Tools for Sustainable Gold Mining in Europe – Final report of SUSMIN -project

ERA-MIN – SUSMIN -Project Final Report

December 2018

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The SUSMIN -project (Tools for sustainable gold mining in EU) was implemented under the ERA-MIN Programme (Network on the Industrial Handling of Raw Materials for European Industries) in the first ERA-MIN Joint Call on Sustainable and Responsible Supply of Primary Resources (2013).

Keywords: Gold, Mining, Environment, Exploration, Mineral processing, Mine waste, Environmental monitoring, Social license to operate

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Tools for Sustainable Gold Mining in Europe – Final report of SUSMIN -project

Abstract

SUSMIN -project developed comprehensive environmental and social management methodologies for sustainable gold mining in Europe. The development work included:

1. Geographical information system and geophysical methods for gold exploration,
2. Chemicals for gold benefication to replace cyanide and piloting traditional gravimetric and flotation benefication techniques,
3. New water treatment chemicals and piloting water treatment on-site,
4. Methods to increase chemical stability in mine backfill and tailings disposal strategies,
5. Geochemical and isotopic characterization of contaminant migration in water phase, new environmental characterization methods to predict contaminant behaviour in recipient waters, environmental risk assessment,
6. Study of social license to operate in Romanian gold mines and road map of research social impact in Finland

The project was coordinated by the Geological Survey of Finland and the project consortium consisted of the Geological Survey of Finland (GTK), Luleå Tekniska Universitet (LTU), Geological Institute of Romania (GIR), Babes-Bolyai University (UBB), Wrocław University of Technology (WUT), University of Porto (UP) and TCD (The Provost, Fellows, Foundation Scholars, and the Other Members of Board, of the College of the Holy and Undivided Trinity of Queen Elizabeth Near Dublin)

In addition following companies participated the project: S.C. Rosia Montanã Gold Corporation S.A., Romania, S.C. Samax Romania SRL/Euro Sun Mining Inc., Romania, Medgold Resources Ltd, Portugal, Agnico Eagle Finland Oy, Finland, Dragon Mining Oy, Finland and Dragon Mining Sweden Ab, Mineral Exploration Network (Suomi) Oy, Finland, Outotec Finland Oy, Finland, Kemira Oyj, Finland, Oulu Water Alliance Oy, Finland

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Map sheet

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1 BACKGROUND

1.1 How and why the project started

Sustainable supply of gold is important for Europe's industry to meet increasing demand without compromising the social and environmental issues of gold mining. Gold mining has challenges in eco-efficiency and extraction methods which often complicates the permitting stage of mine operation. Thus novel sustainable methods and technologies for mineral processing, water treatment and management of environmental and social impacts are needed. Tools for Sustainable Gold Mining in Europe project (SUSMIN) evaluates the whole value chain, from exploration to social impacts, of gold mining in Europe and demonstrates improvements developed in the project.

1.2 Funding bodies

SUSMIN -project was implemented under the ERA-MIN Programme (Network on the Industrial Handling of Raw Materials for European Industries) and it was funded through the first ERA-MIN Joint Call on Sustainable and Responsible Supply of Primary Resources in 2013. Funding was coordinated through National Funding Agencies. The Finnish funding organization was Finnish Funding Agency for Innovation (TEKES). Swedish funding organization was VINNOVA – Verket För Undersökning. Romanian funding organization was Executive Agency for Higher Education (UEFISCDI). Polish funding organization was NCBR - Narodowe Centrum Badań i Rozwoju. Portuguese funding organization was FCT - Fundacão para a Ciência e Tecnologia. Ireland participated in the project by funding its own budget, since they were not yet a partner of ERA-MIN network.

1.3 Project consortium

Effective research approach was achieved by utilizing the expertise of each partner in co-operated case study research within 6 EU member states. The research was carried out by active co-operation with industrial partners, subcontractors, outsourcing services and stakeholders.

Altogether seven research institutes and universities took part in the project:

- Finland: Geological Survey of Finland (GTK), coordinating Partner of the project
- Sweden: Luleå Tekniska Universitet (LTU) division of Geoscience and Environmental Engineering
- Romania: Geological Institute of Romania (GIR) and Babes-Bolyai University (UBB) - Faculty of Environmental Science and Engineering
- Poland: Wrocław University of Technology (WUT) - Faculty of Environmental Engineering
- Portugal: University of Porto (UP) - Faculty of Sciences and Faculty of Engineering
- Ireland: TCD (The Provost, Fellows, Foundation Scholars, and the Other Members of Board, of the College of the Holy and Undivided Trinity of Queen Elizabeth Near Dublin), School of Chemistry – Department of Materials Chemistry and School of Natural Sciences – Department of Geology

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- Outotec Finland Oy, Finland
- Kemira Oyj, Finland
- Oulu Water Alliance Oy, Finland

2 INTRODUCTION

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2.1 Current state of gold mining in Europe

Mining is known to be, with agriculture, human kind´s oldest industry. Development of world´s greatest civilizations has been linked to finding and mastering the exploitation of essential sources of raw materials (*e.g*. gold). Since Roman times gold has been mined in many regions of Europe (*e.g.* Iberian Peninsula, Britain, Ireland, France, Transylvania, Greece and Turkey) and more recently in Scandinavia. At the moment in European countries gold is produced in Finland, Sweden, Bulgaria, Spain, Turkey, Poland, Romania, Serbia, Slovakia, Russia and Greece. In addition, gold mining projects are in permitting stage across in *e.g.* United Kingdom and Portugal. Exploration is also underway in other countries such as France, Italy and Austria.

The value of gold has been more than tripled in the last decade. Almost all of the old gold mining areas in Europe are being explored by several different mining companies. Gold mining is a chance for Europe to increase economic development in the latest economic crisis in the EU. European Association of Mining Industries, Metal Ores & Industrial Materials (2012) states that: “With only about 1.2% of the world’s gold production, but aiming at increasing its economic power and industrial competitiveness, Europe’s focus is to concentrate on the urgency and strategic importance of raw materials and to ensure a sustainable access to them both from within and outside the EU.” However, while the gold demand has been constantly increasing in past years, the commodity findings have been decreasing and the extraction of gold has complicated due to increasing complexity and decreasing grade of the ores. Thus the novel energy and resource-efficient methods and technologies for mineral processing should be developed to concentrate selectively different gold bearing minerals.

2.2 Current challenges in gold mining in Europe

Gold mining has its challenges with eco-efficiency due to the low grade and complexity of the ores and its extraction methods (*e.g.* cyanide leaching). The distribution of trace constituents (trace elements) in ores is paramount for effective extraction. The present knowledge of the very basic trace metal distribution in common ore minerals, many of which are present in nature at vanishingly small concentrations, is limited at best and inadequate in most cases. Regarding extraction methods, gold is often “invisible” in the crystal lattice of sulphides and thus requires pre-treatment (*e.g.* bio-oxidation or pressure oxidation) prior to cyanide leaching. Cyanide readily combines with most major and trace metals, and thus, the most widely used method for gold processing is leaching with sodium cyanide (cyanidation). Cyanide leaching is also accessible, efficient and economic method for gold extraction. However, forms of cyanide present in leaching solutions are highly toxic to humans and aquatic life and the most significant risk from the use of cyanidation is the possible leakage of cyanide into soil and groundwater. Although there are the most restricted thresholds of tolerance for cyanide use in EU (*e.g.* Adopted Directive 2006/21/EC, Directive 96/82/EC, Directive 2000/60/EC), the complete ban on the use of cyanide mining techniques has been raised due to the serious tailing dam failure accidents in Europe (*e.g.* Baia Mare 2000 in Romania, Los Frailes 1998 in Spain). Additionally, cyanide bans have been already implemented in EU Member States (*e.g.* Germany, Czech Republic and Hungary). Hence, there is a need for the study of alternative extraction techniques to cyanide leaching.

Arsenic (As) is a common element in various types of ores in conjunction with precious metals and one of the biggest problems in gold mining activities is the high arsenic concentrations of the ore. The most common arsenic carriers in gold deposits are arsenopyrite (FeAsS), löllingite ($FeAs_2$), cobaltite (CoAsS), gersdorffite (NiAsS) and sometimes pyrite (FeS_2). Arsenic is of particular interest because; 1) it is a frequently a significant component in gold deposits, 2) it is a problematic element due to its relatively high mobility over a wide range of redox-conditions and its toxicity to humans, animals and plants, and 3) arsenic complicates ore beneficiation and the recovery of gold. Previous studies have shown that due to mining operations, concentrations of harmful substances, including As, may exceed thousands of times greater than recommended limits. The sites cannot be used without a proper remediation and rehabilitation processes. By proper water treatment methods (*e.g.* adsorption, ion exchange, chemical precipitation), the amount of As compounds in industrial waste water discharged into receiving water bodies can be reduced to levels that satisfy effluent standards. Ion exchange and/or adsorption have been appeared to be most promising water treatment methods for arsenic removal from industrial waters. Therefore, there is a demand for inexpensive and effective adsorptive materials with a high selectivity and adsorptive efficiency within a range of pH typical for mine process waters and dewatering waters.

Although sustainable use of resources and environmental regulations have been escalated greatly in past few years, waste management has often been inadequate, improper or even non-existent and the mine sites, active, old or abandoned, are still causing serious impacts on human health and the environment. The problems associated with unremediated, abandoned and closed mine sites are often driven from the oxidation of iron-rich sulphides with a consequent formation of acid mine drainage (AMD) and further dissolution of metals and metalloids as well as other harmful substances from water-permeable tailings ponds, waste rock piles and open pits. The problem is widespread in Europe, where during the past centuries several sulphide ores have been in active use and the mine sites abandoned without proper remediation activities. The long-term stability of the wastes and also their stability in connection with other elements and precipitates at actual field condition are rather uncertain and unknown. Thus, it is important to identify the geochemical processes influencing the long-term stability of wastes and formation of stable precipitates when deposited in an impoundment, and also assess if alternative waste management options should be undertaken.

The tailings and old waste dumps can contain fairly high gold concentrations, which could be exploited by utilization of traditional mineral processing methods. The challenge is to find cost effective combination of unit processes for gold separation and recovery. Today, due to the current increase of metal prices, some of the old and abandoned mine sites are about to be opened and operated again and new technologies enabling gold recovery are definitely needed.

Since the closed and abandoned mine sites have been causing serious environmental and health problem all over the world, also the mistrust against the mining companies have increased. Additionally, when mining activities cease, the community is usually faced with socio-economic collapse. Fortunately, the best practices in environmental and social management have been recently recognized within the mining companies. Earning and moreover, maintaining the social license to operate is seen as valuable part of mining operations and thus, the mining companies are putting more effort to communicate with the local community and earn the social acceptance. The experience accumulated in recent mining projects in Europe (*e.g.* Impactmin) and worldwide has shown that gold mining is often differently perceived by the public, with respect to other mineral resources.

2.3 Objectives of the project

The focus of the SUSMIN -project was to increase the transnational cooperation related to best technologies and practices for risk management of gold mining within EU. The project aimed at developing novel sustainable methods and technologies for gold exploration, mineral processing, water treatment and management of wastes and environmental and social impacts of gold mining.

The research supported sustainable and economically viable gold production within EU by improving exploration tools for increasing ore reserves and testing eco-efficient ore beneficiation methods for selective recovery of gold with decreased environmental impacts. The research also provided better knowledge of the mineralogical and petrogenetic features of gold deposits in Europe that can facilitate the knowledge and understanding of the regional distribution of gold deposits enhancing the exploration and exploitation of these important mineral resources. Additionally, the research tested and improved treatment methods for process waters, mine dewatering waters and seepage waters by the development of advanced adsorbents. Furthermore, the research pursued to develop tools for controlling the environmental impacts of mining wastes and new methods for monitoring and assessing environmental risks of contaminant migration from mine sites to surrounding environment. In addition, this project included research on the corporate social responsibility, social acceptance of gold mining and the perception of local communities.

SUSMIN -project provided novel information on potential and reliable geophysical methods combination to enhance the gold exploration. Beneficiation studies provided optimized leaching parameters for gold recovery from both cyanide and alternative leaching methods (*e.g.* thiosulphate) as well as utility of processing aids for selective gold recovery. In addition, water treatment studies verified the effectiveness of different adsorbent materials to treat arsenic containing process effluent, dewatering and seepage waters to meet the environmental standards for mine water quality. Also factors controlling arsenic leaching from gold mine wastes in dynamic conditions were determined. The research verified applicability of environmental monitoring tools and isotopic tracers to assess contaminant migration to mine environment.

Additionally, the study provided new approach for using ecological risk assessment to improve environmental management strategies at mines. Moreover, key issues affecting social license to operate (SLO) at gold mines in EU were canvassed. This knowledge can be utilized to enhance the corporate social responsibility as well as community engagement and management of the relations with the stakeholders in gold mining areas to improve sustainability and long term development of the mining areas.

The outcomes of the SUSMIN -project are summarized in this report. Recommendations for exploration programmes, eco-efficient processing, waste and environmental management as well as to improve sustainable long-term development of the mining areas, are also given.

2.4 References

European Association of Mining Industries, Metal Ores & Industrial Materials. 2012. Newsletter. 1/2012. Gold mining – a chance for Europe.

3 GOLD EXPLORATION

Alexandre Lima[1], Sara Leal[1], Rui Moura[1], Alexander Pivtorak[2], Helena Sant'Ovaia[1], Adriana Baptista[3], Patrícia Santos[3], James Mortensen[4]

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3.1 Introduction

Although the gold demand has been constantly increasing in past years, the commodity findings have been decreasing and the extraction of gold has complicated due to increasing complexity and decreasing grade of the ores. Gold mining is a chance for Europe to increase economic development, but it has challenges. This research promotes sustainable and economically viable gold production within EU by developing and testing geophysical techniques for gold exploration and getting additional value from old stream sediment data available for the same study areas. Additionally, the research improved GIS treatment methods for all this exploration data.

3.2 Objectives

The aim of the research, was to study some key gold deposits in Northern Portugal, in order to obtain a valuable information not only on the geology of the ore deposits themselves, but also on the regional geology and geochemical behaviour of some elements (*e.g*. Ag, As, Sb, etc.) during gold deposit genesis. The better knowledge of the mineralogical and petrogenetical features of these gold deposits would facilitate the knowledge and understanding of the regional distribution of gold deposits. In addition, the research developed recommendations for the exploration programmes to enhance sustainable exploration and exploitation of these important mineral resources.

3.3 Development of Geographical Information System

3.3.1 Study sites

The study areas are located in a region hosted by rocks of the “Valongo Belt”, which is a northwest trending belt of schists and quartzites about 70-80 km long, located in the north of Portugal, just east of Porto and striking close to Viana do Castelo, on the north coast Portuguese (Figure 3.1).

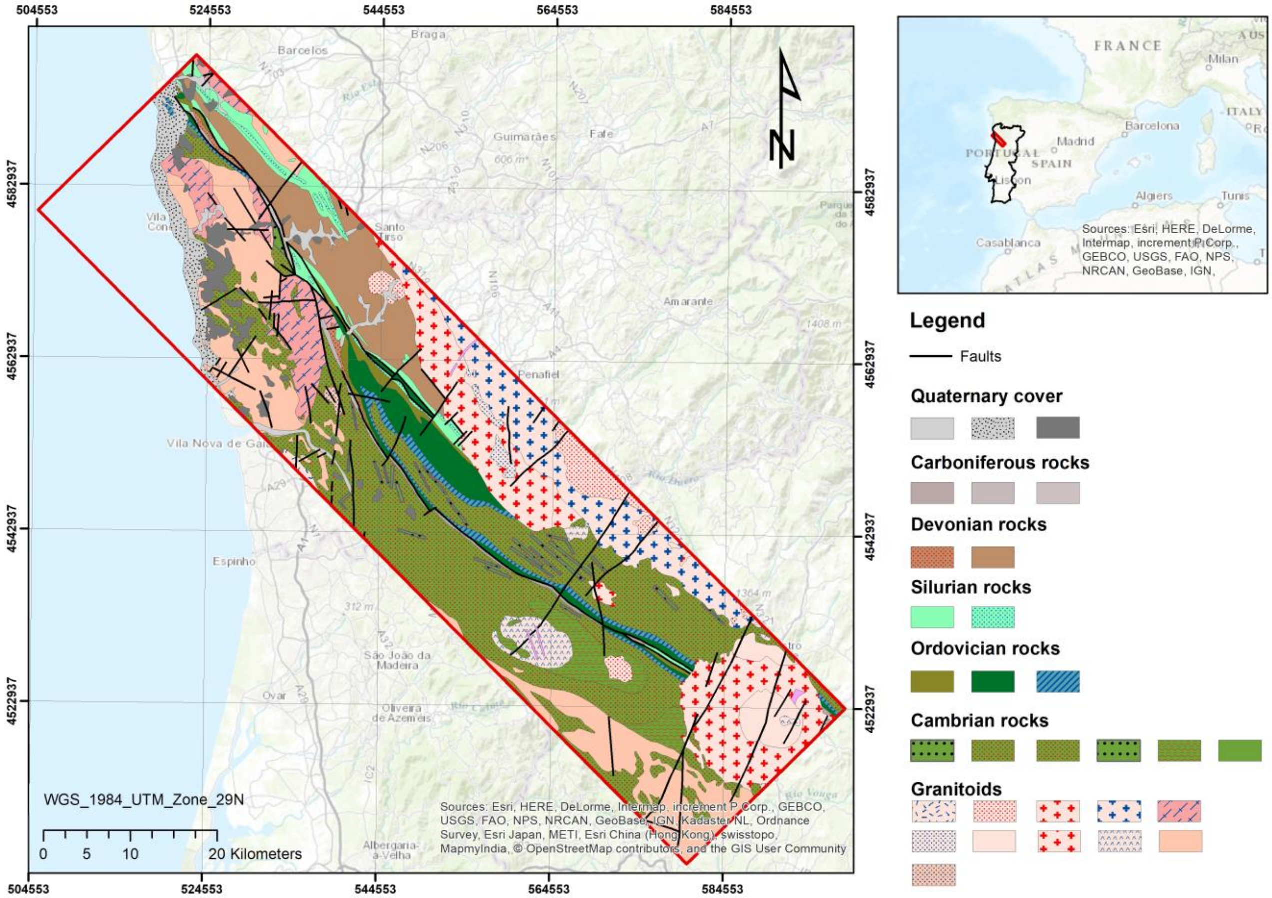


Figure 3.1. Location of study area and simplified geological map.

3.3.2 Geological setting of Valongo belt

The belt is composed largely of Hercynian age (the Variscan orogeny, which lasted from late Carboniferous until middle Permian time). During the Variscan orogeny, the "Central-Iberian Zone" (CIZ) underwent deformation and metamorphism, and experienced polyphase granite emplacement (Figure 3.1). Three main deformation phases have been documented in northern Portugal, namely D1, D2 and D3. Most of the granite intrusions and the associated thermal metamorphic peak are coeval of last phase D3 (Dias & Ribeiro 1995, Noronha et al. 2000). The area has a long history of antimony, gold and tungsten production. Both study areas hosted historic gold mining activity dating back to Roman times and artisan and industrial mining activity during the latter part of the twentieth century. Antimony, tungsten, silver, lead, tin and gold occurrences are confirmed throughout the Valongo mineral belt.

The gold-antimony mining district is situated near the south-western boundary of the axial part of the Iberian Variscan Orogeny, in the CIZ. Country rocks of the area consist of a NW striking band of folded meta-sedimentary rocks, surrounded by pre to post-orogenic Hercynian granites (Couto & Borges 2007).

Three main styles of mineralization have been recognized in the Valongo Belt, based mainly on metal associations: 1) Au-As dominant, 2) Sb-Au dominant, and 3) Pb-Zn-Ag dominant. Most mineralization in the central Valongo Belt is associated with quartz vein systems that are developed mainly in quartzite and conglomerate units, commonly in close proximity to the contact with the overlying and underlying schist units. The Au-As occurrences and deposits are located mainly along the north-eastern flank of the Valongo Anticline, whereas the Sb-Au occurrences appear to be localized along the crest and in the south-western flank of the structure (Couto 1993).

Recent interpretations clearly demonstrate that mineralization within the Valongo Belt was introduced by a series of faults and fractures, and is focused into vein arrays, commonly with zones of massive sulphide and quartz veining in a number of different lithologies.

3.3.3 Methodology

Geographic Information System (GIS) will be used for the inventory, characterization and prediction of gold ores. Integration of all information in a single reference system should be organized in order to make greater use of previous predictive studies performed on gold systems, and also classification of the different kind of gold ore.

The use of GIS in mineral exploration is now beginning to spread, allowing the integration of disparate digital datasets into a single, unified database. The first step was to design the geodatabase according to the information that was going to be needed. In this research all information was compiled in a computer-based GIS, using the software ArcGIS v. 10.2.1 (ESRI software).

3.3.4 Results

3.3.4.1 *Review of Data for Northwest Portugal*

The data compilation for Northwest Portugal contains many datasets: stream sediments, pan concentrates, geological maps and SUSMIN results. However, the quality of these datasets varies, and their coverage is incomplete and inconsistent.

In order to be of practical use in the prospectivity mapping exercise over Northwest Portugal, the datasets used must have complete coverage over the study area, and have a relatively homogeneous level of detail in the mapping. To compute the different spatial statistical analyses, layers of information containing the localization and characteristics of the two study areas, regional geological structures were compiled. All the layers and their content were georeferenced using the ETRS 89 datum for precise results. A summary of the various datasets is provided in Table 3.1.

Table 3.1. SUSMIN database datasets

Feature	Content
Geology	• 1:500 000 geological maps (north and south sheets) Oliveira et al. (1992) • 1:200 000 geological maps (sheets: 1 and 2) Pereira et al. (1989, 2001) • 1:50 000 geological maps (sheets: 9-A (Teixeira & Medeiros 1965); 9-B (Andrade et al. 1986); 9-C (Carríngton da Costa and Teixeira 1957) ; 9-D (Medeiros et al. 1980); 13-A (Teixeira and Perdigão 1962); 13-B (Medeiros et al. 1964))
Geography	• 1: 25 000 military maps (sheets: 82 IGEOE 2011,111 IGEOE 2012a, 123 IGEOE 2012b) • Vectorised drainage network based on SRTM data and delimitation of catchment basins (Balazar area) • Vectorised drainage network based on DTM data and delimitation of catchment basins (Castromil, Lagares area)
DEM	• SRTM of Portugal (cell size 20x20 - D_ETRS_1989 - raster) • DTM Valongo area (cell size 10x10 - D_WGS_1984 - GRID)
Geophysics SUSMIN results	• Location of the geophysical profiles o GPR (Ground Penetrating Radar) o VLF-R (Very-low frequency-resistivity) o ER (Electrical resistivity) o Magnetic search (portable magnetometers)
Geochemistry	• Stream sediments campaign of BRGM (internal report of Consortium Baixo Douro (EDM/ECD/SEREM made in 1988 to 1990) (Viallefond 1990) • Results of chemical analysis obtained during the SUSMIN -project.
Historical mines & Old works of gold mineralization	• SIORMINP from Geological Survey of Portugal

GIS was used in order to produce a mineral potential map. Several methodologies have already been developed and proposed for prospectivity mapping using GIS (Knox-Robinson and Groves 1997, Bonham-Carter 2002, Carranza 2009a). All these approaches have the same objective to integrate cartographic information from various sources in order to locate zones with high exploration potential. Recent applications of such approach have been made for, among others, mining exploration (*e.g.* Cassard et al. 2008, Feltrin 2008, Carranza 2009b, Porwal et al. 2010).

The use of spatial analysis techniques permits to quantify the spatial links between deposits and geological cartographic structure (*e.g.* Carranza 2009b).

3.3.5 Methodology

3.3.5.1 *Catchment basins*

This methodology was used for the delineation of geochemically anomalous areas using GIS, in order to find positive gold anomalies. The catchment basins corresponding to the area of influence upstream of each sampling site were outlined automatically in computer-based GIS, using the Hydrology tool in ArcGIS v. 10.3.

These objects can be delineated from a digital elevation model (DEM) by computing the flow direction raster. The drainage network was produced by extracting water lines of high accumulation zones from the flow accumulation raster. Pan and stream sediment sampling carried out by the BRGM/EDM consortium between 1988 and 1990 (Viallefond 1990) (Figure 3.2) and analysed many elements (*e.g.* Au, As, Sb, W). All these information was compiled in GIS tools in order to obtain some rules for the future gold exploration. The catchment basins are labelled according to the sample number (each stream sediment point) and element contents (Figure 3.3).

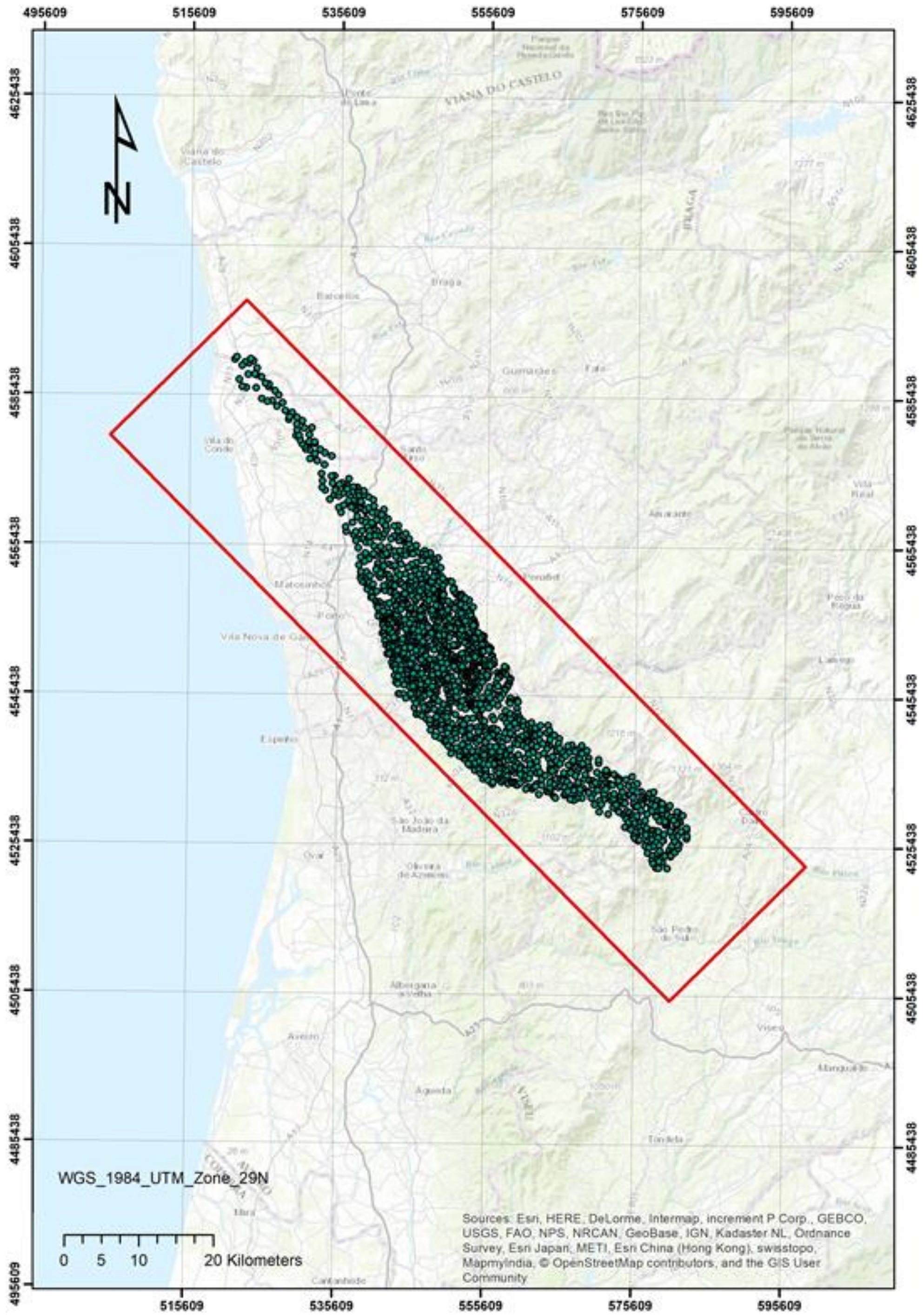


Figure 3.2. Pan and stream sediment sampling carried out by the BRGM/EDM consortium between 1988 and 1990.

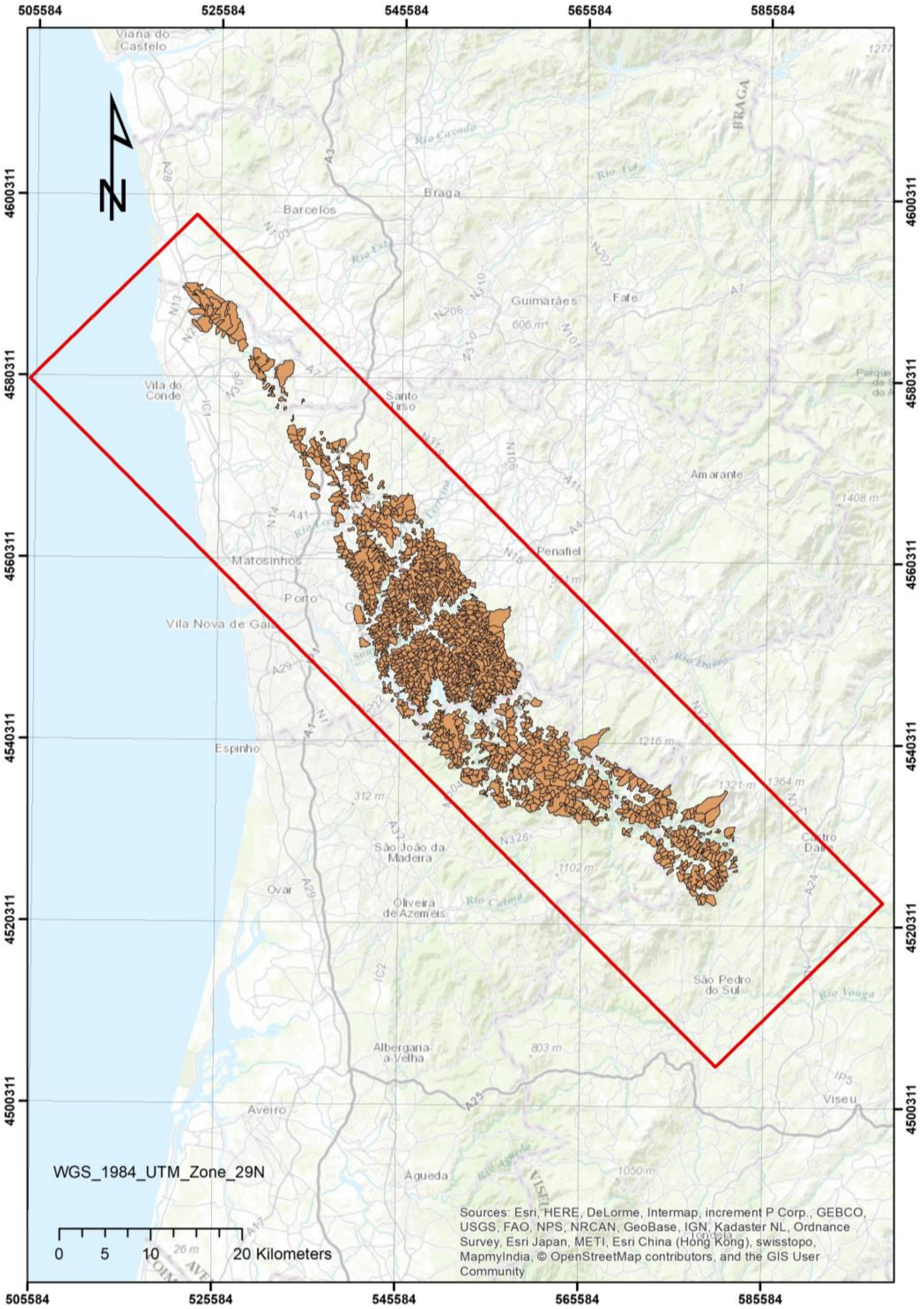


Figure 3.3. Catchment basins of study area.

3.3.5.2 *Spatial analysis*

The distance distribution method for quantifying spatial association between a set of point objects and another set of objects with a particular geometry was formalized and demonstrated by Berman (1977). Further demonstrations of the distance distribution method in quantifying spatial associations between known occurrences of certain types of mineral deposits and geological features can be found in *e.g.* Bonham-Carter (1985), Berman (1985), Carranza & Hale (2002) and Carranza et al. (2008a, 2008b). In the first study, the investigation was focused on the analysis of spatial associations among the geological entities, in particular between the results of stream sediments (Sb content) and surrounding basic rocks. In order to study the basic rocks / stream sediments spatial relationships, Euclidian distance is computed between each point (stream sediment) and its closest line segment (basic rocks). The Euclidean distance is calculated from the centre of the source cell to the centre of each of the surrounding cells. The shortest distance to a source is determined, and if it is less than the specified maximum distance, the value is assigned to the cell location on the output raster.

To compute the different spatial statistical analyses, layers of information containing the localization and characteristics of the two study areas, regional geological structures were compiled.

1. Point layer (Old Sb and Sb/Au mines; geochemical analysis);
2. Line layer (Faults and thrust faults);
3. Polygon layer (Lithology).

Analysis of the shortest distance between old Sb-Au mines and basic rocks (Figure 3.4), shows that 33% of old mines have a range from 0-300 meters and 750 to 1000 meters. And the difference between control points frequency and old Sb-Au mines frequency is very high, which shows a good probable spatial relationship with basic rocks and antimony anomalies.

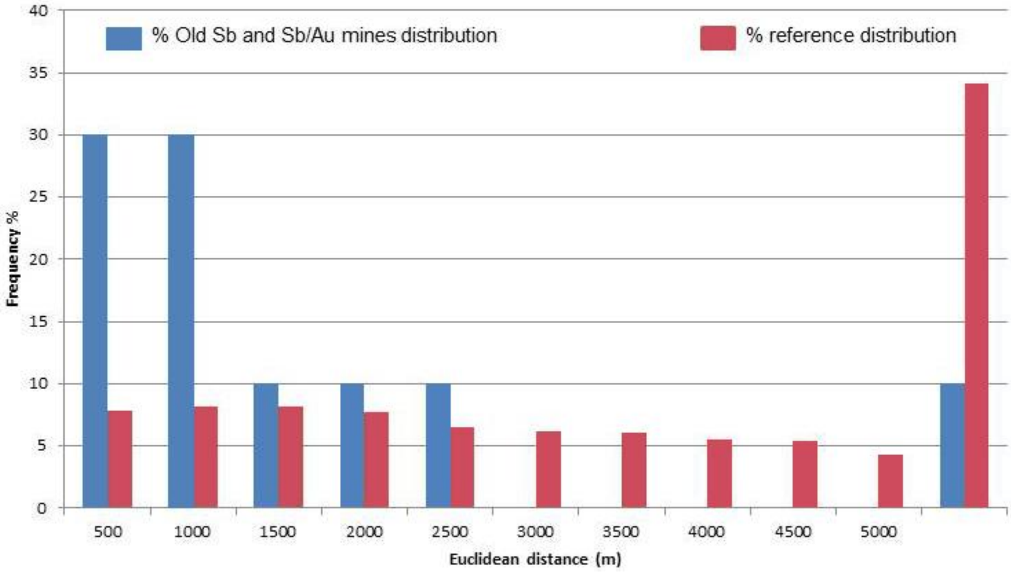


Figure 3.4. Results of the geostatistical tests. Proximity calculation analysed with old Sb-Au mines and basic rocks.

Also the relationship of other features was tested for old mines / faults, gold or antimony mines / faults (Figure 3.5) and gold or antimony mines / azimuth of the faults (Figure 3.6) in the area.

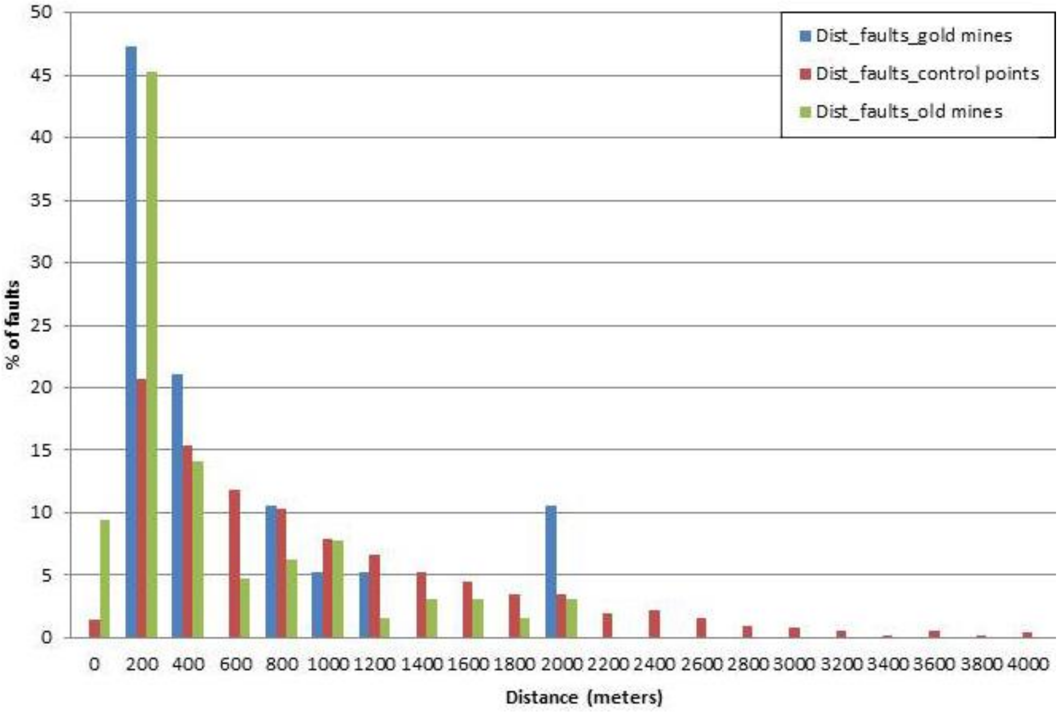


Figure 3.5. Relationship with faults and mines. 46% of faults are related with Au-Sb mines.

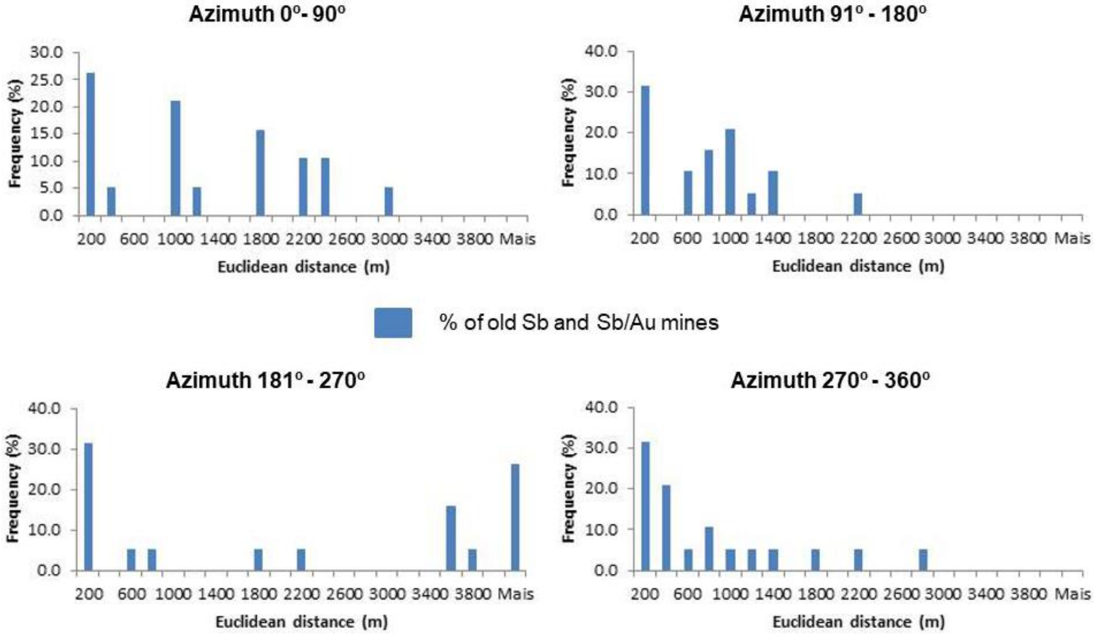


Figure 3.6. Relationship with azimuth of the faults and mines.

The study of relationship with the azimuth of the faults and gold mines indicates an association with trend NW/SE, the direction corresponding to the known shear zones.

Integration of all information in a single reference system should be organized in order to make greater use of previous predictive studies performed on gold systems, and also classification of the different kind of gold ores.

3.3.6 Development of geophysical techniques for gold exploration

The geophysical survey methods have not been extensively used in gold exploration in Northern Portugal. This is based on the fact that most mineralized zones contain low and erratic sulphide contents.

In this work four different types of geophysical surveys were tested combined with geochemical surveys, in order to define anomalies that are closely correlated with the locations of known mineralized zones.

3.3.7 Sites

The aim of the WP1 is to study the gold deposits in Northern Portugal (Lagoa Negra and Castromil) in order to obtain valuable information of the mineralogical and petrogenetically features of these gold deposits, and it's would facilitate the understanding of the regional distribution and formation of gold deposits. This task, aims to do a comparative study of the known Au-deposits based on the integration of different data and define targets were the general characteristics were more distinguishable.

3.3.8 Methods

The four geophysical methods have been used for this study: Low Frequency ground penetrating radar (GPR), very low frequency EM resistivity inversion (VLF-R), 2D electrical resistivity and proton precession magnetometer.

In GPR studies, a Loza-2N system with a 25 MHz antenna was used to image the subsurface. This method detects reflections of the subsurface at interfaces between materials with differing conductivity and dielectric properties such as different lithology, weathered zones and faults.

The VLF-R measurements were done using a Scintrex OMNI IV, which is an electromagnetic instrument capable of detecting electrical conductors by measuring the interference of radio signals, in the 15 to 30 kHz range, caused by certain geologic occurrences and structures. The VLF-R we used easily responded to contacts and fault zones. VLF-R instruments compare the magnetic field of the primary (transmitted) signal to that of the secondary signal (induced current flow within the subsurface electrical conductor). VLF-R survey methods rely on major stations that transmit continuous VLF electromagnetic waves distributed throughout the world. The interaction of the electromagnetic plane waves emitted from these transmitters can be measured as the waves impinge on different material conductors within the earth. Examples of vertical sheet conductors include faults, dykes and fractures or joint zones (Milsom 2003).

The resistivity data, collected with Syscal Switch 48 resistivity meter, consisted of a series of Wenner Schlumberger 2D sections that both improved and confirmed some of the VLF sections. In this method a DC current is injected through electrodes into the ground and potentials measured in millivolts are taken at pairs of electrodes along the same line and according to the chosen geometry (Wenner, Schlumberger or even the Half-Schlumberger geometry).

The magnetic data was collected using a land based proton magnetometer through an irregular walking mode survey and using an internal GPS positioning system. The magnetometer is a Proton Precession Magnetometer designed for measuring the Earths' total magnetic field. Objects and geologic features can be detected due to the disturbance these objects cause in the local magnetic field. The microprocessor provides a direct readout of the magnitude of the local magnetic field directly in units of nanotesla (nT).

3.3.9 Results

3.3.9.1 *Balazar area*

The main objective of geophysical works in this area was to identify the structure considered being associated with regional gold mineralization, which presumably stretches from the northwest to the southeast. In the surrounding area of Lagoa Negra three electromagnetic VLF surveys were performed. More, to the southeast, precisely in Rates, one additional survey was performed along with a soil campaign to establish a link between the presumed structures. For such purposes, the geophysical profiles were disposed in a perpendicular direction to the probable structure (Figure 3.7).

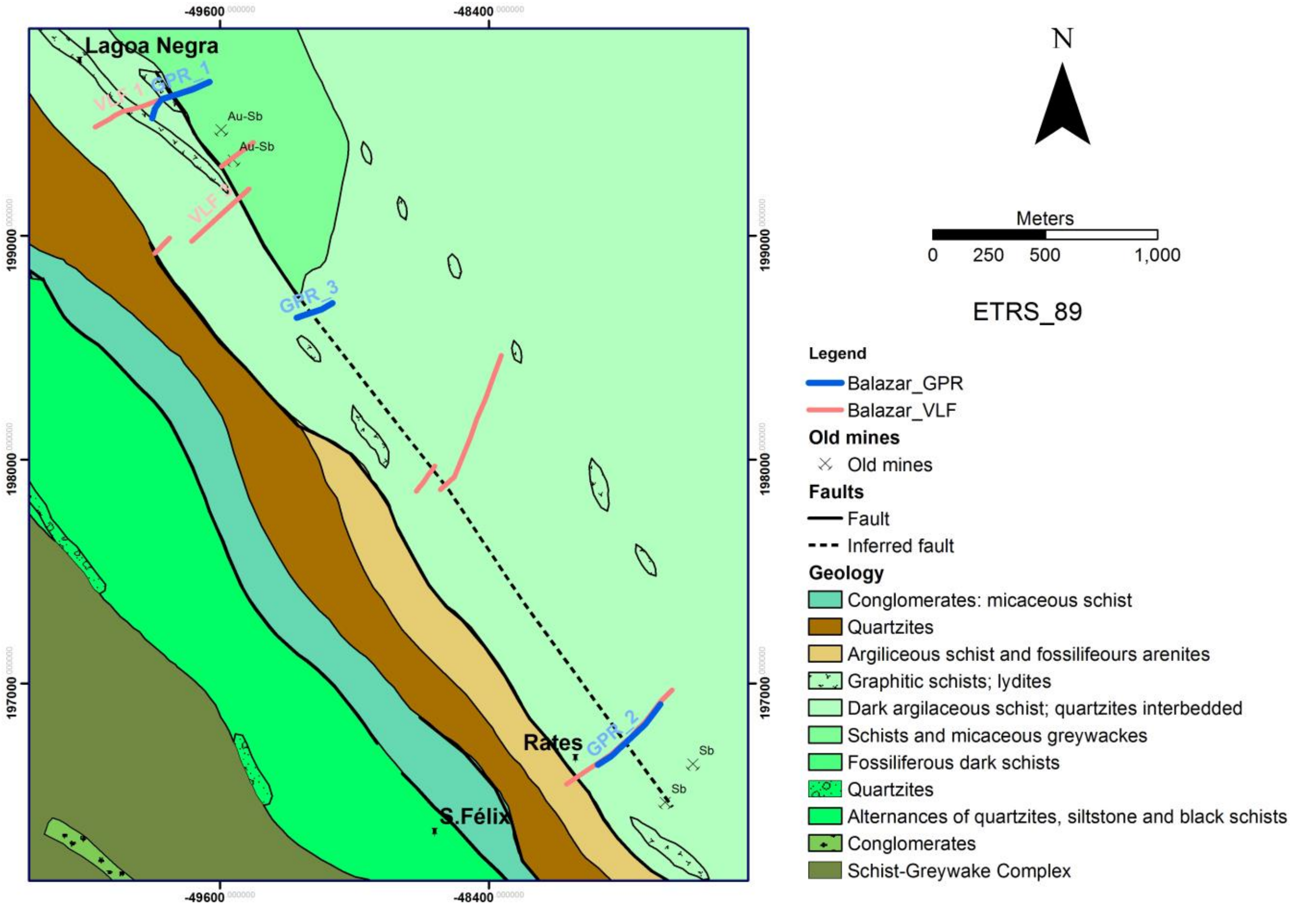


Figure 3.7. Possible structure considered being associated with regional gold mineralization, which presumably stretches from the Northwest to the Southeast.

In the Balazar area the GPR profiles revealed a possible structure, which is interpreted to trend northwest. The model of the geological and geophysical section is represented with the highlighting, based on changes in the electrical properties, of geological and geophysical boundaries, or fractures. The local anomalies have high variations of the signal amplitude and that are depicted in the profile (Figure 3.8).

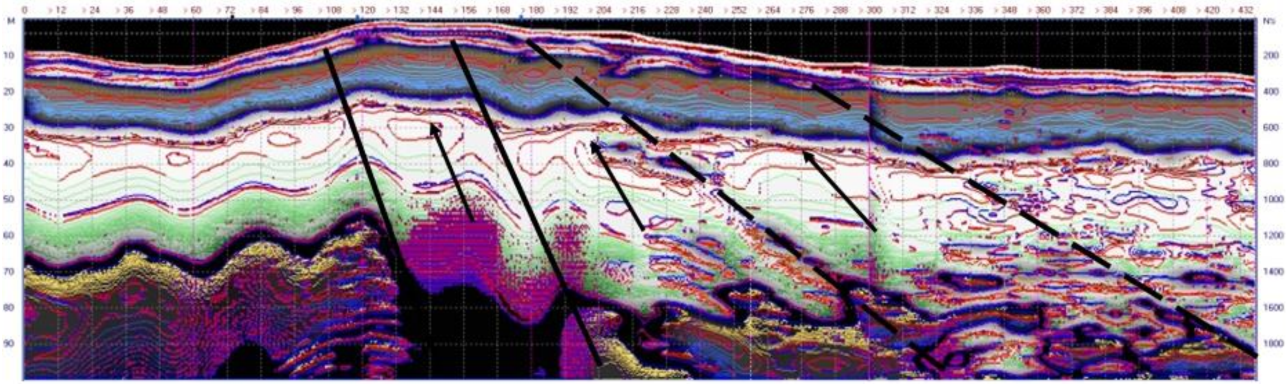


Figure 3.8. Example of a 25 MHz GPR section carried out in the Balazar area. Note the response that was obtained from estimated depths of 90m (1800 ns).

After analysing the VLF profiles it is notable that the anomalous areas are located along the same structure detected by GPR that are shown in Figure 3.9. This also indicates that it must have a planar subvertical form, and probably a fault, due to the form of an antisymmetric anomaly, visible in some profiles. This anomaly was also confirmed in the resistivity section of Figure 3.10. This section although shorter in length was centred on the anomalous VLF and GPR zone.

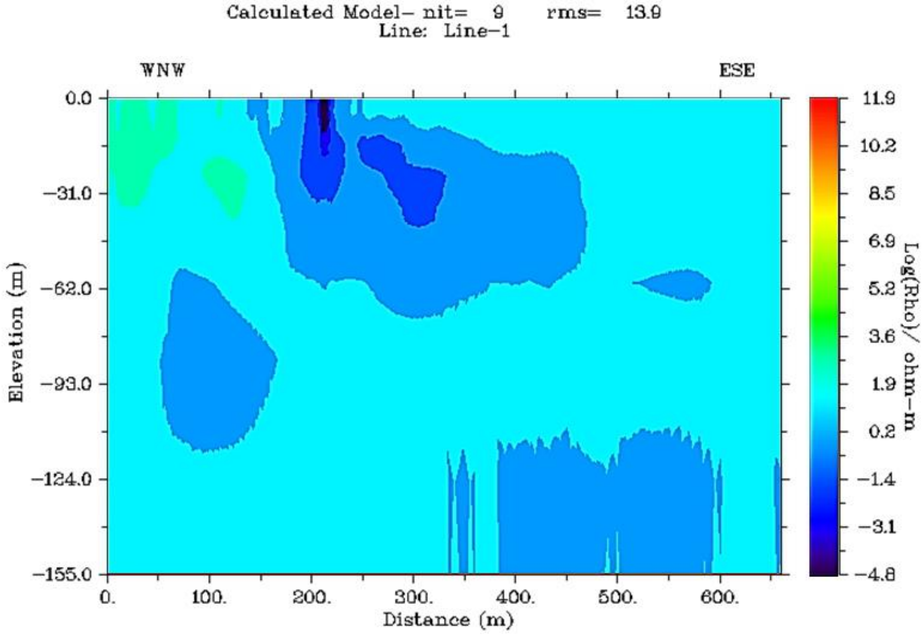


Figure 3.9. Example of an inverted VLF section, carried out in the Balazar area, over approximately the same length of profile as the previous GPR section (Figure 3.8.).

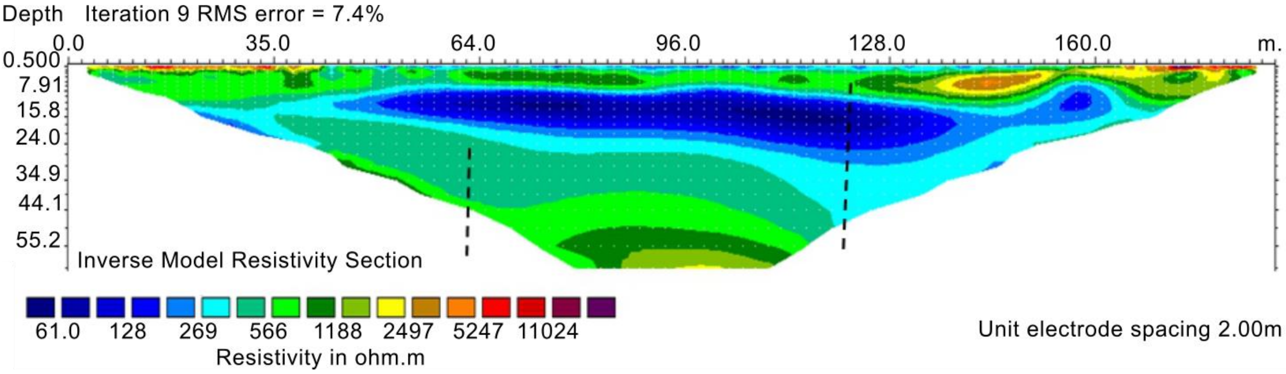


Figure 3.10. Example of an inverted resistivity section, carried out in the Balazar area, over the length of rectangle depicted in the previous VLF profile (Figure 3.9).

The soil geochemistry results (Figure 3.11) demonstrated an anomaly in Sb (mean=170 ppm) and As (mean=114 ppm), representing the best association for the known gold mineralization in this area. The main results show the existence of an antimony and arsenic anomaly in soils which is partially coincident with the Lagoa Negra and Rates old workings and the places where geophysical anomalies were detected.

North of Rates, Medgold Resources performed a soil campaign, and these results were also used to verify geophysical anomalies (Figure 3.11). When depicting the fractures allocated on the geophysical sections along with the soil geochemical anomalies on the map we can see that both anomalies are on the same alignment.

It is proposed that the observed Au-Sb-As anomalies observed at the prospects of Lagoa Negra and Rates are linked by the same northwest-trending fault. Historical mine workings have been identified at both Lagoa Negra and Rates, where rock-chip sampling has yielded a 30 g/t Au result from the Rates prospect. Exploration work at the Balazar exploration is on-going and Medgold Resources is applying observations made in this study to its on-going exploration activities.

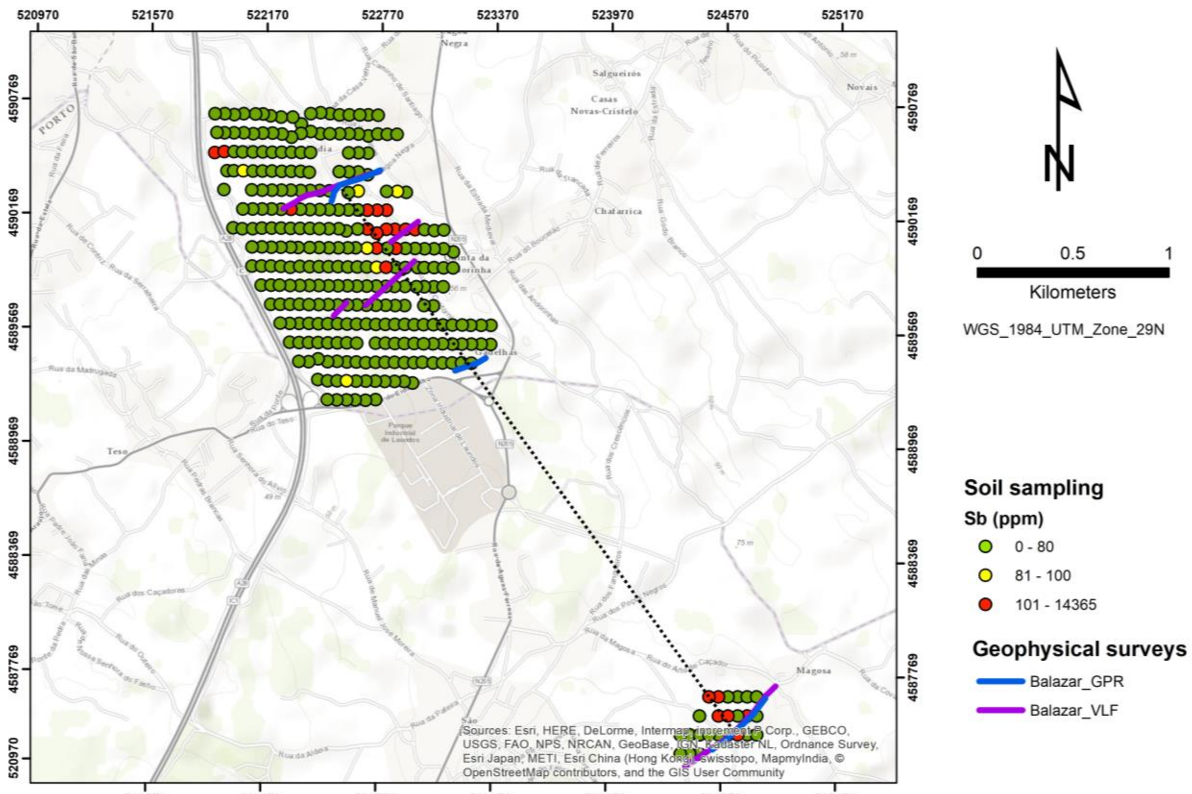


Figure 3.11. Results from Balazar works and direction of the possible structure that host the mineralization.

3.3.9.2 *Castromil area*

In the Castromil area, the gold mineralization is commonly accompanied by vein quartz or disseminated sulphides which cause significant contrasts in electrical properties between the mineralization and the surrounding rocks. Some of the GPR profiles were taken perpendicularly to the granite body intrusion and others parallel to the geological contact, in order to delineate zones with sulphides. As shown in Figure 3.12., a magnetic total field survey was also carried out. The results showed two large but incomplete dipole anomalies probably associated with some sulphide occurrences.

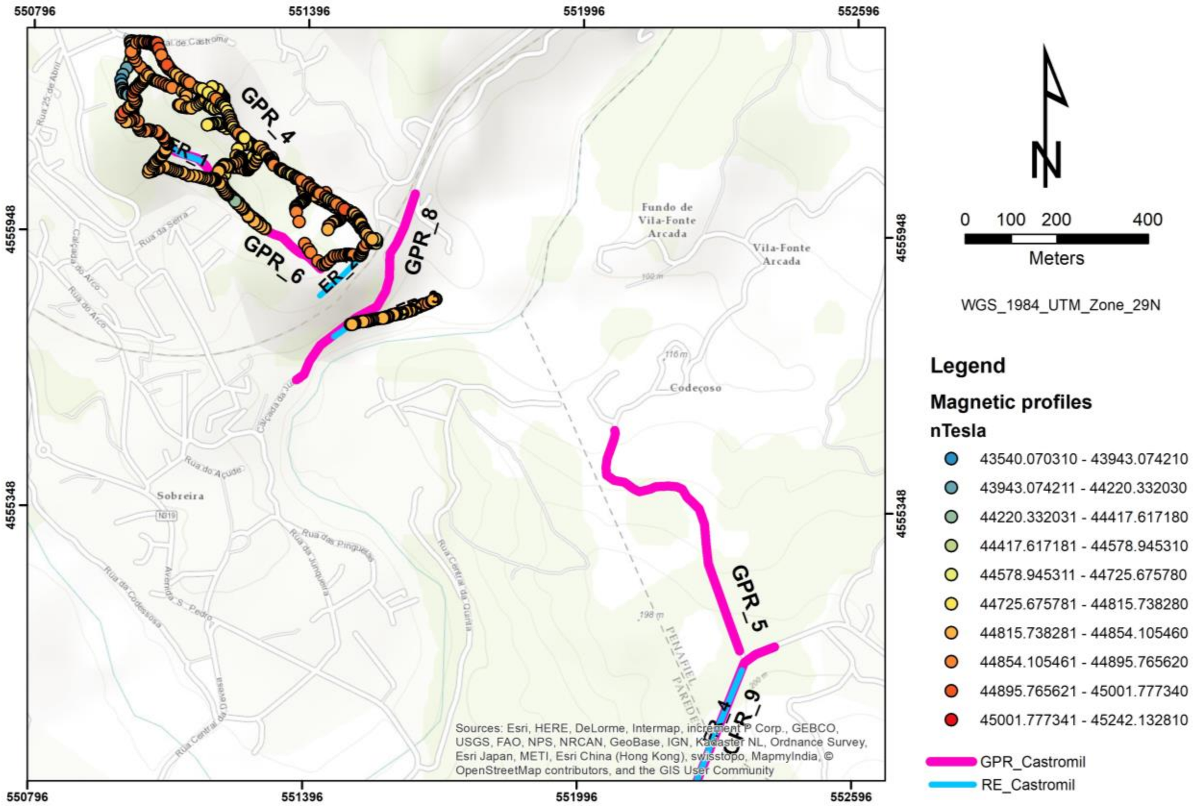
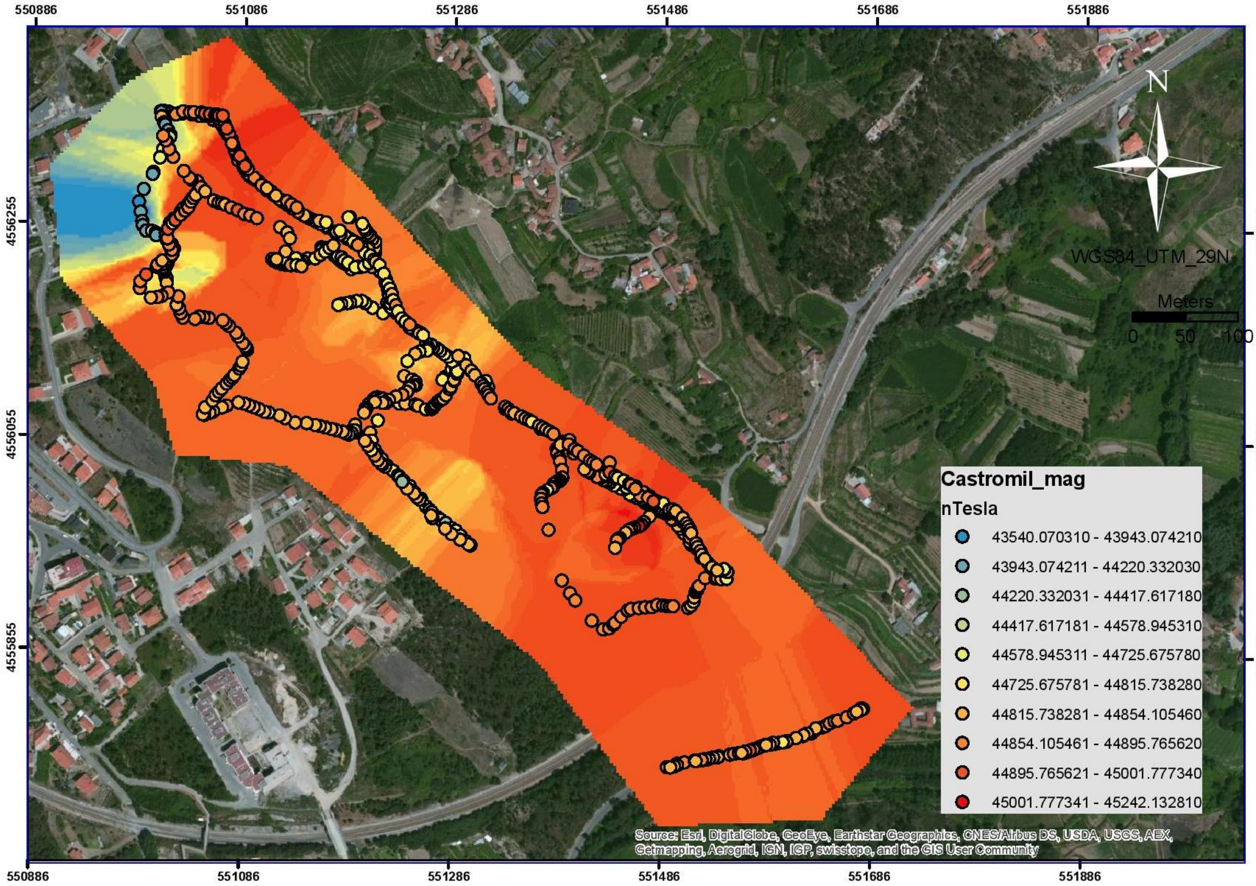


Figure 3.12. Location of geophysical surveys.

At Castromil some GPR profiles beginning in schist and further along the granite massif, in some cases at the end of the profiles, a transition to silicified granite is noticed. In zones of fractures there is a layer spreading which has similar physical property values with altered rock formations in the fracture zone. As a result of the instructional research on the geological sites we were able to identify and map the sulphide-quartz rich dyke zones as well as the identification and mapping of the structural elements (fractures) by pulsed GPR sounding. Magnetic mapping was also able to identify possible sulphide rich zones within the so called mineralized zone (Figure 3.13).



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 3.13. Krigging of magnetic data.

3.4 New U-Pb Zircon Dating in Northern Portugal

One aim of this study was to obtain better constraints on the crystallization and emplacement ages for intrusive rocks in northern Portugal, in order to constrain the age(s) of major faulting events, and the timing of gold and other styles of mineralization in the region. Eleven samples were collected from surface exposures and drill core. Zircons were separated and analysed at the PCIGR at the University of British Columbia, using laser ablation ICP-MS methods, as described by Beranek & Mortensen (2011). The analytical results are shown on conventional U-Pb concordia diagrams and plots of weighted average ^{206}Pb/^{238}U ages in Figures 3.14 – 3.15. Interpreted ages are listed in Table 3.2. Complete discussions of the analytical results and interpretations will be presented in a separate publication.

Table 3.2. Summary of U-Pb zircon dating results for northern Portugal intrusive rocks.

Sample	**Description**	**Interpreted age**
Sample 1	main altered granite at Castromil	305.1 ± 0.7 Ma
Sample 2	unaltered granite at Castromil	305.3 ± 0.8 Ma
Sample 4	granite in footwall of fault at Castromil	304.9 ± 1.1 Ma
Sample 5	aplite in footwall of fault at Castromil	305.0 ± 1.4 Ma
Sample 6	NE-trending dyke cutting Sample 9	304.8 ± 1.5 Ma
Sample 13 M65	NE-trending dyke cutting granite at Serra da Quinta	303.9 ± 1.8 Ma
Sample 11	syn-orogenic granite NE of Castromil	316.4 ± 1.7 Ma
Sample 18	Castro Daire late to post-orogenic intrusion	304.5 ± 1.9 Ma
Sample 9	main granite body NE of Castromil	304.6 ± 1.9 Ma
Sample 7	granite body NE of Castromil	307.0 ± 3.0 Ma

The dating results confirm the general age range that had been reported for granitic magmatism in northern Portugal. Most intrusions that are currently mapped as “late or post-orogenic”) in the region give ages in the range of 303-307 Ma, and two northeast-trending aplite dykes that cut these bodies give essentially the same age. Older, syn-orogenic intrusions give ages of ~316 Ma, and zircon xenocrysts of approximately this age are also abundant within the late and post-orogenic granites, suggesting that ~316 Ma igneous rock is likely present in the subsurface in much of this region.

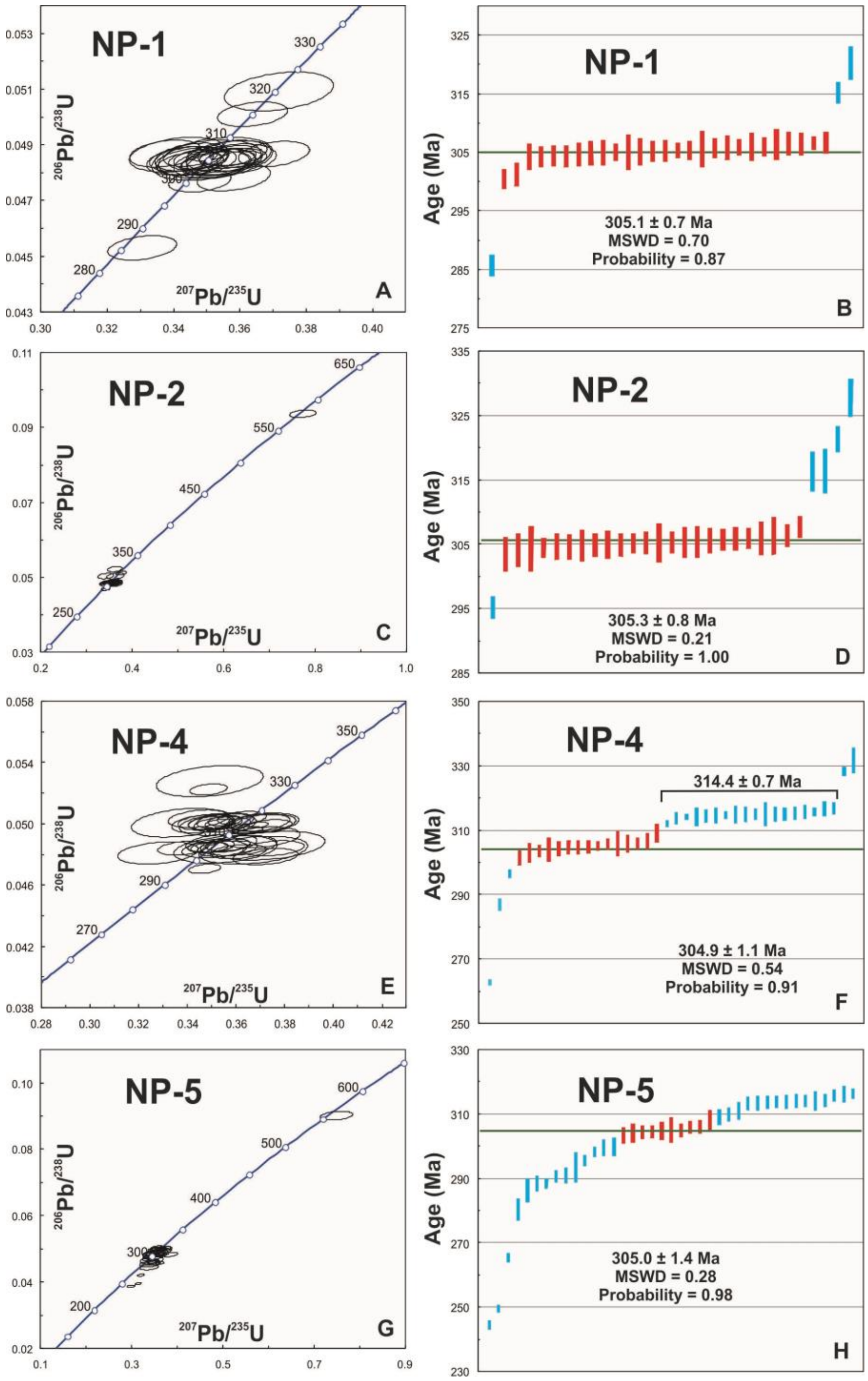


Figure 3.14. U-Pb geochronological results for samples of the Castromil granite and small intrusions in the footwall of the Railway fault at Castromil. Error ellipses in the concordia plots are shown at the 2σ level. Error boxes in the plots of weighted average ^{206}Pb/^{238}U ages are shown at the 1σ level. Analyses shown in red were used to calculate the weighted average ages reported in Table 3.2; analyses shown in blue were omitted.

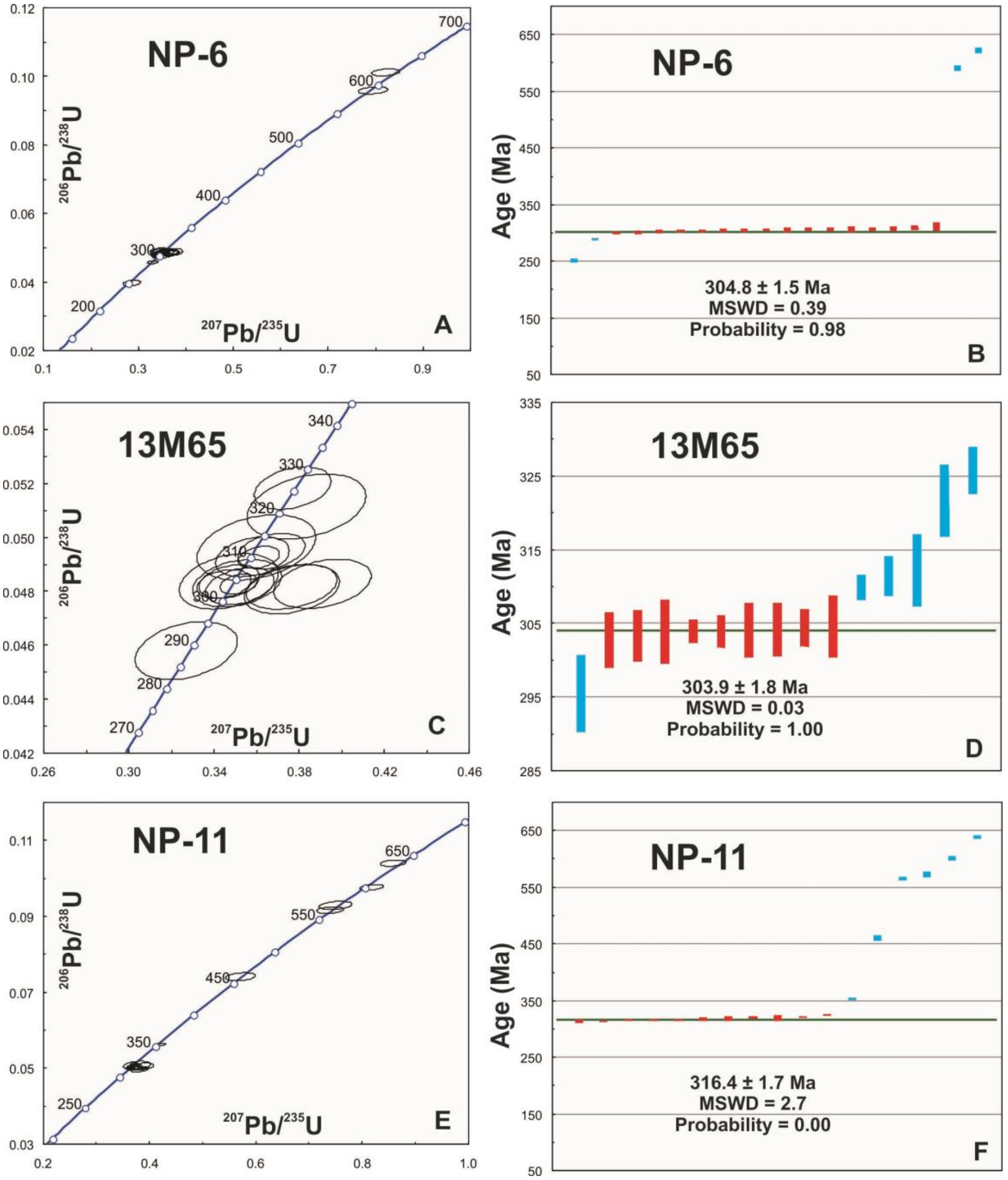


Figure 3.15. U-Pb geochronological results for samples of northeast-trending aplite dykes (NP-6 and 13M65) and syn-orogenic granite northeast of Castromil (NP-11). Errors shown are as in Figure 3.14.

3.5 Conclusions and recommendations

Considerable progress has been made over the past decade in developing better exploration strategies for gold and associated mineralization in north-western Iberia. However, substantial challenges still remain which continue to make gold exploration a challenge. Some of these challenges can be overcome by government geological surveys and others addressed through research ventures.

One of the most productive and cost-effective tools for generating and facilitating regional scale gold exploration activity is a complete regional geochemical dataset, focusing particularly on stream sediments, which effectively sample the largest areas per sample. Particular attention should be paid to obtaining the highest possible quality analyses, and it is critically important that key tracer elements such as Bi, Sb, Te and W are included in the analyses. The sample collection and analysis methods should be standardized as much as possible, so that data can be easily continued from one survey area to the next. Comparison with old report results new GIS approach was proved to be useful.

Ground Penetrating Radar (GPR), Very Low frequency (VLF) electromagnetic methods combined with 2D Electrical Resistivity techniques can be used to define geological structures, and were found to be particularly important where extensive cover exists. They can also play an important role while mapping lithology and lithological contacts. The magnetic surveys revealed and confirmed two possible areas with sulphide mineralization, one with pyrrhotite and other with Fe-sulphide oxidation, which were proven by a drilling campaign done in the area. This work demonstrates how the combination of geophysics and geochemical methods, together with geological sampling, can be used to help delineate possible structures that host gold mineralization. There is no definitive set of predefined methods ideally suited for these types of mineralisation. However the combination does help to overcome some of the ambiguities as well as the lesser clearer anomalies. The encountered difficulties were twofold and were related to their:

- applicability to these types of mineralisations
- applicability to the geographic surroundings

Regarding the first bullet point we refer to the ability that these methods have in detecting any association with the mineralisation itself. Due to the nature of the mineralisations that we studied the strongest anomalies were usually more associated with structures and associated weathering than with the mineral content. However the magnetic anomalies do respond more to the presence of mineralised zones.

Regarding the second bullet point we refer more to the feasibility of the methods in terms of being executable within certain geomorphological conditions, available space and presence of man-made metallic objects as well as electromagnetic noise sources. Within this part of North of Portugal it is rather difficult to apply certain methods, such as resistivity and EM, due to both the topographical variations and the highly spatially irregular and fragmented nature of private property. This leads to difficulties in finding enough space to deploy geophysical profiles long enough to produce adequate depth penetration as well as along the ideal directions and ideal zones. This second bullet point is, in our view, one of the greatest challenges in terms of the feasibility of geophysical surveys applied in areas such as the ones encountered in Northern Portugal.

In areas of limited exposure, airborne geophysical surveys provide critical information regarding the lithologies present, even where covered by substantial amounts of overburden. Low level, high resolution aeromagnetic surveys are one of the most valuable tools that can be used to complement geological mapping. Individual lithological units sometimes show distinctive magnetic signatures, and the magnetic response of specific intrusive suites can be used as a proxy for their oxidation state, which has been shown to be an important constraint on the likelihood of an association with Intrusion Related Gold Deposits (IRGD). Airborne radiometric surveys similarly provide important information regarding the underlying geology, and airborne electromagnetic (EM) surveys help to outline specific structures that may have played a role in localizing fluid flow and gold deposition in Orogenic Gold Deposits (OGD).

IRGDs are known to be associated with intrusions of specific age(s) and composition. Future studies related to IRGDs in north-western Iberia should focus on intrusive suites and phases throughout the region whose relationship to gold mineralization has been well established. Obviously there are far too many intrusions in the region to date them all. Hence the critical intrusions should be dated and characterized in terms of petrography, whole rock and isotope geochemistry, and preferably geophysical response. This will provide a template for the most prospective intrusions that can then be applied regionally.

Structural controls are keys for OGDs, and it is therefore critical to better understand the structural history of north-western Iberia, both in terms of the relative and absolute ages of the various faults that may have influenced hydrothermal fluid flow and gold deposition. This will require detailed structural mapping of the structures and their intersections, and an attempt to obtain absolute ages on as many of the individual structures as possible. Because of the prolonged high heat flow that likely existed throughout much of the region, only a few dating methods, specifically those with relatively high closure temperatures, have any chance of success. Gutiérrez-Alonso et al. (2010) used 40Ar/39Ar dating of white mica within shear zones successfully to constrain the age of shearing along some major fault zones that were interpreted to have been active during the formation of the Cantabrian orocline. Most samples that were dated using the 40Ar/39Ar method in the current study (>20 individual samples), however, show evidence of slow cooling and/or thermal overprinting, such that the resulting data do not permit calculation of a meaningful age. Dating of intrusive rocks, which cut or are cut by structures, using U-Pb methods is a good way to obtain absolute ages for structures, however, most significant faults in the region cross-cut the intrusions and hence this approach will only yield a maximum age for the structures.

It is critical to establish absolute ages of formation for as many examples of IRGD and OGD mineralization in the region, as well as other types of mineralization (*e.g.* W and W-Sn) as possible. This is a challenging task, since only a limited number of dating methods are likely to produce undisturbed and reliable ages. Re-Os dating of molybdenite is one of the most useful and reliable methods to use, however, the method requires that molybdenite is present, and the method is rather expensive. Re-Os dating may also be effective in rare cases for dating arsenopyrite, although in the vast majority of cases there is not enough representative arsenopyrite (especially in OGDs) to make the dating possible. Neiva et al. (1995) and Rosa (2003) used the 40Ar/39Ar method effectively to date alteration and metamorphic white mica at the Jales and Gralheira deposits. Our experience from the current study, however, suggests that the 40Ar/39Ar system in most samples is likely to be too disturbed to yield reliable results. Hydrothermal phosphates (monazite and/or xenotime) may be present within some of the OGD vein systems, and if so, this material could be dated by U-Pb methods using laser ablation ICP-MS or SHRIMP methods (*e.g.* Taylor et al. 2015). Finally, U-Pb dating of cassiterite and/or wolframite from W-Sn deposits using laser ablation ICP-MS methods may give reliable ages for that style of mineralization which could be compared to ages for IRGD and OGD mineralization and finally establish how these deposit styles relate to one another.

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4 MINERAL PROCESSING

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4.1 Introduction

The gold ores with economic relevance are native gold (with a volumetric mass density between 12 and 20 g cm^{-3}, according to the impurities such as silver), calaverite ($AuTe_2$, with approximately 3% of the gold replaced by silver, with a density of 9) and silvanite ($(Ag,Au)Te_2$, with a density from 5.7 to 8.2 g cm^{-3}). Nevertheless, native gold is the most vulgar occurrence of this precious metal forming alloys with silver.

Although gold occurs many times in quartz, it is more frequently mechanically connected to pyrite and less frequently to arsenopyrite, chalcopyrite, antimonite, pyrrhotite and sphalerite. In Portugal gold mostly occurs connected to arsenopyrite and antimonite (stibnite). In the oxidized areas of the sulphide deposits it is also connected to the resulting oxidized minerals. The gold tellurides are also connected to pyrites and other sulphides. Quartz is normally the most frequent gangue.

Relatively to ore processing gold minerals may be divided into the following categories:

- Simple ores (gold connected to quartz or auriferous alluviums);
- Ores of auriferous pyrites;
- Complex ores, those that include minerals that interfere with the extraction of gold and that must be removed or made inert before treatment;
- Ores that contain Au as sub-product of base metals (Pb, Cu, Zn, etc.).

Processes for gold extraction are the following: hydrogravitic concentration (the high density of gold allows its recovery using sluices, jigs, tables, corduroys), amalgamation (free gold forms a liquid alloy with mercury), flotation, cyanidation (leaching by cyanide solutions) and other hydrometallurgical processes that will be reviewed in this report. The first two processes are suitable to recover gold that occurs freely as coarse particles; the other methods are more suitable when gold occurs as fine particles.

Recovery of gold by hydrogravitic methods is applied to the raw ore, such as auriferous alluviums, or after grinding in order to liberate the gold particles.

Amalgamation is one of the oldest processes for recovering native gold. Nowadays it is not practically used due to the environmental problems originated by the usage of mercury, except in artisanal mining in developing countries.

Gold occurring as fine particles (grain size lower than 42 mesh, 354 μm) can be recovered by flotation. Flotation does not allow to produce pure concentrates, but just to increase the grade so that Au will be recovered more efficiently by other processes. Gold may also be depressed by Na_2S, which simultaneously activates pyrites. Other depressors may be also used, such as lime. Starch may be used to depress clay, iron and manganese silts. Gold is floated at a pH 7 and an excess of Na_2CO_3 has a depressing effect.

Gold may be activated by a small dose of fine particles of coke (0.5%) that capture gold allowing the formation of heavier and more consistent foams. This technic is not effective when pyrites are not present in reasonable quantities.

The concentrates are generally leached by cyanides. But cyanidation may have large negative environmental impacts when an accident occurs. For this reason other alternatives for dissolving gold directly from ores or concentrates are available: Pre-treatment and Pressure Leaching (Chemical Oxidation or Pressure Oxidation), or alternative reagents: Malononitrile, Thiourea, Copper-ammonia-thiosulphate system, Thiocyanate, Bromine, Chlorine, Iodine and Bioleaching.

4.2 Objectives

Mineralogical properties of a gold ore are probably one of the most important when selecting the beneficiation methods and thus also indicate the potential environmental impacts of the process. For this reason, the studies are concentrated on the mineralogical and chemical characterization of gold ores, gold concentrates, leaching residues and tailings on selected sites in Finland, Portugal and Romania.

The comminution of gold ores and concentrates is primarily required to liberate gold and gold bearing minerals to make them amenable to next steps of beneficiation process. Gravity separation is the first step for recovery of free gold and gold associated with heavier mineral. Furthermore, the coarse gold particle, which is almost impossible to recover effectively by flotation, can be concentrated by gravity separation methods. The concentrates can be treated by flotation, cyanidation or leaching tests with selective alternatives to cyanide.

The free gold particles and gold bearing sulphides such as pyrite, arsenopyrite and pyrrhotite are commonly separated by flotation. Flotation is also used to control simultaneously the waste rock matrixes. To concentrate selectively different gold minerals and to produce a gold-rich concentrate by flotation, it is necessary to study various factors for example type and amount of chemicals (frothers, activators, collectors, and depressants), pulp and surface properties as well as operating pH/Eh. For example, process chemical residues (*e.g.* xanthates) are known to have an effect in surface chemical reactions during the flotation process, but the phenomena is not well known. Furthermore, each mineral has an optimum flotability area, and thus it is possible to influence the flotation and selective separation of gold bearing minerals by adjusting and controlling the slurry conditions. Process chemistry research focuses in SUSMIN -project on identifying and monitoring the physicochemical interaction in beneficiation processes for developing environmental friendly, efficient and selective process methods to new gold ore types and selected gold containing waste materials. In addition, the effect of different process chemicals to water treatment and recycling will be evaluated.

The hydrometallurgical methods to process gold use leaching to produce a gold bearing solutions, an intermediate product for concentration and purification steps. Currently in Europe, the alkaline cyanides are utilized most commonly for gold dissolution, although there are other lixiviants that are potential alternatives to cyanide leaching, such as thiosulphate, thiourea, ammonium polysulphides, iodine and chlorine. Some of these alternative reagents in relation to cyanides will be tested during the research. Additionally, the development and testing of the alternative and complementary mineral processing combination is relevant.

4.3 Mineralogical and chemical characterization

4.3.1 Characterization and sampling

The aim of this work is to study the key gold deposits in Northern Portugal, in order to obtain valuable information not only about mineralogy, but also on the geochemical behaviour of some elements (*e.g.* Ag, As, Cu, Pb, Zn) usually associated with gold. The better knowledge of the mineralogical and petrological features of these gold deposits would facilitate the knowledge and understanding of the regional distribution of gold deposits and to give useful information for processing.

For this task we developed field work and collected rocks samples in a selected Gold ore deposit from Lagares area (Castromil and Serra da Quinta) in Paredes Municipality (Northern Portugal) where Medgold Resources has an on-going exploration project.

During field work and observation of cores we collected representative samples of the ore and host rock (Figure 4.1 and Figure 4.2) not only from outcrops but also from drill cores from Medgold Resources.

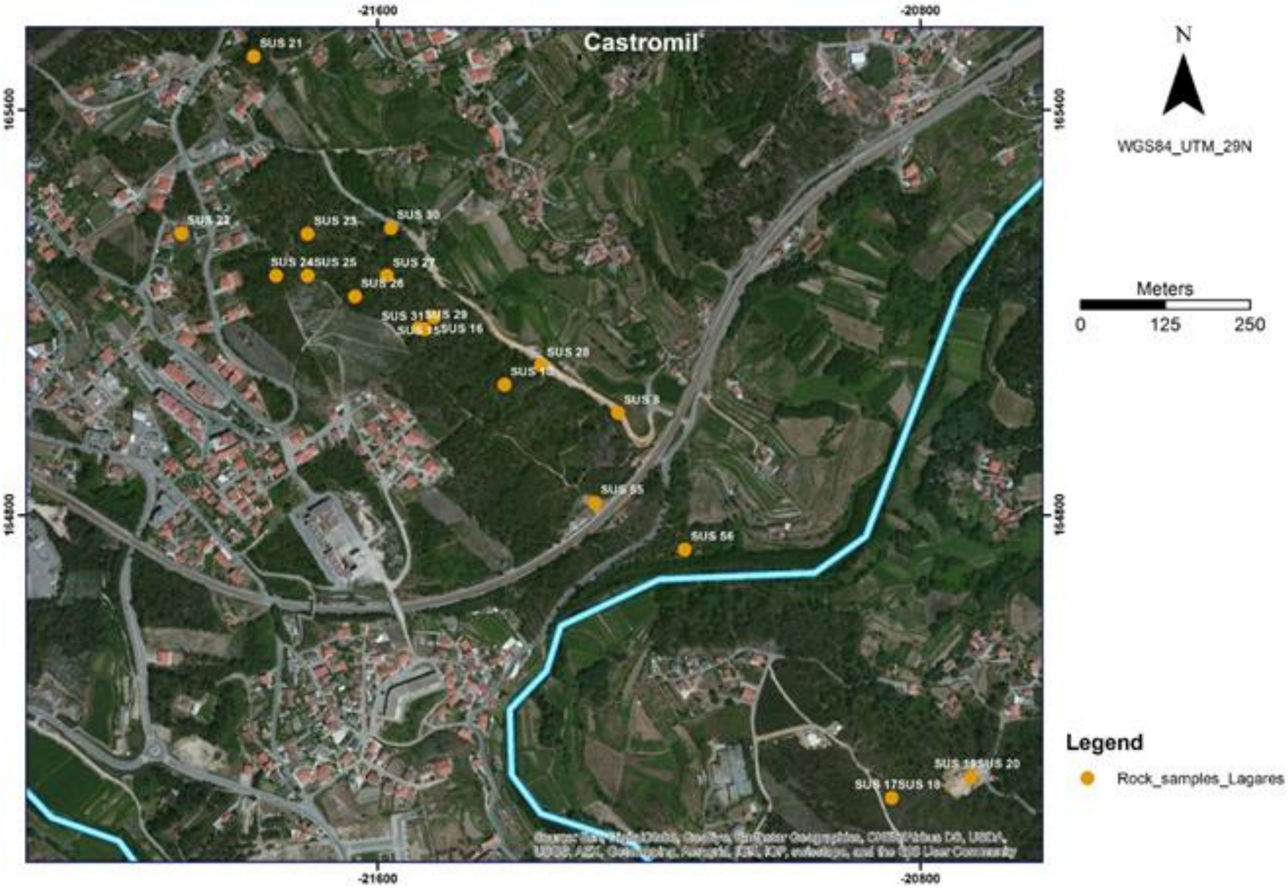
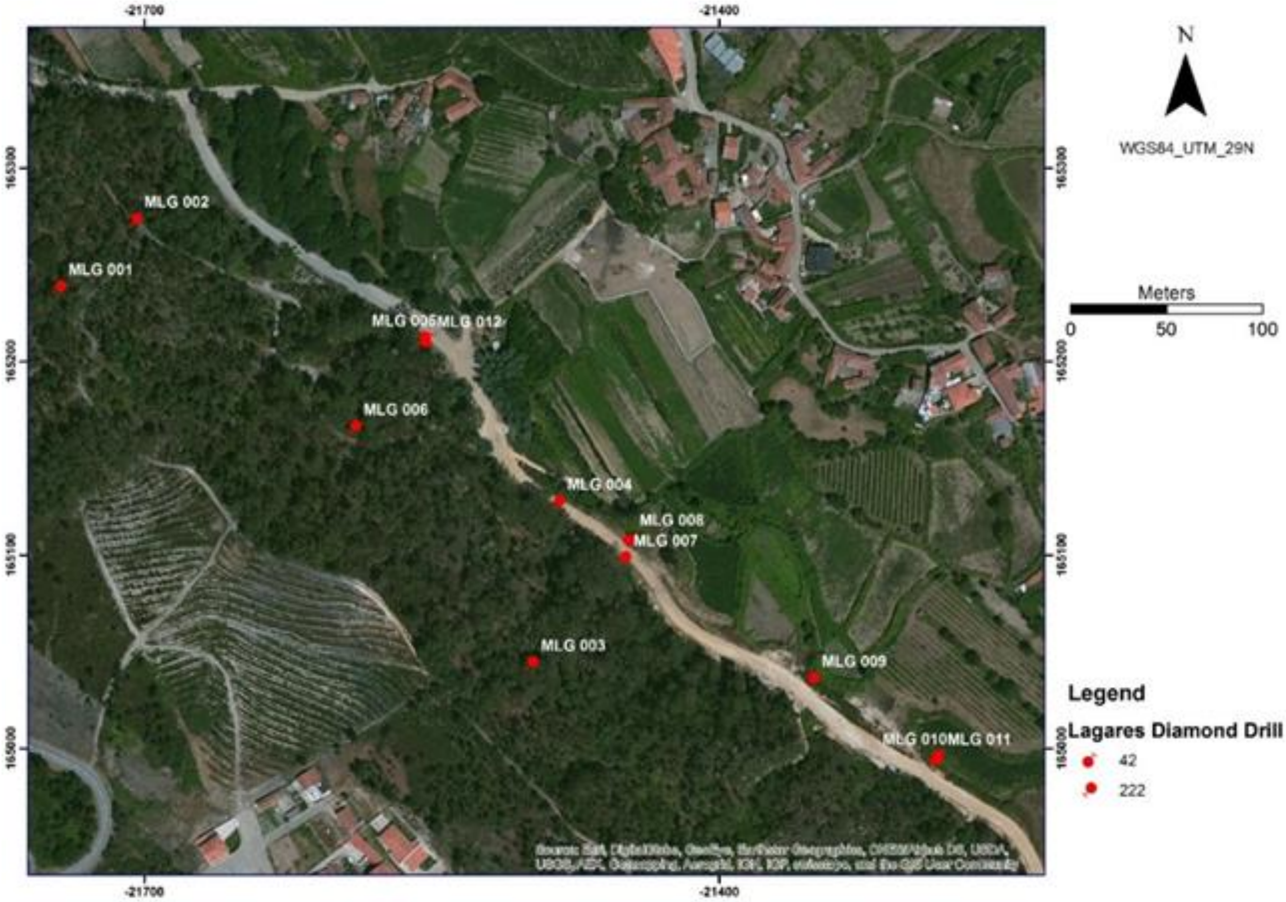


Figure 4.1. Sampling sites of Lagares.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 4.2. Diamond drill of Lagares

4.3.2 Sample preparation and mineralogy study

At the laboratory, the rock samples were firstly cleaned and examined in hand specimen. After this, some samples were selected for preparation of thick and thin sections, as well as, polished sections. The sample preparation and petrographic and metallographic studies were made at the Department of Geosciences, Environment and Spatial Planning (DGAOT) from Faculty of Sciences of University of Porto (FCUP). We prepared polished sections for metallographic study and thick sections for metallographic and/or petrographic studies of Lagares gold project (Table 4.1).

Table 4.1. Description of Lagares samples (PS – polished section; TkS – thick sections; ThS – thin sections; MS – metallographic study; PgS – petrographic study; SEM – Scanning electron microscope; D.C. – drill core; T1 – gold in fractures and/or grain boundary of sulphides; T2 - gold hosted in sulphides; T3 – gold hosted in oxides; n.o. – not observed).

ID	Sample Name	Type	Type of study	Depth	Au ppm (sample)	Au ppm (drill core)	Occurrence of Gold	Short description
SUS 7	CSQ-19	PS	MS+SEM	Surface			T3	Sample from gossan
SUS 8	CS-1	PS	MS+SEM	Surface			n.o.	Sample with Qz and sulphides
SUS 9	CSQ-30A	PS	MS+SEM	Surface			T3	Sample with sulphides
	CSQ-30B	PS	MS+SEM	Surface			T3	Schists from gossan
SUS 10	CS-10	PS	MS	Surface			n.o.	Sample with Qz and sulphides
SUS 16	MC-3	PS	MS+SEM	Surface			T1 (Py), T2 (Py), T3	Greisen with euhedral pyrite
SUS 19	PSQ-1	PS	MS	Surface			T3	Sample near to a fault (N 140º a N 160º); presence of sulphides
	PSQ-1a	ThS	PgS	Surface				Sample near to a fault (N 140º a N 160º); presence of sulphides
	PSQ-2	PS	MS	Surface			n.o.	Sample near to a fault (N 140º a N 160º); presence of sulphides
SUS 30	BIL-5	PS	MS	D.C. Billiton (30.50m)			n.o.	Granite breccia
SUS 31	BIL-9	PS	MS	D.C. Billiton (4.0m)			n.o.	Metasedimentary rock with micro-vein filled by iron oxides/ hydroxides
SUS 14	MC 7	TkS	MS/ PgS	Surface			n.o.	Greisen
SUS 15	MC 9-2	TkS	MS/ PgS	Surface			n.o.	Greisen
SUS 18	SQ a	TkS	MS/ PgS	Surface			n.o.	Greisen
	SQ b	TkS	MS/ PgS	Surface			n.o.	Greisen
SUS 22	PC 2	TkS	MS/ PgS	Surface			n.o.	Black schist
SUS 25	PC 5	TkS	MS/ PgS	Surface			n.o.	Breccia
SUS 26	MC 39	TkS	MS/ PgS	Surface			T3	Black schist
	MC 39-3	TkS	MS/ PgS	Surface			n.o.	Black schist
SUS 27	MC 51	TkS	MS/ PgS	Surface			T3	Greisen (aplite)
	MC 51-1	TkS	MS/ PgS	Surface			T3	Greisen (aplite)
	MC 51-2	PS	MS	Surface			n.o.	Greisen (aplite)
SUS 41	SQ 1	TkS	MS/ PgS	Surface			n.o.	Greisen
	SQ 3	PS	MS	Surface			n.o.	Greisen
SUS 55	SUS 55	PS	MS	Surface			n.o.	Sample with sulphides
SUS 56	SUS 56	TkS	MS	Surface			n.o.	Contact between granite and schist

ID	Sample Name	Type	Type of study	Depth	Au ppm (sample)	Au ppm (drill core)	Occurrence of Gold	Short description
SUS 59	SUS 59A	TkS	MS/ PgS	D.C. MedGold (77.95m)		2.35g/T Au from surface	n.o.	Volcanic-sedimentary rock with few opaque minerals (pyrite)
SUS 60	SUS 60A	TkS	MS/ PgS	D.C. MedGold (75.80m)		2.35g/T Au from surface	n.o.	Volcanic-sedimentary rock with disseminated opaque minerals (pyrite)
	SUS 60B	TkS	MS/ PgS	D.C. MedGold (75.80m)		2.35g/T Au from surface	n.o.	Volcanic-sedimentary rock with disseminated opaque minerals (pyrite)
SUS 62	SUS 62A	TkS	MS/ PgS	D.C. MedGold (19.55m)	0.22	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Granite (with feldspar mega-crystals)
	SUS 62B	TkS	MS/ PgS	D.C. MedGold (19.55m)	0.22	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Granite (with feldspar mega-crystals)
SUS 63	SUS 63A	TkS	MS/ PgS	D.C. MedGold (25.36m)	7.18	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Silicified granite with sulphides
	SUS 63B	TkS	MS/ PgS	D.C. MedGold (25.36m)	7.18	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	T1 (Apy)	Silicified granite with sulphides
SUS 64	SUS 64A	PS	MS/ SEM	D.C. MedGold (24.28m)	1.84	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	T1 (Py), T2 (Py w/ Ccp)	Silicified granite with sulphides
	SUS 64B	TkS	MS/ PgS	D.C. MedGold (24.28m)	1.84	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Silicified granite with sulphides
SUS 65	SUS 65A	PS	MS	D.C. MedGold (23.20m)	19.95	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Silicified granite with massive sulphides (Py, Gn, …)
	SUS 65B	TkS	MS/ PgS	D.C. MedGold (23.20m)	19.95	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Silicified granite with sulphides (Py, Gn)
SUS 66	SUS 66	TkS	MS/ PgS	D.C. MedGold (105.70m)	0.009	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Greisen (granite)
	SUS 66r	TkS	MS/ PgS	D.C. MedGold (105.70m)	0.009	4.45g/T Au from 10m; 22.57-23.40m has 19.95g/T	n.o.	Greisen (granite)
SUS 68	SUS 68	TkS	MS/ PgS	D.C. MedGold (29.80m)	0.03	4.40g/T Au from surface	n.o.	Aplite with sulphide vein
	SUS 68r	TkS	MS/ PgS	D.C. MedGold (29.80m)	0.03	4.40g/T Au from surface	n.o.	Aplite with sulphide vein
SUS 69	SUS 69A	TkS	MS/ PgS	D.C. MedGold (31.0m)	0.101	4.40g/T Au from surface	n.o.	Aplite with sulphides
	SUS 69Ar	TkS	MS/ PgS	D.C. MedGold (31.0m)	0.101	4.40g/T Au from surface	n.o.	Aplite with sulphides
	SUS 69B	PS	MS	D.C. MedGold (31.0m)	0.101	4.40g/T Au from surface	n.o.	Aplite with sulphides
SUS 70	SUS 70	PS	MS	D.C. MedGold (47.00m)	4.51	4.40g/T Au from surface	T1 (Py), T2 (Py)	Epithermal breccia with sulphides
SUS 71	SUS 71	PS	MS	D.C. MedGold (47.15m)	4.51	4.40g/T Au from surface	n.o.	Silicified granite with vein sulphide-richer

Complementary studies were performed using Scanning Electron Microscopy (SEM) and X-Ray Microanalysis (EDS) for characterization of gold ores at *Centro de Materials da Universidad do Porto* (CEMUP). The SEM/EDS exam was performed using a High Resolution Scanning Electron Microscope with X-Ray Microanalysis: JEOL JSM 6301F/ Oxford INCA Energy 350. Samples were coated with a C thin film, by vapour deposition, using the JEOL JEE – 4X Vacuum Evaporator equipment. X-ray intensities are measured by counting photons and the precision obtainable is limited by statistical error.

In order to obtain values of gold and silver contents in electrum particles analysis an Electron Microprobe (JEOL JXA 8500F) was used at National Laboratory of Energy and Geology and in Electron Microprobe (JEOL JXA-8200) at Faculty of Sciences of Lisbon University.

4.4 Metallographic results and short description

A special attention was given for three samples taken for Mineral Processing studies by FEUP with the references CSQ10, CSQ19 and CSQ30. These samples correspond to outcrop samples of three types of ores macroscopically identified and hosted by the regional granite. The first, a less oxidized sample quartz with sulphides (a “sulphide”), the second, a more oxidized gossan labelled CSQ19 (an “oxide”) and a third which is a mixture of both.

All the samples reveal identical mineralogical associations but different quantities of the main minerals.

We must also refer greisen because usually present when the host rock is granitic in composition (granite and/or aplite). It is mostly composed of quartz and white micas and show mineralogical and textural features resulting from the alteration of a granite protolith.

4.4.1 Gossan and hypogene minerals (sulphide and oxide)

The gossan samples reveal free gold associated with different iron oxides resulting from supergenic alteration and enrichment from hypogene minerals.

CSQ-30A and MC-3 shows gold mineralization and represent a mixture of primary sulphides and supergene minerals (oxides). These samples are characterized by pyrite, arsenopyrite, quartz and scorodite and goethite (supergenic minerals). Occasionally, we observed intergrowths with goethite and scorodite. Some pyrite crystals have inclusions of arsenopyrite, chalcopyrite, pyrrhotite, galena and lead. The gold appears hosted by scorodite, encapsulated in pyrite crystals or in fractures/ boundary grains of sulphides. MC-3 sample is important due to unusual association of gold with native lead.

The samples CSQ-19 and CSQ-30B was collected in “gossan” and the samples PSQ-1 and PSQ-2 in faults with sulphides (Nº 140 to N 160º). The mineralogy is similar and is characterized by scorodite and goethite associated with pyrite, arsenopyrite, bismuth, quartz (Figure 4.3). Some pyrite crystals have inclusions of chalcopyrite, pyrrhotite, galena and/or sphalerite (Figure 4.3).

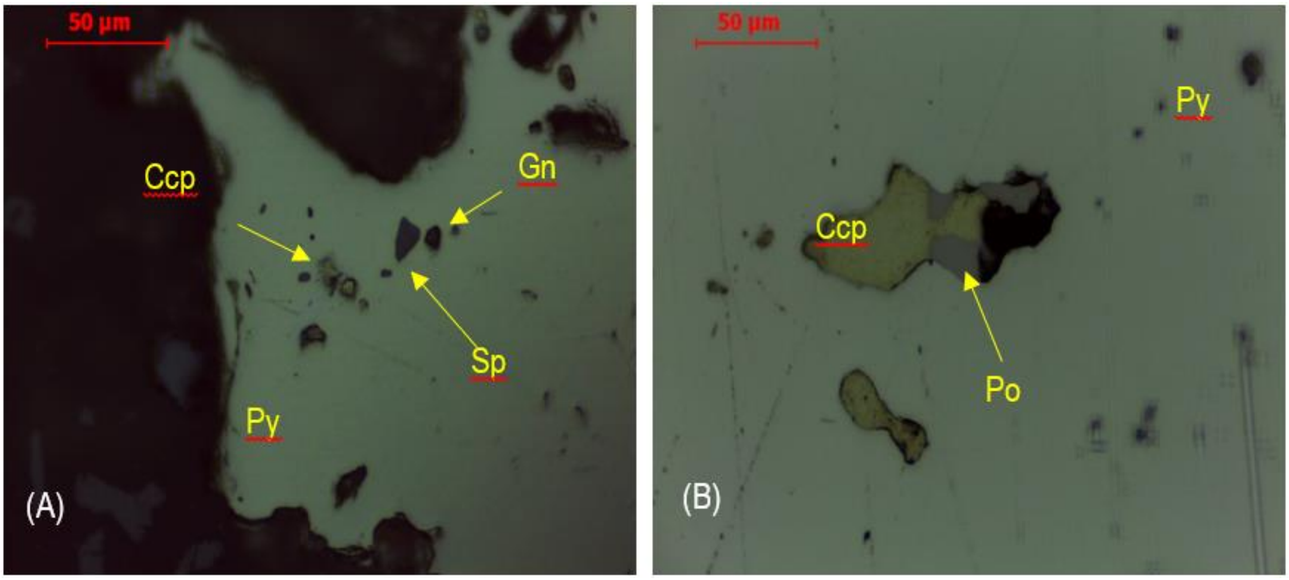


Figure 4.3. Photomicrographs of inclusions in pyrite: (A) sample CSQ-19 (Gn – galena; Sp – sphalerite; Py – pyrite; Ccp – chalcopyrite); (B) sample CSQ-30A (Ccp – chalcopyrite; Po – pyrrhotite; Py – pyrite).

The chalcopyrite, galena and sphalerite inclusions in pyrite of sample CSQ-19, was also observed in SEM (Figure 4.4).

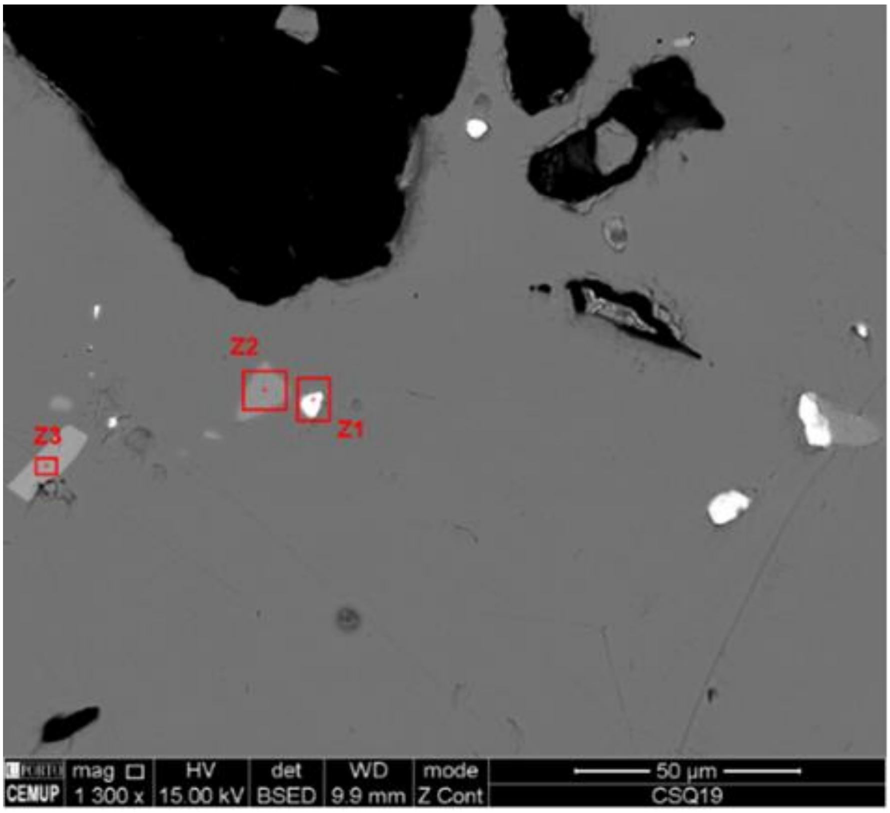


Figure 4.4. Photomicrographs by SEM of inclusions in pyrite in sample CSQ-19.

The samples MC 7, MC 9-2, MC 9-4, MC 51, MC 51-1 and MC 51-2 correspond to greisen where opaque minerals such as pyrite, arsenopyrite and goethite are present. Some analysis in SEM were made in sample MC 9-2 in order to obtain its semi-quantitative composition of arsenopyrite. We can find Interpenetration of scorodite with muscovite.

Arsenopyrite is frequently involved by scorodite and we find plumbogummite (Pb, Al, P oxide) associated with scorodite. The gold is hosted in goethite and scorodite (Figure 4.5).

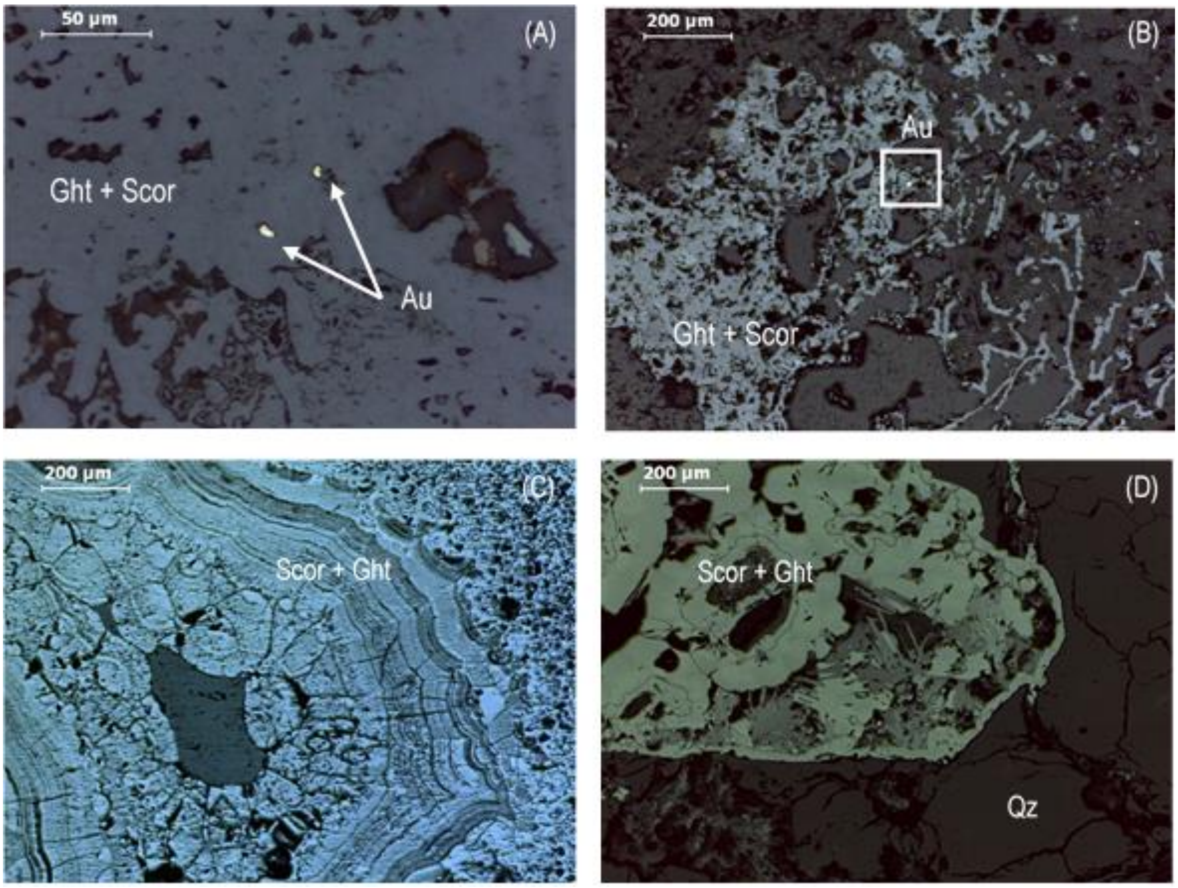


Figure 4.5. Photomicrographs of: (A) and (B) MC 51 sample (Ght - goethite; Scor – scorodite; Au – electrum/gold; (C) MC 51-1 sample and (D) MC 51-2 sample (Scor – scorodite; Ght – goethite; Qz - quartz).

The SUS 55 and SUS 56 samples have minerals like pyrite, arsenopyrite, chalcopyrite, and covellite. Some arsenopyrite crystals have hexagonal shape and has chalcopyrite, pyrrhotite and galena inclusions.

4.4.2 Sulphide samples

CSQ-10 is composed of pyrite, arsenopyrite, scorodite, goethite and quartz. Occasionally pyrite crystals has exsolutions of arsenopyrite, chalcopyrite, pyrrhotite and sphalerite. Gold was not observed in the studied sections (however the geochemical assay reveals 9.23 ppm).

Some arsenopyrites of sulphide rich samples were analysed with SEM in order to observe if the elementary composition of the mineral is constant. A constant composition was observed.

In March 2015**,** Medgold Resources started drilling at Lagares. Twenty-three polished or thick sections were made from the drill cores.

The granite or aplite (SUS 62A, SUS 63A, SUS 63B, SUS 64A and SUS 64B) have mostly pyrite and arsenopyrite crystals. Some pyrite crystals shown inclusions of Chalcopyrite, Pyrrhotite, Galena or Bismuthinite (Figure 4.6). The samples SUS 63B and SUS 64A contain small electrum grains. SEM analysis of samples SUS 63B and SUS 64A shows association with galena, bismuthinite and arsenopyrite (Figure 4.6).

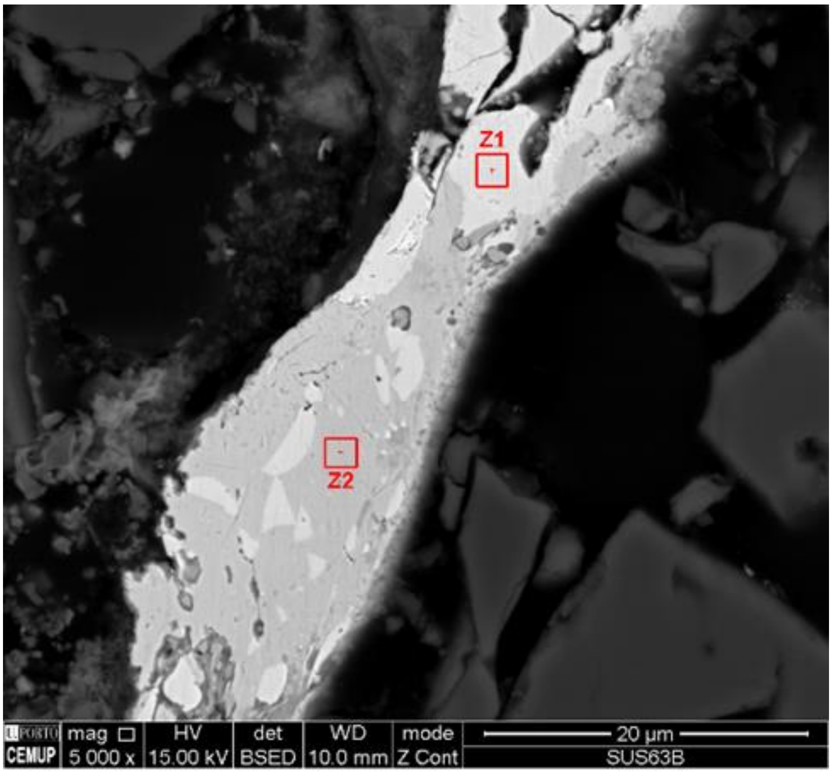


Figure 4.6. Photomicrograph by SEM of galena and bismuthinite (Z1) and arsenopyrite (Z2).

The SUS 65A, SUS 65B, SUS 65C and SUS 65CR samples is composed of greisen with sulphides (Fig 4.7A). The SUS 65A are sulphides-rich and have mostly pyrite, arsenopyrite and galena. In SEM analysis native bismuth in fractures filled by galena was observed (Figure 4.7B). The other samples has mostly pyrite and arsenopyrite (some of these has rhombus and/ or cubic shape). Some of pyrite crystals have inclusions of other minerals, like galena and chalcopyrite, as well as arsenopyrite relicts. The electrum/gold particles appear in the samples SUS 65B, SUS 65C and SUS 65CR (Figure 4.8).

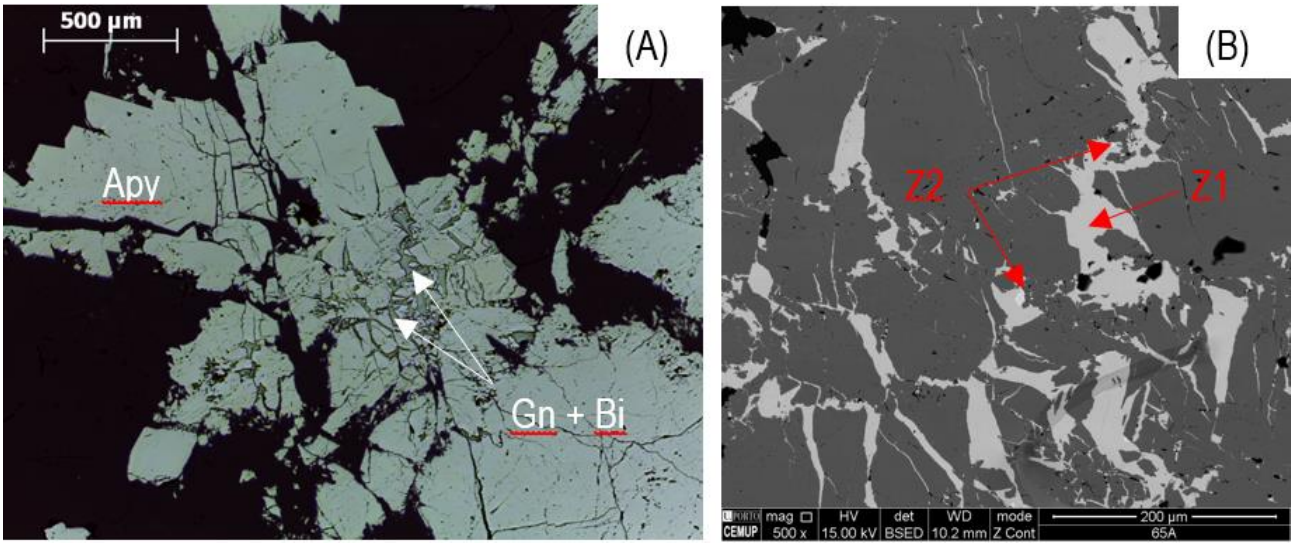


Figure 4.7. Photomicrographs of SUS 65A sample (Apy – arsenopyrite; Gn – galena; Bi – native bismuth).

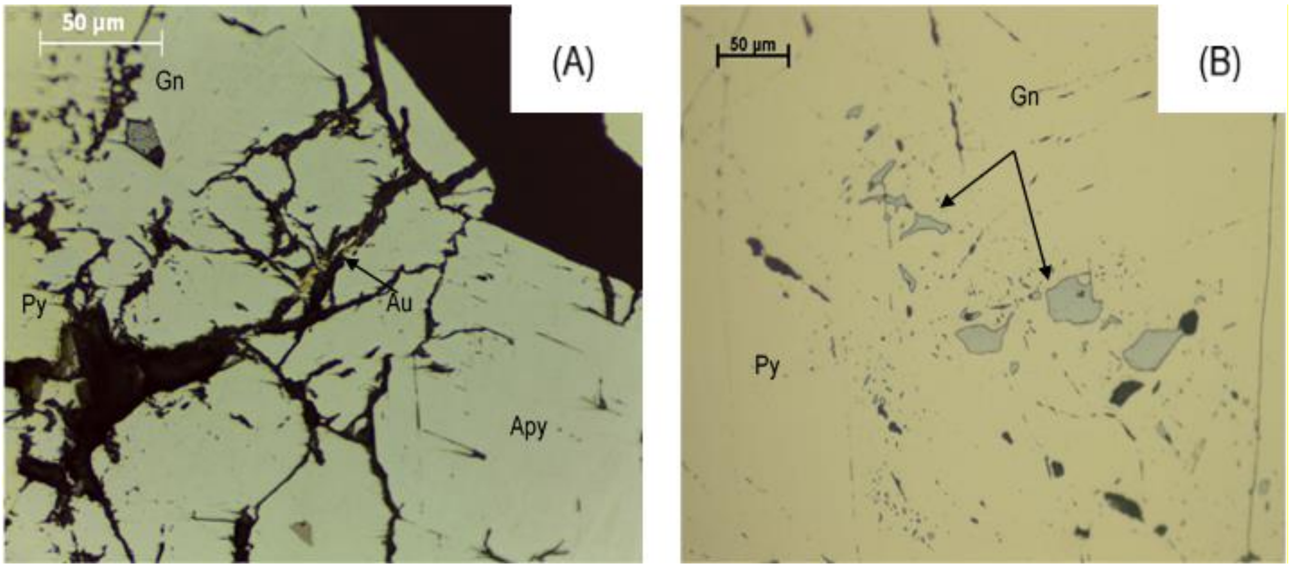


Figure 4.8. Photomicrograph of samples SUS 65C (A) and SUS 65Cr (B) (Gn – galena; Au – electrum/ gold; Apy – arsenopyrite; Py – pyrite).

The samples SUS 66 and SUS 66R, from greisen, and SUS 68, SUS 68R, SUS 69A, SUS 69AR and SUS 69B, from sulphide vein in aplite, have few opaque minerals. These samples have a pyrite micro-vein with inclusions of galena, chalcopyrite, galena ± chalcopyrite, sphalerite, pyrrhotite and/or chalcopyrite ± pyrrhotite ± bismuthinite (Figure 4.9). Some of pyrite crystals have a euhedral shape.

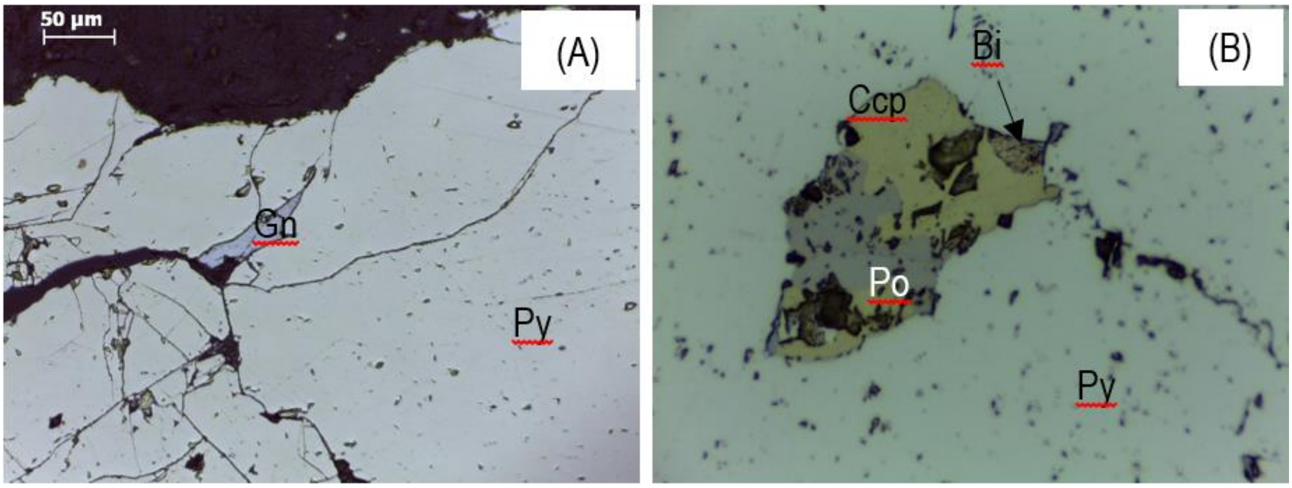


Figure 4.9. Photomicrographs of samples: (A) SUS 66R (Gn – galena; Py – pyrite); (B) SUS 69Ar (Bi – native bismuth; Ccp – chalcopyrite; Po – pyrrhotite; Py – pyrite)

The SUS 70 and SUS 71 samples are from an epithermal breccia with sulphides and greisenised granite with vein sulphide-rich respectively (Figure 4.10). They have mostly pyrite and arsenopyrite crystals and some pyrite crystals have galena and pyrrhotite inclusions. The galena appears to be filling arsenopyrite fractures. The gold mineralization appears in SUS 70 sample.

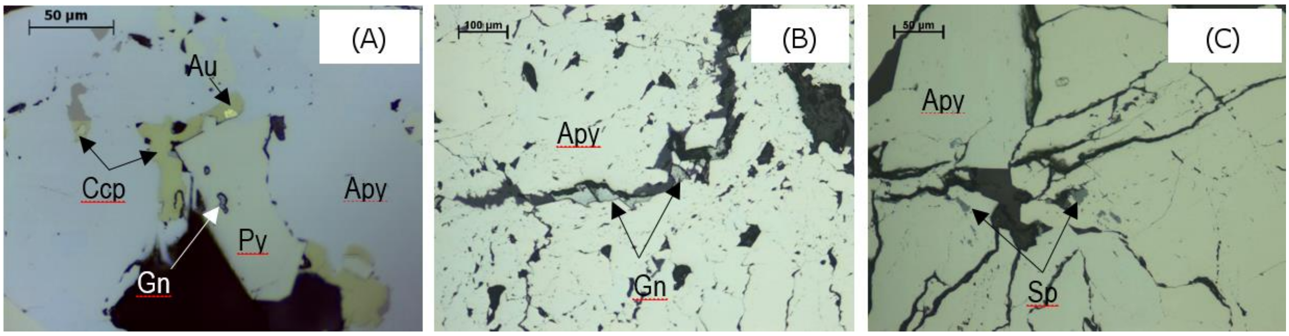


Figure 4.10. Photomicrographs of: (A) SUS 70 sample; (B) and (C) SUS 71 (Ccp – chalcopyrite; Au – electrum/ gold; Py – pyrite; Gn – galena; Apy – arsenopyrite; Sp – sphalerite).

4.5 Gold: nature and occurrence

The present study of the CSQ10, CSQ19 and CSQ30 ore samples confirms precedent studies done by Anamet Services in 1996. “The gold can occur in three ways: primary metallic gold, supergene gold and refractory gold”. According Anamet Services (1996) there are individual particles of gold, with size under 50 µm (fine grained) and tend to occur in clusters of larger particles, one of them being goethite aggregates. It can be also present in discrete stringers or extended bodies, sometimes reflecting prior fractures. The presence of a high proportion of this fine type of gold indicates that it is appropriated to leaching tests. Small particles of electrum (a mixture of gold and silver) can be found growing among scorodite and it is believed that they grow the same way, with the electrum becoming enclosed within arsenopyrite. Figure 4.11 shows this relationship on a computer enhanced electron image as well as the appearance of a cluster of small electrum (yellow) within the scorodite (greenish blue).

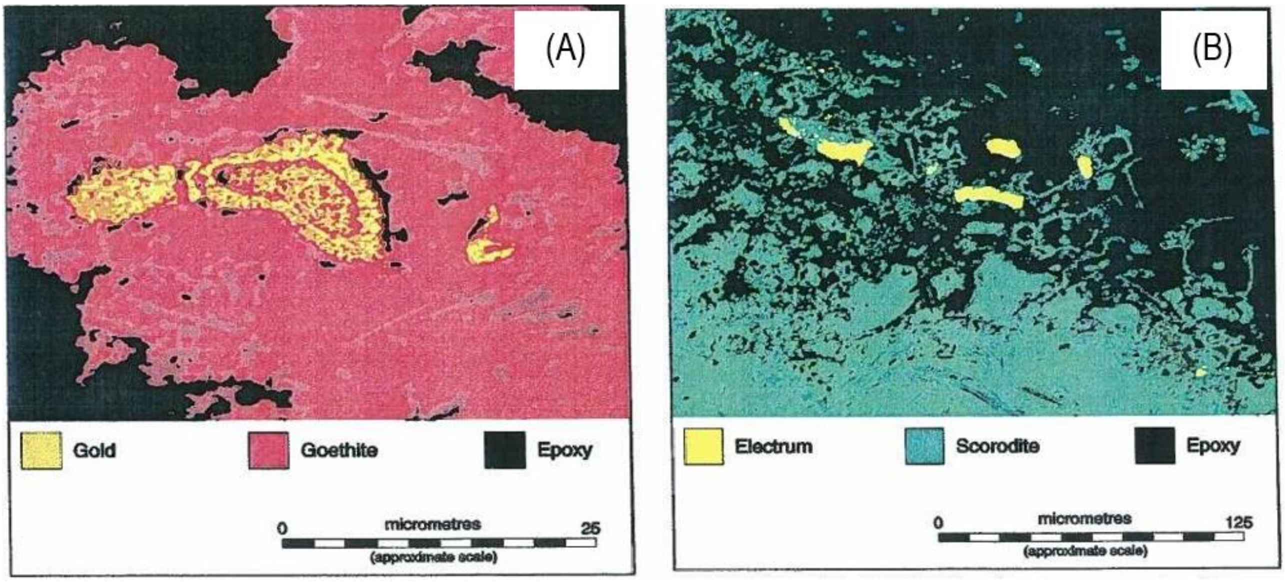


Figure 4.11. Photomicrographs of (A) Gold-goethite relationship and (B) Electrum-scorodite relationship (Anamet Services 1996).

Supergene gold is also found growing within the goethite and developed within the oxidation zone. The remaining refractory gold is abridged within the arsenopyrite and pyrite and it is less than 5% of the total and it occurs in the form of small gold and electrum particles but it also can be attached to quartz.

In the sulphide sample, “the complex nature of the Au-bearing particles may be the result of the decomposition of electrum: it decomposes in oxide environments to form metallic gold, silver halide minerals and silver bearing sulphides. The metal gold might nucleate, forming very irregular and porous aggregates” (Anamet Services 1996).

In conclusion, different electrum/ gold occurrence modes were observed:

1. hosted in iron oxides (Figure 4.12)
2. encapsulated in sulphides (Figure 4.13)
3. included in quartz and in sulphides filling latter fractures or in grain boundaries (Figure 4.14).

The boxwork structures developed in gossan indicate the pre-existing sulphide mineralogy. Presence of gold in gossan is still quite conspicuous and the values interestingly above 2.07 g/T with an average value of about 4.02 g/T (Medgold 2016).

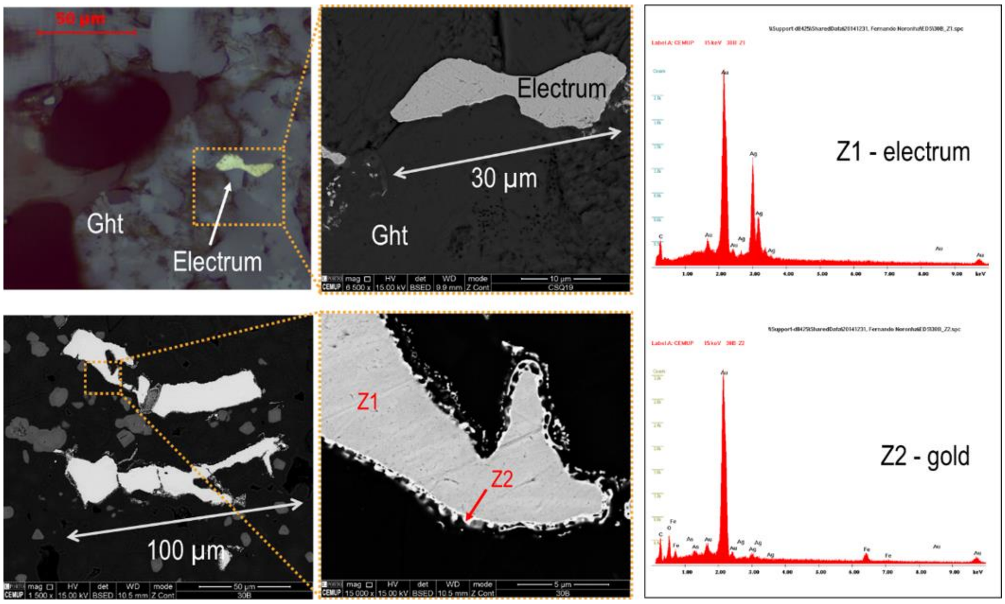


Figure 4.12. Photomicrographs of electrum/gold particles hosted in goethite and EDS spectra of electrum (Z1) and gold (Z2) (Ght – goethite).

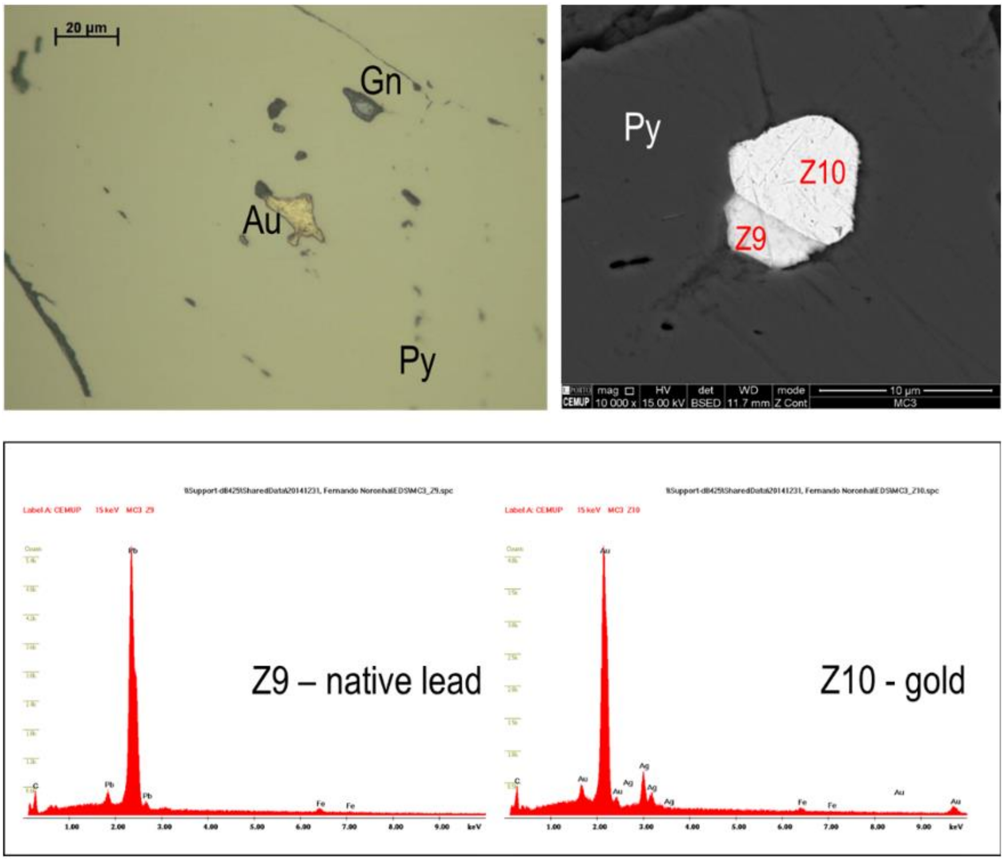


Figure 4.13. Photomicrographs of electrum/gold particles encapsulated in sulphides and EDS spectra of lead (Z9) and gold (Z10) (Gn – galena; Au – native gold; Py – pyrite).

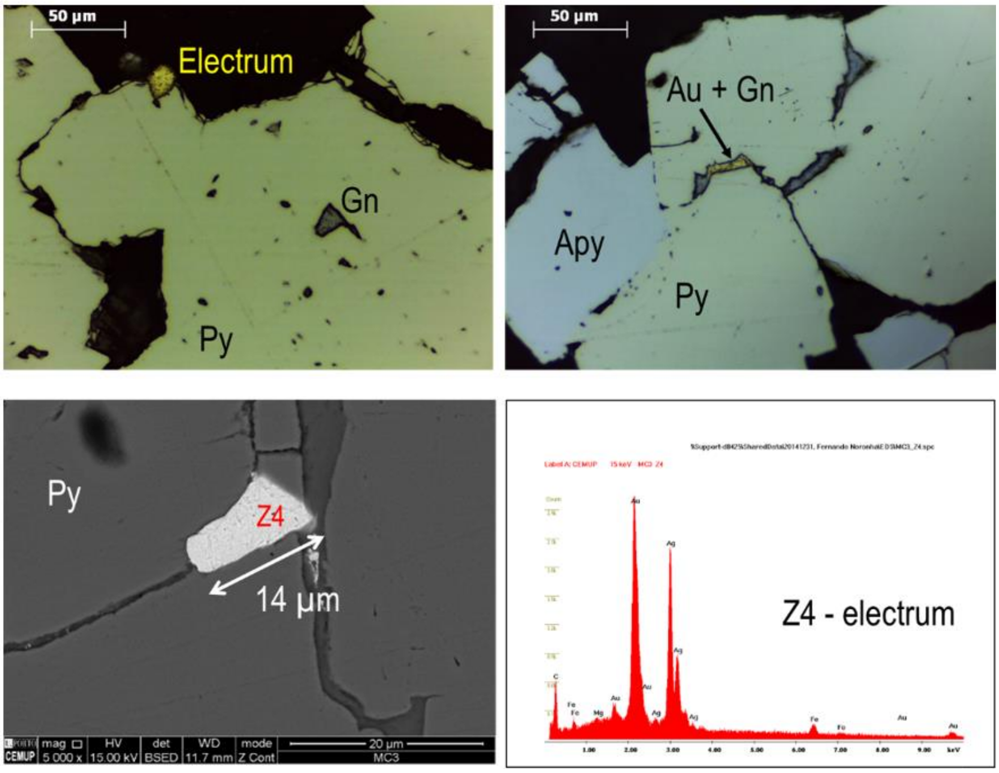


Figure 4.14. Photomicrographs of electrum/gold particles filling latter fractures or in grain boundaries and EDS spectra of electrum (Z4) (Gn – galena; Py – pyrite; Apy – arsenopyrite; Au – electrum/gold).

4.6 Chemical characterization

4.6.1 Semi-quantitative and/or quantitative analyses in gold particles

The SEM-EDS and WDS study of gold particles reveal particles with different contents of Ag (Table 4.2), which allow to conclude the presence of native-gold and electrum particles. The particles encapsulated in sulphides are poorer in Ag (20.43-25.17%) than particles hosted in sulphide fractures or in grain boundaries (37.46-51.45%). In gossan, the referred two main types of particles can be found and are assumed as hypogene in origin, however a supergenic enrichment of these particles can be observed by latter deposition of native-gold (<16.11% Ag). Native-gold in gossan is associated with poorly crystallized iron oxides. The supergene formation enriched in gold results from the mobilization and re-precipitation of this metal.

Table 4.2. WDS data and mean values of Au and Ag contents in auriferous particles

Depth	**Host rock**	**Gold occurrence**	**Mean values**	
			Au	**Ag**
Outcrop	Granite (Serra da Quinta)	Electrum in FeOx	43.07	50.21
Outcrop	Schists (Serra da Quinta)	Electrum in FeOx	58.76	40.76
Outcrop	Greisen (Covas de Castromil)	Electrum in FeOx	54.9	44.83
Outcrop	Greisen (Covas de Castromil)	Au in Py	77.44	20.43
Outcrop	Greisen (Covas de Castromil)	Au+Pb in Py	85.04	15.5
Outcrop	Greisen (Covas de Castromil)	Au in fractures	53.09	43.95
Outcrop	Aplite (Covas de Castromil)	Electrum in FeOx	54.4	43.85
Collected at 23.20m from drill core	Silicified granite (Covas de Castromil)	Electrum in Py	55.35	25.17

4.6.2 Chemical analyses

The three samples CSQ10, CSQ 19 and CSQ30 are similar when referring to mineralogical composition and appearance. However, the degree of mineralization is variable, dominated by rich phases of iron, with greater amounts of primary sulphide minerals on the CSQ10 than on the CSQ19 and CSQ30 samples.

Regarding the primary ore minerals, the weathering transform the main hypogene sulphides, which becomes oxidized and decomposed, with their ions being removed by water or re-precipitated.

The three samples were analysed at ALS Laboratory Group, S.L on February of 2015. The chemical composition is given in Table 4.3.

Table 4.3. Chemical Composition of Castromil Samples.

Element	Sulphid Ore CSQ10	Oxidized Ore CSQ19	Mix Ore CSQ30	Element	Sulphide Ore CSQ10	Oxidized Ore CSQ19	Mix Ore CSQ30
Al (%)	0.32	0.86	0.8	Na (%)	0.01	0.01	0.01
B (ppm)	<10	<10	<10	Ni (ppm)	1	10	12
Ba (ppm)	70	220	180	P (ppm)	370	2950	2610
Be (ppm)	<0.5	4.4	3.1	Pb (ppm)	3490	5620	>10000
Bi (ppm)	94	175	187	S (%)	4.51	0.41	0.41
Ca (%)	0.01	0.01	0.01	Sb (ppm)	48	112	148
Cd (ppm)	<0.5	3.2	2.3	Sc (ppm)	1	1	1
Co (ppm)	<1	3	1	Sr (ppm)	5	19	19
Cr (ppm)	6	18	49	Th (ppm)	<20	<20	<20
Cu (ppm)	94	379	320	Ti (%)	<0.01	<0.01	<0.01
Fe (%)	9.47	20.4	14.65	Tl (ppm)	<10	<10	<10
Ga (ppm)	<10	<10	<10	U (ppm)	10	40	20
Hg (ppm)	<1	2	1	V (ppm)	41	97	91
K (%)	0.12	0.15	0.13	W (ppm)	<10	<10	<10
La (ppm)	10	10	10	Zn (ppm)	4	90	69
Mg (%)	<0.01	0.01	0.01	As (%)	1.91	3.4	1.76
Mn (ppm)	38	32	43	Ag (ppm)	52.8	38.1	>100
Mo (ppm)	<1	28	88	Au (ppm)	9.23	15.75	149.5

It is concluded from chemical composition that the oxidized sample consists of materials derived from the surface weathering, resulting in low sulphur content (0.41), which on the sulphide sample is much greater (4.51). It is also observable that the ”mixed ore” has much more gold than the “sulphide” sample (149.5 against 9.23 ppm) confirming supergene gold enrichments formation resulting from mobilization and re-precipitation of this metal (Figure 4.12).

The high values of As, Pb and Bi indicates that As-bearing phases such as arsenopyrite, galena, lead oxides and native bismuth are present in all samples.

A significant degree of ferruginisation is explained by former Fe-rich phases such as pyrite and arsenopyrite exhibiting replacement by goethite.

Goethite aggregates commonly display a moderate degree of porosity, being very permeable, a detail with enormous importance considering leaching tests – these spaces can enclose small gold particles. It is considered to be the dominant phase in the heavy mineral concentrates, intergrowing with quartz and muscovite.

4.7 Development of mineral processing to concentrate selectively different gold bearing minerals

4.7.1 Preparation of the samples – CSQ10 and CSQ30 Castromil Ore

Initially the size reduction step for the collected samples has conceived. A jaw crusher and a roll crusher were used to crush the samples named as CSQ10 and CSQ30. After that, the material was quartered and kept in stock. Figure 4.15 details the particle size analysis for each type of ore.

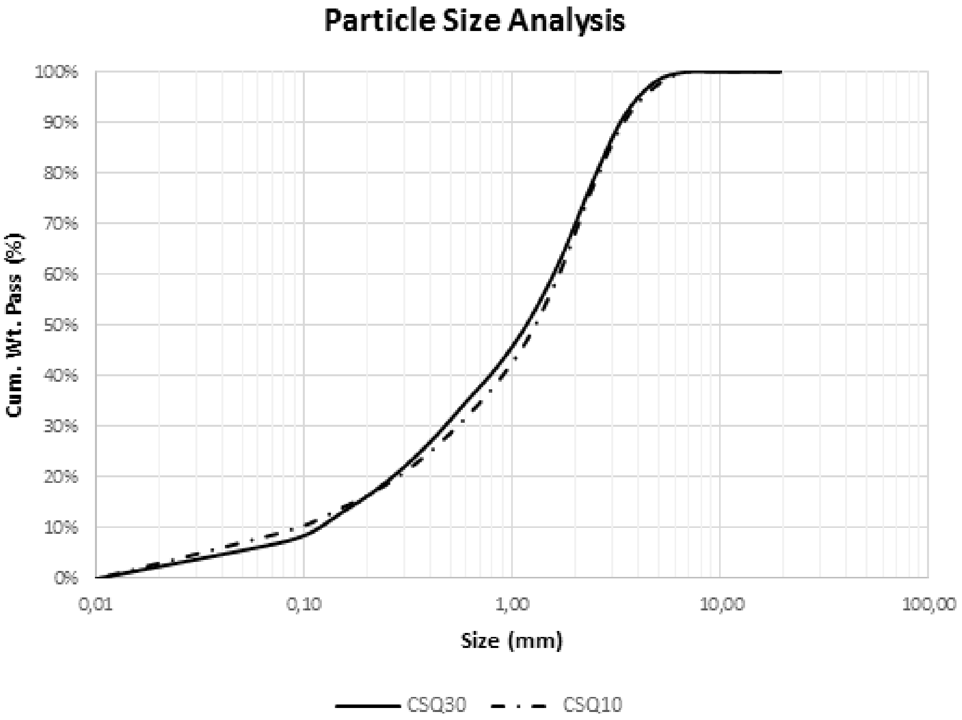


Figure 4.15. Particle size analysis after roll crusher

Analysing Figure 4.15, for both ore samples the d_{80} was 2.36 mm. To carry out these experiments, the particle size should be considerable smaller than 74µm. The material coarser than this limit was then re-grinded by a cutting mill and a vibratory disc mill. Figure 4.16 represents the particle size analysis for each type of ore. The particle size distribution of the final lots were determined with a laser diffraction particle size analyser (Mastersizer 2000).

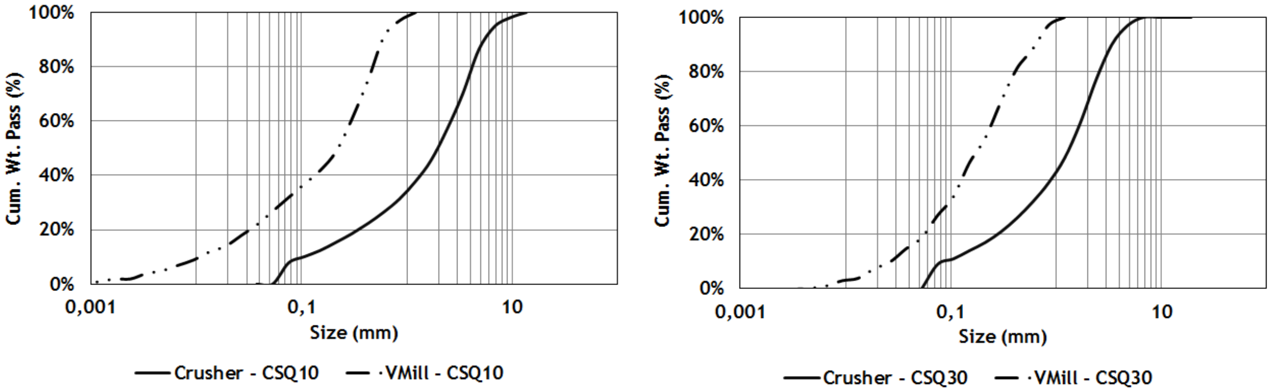


Figure 4.16. Particle size analysis after vibratory mill

It is possible to conclude that size reduction carried out using a roll crusher, a cutting mill and a vibratory disc mill is suitable to obtain a grain size appropriate for leaching, because all material is below 0.2 mm.

4.7.2 Experimental Methodology - Pre-concentration stages

As stated previously, a pre-concentration process was thought of using gravity separation (jig and shaking table) and flotation (Figure 4.17). For the samples CSQ10 and CSQ30, the same process sequence was applied because they are low-grade ores. For the CSQ19, a higher-grade ore, the pre-concentration stage is not mandatory. A new size reduction was carried out with an attrition mill to obtain suitable grain size for the leaching. This last material was also used to perform gravity (only shaking table) and flotation tests.

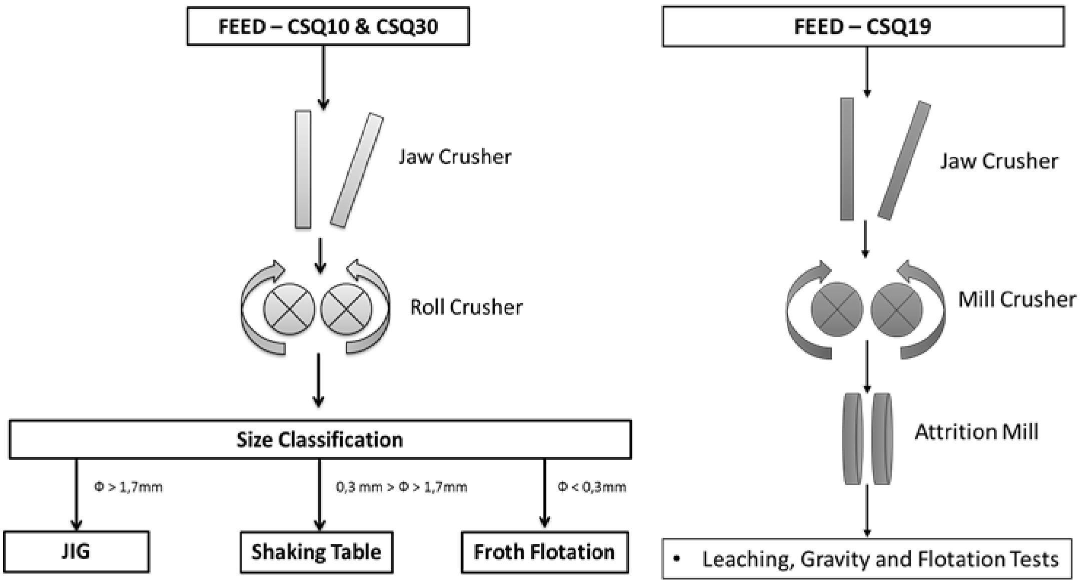


Figure 4.17. Mineral processing diagram for CSQ10, CSQ30 and CSQ19 ore

4.7.2.1 *Pre-concentration stage*

As the oxidized gold ore, CSQ19, is easier to leach and has a higher gold grade than others it does not require any pre-concentration stage. Nevertheless, a test with a shaking table was performed, but the results were not efficient enough to justify a pre-concentration stage before leaching. It was possible to observe the presence of a large quantity of quartz grains in the concentrate of the Wilfley shaking table. The test was carried out with different conditions (inclination and water feed rate).

After the Wilfley test a gravity separation was carried out at laboratory scale using a Mozley separator, performed on the middling and the concentrate of the Wilfley table to ensure that the gravity pre-concentration was not suitable for CSQ19 ore. The results obtained are better than the previous ones, but not good enough to achieve an acceptable pre-concentrate. Pictures of the pre-concentrate were taken with a magnifier (Figure 4.18).

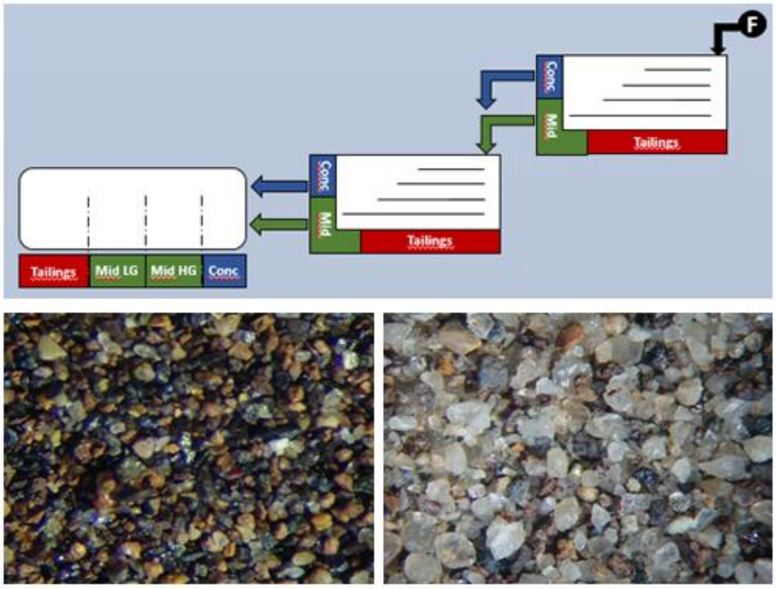


Figure 4.18. Gravity pre-concentration for CSQ19

The following conclusion were obtained:

- The result obtained with the Wilfley table was not as good as expected. It is hard to obtain differentiable products. The concentrate and middling include a lot of quartz grains, which should be included in the tailings.
- With the Mozley table it was possible to obtain a cleaner concentrate (with lower quantity of quartz grains), but also with more losses to middling and tailings.

After that, some flotation tests were performed to assess the feasibility of flotation to concentrate gold. As stated before, flotation could be seen as a pre-concentration stage, although, due to the high gold content of CSQ19 ore, flotation could be the principal method for gold processing in this case. Different reagents and flotation conditions were applied in some exploratory tests, in order to identify suitable conditions for gold flotation. Higher gold recoveries were obtained with collectors D571 (DANAFLOAT) – Test D and AEROPHINE (CYTEC) – Test C, with pH lower than 4.5. These results (Table 4.4) showed that flotation could be a potential to process the Castromil Gold ore. A more detailed study is needed.

Table 4.4. Froth flotation results

ID Lab	**Sample**	**Grade by XRF**					**Recovery**					
		Fe (%)	**As (%)**	**Pb (%)**	**Cu (%)**	**Au (%)**	**Ag (%)**	**Fe (%)**	**As (%)**	**Pb (%)**	**Cu (%)**	**Au (%)**
C1	Conc1	26.96	3.28	2.66	0.70	0.08	0.09	3.63	3.88	5.01	17.07	16.04
C2	Conc2	26.10	3.20	2.52	0.55	0.07	0.08	2.64	2.84	3.56	9.99	10.14
C3	Conc3	16.93	2.19	1.55	0.15	0.02	0.02	14.83	16.84	18.96	23.77	19.07
C4	Tail	12.77	1.41	0.84	0.04	0.01		78.89	76.44	72.47	49.17	54.74
C4	Feed	13.72	1.56	0.98	0.08	0.01						
D1	Conc1	26.93	2.95	2.04	0.06	0.20	0.25	3.22	3.26	3.57	5.40	37.54
D2	Conc2	26.23	3.14	2.54	0.05	0.04	0.05	7.42	8.20	10.51	10.48	15.97
D3	Tail	13.68	1.47	0.90	0.02	0.01		89.35	88.55	85.92	84.12	46.49
D3	Feed	14.42	1.56	0.99	0.02	0.01						

4.8 Investigation of alternatives to cyanide leaching

4.8.1 Introduction

Three leaching reagents were selected: cyanide, for comparison purposes, thiosulphate and bromine, as alternatives.

Cyanide leaching was carried out directly to the reaction vessel with the addition of solid sodium cyanide (NaCN). All tests were carried out with a solid/liquid ratio equal to 1. The pulp was added to the reactor and kept into suspension with a mechanical stirrer. After 1 hour of stirring the sodium cyanide was added. The cyanide concentration in the liquid phase was analysed during the test with a cyanide electrode. Liquid samples were collected at 6h, 12h and 24h.

The thiosulphate leaching tests developed for this study were carried out with the following commercial chemicals: Sodium thiosulphate ($Na_5S_2O_3•5H_2O$), ammonia water (NH_4^+) (28%) and cupric sulphate ($CuSO_4•5H_2O$). Thiosulphate and cupric sulphate were dissolved in demineralized water. They were mixed and ammonia was added to obtain the final leaching solution. Finally, the solution and the ore were inserted into the leaching vessel. It is important to note that the referred concentrations for thiosulphate and copper are related to $Na_5S_2O_3•5H_2O$ and $CuSO_4•5H_2O$. To simplify, they will be respectively referred as thiosulphate and copper concentrations.

A few thiosulphate leaching experiments were carried out initially, in order to determine the best dosage for the chemicals referred above. Reactions were performed in a 1 l borosilicate cylindrical vessel with hemispherical bottom using an agitator Heidolph RZR 2021. The solid/liquid ratio was 40%, and the leaching was performed at room temperature for 7 hours.

Bromine is toxic, causes burns and blisters on the skin, and has a low boiling point (59.5°C) and consequently dangerous to store and handle. Because of that, an alternative method to produce a bromine solution from sodium hypochlorite was tried. Thus, the solution was prepared with the addition of 30 ml (21mmol) of sodium hypochlorite (5.25%, BIOCHEM) to a solution of 4.4 g (43 mmol) of sodium bromide (99%, ACROS) in 42 ml (42 mmol) of 1M hydrochloric acid (35-38%, BIOCHEM) and 28 ml water to produce an aqueous solution of bromine of 3.4 g or 0.021 mol/100 ml, according to the following reaction:

$$2NaBr + NaOCl + 2HCl \rightarrow Br_2 + 3NaCl \cdot H_2O \tag{4.1}$$

Another possibility was the usage of hypochlorous acid with simultaneous formation of chlorine and bromine. Both are gold leaching regents. The reactions are following:

$$2HOCl + 2HCl \rightarrow 2Cl_2 + H_2O \tag{4.2}$$

$$2 * (2NaBr + Cl_2 \rightarrow 2NaCl + Br_2) \tag{4.3}$$

$$2Au + 3Br_2 \rightarrow 2AuBr_3 \tag{4.4}$$

$$2AuBr_3 + 3Cl_2 \rightarrow 2AuCl_3 + 3Br_2 \tag{4.5}$$

All bromine leaching tests were conducted using a 500 ml DURAN reaction vessel, placed in a heating mantle with stirring provided by a Heidolph RZR 2021 agitator. The ore was added to the reactor followed by the water, hydrochloric acid, sodium hypochlorite and finally the sodium bromide. After that, the agitator and heating mantle were turned on to start the tests. All tests were carried out at natural pH (3-4). At the end of residence time, the agitator and the heating mantle were turned off. The reactor was removed from the heating mantle and allowed to cool for 30 minutes at room temperature. After that, the pulp was immediately filtered to obtain the leaching liquor. Then, the residue was re-pulped and filtered once more for washing purposes, prior to final drying. Thus, three products were obtained: a leaching liquor (liquid), a washing solution (liquid) and a residue (solid). The gold content of the liquid solution was analysed with an atomic absorption spectrophotometer. The residues were analysed with a portable X-ray Fluorescence X-MET7500 Mining Analyser, to determine the content of main elements Fe, As, Pb, K, etc.

4.8.2 Cyanide Leaching

A sample of ore from the oxidized zone was leached under the same operating conditions in order to obtain a standard for comparisons. In order to get a standard for comparison of methods, a sample of ore from the oxidized zone was considered for cyanide leaching under the same operating conditions as in the tests that were performed in previously. The sample was designated as CSQ19, classified as ore from oxidized zone, consisted of quartz, disperse sulphides and its products of oxidation, pyrite, chalcopyrite, pyrrhotite, goethite, galena, quartz and with a high grade in gold. It was collected at a gallery in the gossan zone. The liquid phase (the leach liquors) were sampled after 6, 12, 18 and 24 hours and subsequently analysed Table 4.5.

Table 4.5. Cyanide Leaching – Results

	24 hours	12 hours
1st sample		
Leach liquor, Au Concentration [mg/L]	65	62
2nd sample		
Concentration, [mg/L]	84	66
3rd sample		
Concentration, [mg/L]	75	44
Final		
Grade Au [g/t]	19	19
Leach liquor, Volume [L]	0.205	0.215
Leach liquor, Au Concentration [mg/L]	141	67
1st washing		
Volume of solution, [L]	0.22	0.21
Concentration, [mg/L]	34	19
Recovery based on solid phase (%)	79.35	79.35
Recovery based on liquid phase (%)	132.16	85.87

The calculation of the recovery, based on the sampling of the liquid phase, takes into consideration the volumes of the samples that were taken off from the reactor. There is an evident error in the chemical analysis of the sample that was collected after 24 hours, responsible for the final recovery calculated based on the liquid phase. Unfortunately, it was not possible to repeat the determination. The time evolution of the concentrations and corresponding calculations for the first sample are shown in Table 4.6 and for the second test, run in parallel, the results and calculations are shown in Table 4.7.

Table 4.6. Kinetics of leaching (Sample CN_1)

SRS5	**CN_1**					
Time (h)	**Liquor inside the reactor (L)**	**Concentration (mg/kg)**	**Metal Content (mg Au)**	**MQ by stage (mg Au)**	**Au Recovery (mg)**	**Cumulative recovery (%)**
FEED	0.3	92	27.6			
0	0.3	0	0	0	0	0.00
6	0.3	65	19.5	3.25	19.5	70.65
12	0.25	84	21	4.2	24.25	87.86
18	0.2	75	15	3.75	22.45	81.34
24	0.125	141	17.625	17.625	28.825	104.44
Wash	0.225	34	7.65	7.65	36.475	132.16
Residue	0.3	19	5.7			79.35

Table 4.7. Kinetics of leaching (Sample CN_2)

SRS6 **Time (h)**	**CN_2** **Liquor inside the reactor (L)**	**Concentration (mg/kg)**	**Metal Content (mg Au)**	**MQ by stage (mg Au)**	**Au Recovery (mg)**	**Cumulative recovery (%)**
FEED	0.3	92	27.6			
0	0.3	0	0	0	0	0.00
6	0.3	62	18.6	3.1	18.6	67.39
12	0.25	66	16.5	3.3	19.6	71.01
18	0.2	44	8.8	2.2	15.2	55.07
24	0.14	67	9.38	9.38	17.98	65.14
Wash	0.22	26	5.72	5.72	23.7	85.87
Residue	0.3	19	5.7			79.35

Recoveries based on the solid phase are the same while there is a difference in the concentrations of the liquid phase, especially after 24 h. The time evolution of the recovery based on liquid phase for both tests is presented in Figure 4.19.

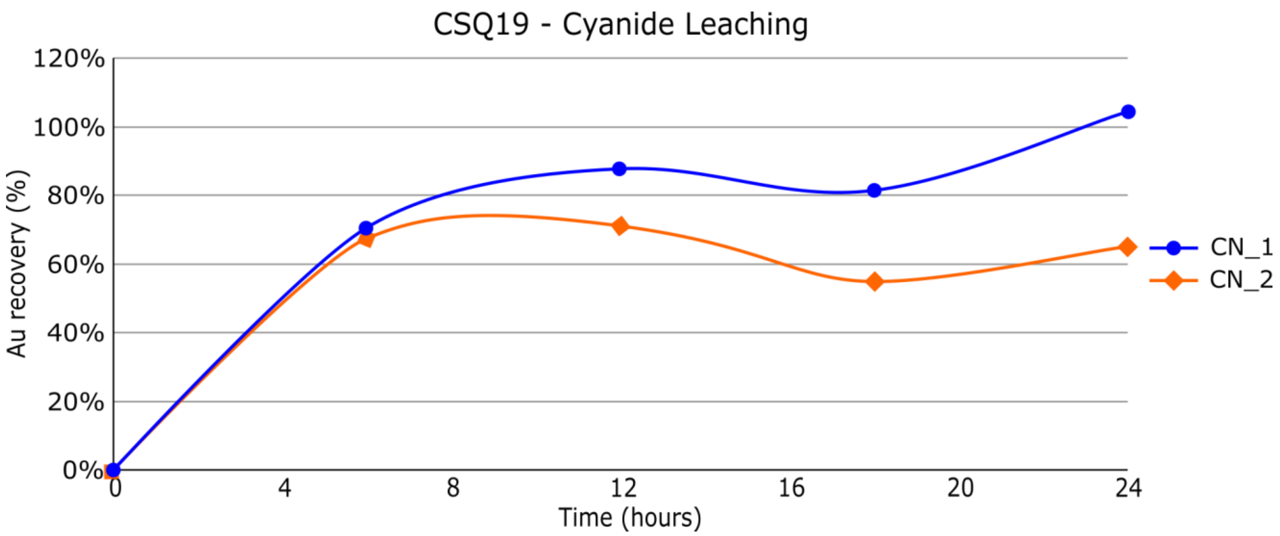


Figure 4.19. Kinetics of cyanide leaching

To verify if the cyanide was consumed excessively in the leaching reaction, so that no available reactant would exist, free cyanide, pH and redox were measured in the previous experiments every two hours. The values obtained are presented in Table 4.8.

Table 4.8. Time evolution of cyanide concentration, pH and Eh

	SRS5			**SRS6**		
Hours	**[CN]***	**pH**	**Eh**	**[CN]***	**pH**	**Eh**
0	5.31	11.22	-257.6	5.31	11.28	-259.1
2	4.58	11.53	-270.1	4.46	11.51	-275.1
4	3.6	11.33	-261.4	4.04	11.28	-260.8
6	2.91	11.29	-260.2	3.22	11.35	-264.5
8	2.01	11.45	-272.1	2.44	11.41	-269.6
12	1.75	11.2	-258	1.87	11.24	-262.1
14	1.52	11.15	-256.2	1.62	11.21	-256.2
16	1.19	11.35	-265.7	1.44	11.25	-261.8
18	1.11	11.25	-258.8	1.37	11.3	-261.8
20	5.2	11.27	-262.5	5.34	11.31	-263.6
22	4	11.3	-259.7	4.25	11.25	-260.4
24	3.23			3.51		

While the pH and the redox potential were kept constant during the experiments, the quantity of free cyanide decreased. For this reason, by the 18th hour more cyanide was added to the solution in order to continue with the dissolution. The measurements are presented in Figure 4.20.

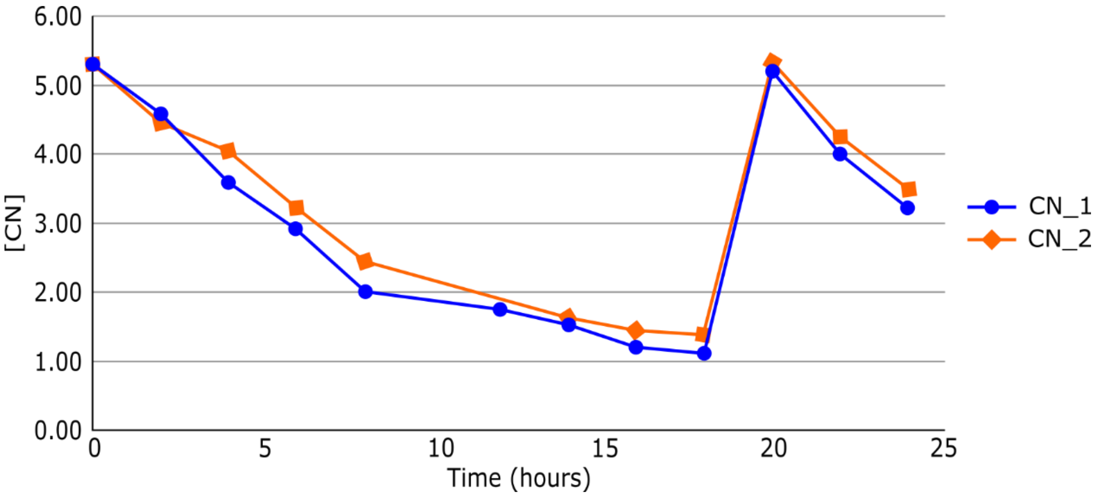


Figure 4.20. Consumption of CN$^-$

4.8.3 Application of the Ammoniac-Thiosulphate leaching to Castromil Ores

4.8.3.1 *Exploratory tests*

Initial leaching test started with the variation of Thiosulphate concentration, maintaining ammonia concentration and without addition of copper. Figure 4.21 presents the concentrations used for the leaching tests.

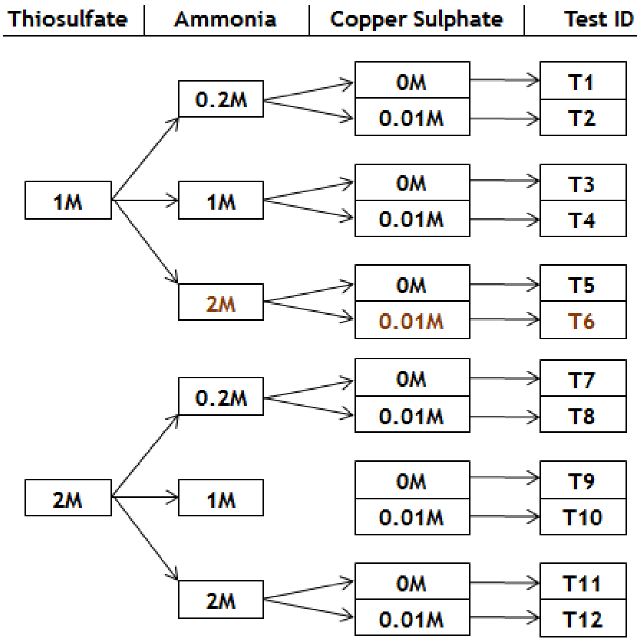


Figure 4.21. Concentration of reagents

The global recovery was lower than expected for an oxidized ore leaching (sample CSQ19). Although, it is possible to predict that the test with both concentrations of thiosulphate and ammonia at 1 M produced a better result than the others (Figure 4.22), a longer leaching time would be required in order to perform a proper comparison.

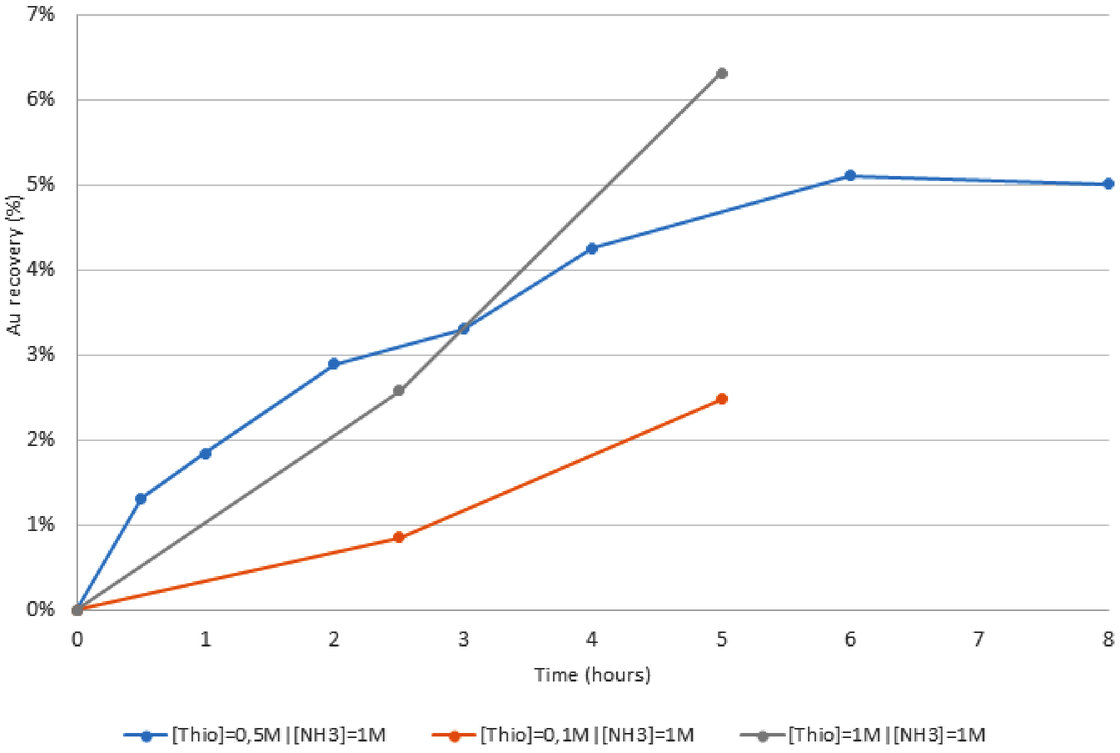


Figure 4.22. Variation of thiosulphate dosage for sample CSQ19.

From the results, the following conclusions can be drawn:

- The increase of the quantity of thiosulphate raised the metal recovery, evidencing that low thiosulphate concentration reduces the rate of gold leaching, so reproduction of SRS3 is mandatory with longer leach time and the development of a new leaching test with larger concentration of thiosulphate;
- A longer leach time is needed to reach a larger metal recovery.
- It is possible to predict that the decrease in metal recovery in SRS1 after 5 hours is due to the passivation of gold by thiosulphate;
- Leaching with rotation of 400 rpm in a 2 litre bowl could create some death-areas (material segregation), so it’s possible that the increase of stirring could raise the metal recovery.

Based on previous findings, a new set of leaching tests was developed in order to obtain better results for the metal recovery in the liquid phase. The stirring was accelerated to avoid death-areas. In this set of leaching assays the variation of the ammonia concentration was tested as well as the increase of thiosulphate concentration (Figure 4.23).

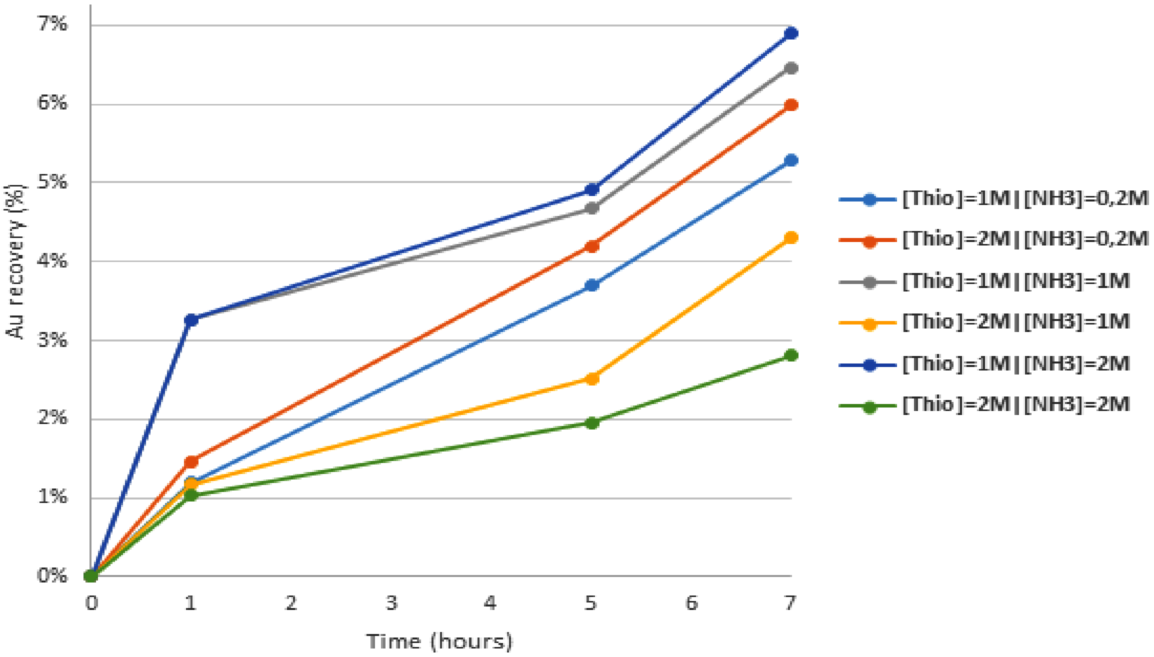


Figure 4.23. Variation of Thiosulphate and Ammonia

The following conclusions can be drawn from this test:

- When the concentration of ammonia is 1M or 2M, the worst recoveries are obtained for a thiosulphate concentration of 2M. When the ammonia concentration is 0.2M the recovery using a thiosulphate concentration of 1M is slightly higher.
- One possible explanation is that higher thiosulphate concentrations hinder the adsorption of ammonia onto gold. This phenomenon is enhanced when the concentration of ammonia is higher, which results in a better performance for the tests with 1M of thiosulphate.
- As can be seen from Figure 4.23 gold leaching increases when ammonia dosage also increases.
- The leaching test performed with 1M of thiosulphate and 2M of ammonia reached the highest Au dissolution.
- The behaviour of the curves represented in Figure 4.23 show an increasing tendency for gold dissolution after 7h, so it’s possible to improve the gold recovery increasing the leaching duration.

After analysing the effect of thiosulphate and ammonia concentration, the effect of copper addition was studied (Figure 4.24). Two leaching tests were carried out for this.

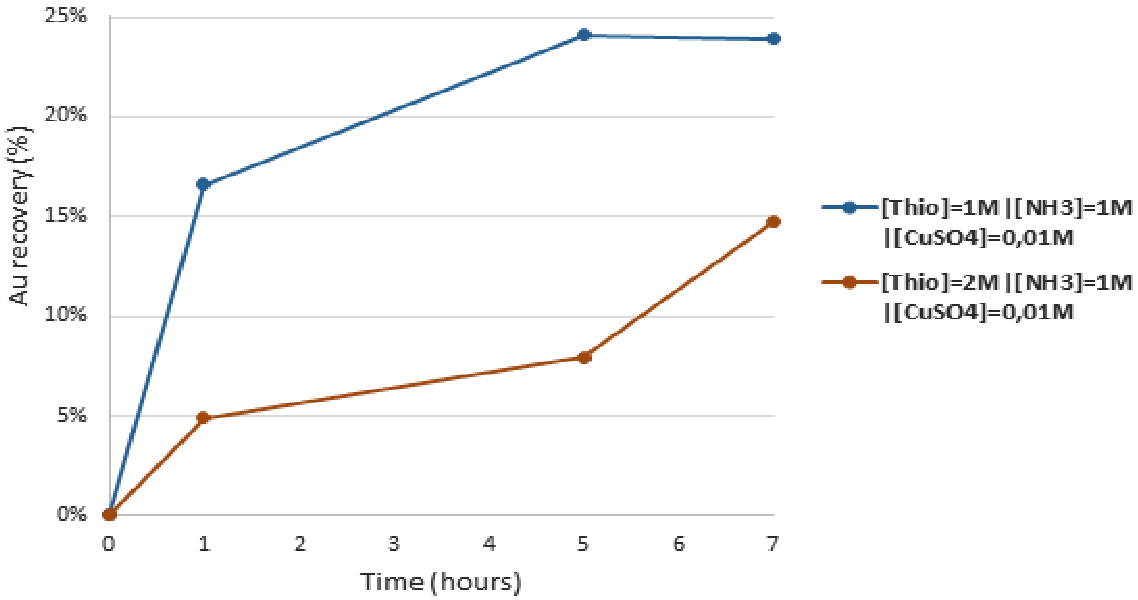


Figure 4.24. The effect of copper addition in ammonia-thiosulphate leaching.

The following conclusions can be drawn from the copper addition tests:

- Au dissolution increases with the addition of copper - verifying what has been stated in the introduction about the catalyst effect of copper ions – and consequently prior results could be improved.
- It's possible to confirm that the increasing of the thiosulphate dosage decreases the Au dissolution, even when copper is added.

Once confirmed that copper addition improves the Au dissolution, all former experiments were repeated but with the addition of copper.

4.8.3.2 *The effect of operating conditions on the recovery to CSQ10 and CSQ30*

As mentioned above, the leaching performance depends on the concentration of thiosulphate, ammonia and copper on the leaching solution. Thus, the first step of this work was to determine the best concentration for leaching solution. A factorial plan was applied to CSQ10 and CSQ30 ore. An agitator Heidolph RZR 2021 was used to agitate the pulp at 450 rpm.

The conditions stipulated for the control experiment were based on previous works:

- Solid percentage (w/w): 40
- Thiosulphate concentration: 0.5 M
- Ammonia concentration: 1 M
- Copper concentration: 0.001 M
- Medium rotation speed (level 1 of stirring).
- Room temperature
- Residence time: 5 hours

During the tests pH and oxidation-reduction potential (ORP) was measured, maintaining the pH 11 by adding sodium hydroxide 20 M. Alkaline solutions were used to prevent the decomposition of thiosulphate, leading to a poor leaching process. The operating parameters are shown in Figure 4.25.

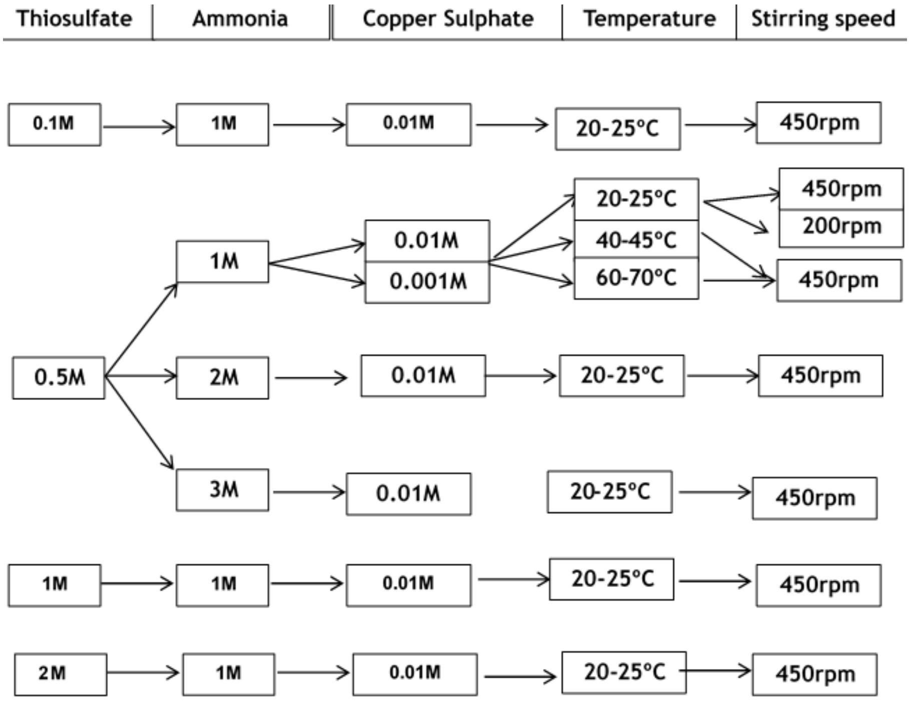


Figure 4.25. Operating parameters of the tests.

Each sample with 250 g of ore was mixed with a 375 ml solution of thiosulphate 0.5 M, kept at room temperature, using a stirring speed 450 rpm during 5 hours in order to determine whether the leaching was effective or not.

Kinetic tests were carried out to study the effect of time on the leaching process. The duration of the test was expanded to 8 hours, with collection of liquid phase samples after 1, 3, 5 and 8 hours.

4.8.3.3 *Results – Sulphide Ore -CSQ10*

Twelve tests were performed with the ‘sulphide ore’ – CSQ10 and another 12 with the ‘oxidized’ ore – CSQ30. In test 5, the grade of the residue was higher than the grade of the ore. For this reason, the test was considered as invalid (Table 4.9).

Table 4.9. Results Thiosulphate leaching with sulphide ore

	T1	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**	**T8**	**T9**	**T10**	**T11**	**T12**
Mass of ore (g)	250	250	250	250	250	250	250	250	250	250	250	250
Grade (g/t)	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5
Initial Gold content (microg.)	1375	1375	1375	1375	1375	1375	1375	1375	1375	1375	1375	1375
Au content residue (mg/kg)	2.2	4.6	4.2	2.2		2.1	0.96	4.7	3.6	3.9	0.72	1.9
Solution volume (ml)	375	375	375	375	375	375	375	375	375	375	375	375
Concentration (mg/L Au)	0.067	0.22	0.68	0.25	0.008	0.2	1.8	1.5	1.4		0.03	0.04
Filtrated solution volume (ml)	204		260	240	243	248	248	215	203	200	217	199
Concentration (mg/L Au)	0.19		1.2	0.04	0.025	0.5	1.8	0.28	0.37		0.13	0.73
Gold content liquid phase (mg)	71.3	82.5	450.0	93.8	9.4	187.5	675.0	562.5	525.0	0.0	48.8	273.8
Washing solution volume (ml)	325		290	345	330	325	305	332	305	350	349	318
Concentration (mg/L Au)	0.049		0.25	0.11	0.12	0.15	0.52	0.11	0.1		0.03	0.27
Gold content washing liquor (mg)	15.9	0.0	72.5	38.0	39.6	48.8	158.6	36.5	30.5	0.0	10.5	85.9
Recovery base on solids (%)	60.0	16.4	23.6	60.0		61.8	82.6	14.6	34.6	29.1	86.9	65.5
Recovery liquid phase (%)	6.3	6.0	38.0	9.6	3.6	17.2	60.6	43.6	40.4	0.0	4.3	26.2

The recovery based on the liquid phase was calculated considering all the available volume of liquid, *i.e*. it includes the liquid phase absorbed by the ore and it also considers the highest concentration obtained, either in the sample collected when the test was concluded or after filtration.

There are several discrepancies in the results obtained in the tests (Table 4.10):

- The concentration of both liquid phases – the sample taken when the test was finished and the sample collected from the filtrated solution – should be identical, but the results indicate very high discrepancies, with exception of test 5.
- The concentrations in the liquid phase obtained after filtration are always higher than the ones obtained from the same solution but before filtration.
- Recoveries calculated based on the grade of the residue and on the concentration of the liquid phase are not in agreement. Recoveries obtained from the solid phase are generally higher than those calculated from the liquid phase; exceptions are tests 3 and 8.

Table 4.10. Discrepancies between recoveries.

	Test 1	**Test 2**	**Test 3**	**Test 4**	**Test 5**	**Test 6**	**Test 7**	**Test 8**	**Test 9**	**Test 10**	**Test 11**	**Test 12**
Discrepancy between liquid phases (mg/L Au)	71.2	82.3	449.3	93.5	9.4	187.3	673.2	561.0	523.6	0.0	48.7	273.7
Relative difference between recoveries (%)	89.4	63.3	-60.8	84.0		72.2	26.6	-199.5	-16.9	100.0	95.0	60.0

The recoveries calculated based on the solid phases, ore and residue, are considered more accurate. Following conclusions can be drawn:

- Recoveries vary between 14.5 % and 86.9 %.
- The average value is 48.6 % and the standard deviation is 0.26.

In test No 2 several samples of the liquid phase were collected after 1, 3, 5 and 8 hours and were analysed in order to study the kinetics of the reaction. The results were completely incongruent (Figure 4.26).

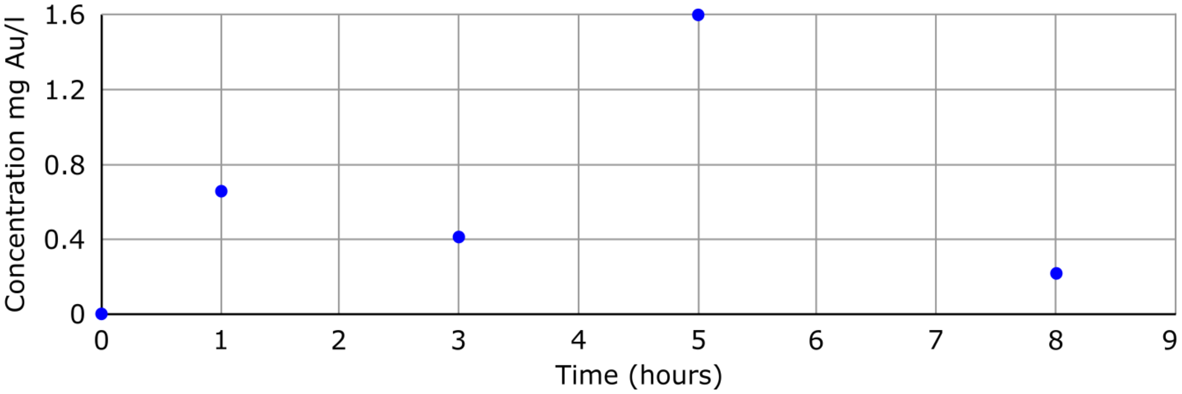


Figure 4.26. Leaching kinetics in test 2.

The chemical analysis were accomplished by LNEG, a laboratory with international certification, using atomic absorption and the regular method for chemical assay of gold in liquid phases. It is concluded that some interferences exist that are not considered in the analytical method used. In fact, due to the time evolution of the results, re-sorption of gold cannot be considered the cause of the incongruences.

In the interpretation of the results only the recoveries obtained from the analysis of the solid phase were considered reliable, although they are also doubtful in some cases. The mean recovery was 48.6 %, with a standard deviation between tests 0.26: The minimum recovery was 14.5 % and the maximum recovery, was 86.9 %.

The correlation coefficients between the recovery and the operating variables are shown in Table 4.11. Overall, the correlation coefficients are low. Correlation with residence time was not considered as there was only one experiment where this parameter was changed. The highest correlations are seen with copper and ammonia concentrations. Temperature shows the lowest correlation because the two tests with temperatures higher than the environmental temperature show contradictory values: one of them lowers the recovery while the other one increases the recovery.

Table 4.11. Correlation between recovery and operating conditions

S/L Ratio	Thiosulphate Conc. (M)	Copper Conc. (M)	Ammonia Conc. (M)	T (ºC)	Residence time (h)	Stirring Speed (rpm)
0	0.30	0.39	-0.37	0.00	Not considered	0.11

In order to try to understand how the operating variables affect the results, a correspondence analysis was performed. We followed the methodology proposed by Lebart et al. (1984). This methodology allows a simultaneous representation of the tests and the variables involved in each test (Figure 4.27).

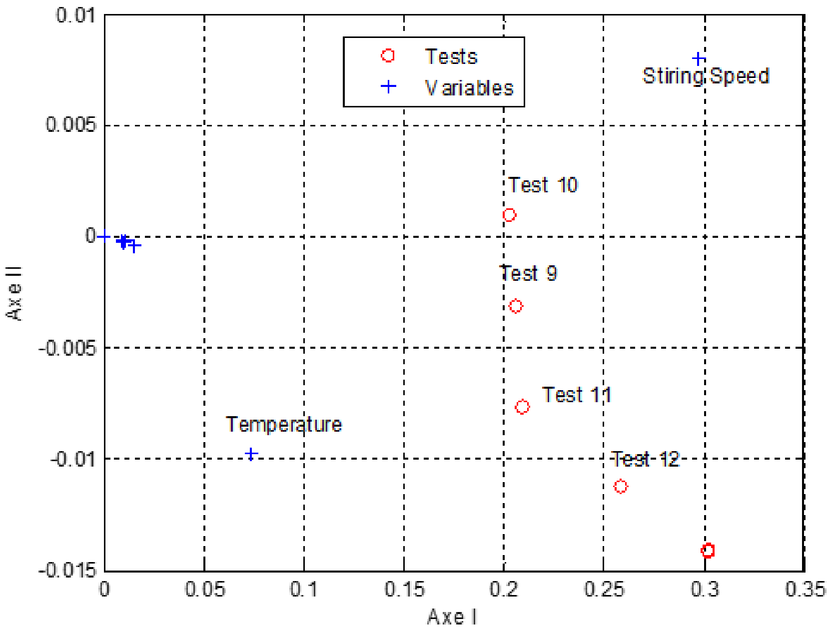


Figure 4.27. Correspondence Analysis of tests for sulphide ore

We can conclude that the tests 1 to 8 are all similar, while tests 9 to 12 evidence a different behaviour. The two operating parameters that affect the experiment are the stirring speed (lower speed favours recovery) and the temperature that increases the recovery. All the other operating parameters do not affect significantly the final recovery.

4.8.3.4 *Results – Oxidized Ore*

In total, 12 beneficiation tests were done for sample CSQ30, which contains oxidized ore (Table 4.12).

Table 4.12. Results of Thiosulphate leaching with oxidized ore – sample CSQ30

	T1	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**	**T8**	**T9**	**T10**	**T11**	**T12**
Mass of ore (g)	250	250	250	250	250	250	250	250	250	250	250	250
Grade (g/t)	8.98	8.98	8.98	8.98	8.98	8.98	8.98	8.98	8.98	8.98	8.98	8.98
Initial Gold content (microg.)	2245	2245	2245	2245	2245	2245	2245	2245	2245	2245	2245	2245
Au content residue (mg/kg)	5.5	4.9	6	6.7	7	4.4	1.4	0.03	4	4.5	0.08	0.2
Solution volume (ml)	375	375	375	375	375	375	375	375	375	375	375	375
Concentration (mg/L Au)	0.054		0.42	0.33	0.21	0.86	12	2.6	3.5	0.63	0	0.051
Filtrated solution volume (ml)	200		245	248	265	258	245	209	205	204	208	205
Concentration (mg/L Au)	0.32		0.26	0.21	0.3	0.73	3	2	2.6	0.26	1	0.04
Gold content liquid phase (mg)	120	0	157.5	123.75	112.5	322.5	4500	975	1312.5	236.25	375	19.125
Washing solution volume (ml)	278		290	252	340	342	325	340	300	345	350	270
Concentration (mg/L Au)	0.34		0.15	0.25	0.2	0.32	1.4	0.47	0.56	0.57	0.05	0.44
Gold content washing liquor (mg)	94.52	0	43.5	63	68	109.44	455	159.8	168	196.65	17.5	118.8
Recovery base on solids (%)	38.8	45.4	33.2	25.4	22.1	51	84.4	99.7	55.5	49.9	99.1	97.8
Recovery liquid phase (%)	9.6	0	9	8.3	8	19.2	220.7	50.6	66	19.3	17.5	6.1

The recovery calculated from the liquid phase considers not only the filtration volume but also the liquid that remains as residual moisture in the ore. Solutions are analysed before and after filtration and the highest one is considered in the calculation of the recoveries.

There are several discrepancies in the results obtained in the tests (Table 4.13):

- The concentration of both liquid phases – the sample taken when the test was finished and the sample collected from the filtrated solution – should be identical.
- The concentrations in the liquid phase obtained after filtration are always higher than the ones obtained from the same solution but before filtration, with the exception in tests 7 and 9. In the first of these tests the gold concentration is evidently erroneous, once it would imply a gold content in the liquid phase higher than the one that existed in the ore.
- Recoveries calculated based on the grade of the residue and on the concentration of the liquid phase are not in agreement. Recoveries obtained from the solid phase are generally higher than those calculated from the liquid phase; exceptions are test 7 and 9.

Table 4.13. Discrepancies between recoveries

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12
Discrepancy between liquid phases (mg/L Au)	78	0	45	4	75	84	80	131	95	141	142	65
Relative difference between recoveries (%)	75.3	100	73	67.2		62.3	-162	49.3	-18.9	61.3	82.4	93.7

The recoveries calculated based on the solid phases are more precise. We may conclude the following:

- Recoveries vary between 22.1% and 99.7 %.
- The average value is 58.5 % and the standard deviation is 0.29.

The correlation coefficients between the recovery and the operating variables are shown in Table 4.14.

Table 4.14. Correlation between recovery and operating conditions (ox. ore)

S/L Ratio	Thiosulphate Conc. (M)	Copper Conc. (M)	Ammonia Conc. (M)	T (ºC)	Stirring Speed (rpm)
0	-0.404	0.299	0.235	0.123	-0.494

The correlation coefficients are low. The correlation coefficient with residence time was not considered as there was only one experiment where this parameter was changed. The highest correlations are with the stirring speed and with Thiosulphate concentration. Correlation with temperature is the lowest. The results were also analysed by correspondence analysis (Figure 4.28).

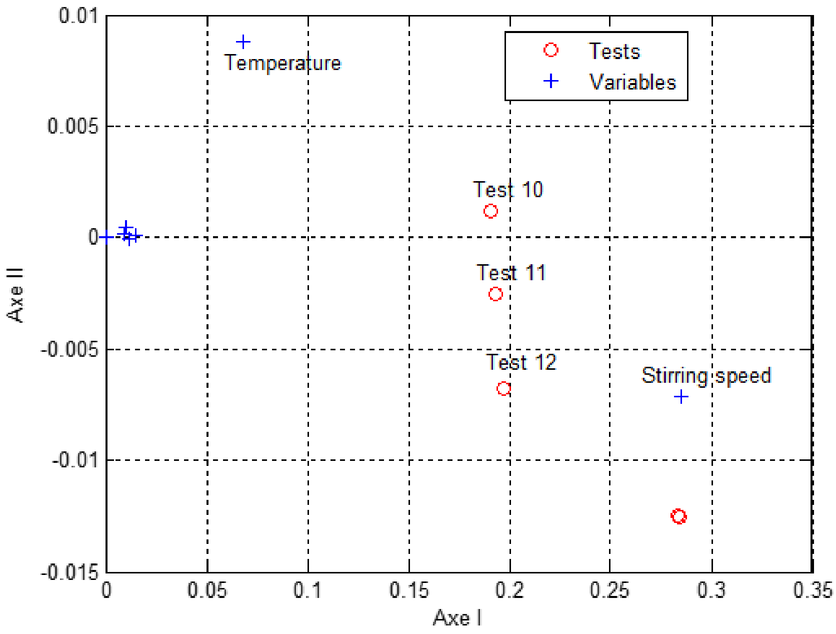


Figure 4.28. Correspondence Analysis (ox. ore)

We can conclude that the tests 1 to 9 are all similar, while the tests 10 to 12 show evidence of different behaviour. There are two operating parameters that affect recovery the most: the stirring speed (lower speeds favours recovery), and the temperature that increases the recovery. All the other operating parameters do not affect significantly the final recovery.

4.8.4 Bromine Leaching

4.8.4.1 *Exploratory tests*

The composition of a leaching solution, temperature, pH/Eh, solid/liquid ratio, stirring speed and residence time are the most important parameters that affect the performance of a leaching process. The exploratory tests aimed to assess the applicability of the chosen leaching solution, and to evaluate the parameters with higher impact in the bromine leaching effectiveness – temperature and solid/liquid ratio. As mentioned above, the studied method has applicability over a wide range of pH values and, consequently, this parameter was not studied. The variation of residence time was not included in the exploratory tests because bromine leaching presents a fast leaching rate, reaching the maximum efficiency in a few hours. The stirring speed only influences the kinetic of the process and for this reason was also excluded for the exploratory tests. Thus, some exploratory tests were performed just to confirm the feasibility of the bromine leaching process for the ore of the Castromil orebody. Figure 4.29 indicates the results of the exploratory tests and Table 4.15 the operating conditions that were used.

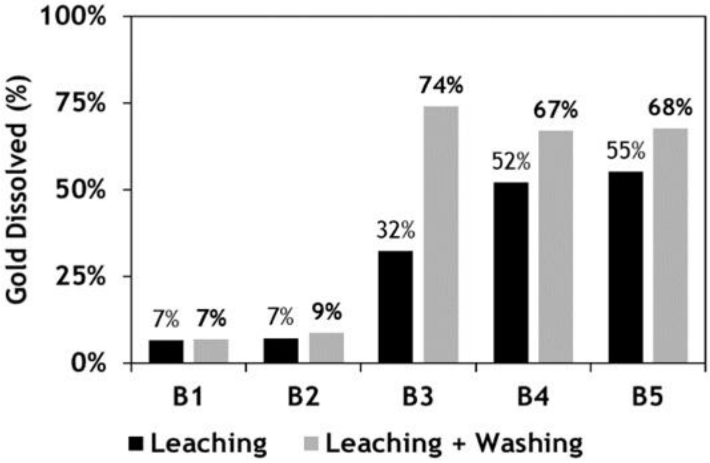


Figure 4.29. Exploratory tests

Table 4.15. Operating conditions of preliminary tests

Test	T (°C)	S/L ratio	Stirring (rpm)
B1	25	1	450
B2	25	0.5	450
B3	100	1	450
B4	100	0.5	450
B5	50	1	450

Test B3 achieved the highest gold dissolution ratio (74%), when heating the reactor to a temperature of 100°C (external temperature), with a solid/liquid ratio of 1. The results showed that higher temperatures are needed to obtain higher gold dissolution ratios, although, serious volume losses of leaching solution (almost 50%) were observed due to evaporation. The efficiency of the leaching process increased when a solid/liquid ratio of 1 was applied, so lower quantities of leaching solution are needed, which could be economically advantageous in terms of reagents costs and plant design. Solid/liquid ratios higher than 1 were not tried due to the difficulty to keep the pulp in suspension.

4.8.4.2 *Effect of solution composition*

Once it was proven that the bromine solution could lead to high quantities of gold dissolved from the ore, it was possible to assess the effect of other parameters in the leaching performance. Therefore, the possibility to reduce the quantity of reagents on the leaching solution was assessed. New tests with lower concentrations of NaBr, HCl and NaOCl were executed. Due to the vaporization losses a relevant change was implemented in the leaching reactor, with the installation of a condenser in one of the reactor outlets. The condensed vapours returned to the reactors. For this reason, test B6 was a replica of Test B3, upgrading the reactor efficiency. Tests B7 and B8 were carried out with a reduction of the concentration of NaBr, HCl and NaOCl in the leaching solution.

The obtained results are presented in Figure 4.30 and the reagents dosage in Table 4.16. It is clear that the decrease in the concentration of reactants also reduces the gold dissolution ratio that appears to be very sensitive to small changes in the chemical composition. Thus, the original solution was used as a standard for the upcoming tests.

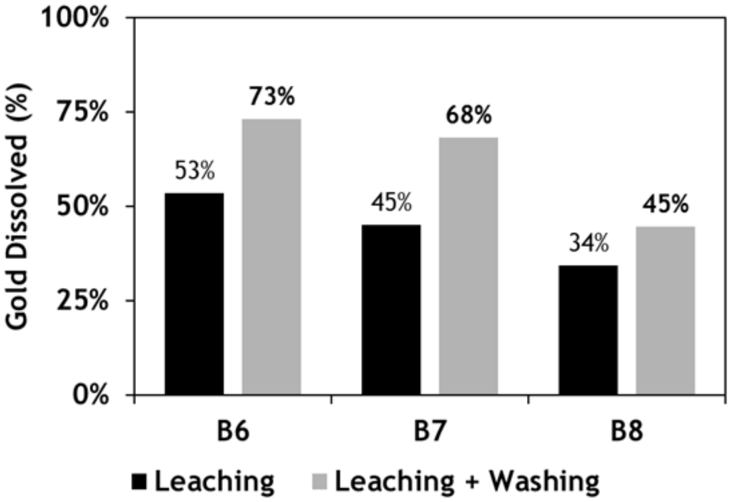


Figure 4.30. Recoveries

Table 4.16. Composition of bromine leaching solutions (per 100ml).

Test	NaBr (g)	NaOCl (mL)	HCl (mL)	H_2O (mL)
B6	4.4	30	42	28
B7	3.1	20	30	50

4.8.4.3 *Effect of stirring speed*

As stated above, the variation of stirring speed could affect the dissolution kinetic rate. It was mandatory to evaluate the effect of increasing and decreasing this parameter to compare with the Test B6. Low stirring speed could reduce the contact between the solution and the ore. High stirring speeds could create turbulence, which might affect the leaching performance. Until this point, all tests were carried out at 450 rpm, a common value for laboratory leaching tests because it allows the suspension of the pulp and avoids death-areas inside the reactor. In order to assess the stirring speed effect, two new attempts were performed (Table 4.17). The results are presented in Figure 4.31.

Table 4.17. Variation of stirring speed

Test	T (°C)	Stirring (rpm)	S/L ratio
B9	100	300	1
B6	100	450	1
B10	100	600	1

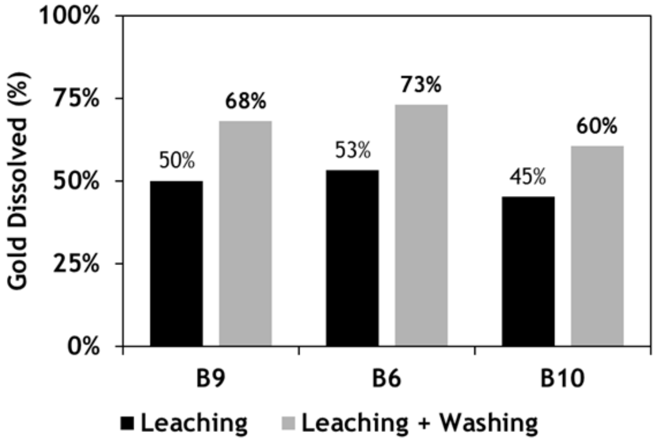


Figure 4.31. Effect of stirring on bromine leaching.

When the stirring speed was decreased from 450 to 300 rpm, the final conversion of gold decreased from 73% to 68%, which represents a slight reduction. When the stirring speed was further increased from 450 to 600 rpm, the dissolution of gold decreased from 73% to 60%. It was clear that 450 rpm is an optimal stirring speed for bromine leaching processes, when a solid/liquid ratio equals to 1 and a temperature of 100°C is applied. It was also possible to conclude that the effect of increasing the stirring speed caused a higher negative effect than decreasing the stirring speed.

4.8.4.4 *Effect of Residence Time*

It has been reported that bromine leaching process presents a faster dissolution rate, which means that short residence times are needed to convert the gold from the ore to the liquid solution. All previous tests were carried out for 4 hours, which was predicted enough for high gold dissolution. A new attempt was performed with longer residence time (Test B11). The duration of Tests B6 and B11 were respectively 4 and 6 hours. A kinetic test was performed (Test B12), for 6 hours, with sampling at 1, 2, 4 and 6 hours (Tests B6 and B11 allowed for a discontinuous kinetic analysis, while Test B12 allowed for a continuous kinetic analysis). This methodology also allowed for track potential sampling errors related to continuous kinetic analysis, due to the necessity of open the reactor to obtain liquor samples. The kinetic analyses are presented in Figure 4.32, and the residence and sampling times in Table 4.18.

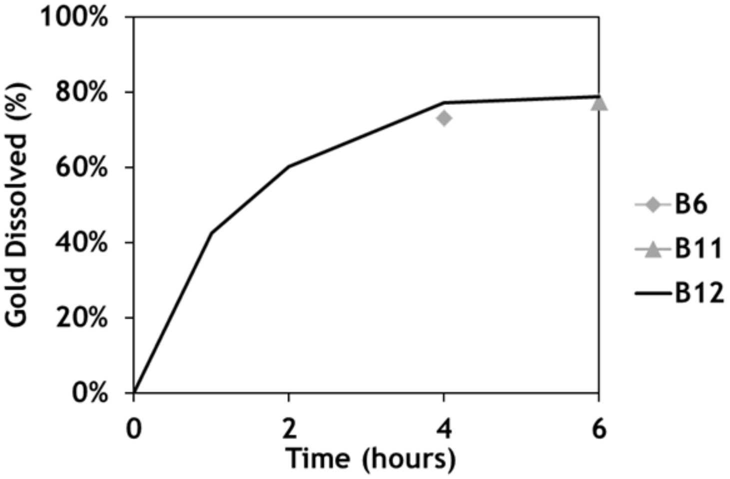


Figure 4.32. Effect of residence time

Table 4.18. Variation of residence time

Test	Residence Time (h)	Sampling time
B6	4	4h
B11	6	6h
B12	6	1h, 2h, 4h, 6h

It is possible to conclude that bromine leaching presents a fast dissolution rate, with ≈40% of gold dissolved after 1 hour, 60% after 2 hours and 77% after 4 hours. Between 4 and 6 hours the gold dissolution ratio remained practically constant, thus 4 hours could be the optimal residence time. These results are similar to those obtained with Test B6 and Test B11, indicating that the sampling methodology applied on continuous kinetic test (B12) was suitable for this kind of analysis and could be applied for future works.

4.8.4.5 *Pre-treatment effect*

Pre-treatment processes could improve the gold dissolution ratio during the leaching stage, essentially when the ore is considered as refractory, which means that gold particles are encased by sulphide matrix minerals, essentially pyrite and arsenopyrite. This type of refractoriness can be treated by a pre-treatment process that could be fine grinding, pressure oxidation, roasting, chemical oxidation or bio-oxidation. Thus, the effect of fine grinding and roasting pre-treatments were assessed. First, the original sample used in the previous tests, was comminuted in a closed circuit. Two new samples were obtained. Figure 4.33 represents the comminution diagram applied. Then, the roasting process was tested by heating the original sample at 500°C during 30 minutes. These three new samples were leached in the same conditions as Test B6. The results are presented in Figure 4.34 comparing the dissolution of gold obtained with non-pre-treated ore (B6) and pre-treated ore (B13, B14, B15). Table 4.19 presents the method applied for each test.

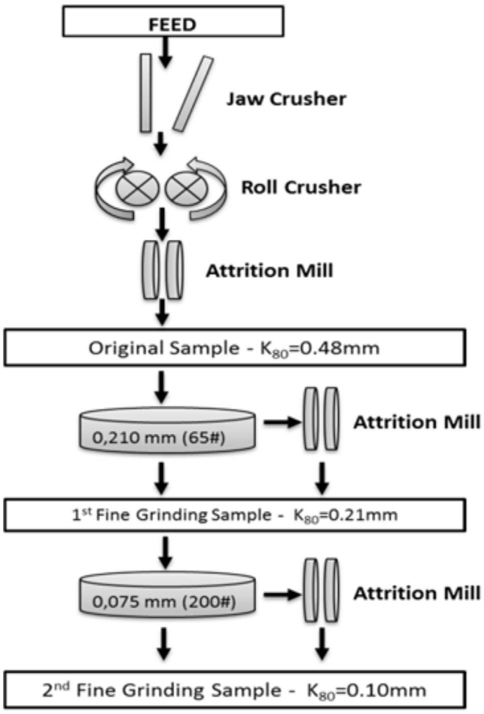


Figure 4.33 . Fine Grinding Circuit

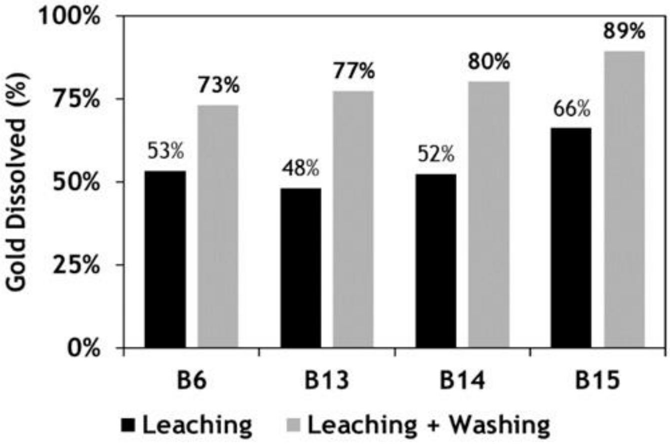


Figure 4.34. Effect of pre-treatments in the recovery. The dissolution of gold with non-pre-treated ore (B6) and pre-treated ore (B13, B14, B15)

Table 4.19. Pre-treatment alternatives

Test	Pre-treatment	Method
B6	Original Sample	Non-pre-treated
B13	Re-grinded to K_{80}=0.21mm	Fine grinding
B14	Re-grinded to K_{80}=0.10mm	Fine grinding
B15	Heated at 500°C for 30 min.	Roasting

Upon observation of the Figure 4.34 it is evident that gold dissolution increased for the pre-treated samples. A slight increase of gold conversion was observed for the fine grinding pre-treatment. It was also observed that a more intense grinding (Test B14) allowed for better leaching performance, which means that this ore presents a low liberation size. In what concerns roasting pre-treatment, a higher increase was observed (Test B15), with 89% of gold dissolved into the liquid phase. This result allowed to conclude that an oxidation pre-treatment is required to reduce the quantity of gold particles encased by sulphide matrix minerals, increasing the quantity of leaching solution available to react directly with gold.

4.8.4.6 *Residue analysis*

The residues from the leaching stage were analysed with X-Ray Fluorescence (XRF), to determine the content of the main elements (Fe, As, Pb, Cu, K). With this analysis it was also possible to determine other elements that were dissolved into the leaching solution. Table 4.20 presents the residues analysis of the tests that obtained higher gold dissolution ratios.

Table 4.20. Residue analysis from X-Ray Fluorescence

Test	Fe		As		Pb		Cu		K	
	Grade (%)	Rec (%)	Grade (%)	Rec (%)	Grade (%)	Rec (%)	Grade (%)	Rec (%)	Grade (%)	Rec (%)
B6	16.3	94.47	1.78	87.2	0.94	79.66	0.02	80.09	0.69	62.69
B12	13.54	78.47	1.42	69.47	0.74	63	0.01	63.51	0.54	49.01
B14	15.51	89.87	1.62	79.49	0.86	73.41	0.02	76.3	0.74	66.88
B15	13.65	79.11	1.39	68.12	0.6	51.07	0.01	49.29	0.54	48.86
B22	14.76	85.52	1.53	75	0.8	68.03	0.02	73.46	0.72	65.65
FEED	17.26	0	2.04	0	1.18	0	0.02	0	1.1	0

Relatively to the tests B6 and B12, longer residence times (B12) caused higher dissolution of gangue elements Fe, As, Pb, Cu and K, while the quantity of gold dissolved into the liquid phase remained almost the same. In what concerns the effect of the pre-treatment, it was possible to observe that fine grinding (B14) caused a slight increase in the gangue dissolution, while the roasting pre-treatment (B15) originated a higher increase, that could be caused by the easier leaching of the minerals resulting from the oxidation of the sulphides. Finally, about the effect of H_2O_2 and $FeCl_3$ addition, a slight increase in the dissolution of gangue elements was verified, which could be due to the higher leaching efficiency of the bromine solution.

4.8.4.7 *Liquor analysis*

The X-Ray Florescence (XRF) equipment used to analyse the leaching residues, can also be used to obtain the spectrum of liquid samples. XRF is based on the principle that individual atoms emit photons of a characteristic energy or wavelength when excited by an external energy source (X-ray). Thus, the elements present in leaching liquors could be identified and quantified by counting the number of photons emitted by a sample within each energy level. So, the leaching liquor from tests B6, B14 and B22 were analysed in order to obtain the number of counts for Br, Fe, As and Pb, using a filter with 45 keV of voltage and 10 µA of current (Table 4.21). A partial spectrum is shown in Figure 4.35.

Table 4.21. XRF Analysis of leaching liquors

Elements/Test	B6	B14	B22
Br (11.91 keV)	598204	650755	691731
Fe (6.39 keV)	1931	1836	27070
As (10.52 keV)	1493	3202	3062
Pb (10.54 keV)	1479	3288	3141

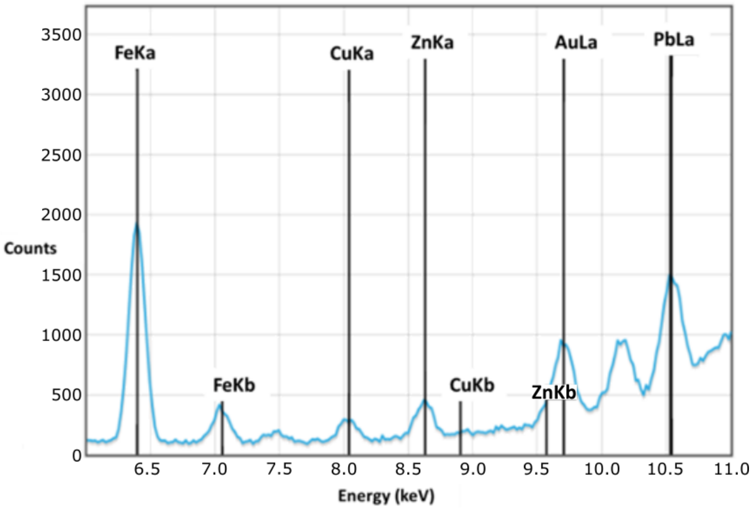


Figure 4.35. Partial Spectrum of leaching liquor of Test B6

As it was expected considering the previous analysis of the residues, the leaching liquor reveals a high quantity of Fe, As and Pb that were dissolved from the ore. The quantity of Br was also determined to quantify the reagent consumption. Test B14 was developed after a fine grinding pre-treatment and Test B22 was carried out with addition of iron (III) chloride and hydrogen peroxide and presented a higher gold dissolution than Test B6, although the consumption of Br was lower. According to these results it is possible to confirm that the efficiency of bromine leaching is higher when a pre-treatment is applied or when $FeCl_3$ and H_2O_2 are added to the bromine solution, reaching higher quantities of gold dissolved and consuming lower quantities of Br. The dissolution of As and Pb increased from Test B6 to Tests B14 and B22, due to the higher efficiency of the leaching process. Otherwise, the quantity of Fe dissolved was similar for tests B6 and B14, which could be due to the dissolution of Fe is independent of the efficiency of the process. Test B22 presented a higher quantity of Fe due to the addition of $FeCl_3$ to the leaching solution.

4.8.5 Final conclusions in relation to bromine

This study is part of a research work that aims to contribute for the knowledge about the leaching process of the Castromil gold ore deposit and simultaneously study alternative leaching reagents that could replace the use of cyanide. An analysis of the most relevant operatory conditions that could affect the performance of bromine leaching showed that: a) high temperatures are needed to increase the dissolution of gold; b) higher solid/liquid ratio increases the gold recovery; c) stirring speed should be about 450 rpm; d) no pH adjustment is required to achieve high gold dissolution. Thus, the optimal operatory conditions were defined as follows: leaching solution composed by 4.4 g of NaBr, 30 ml of NaOCl, 42 ml of HCl and 28 ml of H_2O per 100 ml of solution, at 100°C using a solid/liquid ratio of 1, with a stirring speed of 450 rpm at natural pH. With these conditions, 73% of gold was solubilized.

It has been reported that the usage of a pre-treatment stage before leaching, could improve the quantity of gold dissolved. Therefore, a mechanical pre-treatment – fine grinding, and a roasting pre-treatment were applied to the Castromil ore. It was possible to observe in both cases an increase in the bromine leaching performance, particularly for the roasting process, which allowed to dissolve 89% of gold with a simultaneous decrease in the bromine consumption caused by the absence of the sulphides.

The effect of adding oxidants, peroxide hydrogen and iron (III) chloride, to the bromine solution was also assessed. It was possible to observe that the effect of adding H_2O_2 reduced the efficiency of the leaching process and the addition of $FeCl_3$ is only relevant for quantities equal or higher than 10 mg of iron chloride per 100 ml of bromine solution. Although, when these compounds were added simultaneously to the bromine solution 80%

of gold was dissolved, which represents an improvement for the leaching process. The analysis of residues and leaching liquors allowed to conclude that higher gold dissolution could be enhanced with optimized leaching processes that consume lower quantities of Br.

4.8.6 Comparison between Thiosulphate, Cyanide and Bromide Leaching

Once analysed the performance of thiosulphate, cyanide and bromine as alternatives reagents for leaching, it was mandatory to compare these three processes. In order to that, the kinetic tests T15, B8 and CN1, were compared. These tests were carried out with the original samples, and concerns the best exploratory test for each alternative (Figure 4.36).

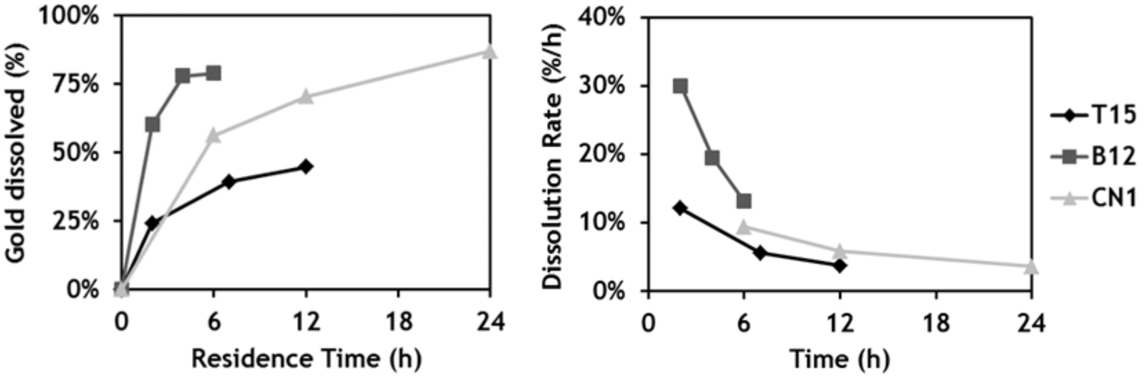


Figure 4.36. Comparative tests – recoveries and kinetics

Comparing the different alternative leaching reagents, the following conclusions can be drawn:

- In relation to gold dissolution, the cyanidation process produces the highest gold recovery (86.96%) against 78.90% and 44.70% achieved respectively by bromide and thiosulphate leaching.
- Nevertheless, the kinetics of cyanidation is slower: 24 hours are required against 12 hours for thiosulphate and 6 hours for bromide leaching.
- Thus, bromine leaching has the fastest rate. In fact, bromine leaching requires 6 hours to dissolve almost 80% of gold present in the solid phase while cyanide leaching requires almost 20 hours to attain the same value. Thiosulphate leaching only dissolved 44% of gold in 12 hours, and it was not expected that this process could achieve 80% of dissolution.

It is clear that, for the original sample – sample # 1 – without any type of pre-treatment, the bromine leaching may be the optimal process for Castromil ore, with 78.90% of gold dissolved into the leaching solution, which for an industrial process could represent a good result.

However, the original sample (sample # 1) could be pre-treated in order to optimize the studied leaching processes. Two types of pre-treatment were studied: a) Fine grinding – a new grinding process was applied to sample #1 in order to obtain two finer classes of material – sample # 2 and sample # 3; b) roasting – the original sample was roasted for 30 minutes at 500°C. The effect of these processes were verified for the three leaching methods.

4.8.6.1 *Fine grinding*

As mentioned above, to determine the effect of fine grinding, the three leaching methods were applied to sample # 2 (T18, B13 and CN4) and to sample # 3 (T19, B14 and CN5). The results are presented in Figure 4.37.

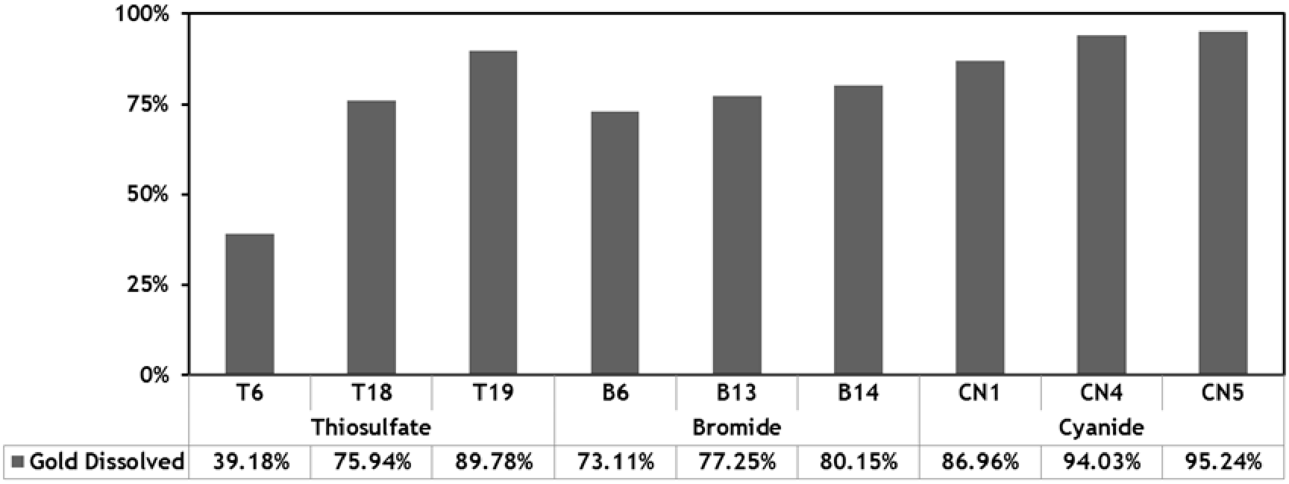


Figure 4.37. The effect of grinding in thiosulphate, cyanide and bromide leaching.

Some conclusions can be stated:

- As expected, increasing the grinding time the gold dissolution also increases due to a higher liberation of gold particles. This was verified for all the three alternatives.
- The effect of increased grinding time was especially noticeable in thiosulphate leaching, with an increase of 194% and 229% of gold dissolution for sample # 2 and sample # 3, respectively. In case of bromine leaching, the increase was 103% and 104%, while for cyanidation it was 108% and 110%, respectively.

The previous analysis showed that: a) the particle size distribution has an important role in thiosulphate leaching while for bromine and cyanide the dependency on liberation is smaller; b) in exploratory tests the thiosulphate leaching showed poor results; although, with a fine grinding similar results to the other alternatives could be obtained.

4.8.6.2 *Roasting*

In order to study the effect of roasting, the three leaching alternatives were applied to a roasted sample (T16, B15 and CN3). The results are presented in Figure 4.38.

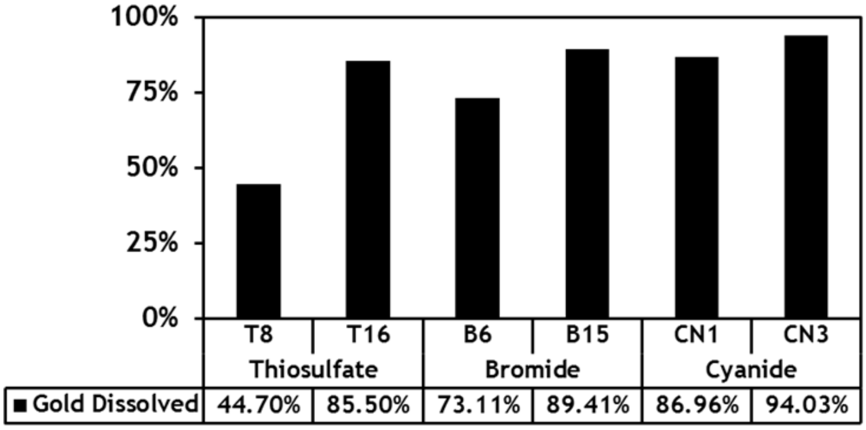


Figure 4.38. Effect of roasting in thiosulphate, bromine and cyanide leaching.

The most important conclusions are

- The roasting pre-treatment increases the quantity of gold dissolved for all the alternatives;

- For thiosulphate leaching, the quantity of gold dissolved increased 191%, while for bromine the increase was 115% and for cyanide 108%. The same conclusion could be drawn from the fine grinding pre-treatment;
- Thiosulphate leaching, after roasting, was able to generate recoveries similar to bromine and cyanide.
- It can also be concluded that bromine leaching can enhance recoveries similar to those attained by cyanidation (83.5%) and higher than those obtained by thiosulphate leaching (44.7%).

If a pre-treatment stage is applied, bromine leaching allows for dissolving 89% of the gold, while thiosulphate only allows for 85.5% (Table 4.22). Nevertheless, the bromine leaching process presents a higher recovery, taking only 4 hours to dissolve 80% of gold, while cyanide leaching needs 24 hours for a similar result.

Table 4.22. Gold dissolved in each method for each feed sample

Ore	**Leaching solution**		
	Thiosulphate	**Cyanide**	**Bromide**
Sample No. 1	44.70 %	86.96 %	73.11 %
Sample No. 2	75.94 %	94.03 %	77.25 %
Sample No. 3	89.78 %	95.24 %	80.15 %
Roasted ore	81.24 %	95.98 %	89.41 %

4.9 Beneficiation tests with Romanian gold ore samples

Two gold ore samples Colnic Rovina and Ciresata from the Rovina Valley in Romania were studied. Both flotation and gravity concentration tests were done in order to recover the gold and copper. Some basic mineralogical studies of the feed materials were also made.

Prior the mineralogical studies and beneficiation tests both ore samples were crushed by the jaw- and roller crusher to suitable < 1 mm particle size. The ore samples were homogenized by mixing and divided into suitable 1.5 kg sub samples for the bench scale tests.

4.9.1 Mineralogical studies

The mineralogical content of the feed material and occurrence of the gold and copper were determined for both ore samples by Mineral Liberation Analyser (MLA) equipment. The samples of the following grinding finenesses were studied: Colnic Rovina Blend P80 < 77 µm and Ciresata P80 < 85 µm. The polished sections were made from every sieve fraction of both samples.

The mineralogical content of the Colnic Rovina ore sample is presented in Table 4.23. The main minerals in Colnic Rovina ore sample were silicates 88.6 %, carbonates 2.5 % and pyrite 4.8 %, the copper was carried by chalcopyrite.

Table 4.23. Colnic Rovina, Modal mineralogy 20 min ground feed ore P80 < 77 µm.

Mineral	+90µm (Wt%)	63-90µm (Wt%)	32-63µm (Wt%)	-32µm (Wt%)	Bulk (Wt%)
Silicates	92.29	88.67	87.49	87.87	88.57
Apatite	0.28	0.46	0.34	0.32	0.34
Fluorite	n.d.	0.01	0	0	0
Gypsum	0	0.01	0.01	0.01	0.01
Carbonates	2.13	2.11	2.19	2.7	2.45
Ti Oxides	0.1	0.09	0.08	0.18	0.14
Fe Oxides	0.48	0.69	0.73	1.34	1.02
Chalcopyrite	0.26	0.15	0.39	0.56	0.44
Pyrite	3.98	7.17	7.44	3.68	4.78
Pyrrhotite	0.11	0.26	0.42	0.6	0.46
Pentlandite	n.d.	n.d.	0.01	n.d.	0
Sphalerite	0.02	0.01	0.02	0.05	0.04
Molybdenite	n.d.	n.d.	0.01	n.d.	0
Au_alloy_mix	n.d.	n.d.	0.4	n.d.	0.04
Other	n.d.	0.01	n.d.	0.02	0.01
Unclassified	0.35	0.38	0.46	2.66	1.66
Total	100	100	100	100	100

**n.d. = not detected.*

Most of the copper, about 71 % occurred in - 32 µm size fraction (Table 4.24). The liberation degrees of chalcopyrite by size fractions are presented in Figure 4.39 which shows that 78 % of chalcopyrite particles were totally liberated. The liberation degrees were the highest in - 32 µm size fraction (85 % of chalcopyrite totally liberated) and poorest in + 90 µm size fraction (only 16 % of chalcopyrite totally liberated).

Table 4.24. Colnic Rovina chalcopyrite distributions, 20 min ground feed ore P80 < 77 µm.

Colnic Rovina Blend	Mass (%)	Chalcopyrite (Wt%)	Chalcopyrite mass (%)	Chalcopyrite distribution (%)
-32 µm	55.7	0.56	0.31	71.1
32-63 µm	18.1	0.39	0.07	16.1
63-90 µm	10.7	0.15	0.02	3.7
+90 µm	15.4	0.26	0.04	9.1
Total	100		0.44	100

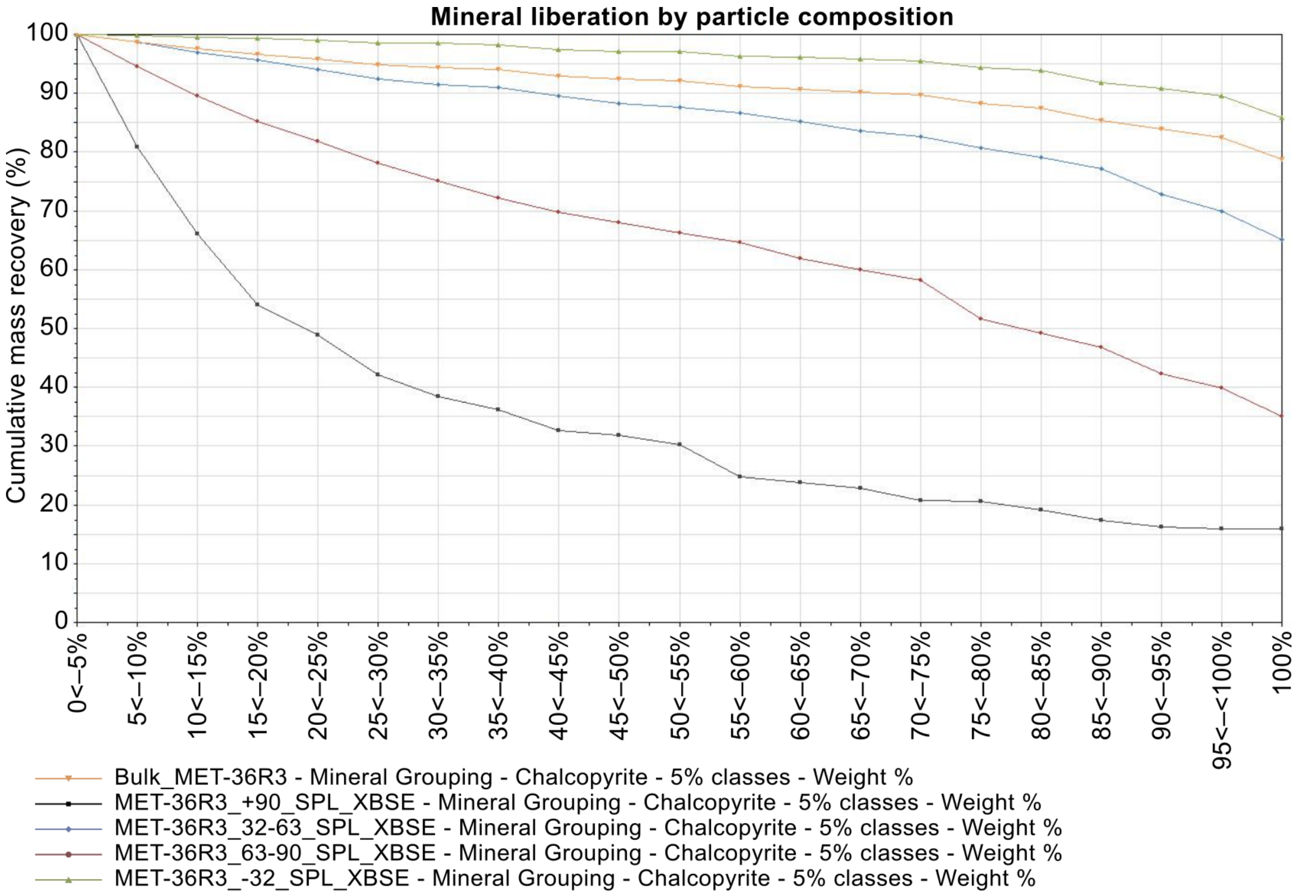


Figure 4.39. The liberation degrees of chalcopyrite, 20 min ground feed ore P80 < 77 µm, Colnic Rovina.

The gold occurred mostly as native gold or electrum. The gold grains contain Au >90 Wt% and the electrum grains contain Au 70-90 Wt%. The particle sizes of gold and electrum grains were rather small, usually < 10 µm, and only a few totally liberated particles were found.

There is one Electrum grain in the +90µm fraction, associated with Chalcopyrite. The particle contains mainly silicates (K-feldspar, Actinolite, Chlorite, Hornblende, Titanite, Plagioclase, Illite, Smectite, Tourmaline, Clinozoisite, Muscovite and Quartz) and some Fe-oxide and carbonate (Calcite) grains and one Pyrite grain (Figure 4.40).

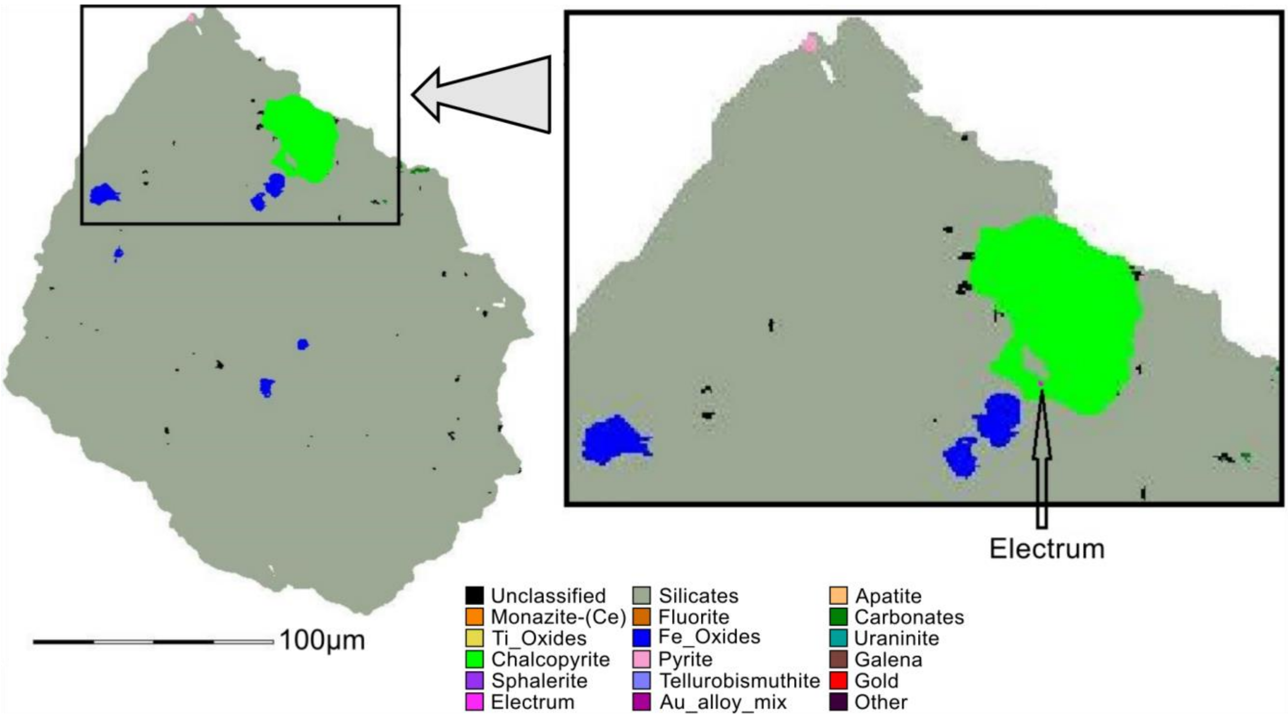


Figure 4.40. Colnic Rovina, occurrence of gold + 90 µm size fraction.

Fraction 75-90µm contains two Gold grains. The Gold grain in the particle on the left side is associated with Quartz, but the same particle contains also Chlorite, Titanite, Plagioclase, Biotite, Illite, Hornblende, Smectite and Clinozoisite. On the right side, the Gold grain is associated with Plagioclase, Chlorite and Electrum. The particle contains mainly silicates (Plagioclase, Chlorite, K-feldspar, Biotite, Muscovite, Illite and Tourmaline) but also carbonate (Calcite) and Electrum (Figure 4.41).

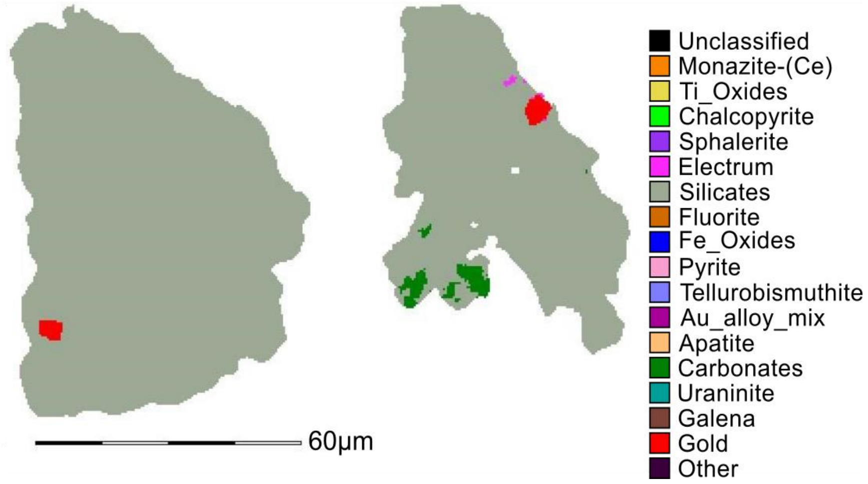


Figure 4.41. Colnic Rovina, occurrence of gold 75-90 µm size fraction.

Finally, in the smallest -20µm fraction there are three Gold grains. On the left side, the Gold grain is associated with K-feldspar. In the middle and on the right side the gold grains are totally liberated (Figure 4.42).

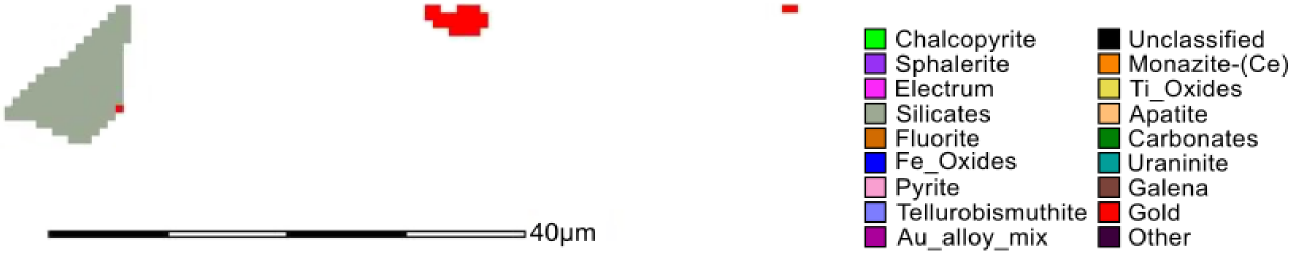


Figure 4.42. Colnic Rovina, occurrence of gold - 20 µm size fraction.

The mineralogical content of the Ciresata ore sample is presented in Table 4.25. The main minerals were silicates 89.8 %, carbonates 3.0 % pyrite 2.5 %, apatite 1.4 % and iron oxides 1.2 %. The copper was carried by chalcopyrite.

Table 4.25. Ciresata, Modal mineralogy 50 min ground feed ore P80 < 85 µm.

Mineral	**+90µm (Wt%)**	**63-90µm (Wt%)**	**32-63µm (Wt%)**	**-32µm (Wt%)**	**Bulk (Wt%)**
Silicates	94.72	92.24	90.2	86.92	89.8
Apatite	2.08	1.86	1.02	1.11	1.38
Monazite	n.d.	n.d.	n.d.	0	0
Barite	n.d.	n.d.	n.d.	0.02	0.01
Carbonates	1.54	2.12	3.24	3.84	3.04
Ti Oxides	0.06	0.08	0.09	0.24	0.15
Fe Oxides	0.21	0.31	0.83	2.14	1.24
Chalcopyrite	0.12	0.33	0.43	0.69	0.48
Pyrite	0.93	2.5	3.56	2.54	2.47
Pyrrhotite	0.01	n.d.	0.03	0.04	0.03
Pentlandite	n.d.	n.d.	0.01	n.d.	0
Sphalerite	n.d.	n.d.	n.d.	0.01	0
Other	0.02	0.02	n.d.	n.d.	0.01
Unclassified	0.32	0.55	0.6	2.44	1.39
Total	100	100	100	100	100

**n.d. = not detected.*

Most of the copper, *ca.* 66 % occurred in - 32 µm size fraction (Table 4.26). The liberation degrees of chalcopyrite by size fractions are presented in Figure 4.43 which shows that 72 % of chalcopyrite particles were totally liberated. The liberations degrees in the two coarsest + 90 µm and 63- 90 µm size fractions were poor only 8 % to 20 % of chalcopyrite was totally liberated.

Table 4.26. Ciresata chalcopyrite distributions, 50 min ground feed ore P80 < 85 µm.

Ciresata	**Mass (%)**	**Chalcopyrite (Wt%)**	**Chalcopyrite mass (%)**	**Chalcopyrite distribution (%)**
-32 µm	46.1	0.69	0.32	66.2
32-63 µm	20.5	0.43	0.09	18.4
63-90 µm	16.2	0.33	0.05	11.1
+90 µm	17.2	0.12	0.02	4.3
Total	100		0.48	100

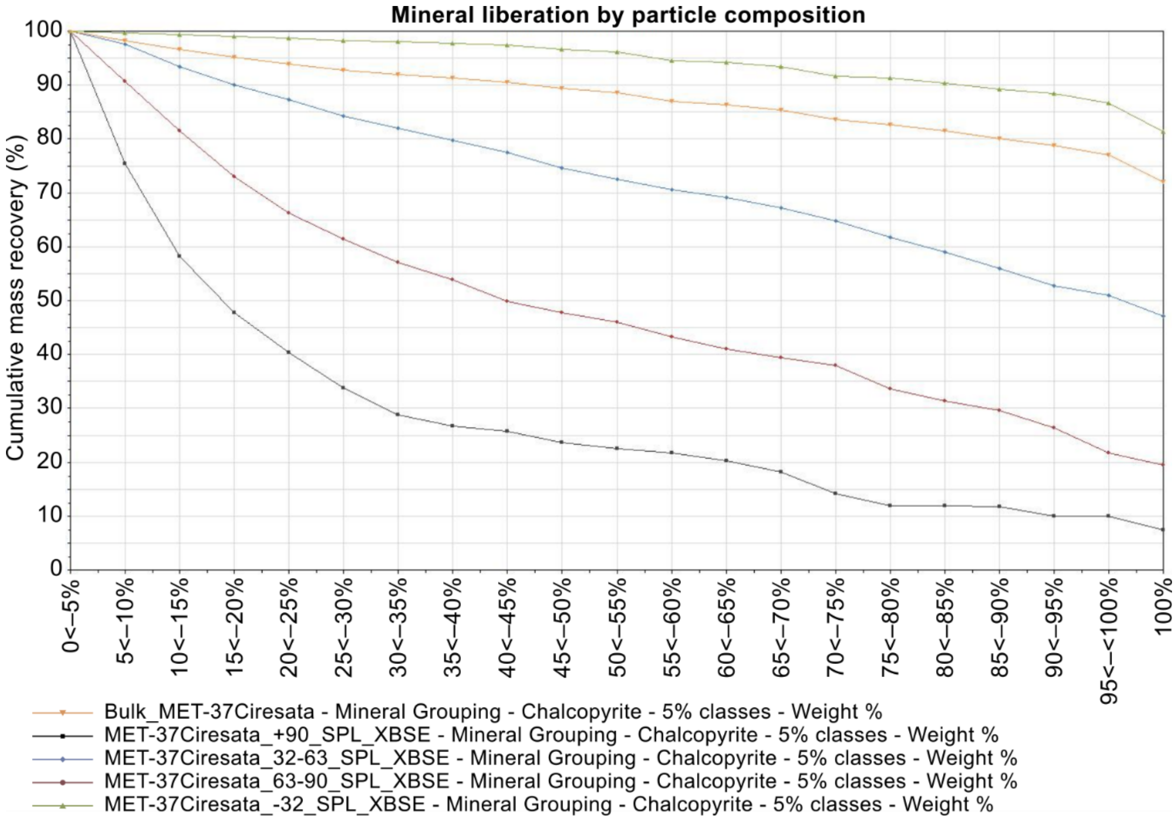


Figure 4.43. The liberation degrees of chalcopyrite, 50 min ground feed ore P80 < 77 µm, Ciresata sample.

The gold occurred mostly as native gold or electrum. There was also one grain which is named as Au_alloy_mix because it was impossible to identify it more specific. The particle sizes of gold and electrum grains were small, usually < 10 µm and only a few totally liberated particles were found, as in Colnic Rovina ore.

In the +90µm fraction there seems to be one grain containing Au, but it was impossible to identify the grain accurately. Therefore the grain has been labelled as Au_alloy_mix. This grain is associated with Plagioclase, Chlorite and Galena (Figure 4.44).

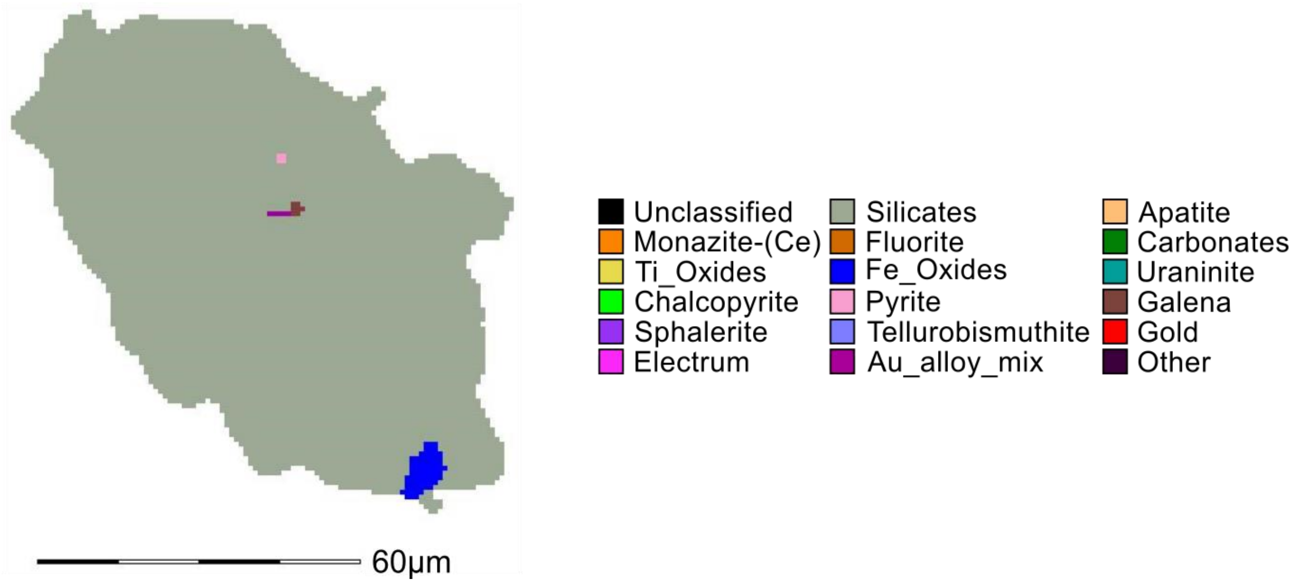


Figure 4.44. Ciresata, occurrence of gold + 90 µm size fraction.

In the fraction 20-32µm, there are four Gold grains. Three of them are associated with Pyrite and one is associated with Chalcopyrite (Figure 4.45).

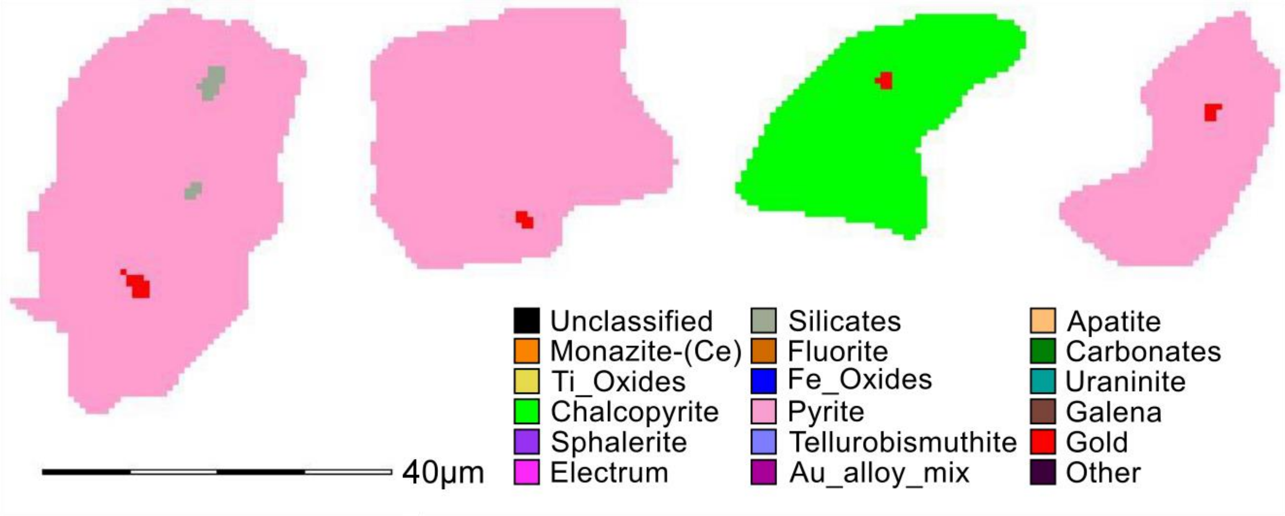


Figure 4.45. Ciresata, occurrence of gold 20-32 µm size fraction.

In the smallest -20µm fraction there are three Gold grains. Two of them are totally liberated and one is associated with Chalcopyrite (Figure 4.46).

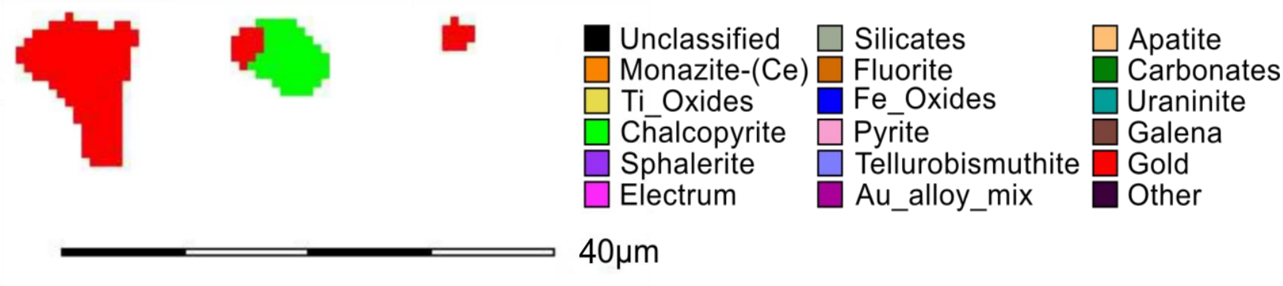


Figure 4.46. Ciresata, occurrence of gold -20 µm size fraction.

4.9.2 Flotation tests Colnic Rovina

Totally eight rougher flotation tests were done, three of them were combined gravity and flotation tests. The grinding was done with the mild steel ball mill for the crushed < 1 mm ore samples. The used ore sample was 1.5 kg, water 0.9 l and the ball charge 8 kg. The flotation tests were done in a four litre flotation cell with 1800 rpm stirring speed, 3 l/min air flowrate and natural pH. The main test parameters were grinding fineness, collector chemicals and their dosages. The used test variables are described below and shown in Table 4.27.

Table 4.27. Flotation test parameters, Colnic Rovina ore.

Test ID	Test parameters
R1	Grinding fineness P80~99 µm, flotation time 15 min, Aerophine 3418A was used as collector 100/t and Dowfroth as frother.
R3	Grinding fineness P80~77 µm, flotation time 15 min, Aerophine 3418A was used as collector 50/t and Dowfroth as frother.
R4	Repeat of Test R1.
R6	Grinding fineness P80~77 µm, flotation time 20 min, two collector chemicals Aerophine 3418A 100/t and KAX 20 g/t, also copper sulphate was used 50 g/t to activate copper and improve the flotation.
R7	Grinding fineness P80~77 µm, flotation time 15 min, Aerophine 3418A 100/t as collector, also Kemira's Grinding aid 2 was used 1000 g/t.
R8	Grinding fineness P80~77 µm, then Knelson concentration followed by flotation for the Knelson tailings. Aerophine 3418A 100/t and KAX 50 g/t were used as collector chemicals.
R10	Grinding fineness P80~57 µm, then Knelson concentration followed by flotation for the Knelson tailings. Aero 3894 100/t and KAX 50 g/t were used as collector chemicals.
R11	Grinding fineness P80~57 µm, then Knelson concentration followed by flotation for the Knelson tailings. Aero 3894 100/t and KAX 50 g/t were used as collector chemicals, in addition Kemira's Grinding aid 1 was used 500 g/t.

4.9.3 Flotation test results and conclusions Colnic Rovina ore

The main results from the beneficiation tests are shown in Table 4.28 and in Figures 4.47 – 4.48. The copper recoveries were modest in rougher flotation tests R1-R7, only 57 – 66 % and the corresponding gold recoveries were 70 – 83 %.

The flotation tailings of Test R3 were investigated in order to find some reasons for the modest copper recoveries. According to mineralogical studies, the liberation degree of chalcopyrite in flotation tailings was 65 %, in the coarsest + 63 µm and + 90 µm size fractions the liberation degree was only 1 – 3 %. Probably the finer grinding will improve the copper recoveries (Test R3 P80~77 µm).

The best gold and copper recoveries were achieved when both gravity concentration and flotation were applied. In tests R10 – R11, the copper recovery was about 74 % with 0.61 % grade and gold recovery 85 – 87 % with grade 2.3 – 2.4 g/t. According to the results, finer grinding improved both copper and gold recoveries. The Kemira's grinding aids didn't improve the copper or gold recoveries but more testing should be performed to verify this. In the earlier studies on Tekes funded Pregold project it was discovered that the grinding aid 1 might improve the gold recoveries and grinding aid 2 rejects the arsenic. The copper sulphate seemed to have positive effect on the copper flotation kinetics in the first rougher flotation stage in Test R6 compared with Tests R1, R3, R4 and R7.

Table 4.28. The main test results, Colnic Rovina ore.

Test	Product	Mass	Cu (XRF)		Au (FA)		S (Eltra)	
		%	%	Rec%	g/t	Rec%	%	Rec%
R1	RC1-5	11.9	0.8	56.6	3.36	74.4	16.9	75.8
R3	RC1-5	17.7	0.62	66	2.23	83.2	14.1	87.6
R4	RC1-5	16.7	0.64	65.1	2.6	77.3	13.8	87.6
R6	RC1-6	13.8	0.81	65.1	3.76	69.8	16.4	90.6
R7	RC1-5	12.8	0.79	57.7	3.25	75.7	15.7	77.8
R8	Knelson concentrate	5.2	0.43	12.9	4.46	42.4	24.7	48.8
R8	RC1-6	9.1	0.95	49.3	2.3	37.4	12.3	42.3
R8	Knelson concentrate + RC1-6	14.3	0.76	62.2	3.06	79.8	16.8	91
R10	Knelson concentrate	4.6	0.43	11.1	4.93	37.7	21	37.9
R10	RC1-6	16.7	0.66	62.6	1.75	49.1	8.41	55.5
R10	Knelson concentrate + RC1-6	21.3	0.61	73.7	2.44	86.8	11.1	93.3
R11	Knelson concentrate	4.4	0.39	9.6	4.56	35.5	25.3	40.2
R11	RC1-6	16.8	0.67	64	1.65	49.1	8.8	53.4
R11	Knelson concentrate + RC1-6	21.1	0.61	73.6	2.25	84.6	12.2	93.6

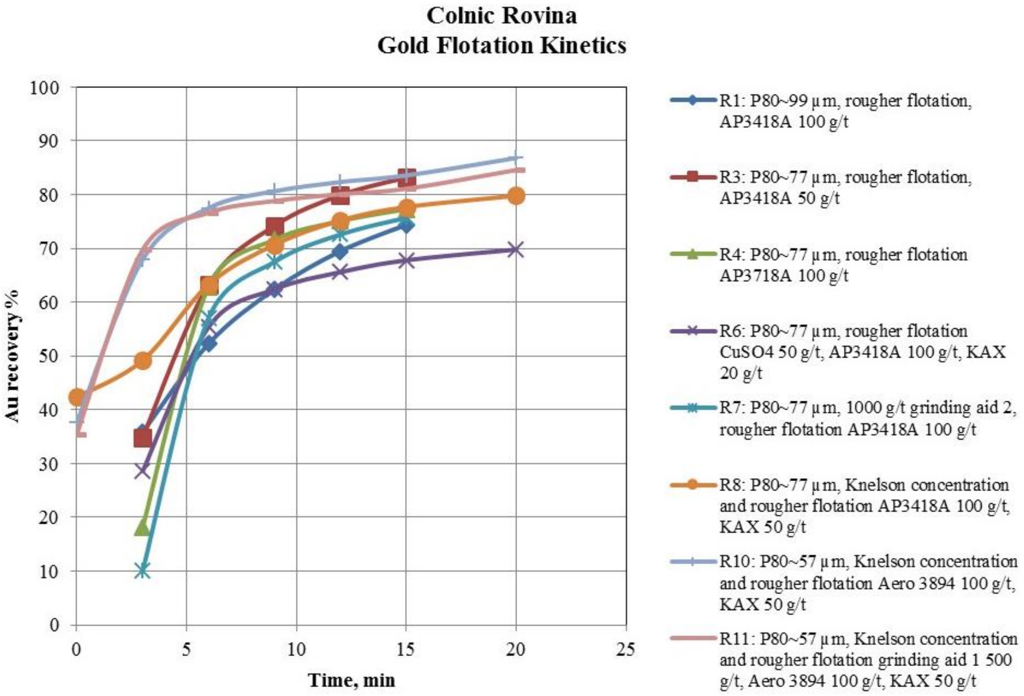


Figure 4.47. Colnic Rovina ore, gold flotation kinetics.

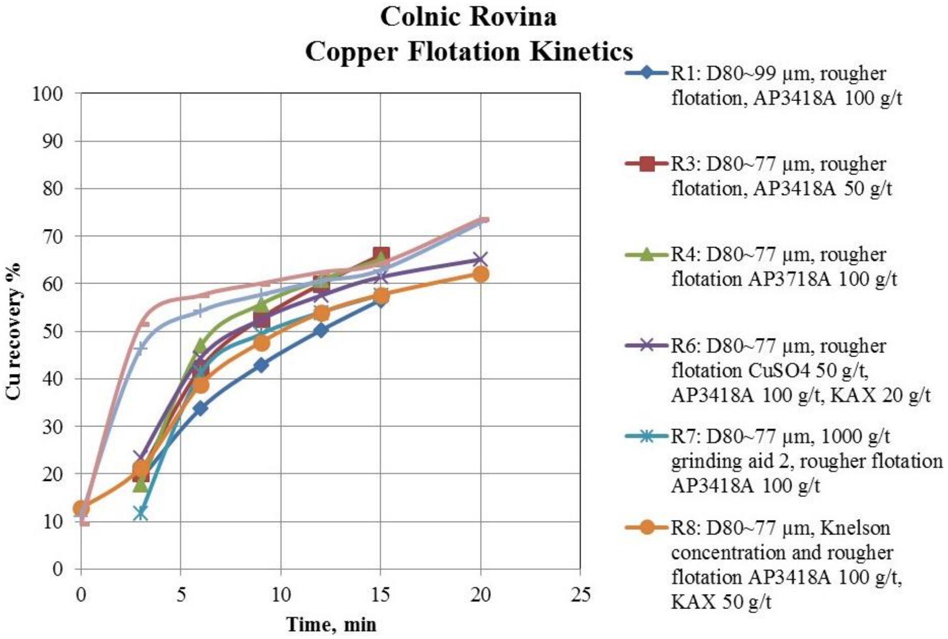


Figure 4.48. Colnic Rovina ore, copper flotation kinetics.

The liberation degrees of chalcopyrite in Test R3 flotation tailings are presented in Figure 4.49 and the distributions of chalcopyrite in the size fractions in Table 4.29.

Table 4.29. Colnic Rovina chalcopyrite distributions, Test R3, flotation tailings.

Test R3 Tails	**Mass (%)**	**Chalcopyrite (Wt%)**	**Chalcopyrite mass (%)**	**Chalcopyrite distribution (%)**
-32 µm	51	0.22	0.11	72.5
32-63 µm	19.9	0.07	0.01	9
63-90 µm	12.4	0.07	0.01	5.6
+90 µm	16.7	0.12	0.02	12.9
Total	100		0.15	100

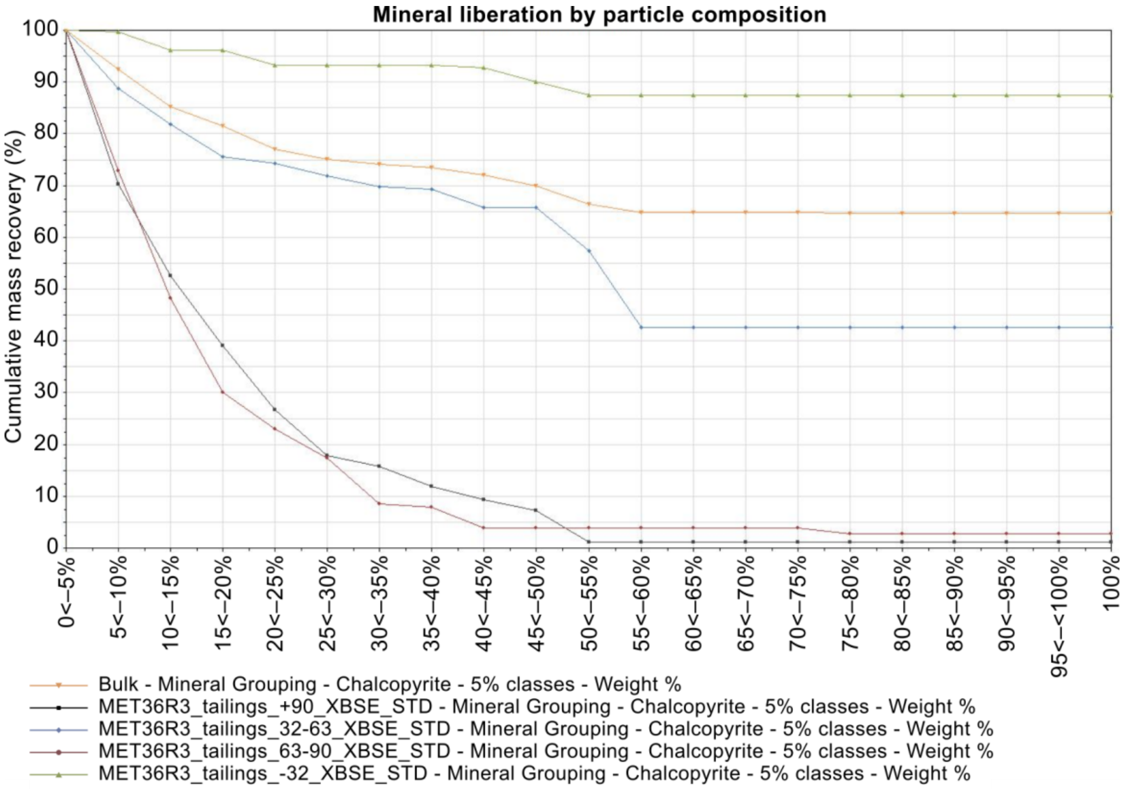


Figure 4.49. The liberation degrees of chalcopyrite, Test R3, flotation tailings.

4.9.4 Flotation tests Ciresata ore

The used test variables are described below and shown in Table 4.30. At the beginning one rougher flotation test and one cleaning flotation were done. Also three combined gravity and rougher flotation tests were conducted. The grinding was done with the mild steel ball mill for the crushed < 1 mm ore samples. The used ore sample was 1.5 kg, water 0.9 l and the ball charge 8 kg. The flotation tests were done in a four litre flotation cell, stirring speed was 1800 rpm and air flowrate 3l/min. The main test parameters were grinding fineness, collector chemicals and their dosages. Flowsheets for tests R2 and R13 done on Cirecita ore are shown respectively in Figures 4.50 and 4.51.

Table 4.30. Flotation test parameters, Ciresata ore.

Test ID	Test parameters
R2	Grinding fineness P80~85 µm, flotation time 15 min, Aerophine 3418A was used as collector 100/t and Dowfroth as frother.
R5	Grinding fineness P80~85 µm, rougher flotation similar as in Test R2. In 1st cleaning stage 5 g/t of Aerophine 3418A were used and pH 11 was applied. The 2nd cleaning stage was done in pH 11.5. The idea was to produce higher grade copper concentrate. Flowsheet for the test is shown in Figure 4.50.
R9	Grinding fineness P80~85 µm, then Knelson concentration followed by flotation for the Knelson tailings. Aerophine 3418A 100/t and KAX 50 g/t were used as collector chemicals.
R12	Grinding fineness P80~57 µm, then Knelson concentration followed by flotation for the Knelson tailings. Aero 3894 100/t and KAX 50 g/t were used as collector chemicals.
R13	Grinding fineness P80~57 µm, then Knelson concentration followed by flotation for the Knelson tailings. Aero 3894 100/t and KAX 50 g/t were used as collector chemicals, also Kemira's Grinding aid 1 was used 500 g/t. Flowsheet for the test is shown in Figure 4.51.

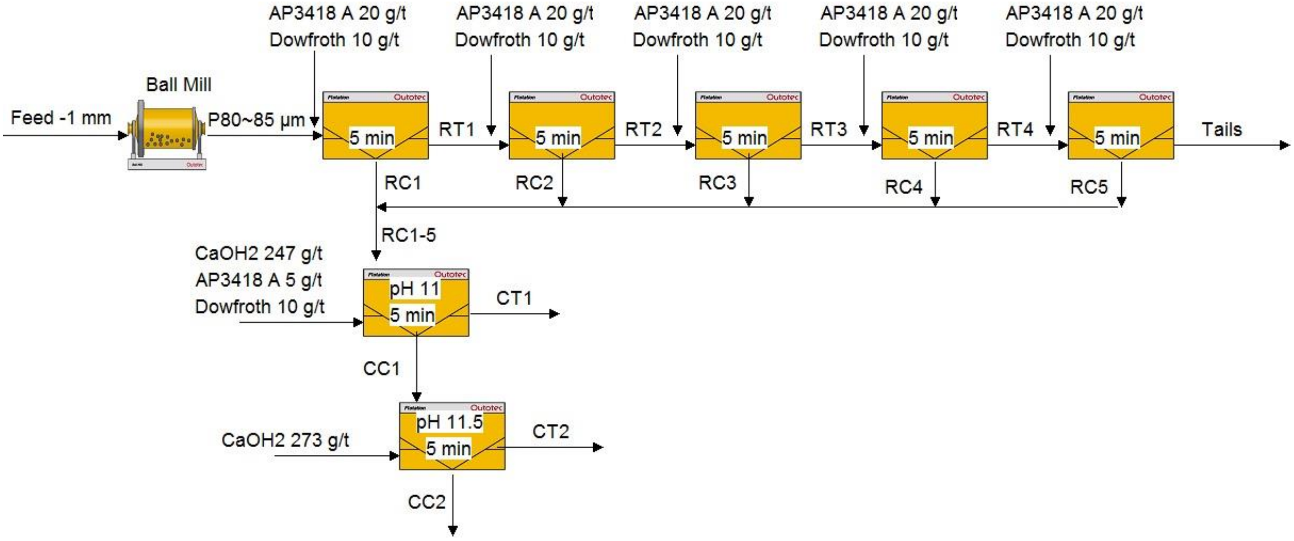


Figure 4.50. Flotation flowsheet, Test R5, Ciresata ore.

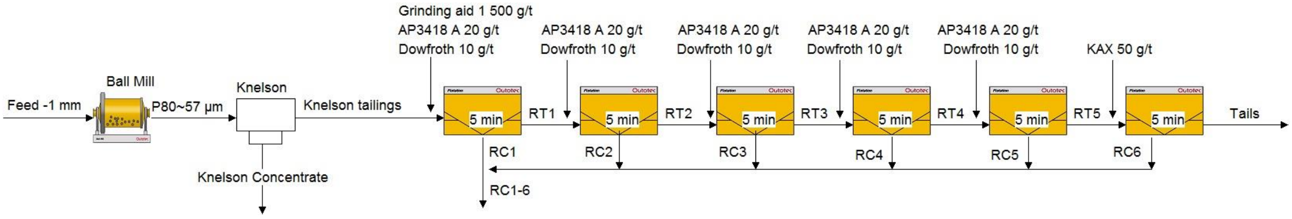


Figure 4.51. Flotation flowsheet, Test R13, Ciresata ore.

4.9.5 Flotation test results and conclusions Ciresata ore

The main results from the beneficiation tests are shown in Table 4.31 and in Figures 4.52 and 4.53. Fairly good copper recovery 86 % and gold 80 % were achieved in the Test R2. The upgrading of copper and gold was modest, after two cleanings in Test R5 the copper grade was 6.4 % with 40 % recovery, the corresponding gold grade was 27 g/t with 32 % recovery.

The combination of gravity concentration and flotation produced the highest copper recoveries about 89 – 90 % in Tests R9 – R13. About 8 – 9 % of total copper and 23 – 26 % of gold was recovered by Knelson concentrator. The gravity concentration did not improve the total gold recovery. Overall, the gold recoveries varied from 78.9 – 80.6 %. Also, there was not much difference in copper and gold recoveries by using different grinding fineness's. The Kemira's "Grinding aid 1" didn't seem to improve the copper or gold recoveries, but need to be tested with higher dosage.

Table 4.31. The main test results, Ciresata ore.

Test	Product	Mass	Cu (XRF)		Au (FA)		S (Eltra)	
		%	%	Rec%	g/t	Rec%	%	Rec%
R2	RC1-5	9.5	1.34	86	5.8	80.1	10.3	9.9
R5	RC1-5	11	1.15	85.5	5.7	79	9.5	91.3
R5	CC1	1.5	4.24	4.8	19.6	37.5	31.6	42
R5	CC2	0.9	6.43	40.4	27.4	31.9	40.8	33
R8	Knelson concentrate	4	0.38	9.3	6	26.2	11.8	41.6
R8	RC1-6	11.2	1.16	79.7	4.5	54.4	5.5	53.9
R8	Knelson concentrate + RC1-6	15.2	0.95	89	4.9	80.6	7.2	95.5
R10	Knelson concentrate	3.3	0.39	8.1	7.2	24.2	11.9	33.2
R10	RC1-6	17.8	0.72	81.4	3.01	55.2	4.1	62.4
R10	Knelson concentrate + RC1-6	21.1	0.67	89.5	6.67	79.4	5.3	95.6
R11	Knelson concentrate	3.3	0.38	7.9	6.49	23	11.8	33.9
R11	RC1-6	17.3	0.75	82.5	3.03	55.8	4.1	61.7
R11	Knelson concentrate + RC1-6	20.6	0.69	90.4	3.6	78.9	5.4	95.6

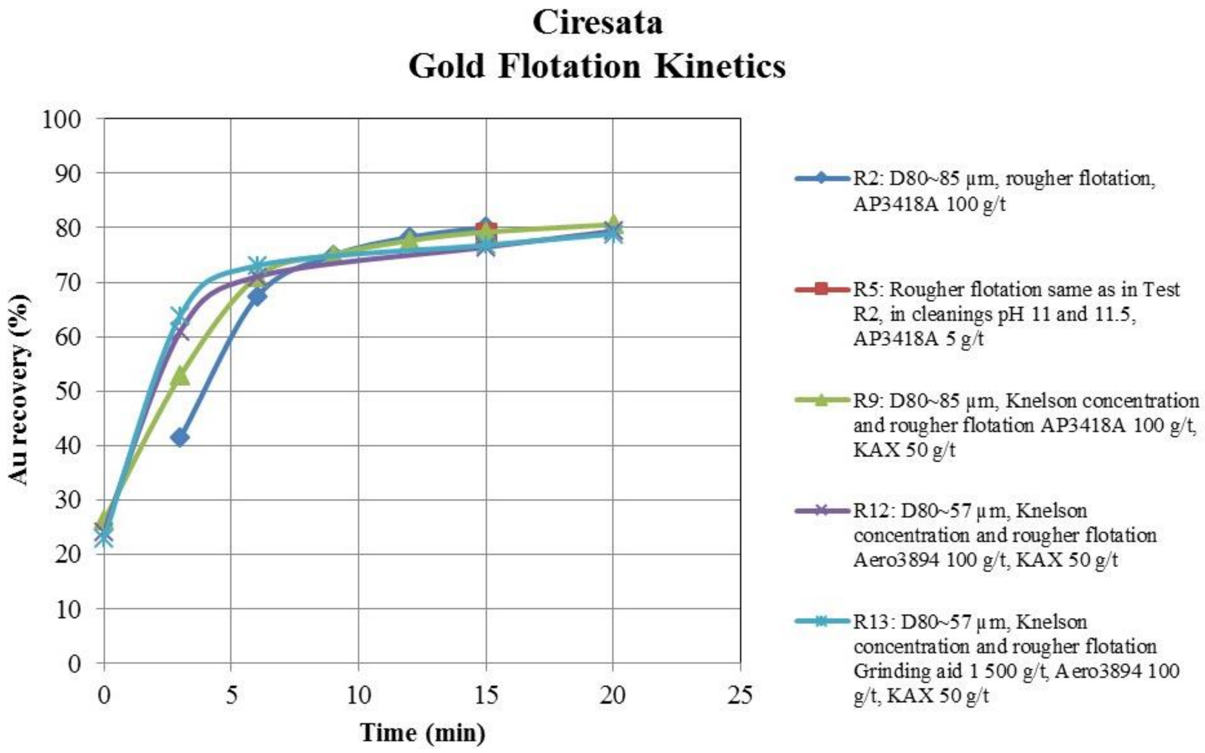


Figure 4.52. Ciresata ore, gold flotation kinetics.

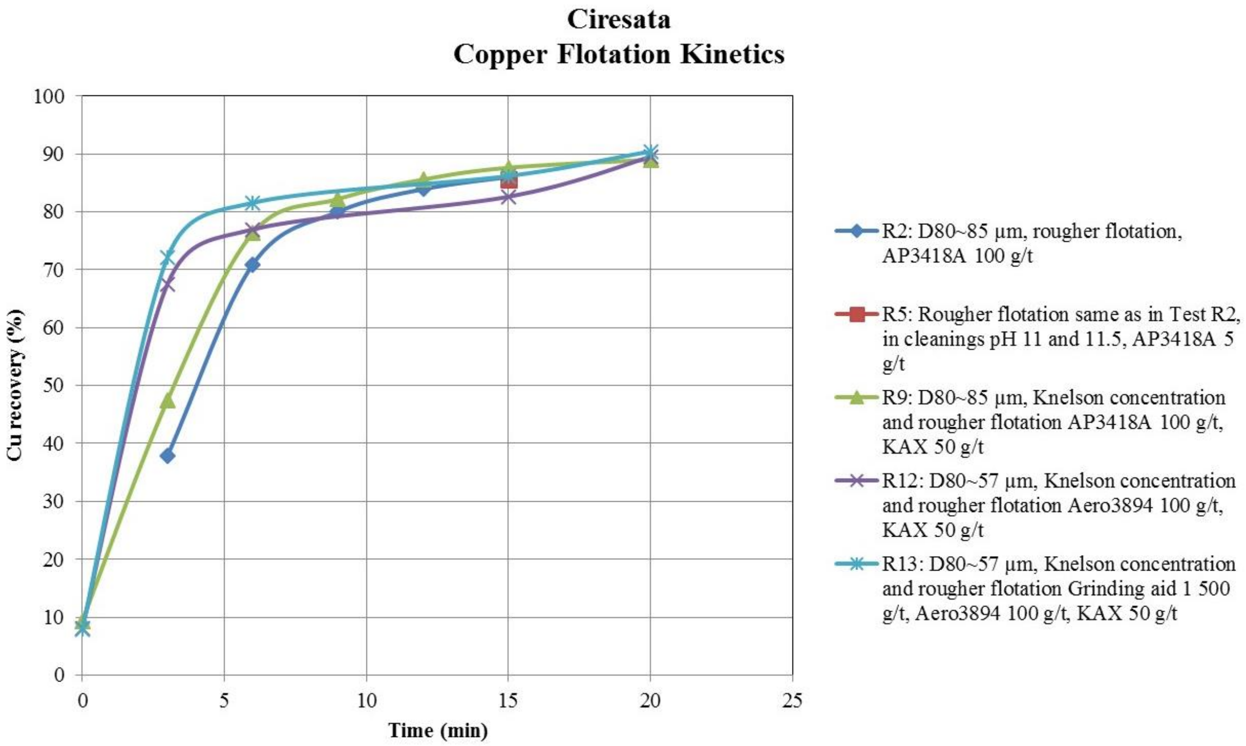


Figure 4.53. Ciresata ore, copper flotation kinetics.

4.10 Beneficiation tests with Finnish gold ore samples

Two gold ore samples Kuikka 1 and Kuikka 2 located in Suomussalmi area in Finland were studied. Both flotation and gravity concentration tests were done to recover the gold. Also some mineralogical studies were made.

Prior to the mineralogical studies and beneficiation tests both ore samples were crushed by the jaw- and roller crusher to suitable < 1 mm particle size. Then the ore samples were homogenized by mixing and divided into suitable 1.5 kg and 5 kg sub samples for the bench scale tests.

4.10.1 Mineralogical studies

Crushed materials were crushed more up to grain size minus 1 mm. The samples were ground 40 min and sieved to the fractions +75 µm, 45-75 µm, 20-45 µm and -20 µm.

One polished vertical section was prepared from each sieving fraction. Modal mineralogy was measured with Mineral liberation analyser (MLA) equipment from fractions +75 µm, 45-75 µm and 20-45 µm using measurement type XMOD_std and from fractions -20 µm measurement type XBSE.

The main minerals in Kuikka 1 were Quartz (57 %), Albite (5.6 %), Plagioclase (14.5 %), Muscovite (1.6 %), Biotite (4.5 %), Chlorite (6.4 %), Hornblende (1.5 %), Clinozoisite (3.7 %), and Arsenopyrite (1.3 %). The main minerals in Kuikka 2 were Quartz (45.5 %), Albite (7.7 %), Plagioclase (26.8 %), Muscovite (1.6 %), Biotite (5.5 %), Chlorite (4.4 %) and Arsenopyrite (2.9 %)

Table 4.32. The modal mineralogy of the sieved fractions and calculated bulk, Kuikka 1.

Measurement type	**XMOD**	**XMOD**	**XMOD**	**XBSE**	**Calculated Bulk**
Mineral	**+75 µm**	**45-75 µm**	**20-45 µm**	**-20 µm**	
	Wt%	**Wt%**	**Wt%**	**Wt%**	**Wt%**
Quartz	70.7	61.2	51.8	41	57
Albite	3.91	5.63	6.43	6.41	5.56
Plagioclase	9.95	14.9	16.8	16.8	14.5
K-feldspar	0.45	0.4	0.45	0.67	0.48
Muscovite	1.05	1.19	2.07	2.47	1.64
Biotite	3.31	3.67	5.61	5.81	4.5
Chlorite	4.03	4.43	7.14	11.1	6.38
Smectite	0.35	0.56	0.41	0.69	0.5
Hornblende	1.12	1.25	1.61	2.02	1.47
Clinozoisite	2.89	3.93	3.97	3.88	3.67
Titanite	0.36	0.43	0.37	1.37	0.6
Arsenopyrite	0.71	1.13	1.21	2.15	1.26
Goethite	0.33	0.39	0.58	1.91	0.74
Total	100	100	100	100	100

Table 4.33. The modal mineralogy of the sieved fractions and calculated bulk, Kuikka 2.

Measurement type	**XMOD**	**XMOD**	**XMOD**	**XBSE**	**Calculated Bulk**
Mineral	**+75 µm**	**45-75 µm**	**20-45 µm**	**-20 µm**	
	Wt%	**Wt%**	**Wt%**	**Wt%**	**Wt%**
Quartz	56.5	45.8	42.9	34.2	45.5
Albite	7.41	8.01	7.19	8.01	7.67
Plagioclase	23.5	31	28.2	22.9	26.8
K-feldspar	0.43	0.38	0.41	0.62	0.45
Muscovite	1.17	1.14	1.24	2.5	1.44
Biotite	2.94	4.1	7.91	8.34	5.52
Chlorite	2.91	3.14	4.85	7.99	4.44
Smectite	0.43	0.5	0.51	0.82	0.55
Clinozoisite	0.65	0.77	1	1.34	0.91
Titanite	0.59	0.8	0.95	2.44	1.11
Arsenopyrite	2.31	3.08	2.69	3.59	2.9
Goethite	0.46	0.5	0.64	2.39	0.9
Total	100	100	100	100	100

In Kuikka 1, *ca*. 80 % of gold occurred in < 40 µm particle size. Approximately 70 % of gold particles were free, 24 % of gold is associated with silicates, about 6 % with arsenopyrite and the rest with sulphides and Fe-arsenate (Figure 4.54). Only a few gold grains were observed in sample Kuikka 2.

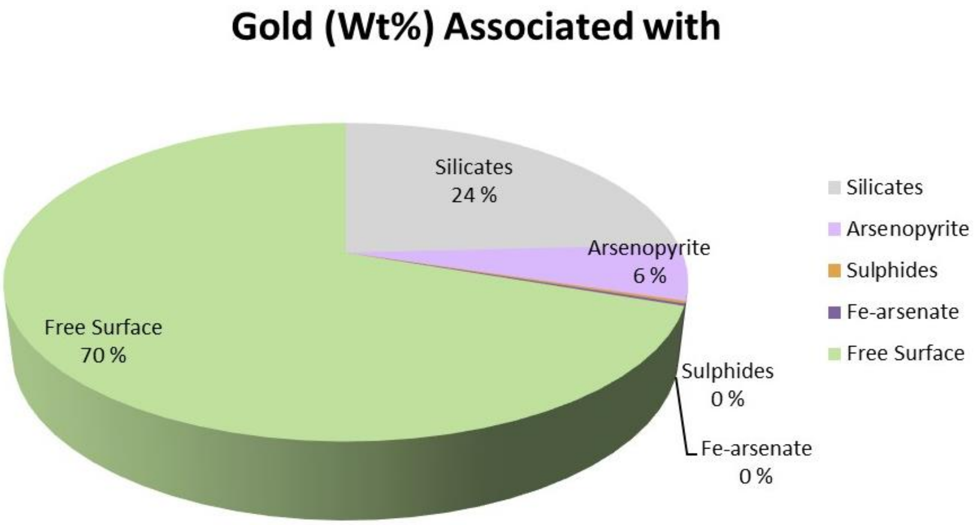


Figure 4.54. Association of gold, Kuikka 1.

4.10.2 Test program Kuikka 1

The used test variables in the flotation tests are shown in Table 4.34. The rougher flotation stage was done in four litre flotation cell, stirring speed was 1800 rpm and air flowrate 3l/min. The grinding was done with the mild steel ball mill for the crushed < 1 mm ore samples. The used ore sample was 1.5 kg, water 0.9 litre and the ball charge 8 kg. Also the gravity separation and the combination of both gravity separation and flotation were investigated too.

Table 4.34. Flotation test conditions, Kuikka 1 gold ore.

Test ID	Test conditions
Test 1	Grinding fineness P80~81 µm, flotation time 15 min, Aerophine 3418A was used as collector 100/t and Dowfroth as frother 50 g/t.
Test 4	Grinding fineness P80~81 µm, rougher flotation similar as in Test 1. The rougher concentrates RC1-5 were cleaned twice.
Test 7	The rougher tails from the Test 1 were reground 20 minutes and then scavenger flotation was conducted in order to improve the gold recoveries. The potassium amyl xhantate (KAX) and Aerophine 3418A were used as collector chemicals.

The flowsheet of the gravity separation test is presented in Figure 4.55. The test was done with 5 kg ore batch, the grinding fineness was 80 < 86 µm. After the grinding gravity separation was done by the small shaking table and the rougher shaking table concentrate was cleaned twice.

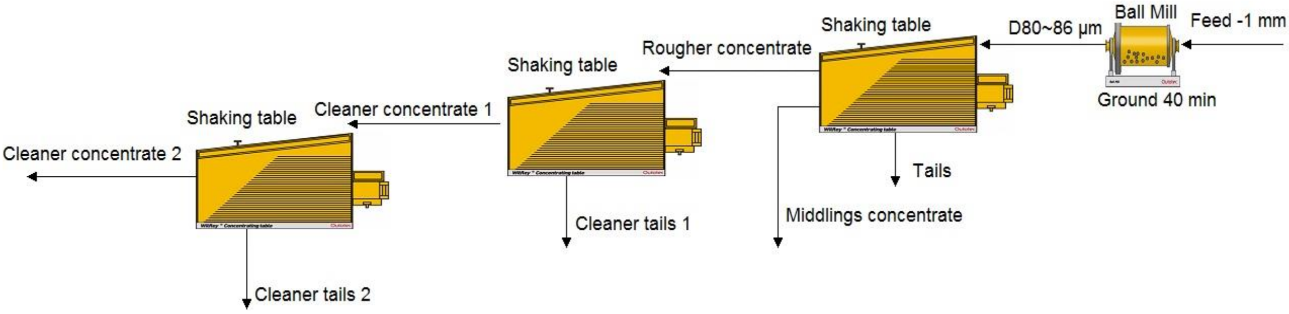


Figure 4.55. Gravity separation test with shaking table.

The flowsheet of the combined gravity separation and flotation test is shown in Figure 4.56. Generally, the shaking table tailings, middlings concentrate, 1st cleaner tails and 2nd cleaner tails were combined and reground 20 minutes prior the rougher flotation. The rougher flotation concentrates RC1-5 were then cleaned twice.

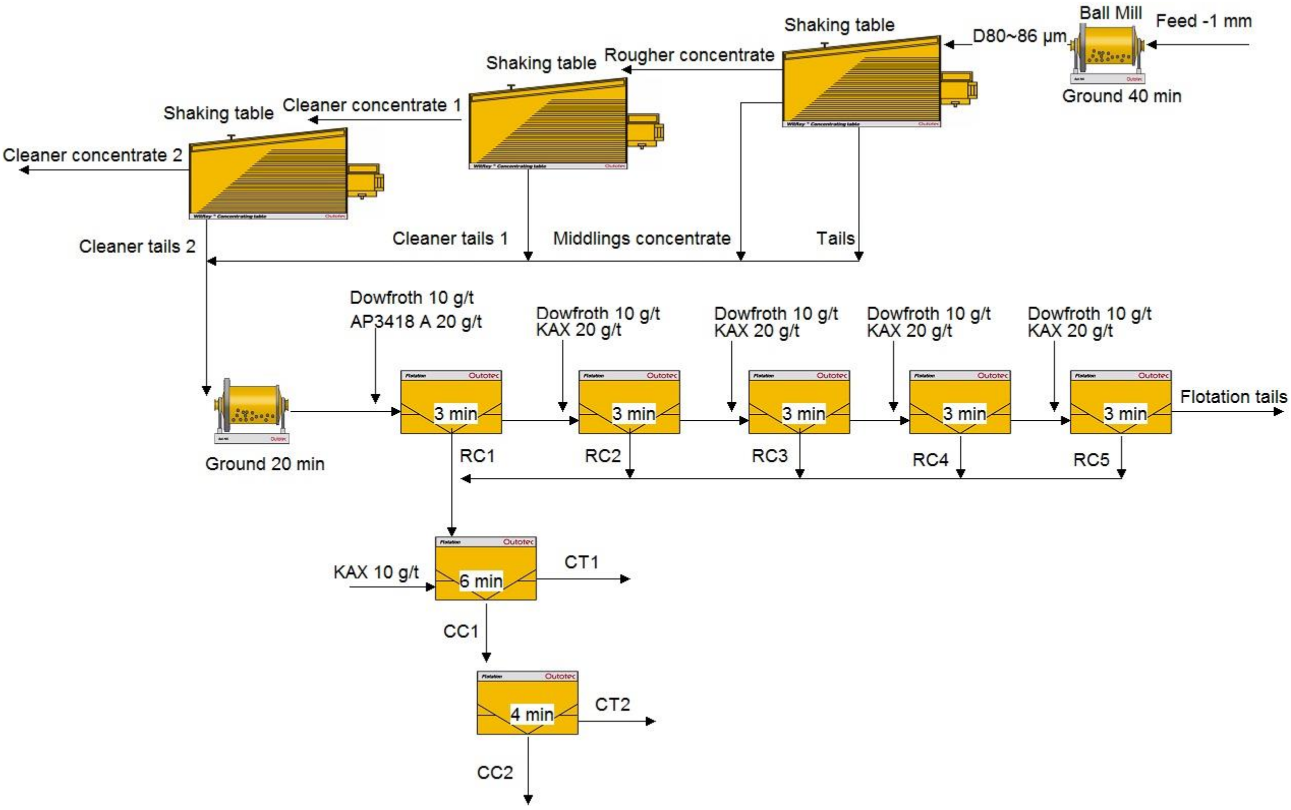


Figure 4.56. The combined gravity separation and flotation test 1.

4.10.3 Test results and conclusions Kuikka 1

According to the results, it seems that it is possible to produce very high grade gold concentrates with high recoveries (Tables 4.35 – 4.36) from Kuikka 1 ore. In Test 4, about 93 % gold recovery with 3690 g/t grade was achieved in rougher flotation, after 2nd cleaning the gold grade was 6557 g/t with 72 % recovery. The harmful arsenic tends to float easily with the gold. The arsenic grade in 2nd cleaning concentrate was 21.7 % with 55.6 % recovery.

In Test 1 the grinding fineness and the collector dosages were the same as in the Test 4, anyhow, for some reason the gold recovery was lower 84 % and the gold grade in the flotation tailings was very high 18 g/t. The flotation tailings of Test 1 were reground and scavenger flotation was performed in Test 7, in order to find out the possibility to improve the gold recoveries. After four stage scavenger flotation, the gold recovery was improved from 84 % up to almost 97 %. Anyhow, there was still 3 g/t of gold in the flotation tailings.

Table 4.35. Flotation test results, Kuikka 1 ore sample.

Test no:	**Product**	**Mass**	**Au (FA)**		**S (Eltra)**		**Fe (XRF)**		**SiO$_2$ (XRF)**		**As (XRF)**	
		%	**g/t**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**
1	RC1-5	2.4	3942.8	84.4	15.3	77.7	17.9	13.4	38	1.2	15.3	75.9
1	Tails	97.6	18	15.6	0.1	22.3	2.9	86.6	79.1	98.8	0.1	24.1
1	Calculated feed	100	113	100	0.5	100	3.2	100	78.1	100	0.5	100
4	RC1-5	2.8	3690.1	93.2	11.3	74.7	16	13.8	42.9	1.5	13	76.4
4	CC1	1.5	6217.6	81.9	17.2	59.2	22	9.9	27.5	0.5	19.8	60.9
4	CC2	1.2	6557	72.1	18.7	53.7	23.6	8.9	23.2	0.4	21.7	55.6
4	Tails	97.2	7.7	6.8	0.1	25.3	2.9	86.2	79.2	98.5	0.1	23.6
4	Calculated feed	100	110.5	100	0.4	100	3.2	100	78.2	100	0.5	100
7	RC1-5	2.4	3942.8	83.6	15.3	71.4	17.9	13.3	38	1.2	15.3	77.3
7	RC1-5 + SC1-2	3.3	3283.1	96.2	11.9	76.8	15.4	15.9	45.2	2	11.9	83.1
7	RC1-5 + SC1-4	4.4	2528	96.9	9.5	79.7	13.6	18.4	50	2.9	9.3	85.6
7	Tails	95.6	3.7	3.1	0.1	20.3	2.8	81.6	76.3	97.1	0.1	14.4
7	Calculated feed	100	114.1	100	0.5	100	3.2	100	75.1	100	0.5	100

The gravity separation by the shaking table produced fairly good results (Table 4.36). The gold recovery in rougher concentrate was 69 % with grade 550.7 g/t and in the combined rougher and middlings concentrate 222.7 g/t with the 79 % recovery. After cleaning the rougher concentrate twice, the gold grade was upgraded to 6748 g/t with 52.3 % recovery. Most likely, the finest gold particles were lost in shaking table tailings which gold grade was high 24.7 g/t.

The combination of gravity separation and flotation resulted in higher gold recoveries compared with gravity separation. The overall gold recovery was 94.5 % with grade 1710 g/t (the combined 2nd cleaner gravity concentrate and rougher flotation concentrate RC1-5). Thus, the gold grade was still relatively high 4.6 g/t in the flotation tailings.

Table 4.36. Gravity separation and combined gravity separation and flotation results.

Test no:	**Product**	**Mass**	**Au (FA)**		**S (Eltra)**		**Fe (XRF)**		**SiO_2 (XRF)**		**As (XRF)**	
		%	**g/t**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**
1	Rougher + Middlings concentrate	29.3	222.7	78.9	0.4	32.1	2.7	25.1	81	30.3	0.8	45.2
1	Rougher concentrate	10.4	550.7	69	0.5	15.4	3	9.6	80.7	10.7	1.3	24.9
1	Cleaner concentrate 1	3.1	1572.2	59.1	1.2	10.4	4.6	4.5	75.8	3	3.3	18.8
1	Cleaner concentrate 2	0.6	6748	52.3	2.9	5.1	9.8	2	59	0.5	9.8	11.6
1	Tails	70.7	24.7	21.1	0.4	67.9	3.4	74.9	77.4	69.7	0.4	54.8
1	Calculated feed	100	82.8	100	0.4	100	3.2	100	78.5	100	0.5	100
1B	Cleaner concentrate 2	0.6	6748	52.3	2.9	5.1	9.8	2	59	0.5	9.8	11.6
1B	RC1-2	3.7	841.5	39.7	6.7	72.3	12.6	14.6	54.3	2.6	7.8	67.4
1B	CC1	1.5	1951.1	37.6	13.9	61.6	20.4	9.6	33.8	0.7	17	60.3
1B	CC2	1.2	2475.3	36.4	16.5	56.1	23	8.3	26.4	0.4	20.7	56.1
1B	Cleaner concentrate 2 + RC1-5	4.4	1710.4	94.5	6.1	77.7	12.2	16.6	55	3.1	8.1	82
1B	Cleaner concentrate 2 + CC1	2.2	3374.1	92.4	10.6	67	17.3	11.6	41.3	1.2	14.9	74.8
1B	Cleaner concentrate 2 + CC2	1.8	3994.9	91.3	11.7	61.5	18.3	10.3	38	0.9	16.8	70.6
1B	Tails	95.6	4.6	5.5	0.1	22.3	2.8	83.4	78.5	96.9	0.1	18
1B	Calculated feed	100	79	100	0.3	100	3.2	100	77.5	100	0.4	100

Test 1: gravity separation test by the shaking table.
Test 1B: combined gravity separation and flotation test.

4.10.4 Test program Kuikka 2

Totally six rougher flotation tests and one cleaning flotation test were done. The used test conditions are described below and presented in Table 4.37 and in Figure 4.57. The grinding was done with the mild steel ball mill for the crushed < 1 mm ore samples. The used ore sample was 1.5 kg, water 0.9 litre and the ball charge 8 kg. The rougher flotation stage was done in four litre flotation cell, stirring speed was 1800 rpm and air flowrate 3 l/min. The effect of Kemira’s grinding aids were especially investigated against arsenic and gold recoveries.

Table 4.37. The flotation test conditions, Kuikka 2 gold ore.

Test ID	Test Conditions
Test 2	Grinding fineness P80~82 µm, flotation time 15 min, Aerophine 3418A was used as collector 100/t and Dowfroth as frother 50 g/t.
Test 5	Grinding fineness P80~82 µm, rougher flotation similar as in Test 2. The rougher concentrates RC1-5 were cleaned twice.
Test 11	Grinding fineness P80~82 µm and Kemira's "Grinding aid 2" was fed 1000 g/t in grinding. Otherwise the rougher flotation was done the similar way as in the previous tests.
Test 12	Kemira's "Grinding aid 2" was fed totally 1000 g/t during the rougher flotation, 200 g/t in every rougher flotation stage. Otherwise the test procedure was similar as in the previous tests.
Test 17	Kemira's "Grinding aid 1" was fed 1000 g/t in grinding, otherwise the test procedure was the same as in the previous tests.
Test 18	The finer grinding was applied P80~60 µm. The rougher flotation stages 1-5 were done the similar way as previous tests by using Aerophine 3418A as collector 100/t and Dowfroth as frother 50 g/t. Additional 6th rougher flotation stage was added where 50 g/t KAX was used as collector in order to improve the gold recoveries.
Test 19	Kemira's "Grinding aid 2" was fed 500 g/t in the 1st rougher flotation stage, otherwise the test conditions were the same as in Test 18.

4.10.5 Test results and conclusions Kuikka 2

Generally, the gold recoveries in the rougher flotation varied from 77.6 – 83.9 % and gold grades 18.8 – 47.4 g/t. Only one cleaning flotation test was conducted where 78.8 g/t gold grade with 54.2 % recovery was achieved after 2nd cleaning (Test 5) (Table 4.38, Figure 4.57).

The finer grinding P80~60 µm with additional rougher flotation stage in Test 18 improved the total gold recovery slightly 83.9 % compared with tests of similar kind (Tests 2-5) with coarser grinding P80~82 µm which produced 79.4-80.4 % recovery (Table 4.38, Figure 4.57).

The Kemira's "Grinding aid 2" reduced the arsenic recoveries in gold concentrates. The arsenic recovery was about 81-85 % in Tests 2-5 without grinding aid. In similar Test 11 "Grinding aid 2" was fed 1000 g/t in grinding and then the overall arsenic recovery was 75.7 %. The arsenic recovery was reduced furthermore below 70 % in Test 12 when the "Grinding aid 2" was fed 1000 g/t during the flotation (Table 4.38, Figure 4.57).In Test 19, the arsenic recovery was high 87 % and only slightly lower than in similar Test 18 without the grinding aid. Probably due to finer grinding fineness P80~60 µm and the lower 500 g/t "Grinding aid 2" dosage the arsenic recoveries were high. The finer grinding the most likely requires higher dosages of grinding aid in order to depress the arsenic. Further testing would be needed (Table 4.38, Figure 4.57). The effect of "Grinding aid 1" was neutral for the both gold and arsenic recoveries, more testing should be done.

Table 4.38. Flotation test results, Kuikka 2 ore sample.

Test no:	**Product**	**Mass**	**Au (FA)**		**S (Eltra)**		**Fe (XRF)**		**SiO_2 (XRF)**		**As (XRF)**	
		%	**g/t**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**	**%**	**Rec%**
2	RC1-5	3.5	47.4	80.4	17.1	80.2	23.2	26.6	21.3	1.1	24.3	84.8
2	Tails	96.5	0.4	19.6	0.2	19.8	2.3	73.4	72.8	98.9	0.2	15.2
2	Calculated feed	100	2.1	100	0.7	100	3.1	100	71	100	1	100
5	RC1-5	4	53.8	79.4	14.3	79.9	20.4	26.5	28.5	1.5	20.7	81.1
5	CC1	2.2	77.6	62.6	19.6	59.9	26.4	18.7	13	0.4	27.8	59.1
5	CC2	1.9	78.8	54.2	20.7	53.8	27.6	16.7	9.7	0.2	29.4	53.6
5	Tails	96	0.6	20.6	0.2	20.1	2.4	73.5	76.6	98.5	0.2	18.9
5	Calculated feed	100	2.7	100	0.7	100	3.1	100	74.7	100	1	100
11	RC1-5	4.9	36.4	79.5	13.1	80.8	17.2	26.8	37.8	2.5	16.5	75.7
11	Tails	95.1	0.5	20.5	0.2	19.2	2.4	73.2	76.3	97.5	0.3	24.3
11	Calculated feed	100	2.2	100	0.8	100	3.1	100	74.4	100	1.1	100
12	RC1-5	5.7	33.1	81.9	9.2	73.6	15.2	28.7	43.4	3.4	13.9	69.8
12	Tails	94.3	0.4	18.1	0.2	26.4	2.3	71.3	74.3	96.6	0.4	30.2
12	Calculated feed	100	2.3	100	0.7	100	3	100	72.5	100	1.1	100
17	RC1-5	5	31.5	77.6	12	80	17.8	28.1	36.2	2.4	17.2	82.6
17	Tails	95	0.5	22.4	0.2	20	2.4	71.9	76.4	97.6	0.2	17.4
17	Calculated feed	100	2	100	0.7	100	3.1	100	74.4	100	1	100
18	RC1-6	10.6	18.8	83.9	6.1	87.4	10.6	35.3	54.4	7.9	8.2	87.9
18	Tails	89.4	0.4	16.1	0.1	12.6	2.3	64.7	75	92.1	0.1	12.1
18	Calculated feed	100	2.4	100	0.7	100	3.2	100	72.8	100	1	100
19	RC1-6	11	19.3	81.2	5.9	86.5	10.2	34.9	55.6	8.4	8.1	87
19	Tails	89	0.6	18.8	0.1	13.5	2.4	65.1	74.8	91.6	0.1	13
19	Calculated feed	100	2.6	100	0.7	100	3.2	100	72.8	100	1	100

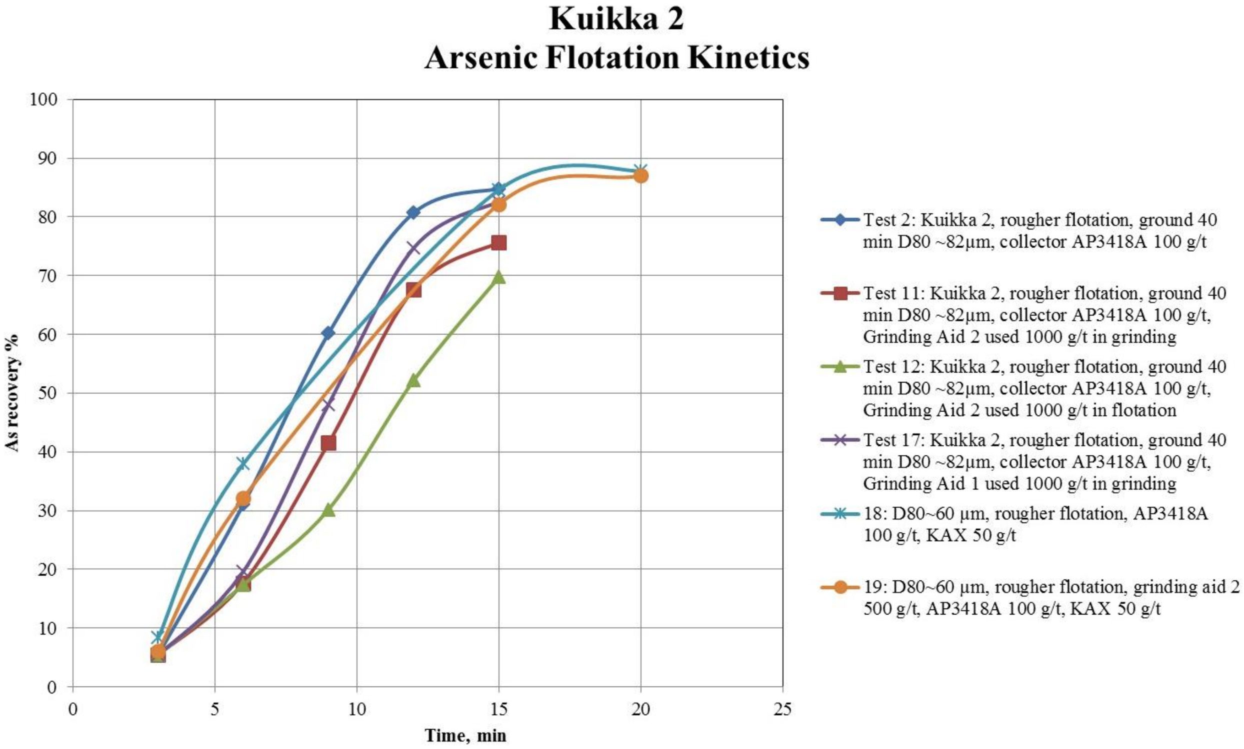


Figure 4.57. Arsenic flotation kinetics in rougher flotation tests, Kuikka 2 ore sample.

4.11 Characterization of process chemical residues and their surface chemistry in flotation

Chemical compounds in process waters and their effects on the properties of the flotation pulp and mineral surfaces were studied. Two reagents, polyacrylic acid and polyacrylamide based chemicals according to their manufacturer, Kemira Oyj, were in special interest. The chemical are called Aid 1 and Aid 2 in this work. In some previous studies carried out at GTK Mintec, these process chemicals had been observed to decrease the recovery of arsenic into gold concentrates. In the present investigation the main goal was to get a deeper understanding of how Aid 1 and Aid 2 work in the flotation of low-sulphide gold ores. Bench scale batch flotation tests on the Colnic Rovina Blend, Ciresata, and Kuikka 2 gold ores were carried out as described elsewhere in this report. First, the flotation tests were conducted without using Kemira's reagents. Then the tests were repeated and either Aid 1 or Aid 2 was added to the pulp before starting flotation. Otherwise the flotation parameters and test conditions were the same (Table 4.39). Aid 1 was used when processing the Colnic Rovina Blend and Ciresata ores, while Aid 2 was used when processing the Kuikka 2 ore.

Table 4.39. Details of the tests carried out to study the effects of Kemira's reagents Aid 1 and Aid 2.

Ore sample	**Test ID**	**P_{80} (µm)**	**Flotation time (min)**	**Reagent dosage (g/t)**					
				Aerophine 3418A	**Aero 3894**	**PAX**	**Aid 1**	**Aid 2**	**Dowfroth 250**
Colnic Rovina Blend	R10	57	20		100	50			50
Colnic Rovina Blend	R11	57	20		100	50	500		50
Ciresata	R12	85	20		100	50			50
Ciresata	R13	85	20		100	50	500		50
Kuikka 2	18	60	20	100		50			50
Kuikka 2	19	60	20	100		50		500	50

During the flotation tests, pulp (redox) potential, some mineral electrode potentials, and pH of the mineral slurry were monitored. Dynamic viscosity of slurry before and after flotation was determined using the Bohlin Visco 88 BV rotational viscometer (Bohlin Reologi AB). In addition, possible effects of the reagents on the degree of non-sulphide gangue entrainment was estimated. Mechanical entrainment is a consequence of particles suspended in the pulp phase following the water into the froth and ultimately into the concentrate (Runge 2010). Entrainment may have a prominent effect on the gangue contents of the concentrate and, thus, its quality. Slurry rheology is potentially an important factor affecting entrainment (Wang et al. 2015).

To evaluate the effect of Kemira's reagents on hydrophobicity/wettability of selected minerals, static contact angle measurements were performed using the CAM 200 optical contact angle meter (KSV Instruments). The recovery and selectivity in flotation depends ultimately on relative hydrophobicities of different mineral phases. The hydrophobicity and, thus, the average contact angle for a specific mineral phase is principally determined by surface chemistry (Smart et al. 2007). Therefore, contact angle measurements can provide information on possible changes in surface chemistry. Finally, NMR spectroscopy was used to analyse organic reagents in process waters. The spectra of the samples were measured at the University of Eastern Finland by using a Bruker AVANCE-III HD 600 NMR instrument operating for ^{1}H nucleus at 600.13 MHz (Bruker-Biospin GmbH, Karlsruhe, Germany) and equipped with a cryo-probe. The compounds were identified based on the chemical shifts and coupling constants. Quantities of compounds were estimated based on the known 3-(trimethylsilyl)propionic acid sodium salt (TSP) concentration.

The 200 mg/l solution (corresponding a dosage of 500 g/t in flotation) of Aid 1 was measured to be basic (pH 9.5) while that of Aid 2 was acidic (pH 5.0). Correspondingly, Aid 1 increased the pulp pH and Aid 2 decreased it compared to the flotation tests where the Kemira's reagents were not used. Neither Aid 1 nor Aid 2 had any obvious effect on the pulp potential or the potentials of gold, arsenopyrite, pyrite or chalcopyrite mineral electrodes. Thus, the reagents appeared to be electrochemically inactive.

Both Aid 1 and Aid 2 (500 g/t) had only a slight effect on the viscosity of the slurry and this effect did not seem to depend on the ore sample. The viscosity of the flotation feed (slurry density 30% w/w) was about 9 mPa·s before adding the chemical and about 8 mPa·s after the addition. The viscosity of the flotation tailings was about 7 mPa·s whether the chemical was used or not.

Entrainment was found to be the most important recovery mechanism for the non-sulphide gangue in the flotation of the Colnic Rovina Blend sample – about 12% of the gangue was recovered by entrainment and 3% by true flotation. Kemira's chemicals did not have any significant effect on the predominant gangue recovery mechanism in the flotation tests. This result is in line with the minor effect of Aid 1 and Aid 2 on slurry viscosity.

Results of the contact angle measurements implied that Aid 1 and Aid 2 had no effect on the contact angle of quartz or talc. Instead, the average contact angle of gold increased by 9° (Aid 1) and 5° (Aid 2) implying an increase in hydrophobicity, whereas the average contact angle of arsenopyrite decreased by 5° (Aid 1) and 7° (Aid 2), implying an increase in hydrophilicity. The confidence level for these results was 94–99% according the two-sample t-test.

According to the NMR measurements, the Dowfroth 250 frother was present in all process water samples and its concentration varied between 0.27 and 1.26 mM. Small concentrations of acetic acid (0.01 mM) and formic acid (up to 0.06 mM) were also found in many process waters. Neither acetic acid nor formic acid were used as flotation reagents so they were either degradation products or impurities/additives in the reagents. Two clear sets of signals were observed for O-isopropyl-N-ethyl thionocarbamate (Aero 3894). This suggested that thionocarbamate existed as two stable conformations (ratio 55:45). The concentration of thionocarbamate was estimated to vary between ca. 0.05 and 0.30 mM. The signals originating from sodium di-isobutyl dithiophosphinate (Aerophine 3418A) and its reaction products with water were identified in the process waters of tests 18 and 19. The concentrations of these compounds were estimated to be 0.05 mM at most. It is notable that Aid 1, Aid 2 and PAX could not be detected by NMR in the process waters. A possible explanation is that these chemicals had adsorbed on the mineral surfaces for the most part leaving none or only trace amount of molecules in the water phase.

For future studies, zeta potential measurements, attenuated total reflection infrared (ATR-IR) spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are suggested as tools that could give more information about the surface chemistry of Kemira’s process chemicals and other reagents as well.

4.12 Conclusions and Recommendations

4.12.1 Conclusions

- Pre-treatment by gravity methods may not be suitable for Castromil gold ore
- Pre-treatment by roasting and high size reduction increases the performance of leaching stages, namely for the thiosulphate leaching
- Thiosulphate leaching could be an alternative to cyanidation, but a pre-treatment stage is mandatory
- Bromine leaching could be an alternative to cyanidation for the Castromil ore, even without a pre-treatment stage, which is mandatory to obtain similar results with thiosulphate leaching
- Froth flotation process showed promising results for gold recovery.

4.12.2 Recommendations

- The conversion of gold from liquid phase to solid phase should be studied for the three leaching methods, namely by activated carbon
- The froth flotation process presented a good performance on gold recovery and should be carefully analysed, namely with a size liberation study
- Different pre-treatment methods could be applied, namely by high pressure oxidation
- The flotation of arsenic from the leaching residues could have an important role on the reduction of the environmental impact of waste disposal.

4.13 References

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5 MINE WATER TREATMENT TECHNOLOGIES

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5.1 Introduction

Anomalous arsenic (As) concentrations in natural waters may be caused by natural dissolution of minerals or originate from agricultural and industrial sources. In an aquatic ecosystem, As is typically present in inorganic forms, mainly in two oxidation states (+5, +3). As(III) is dominant in the presence of reducing conditions, whereas As(V) is mostly observed in the oxidizing environment. Toxicity depends upon the chemical species and, in general, As(III) is 25 to 60 times more toxic than As(V) (Pokhrel et al. 2005).

As occurs as a major constituent in more than 200 minerals, including elemental As, arsenides, sulphides, oxides, arsenates and arsenites. The main As mineral in most As-bearing natural occurrences is arsenopyrite (FeAsS), which is usually present in sulphide ores associated with sediment-hosted gold deposits (Cama et al. 2008).

As concentrations in clean surface water and in groundwater are normally in the range of 1-10 µg/L. Nevertheless, high levels of As originating from natural sources can be found in many places around the world. The level of As in natural waters may be accelerated by a number of human activities like mining.

For instance, in Portugal and Spain it is possible to find concentrations of As in former mining areas ranging from 100 to 2000 µg/L (Fiúza at al. 2014), whereas in Poland significant As concentrations, up to 26 mg/L, were found in water in areas of old mining excavations (Marszałek & Wąsik 2000).

Generally, the water contamination at a mine site depends on type of mined ore, chemicals used in the mineral preparation and metal extraction processes, life stage of the mine as well as environmental management practises (Mining facts 2016, Society for Mining, Metallurgy and Exploration Inc. 2015). Mining and mineral processing operations generate liquid effluents that require treatment before recycling or partial discharge. In particular, effluents resulting from gold mining and mineral processing plant, may contain high levels of As. Therefore, a major concern in gold mine industry is to maintain good quality of effluents discharged in large volumes into water bodies. This requires constant quality monitoring to guarantee the efficient protection of the receiving waters and to react quickly to possible negative impacts of contamination within local communities.

A number of proven methods are available for As removal including oxidation and precipitation techniques, coagulation, ion exchange and adsorption methods as well as membrane separation (Szlachta et al. 2016). A commonly applied active method for the treatment of As-rich mine effluents, is co-precipitation with ferric or aluminium (Al) salts. However, As(III) does not precipitate to the same extent as As(V), and thus is more difficult to remove from water. The oxidation of the As species by air is a slow process; therefore, chemical oxidation by potassium permanganate, sodium hypochlorite or hydrogen peroxide is required (Straskraba & Moran 1990).

Effective removal of various As species is possible by application of sorption technique with use of iron (Fe) based sorbents (IBS) and Fe nanoparticles. Many studies have confirmed that As has a natural affinity for Fe compounds under various operating conditions (Mohan & Pittman 2007, Vu et al. 2003). Therefore, adsorption on Fe-containing surfaces may offer a good solution for the robust and cost-effective treatment of mine waters with elevated concentrations of As. Additionally, sorption is considered as a feasible technique for the treatment large volumes of mine effluents due to the low operational and maintenance costs, flexibility in design, simple operation as well as easy adaptation to in-situ remediation solutions.

In recent years, the in-situ technologies have gained high interest in terms of practical applications. Some alternatives are available like: bioremediation, permeable reactive barriers, in-situ chemical treatment, enhanced natural attenuation and electro-kinetics. The implementation of IBS in a permeable reactive barrier is promising in-situ technology that has received high attention and some applications were already successfully employed in several countries (Litter et al. 2014).

5.2 Objectives

There is a large number of studies available in the literature on selective ion exchange and porous materials for As removal. However, many of them are not technically applicable or economically feasible in the treatment of As contaminated mine effluents.

Due to the specificity of mine waters, the potential ion exchangers/adsorbents must meet several criteria, including a high adsorptive capacity, selectivity towards the As species, good stability, proper particle size or good hydraulic properties. It is known that As has a strong affinity for Fe based materials. Therefore, ion exchange/adsorption on Fe-containing surfaces provide the most suitable treatment of mine waters with elevated concentrations of As.

For this reason, attention was given to the adsorption onto Fe based sorbents and Fe nanoparticles, as an active and passive method for the treatment of As-rich mine waters.

Specific objectives of WUT and UP study were as follows:

- Physical and chemical characterisation of adsorptive/ion exchange materials and nanoparticles used in the study (WUT, UP).
- Assessment of the capacity of Fe based sorbents of the oxides-hydroxides type, as an active reagent for permeable reactive barriers (UP).
- Testing methods for preparing “green” nano Zero Valent Iron nanoparticles (nZVI) and quantification of the removal of As species (III and V) by determining the “green” nZVI isotherms and comparing with nZVI produced by classical chemical methods (UP).
- Assessment of the efficiency of Fe-based sorbents as an active treatment of mine waters, on the basis of batch adsorption tests and fixed bed column experiments with use of model solutions and raw mine waters from the selected two gold mines in Finland (Kittilä Gold Mine, Agnico Eagle and Jokisivu Gold Mine, Dragon Mining) (WUT).
- Testing the performance of selected iron based material in the pilot scale at the gold mine site in Finland (Jokisivu Gold Mine, Dragon Mining) (WUT).

5.3 Materials and methods

5.3.1 Characterization of iron based sorbents and iron nanoparticles

Particle size distribution of tested sorbents and nanoparticles was determined by Mastersizer 2000 laser diffraction particle size analyser (Malvern Instruments). The specific surface area (S_{BET}) and pore size distribution were determined on the basis of nitrogen adsorption/desorption analysis (Autosorb-1, Quantachrome). A scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM/EDS) (JEOL JEM-6301F and JSM-7500F) was used to analyse the chemical composition and properties of tested IBS and nZVI.

5.3.2 Production and testing of “green” nano Zero Valent Iron

The production of “green” nano Zero Valent Iron (NZVI) using vegetable extracts is known as a simple and low-cost method for producing Fe nanoparticles. Within this WP3, several methods with use of various vegetable extracts were considered for the production of the nZVI particles. The materials used in the experimental work were eucalyptus, oak and strawberry leaves, potatoes and carrot peels (Herlekar et al. 2014, Machado et al. 2013a, Machado et al. 2013b, Kharissova et al. 2013). The peels were chosen by their antioxidant behaviour resulting from their high content in phenolic compounds. The selection of the most promising production methods has been done.

The following reagents were used without further purification to obtain the reductive extract from the natural materials: Fe(III) chloride hexahydrate (99 %), Tween 20 and 80, As(III) oxide (99 %), As(V) oxide and distilled water. The mining effluent used in this study was collected in an abandoned mining area (Penedono, Portugal) from former tailings and mine galleries.

The vegetables were dried at 50 ºC in an oven for 48 h and then milled using a cutting mill Retsch SM 2000. After they were sieved and only the fraction with grain size below 4 mm was used. The extract was obtained by a simple procedure: the dried vegetables were weighed and transferred to Erlenmeyer flasks previously filled with 100 mL of distilled water warmed to a temperature of 80 ºC. The contact time was 30 minutes with occasional stirring. The extract was then filtered and left to cool down. Chosen volumes of a solution 0.1 mol/L of Fe(III), prepared from ferric chloride hexahydrate, were added to the extracts and slightly mixed. The reaction occurs immediately and the solution changes from an orange colour to a strong black, indicating the formation of Fe particles (Pattanayak & Nayak 2013).

The removal of As species (III and V) was quantified by determining the “green” nZVI isotherms and comparing with nZVI produced by classical chemical methods. A characterization by visual inspection of the colour evidenced that some extracts were not suitable for the production of nZVI. The remaining coloured solutions were analysed using a particle size analyser (Figure 5.1). The presence of nZVI was confirmed for extracts made with eucalyptus, oak and strawberry leaves. In all three cases the extract was made with 10 g of leaves in 100 mL of distilled water using a ratio of Fe(III) solution / extract of 1:1.

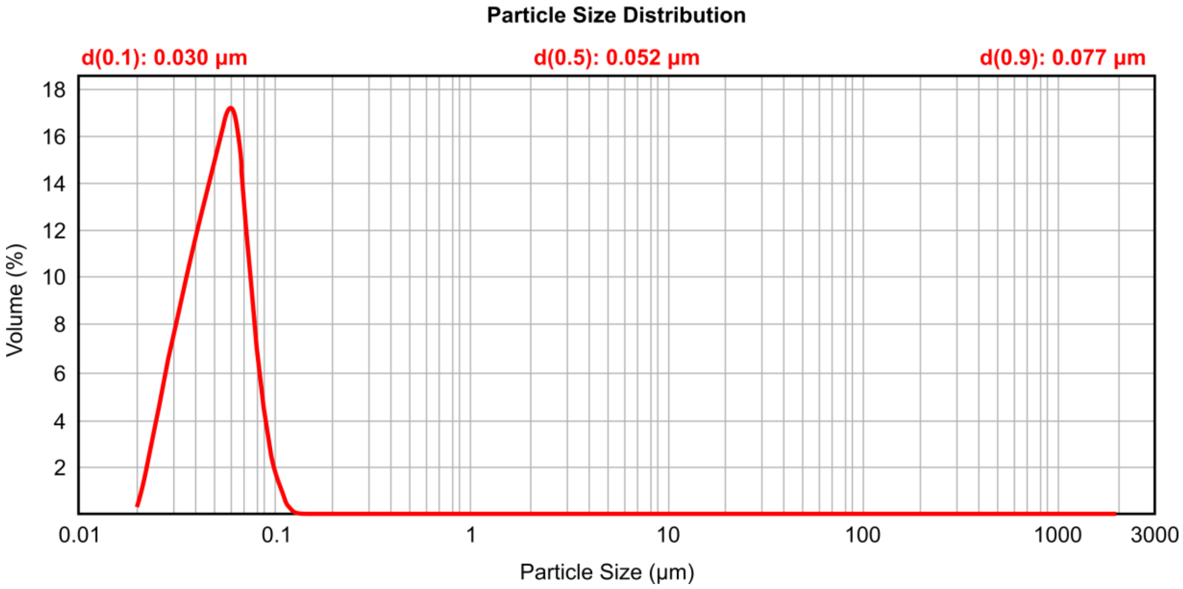


Figure 5.1. Perfect grain size distribution of produced “green” nanoparticles

The nZVIs produced from the eucalyptus leaves were selected for kinetic characterization studies. The role of two surfactants Tween 20 and Tween 80 in the stabilization of the nanoparticles, avoiding aggregation, was also assessed allowing to conclude that Tween 80 could partially avoid and delay the particle aggregation.

Two samples were submitted to SEM/EDS analysis. The analysis evidenced the presence of Fe and carbon and some minor elements such as P and chloride (Cl). The structure was not crystalline but evidenced an amorphous nature and carbon is probably of organic origin.

The second part of the experimental work was focused on the As removal from the mining effluents. The solutions were prepared in different conditions: beakers with 100 mL of effluent each and different volumes of nZVIs that were left to react for 8 hours with slight stirring. After, the solutions were filtered and analysed by Hydride Generation Atomic Absorption Spectroscopy. Industrial nZVIs were also tested for comparative purposes using an As solution with a concentration of 500 µg/L.

Kinetic tests with nZVI were performed using flasks with 500 mL of a solution with a concentration in As of 1.1 mg/L and adding different masses of nZVI: 0.1, 0.2 and 0.55 g. The flasks were incubated in an orbital shaker during 48 hours. During this time 5 samples of 10 mL were collected from each flask and preserved by adding 100 µL of HCl at 37%.

5.3.3 Sorption tests of arsenic by iron based sorbents - ARM 300 and GEH 102

The commercial sorbents ARM 300 and GEH 102 used in the study were supplied by BASF and Wasserchemie GmbH & Co, respectively. The sand used was pure quartz that was washed, dried and sieved to grain sizes between 710 and 1000 µm.

Column tests were performed at 20 ºC. The solutions contaminated with As were artificially prepared and they were pumped from a large volume container using a peristaltic multi-channel Ismatec BV-GES pump into an Omnifit column with an internal diameter of 2.5 cm and a total height of 15 cm. Later, larger columns (3.1 cm in diameter and 40 cm in height) were also used. Cumulative effluent volumes were periodically measured and samples were simultaneously collected for chemical analysis.

Samples of two sorbents were collected after their usage in fixed bed columns and analysed using an Electron Microprobe Analyser. The samples were impregnated in resin and polished with diamond paste for examination and analysis by a Field Emission Electron Microprobe (EPMA), model Jeol JXA-8500F.

The sorption isotherms were obtained using flasks with 100 mL of a solution with an As concentration of 5 mg/L and adding different mass of sorbent. Control tests were simultaneously performed in the same way but without sorbent. The flasks were incubated in an orbital shaker (Ritabit, Selecta) during 24 hours. Next, the pH was measured and the content was filtered under pressure; a sample of 10 mL was collected from each flask and preserved by adding 100 µL of HCl at 37%. This procedure was used both for As(III) and As(V).

Total As determinations were carried by ICP-OES with coupled hydride generation. As(III) was determined by cathodic stripping voltammetry with square wave using a hanging mercury drop electrode as described by Ferreira & Barros (2002). Samples that were not analysed immediately, were preserved by acidification to a pH lower than 2 with concentrated HCl and stored in acid washed high-density polyethylene containers. All samples were analysed within seven days after collection. The pH values were obtained by immediate measurement using a pH meter (Crison, GLP22).

All chemicals were reagent grade that were used without any further purification. All solutions were prepared with deionized water. All glassware was cleaned by soaking in 10% HNO_3 and rinsed with deionized water. As solutions were prepared by direct dilution of a 1000 mg/L standard solutions from Fluka for As(V) and from Panreac for As(III) and were kept in dark glass flasks for the preparation of all the required diluted solutions.

5.3.4 Sorption tests of arsenic by iron based and other sorbents

In the study, preliminary batch adsorption tests in the laboratory scale were performed to evaluate the efficiency of various sorbents/ion exchangers in terms of As(III) and (V) removal, and select the most promising one:

- Granular Fe hydroxides CFH12 (Kemira Oyj, Finland),
- Ground impure dolomite (Aquaminerals/Oulu Water Alliance Oy Ltd., Finland),
- Material F7M/AQM based on natural minerals, (Aquaminerals/Oulu Water Alliance, Finland),
- Partially oxidized Fe carbonates GHE (Romania),
- Biosorbent (Outotec, Aalto University, Finland),
- Activated carbon (GryfSkand, Poland).

From among tested materials granular Fe hydroxides CFH12, mineral material F7M/AQM and oxidized Fe carbonates GHE were selected for the extended tests with model solutions and mine real waters in the laboratory scale.

Several types of sorption experiments were conducted, namely:

- Batch tests with use of synthetic water (with different contact time, material dose, solution composition, pH and temperature, presence of sulphate and chlorides in the solution), to determine the optimal operating process parameters. Laboratory tests were performed at Wrocław University of Technology (WUT), Poland.
- Fixed-bed column experiments with use of synthetic water (with different solution composition and bed height), to assess the materials performance under dynamic conditions. Laboratory tests were performed at Wrocław University of Technology (WUT), Poland.
- Batch adsorption tests with real mine waters from Kittilä Gold Mine, Agnico Eagle and Jokisivu Gold Mine, Dragon Mining in Finland (different contact time and material dose) to select the most suitable material for piloting test at a mine site. Laboratory tests were performed at Savonia AMK, Finland.

Synthetic water for batch tests was freshly prepared using Milli-Q water and spiked with As(III) and/or As(V). The adsorption equilibrium experiments were conducted using the bottle point method. The solution with various initial concentration of As(III) or As(V) was added into capped tubes containing pre-weighted material. The samples were agitated in a shaker incubator (IKA) at 22 ºC until equilibrium was reached. The experiments with various material dose (1–10 g/L), solution pH (2–11) and temperature (5–35 ºC) were conducted in the similar way. In the kinetics tests, dry pre-weighted material was added to 500 mL of water sample spiked with As(III) and/or As(V). The test was performed for five hours using a magnetic stirrer.

Figure 5.2. Laboratory set-up for batch adsorption tests (WUT, Poland)

Feed solutions for fixed-bed column experiments were prepared with used of dechlorinated tap water and spiked with the As solution. Column were loaded with granular Fe hydroxides CFH12 and oxidized Fe carbonates GHE. The set-up for fixed-bed columns adsorption tests consist of custom-made PMMA columns. Feed water was passed through the columns downward with continuous flow rate using the Masterflex peristaltic pump. The samples were collected periodically using the automated samples collector.

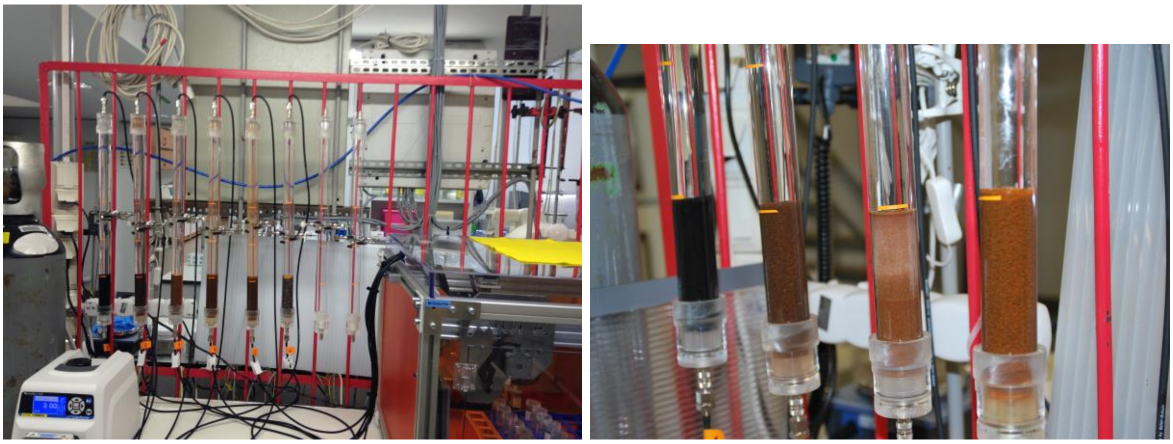


Figure 5.3. Laboratory set-up for fixed-bed column tests (WUT, Poland)

The real mine water collected from Kittilä Gold Mine and Jokisivu Gold Mine was the underground mine water from pumping level of 225 m and 350 m, respectively. The batch adsorption experiments were conducted to verify the As uptake by tested materials (CFH12, F7M/AQM and GHE) and influence of contact time and sorbents dose on their performance. The tests procedures were the same as applied in experiments with synthetic water. In collected samples, apart from As, concentration of nickel (Ni) and antimony (Sb) was analysed in case of water from Kittilä Mine and concentration of Ni and U in case of water from Jokisivu Mine; pH, temperature and conductivity were also measured.

Figure 5.4. Laboratory set-up for batch adsorption tests (Savonia AMK, Finland)

Chemicals used in all experiments were of reagent grade, and stock solutions were freshly prepared using Milli-Q water. The stock solutions of As(III) and As(V) were prepared using $NaAsO_2$ and $Na_2HAsO_4\cdot 7H_2O$ (Merck, Sigma-Aldrich), respectively. The initial pH of the solution was adjusted by the addition of either 0.1M HCl or 0.1 M NaOH (Merck). Temperature, conductivity and pH were measured using Hach-Lange HQ40d multi-meter.

The initial and residual As concentration, as well as concentration of Ni, Sb and U, was determined using ICP-OES or ICP-MS technique.

5.3.5 Pilot tests at the mine site

The pilot scale adsorption tests in batch and continuous mode were performed at the mine site of Jokisivu Gold Mine, Dragon Mining in Finland. F7M/AQM based on natural minerals was provided for the pilot tests.

The adsorption tests in a batch mode were performed with different material dose (0.5–10 kg/m^3). Each individual run took five hours, followed by two hours of clarification. In this system, the material was dosed manually into the tank of 1 m^3 volume and manually collected after the clarification. Schematic of batch process in shown in Figure 5.5 and the set-up at the mine site in Figure 5.7a. Samples were collected at selected time intervals and analysed for Ni, As and U using ICP-MS. The pH and temperature were monitored and logged on-line during the process, while conductivity was measured before and after the process.

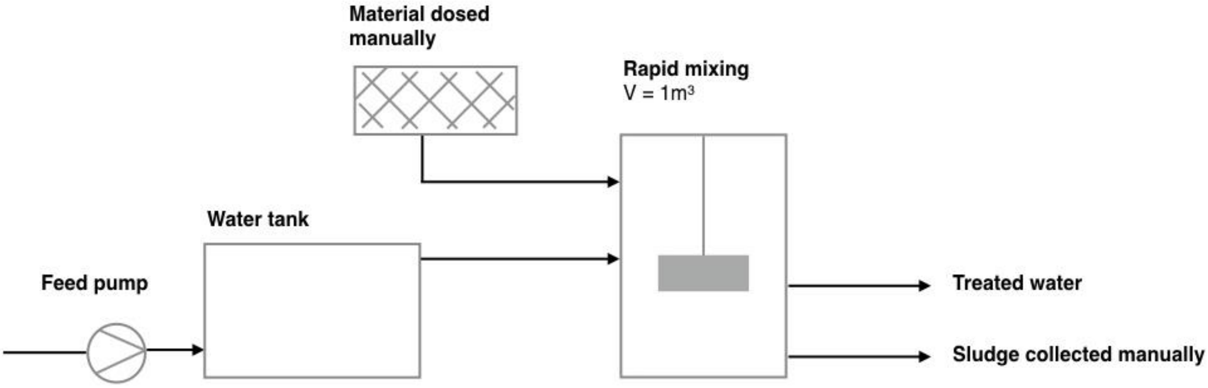


Figure 5.5. Schematics of a batch process at pilot scale

The adsorption tests in a continuous mode were performed with different material dose (0.5–10 kg/m^3) and different retention time (15–60 min). Single run took from six to nine hours. The constant flow rate of 1 m^3/h and 2 m^3/h was applied. In this system, the material was dosed into the tank using automated powder dispenser and collected in the lamella clarifier. Schematic of continuous process in shown in Figure 5.6 and the set-up at the mine site in Figure 5.7. Samples were collected from tank and after clarifier and analysed for Ni, As and U.

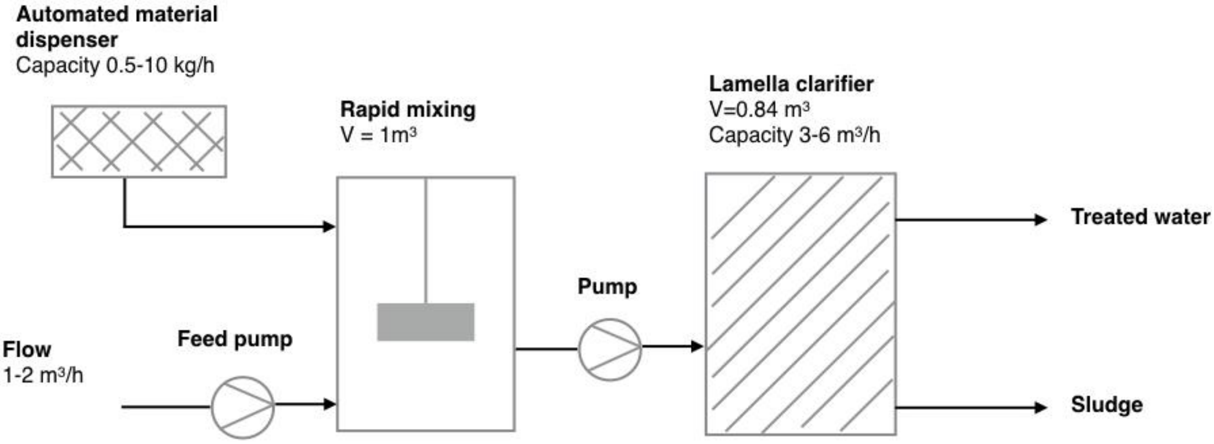


Figure 5.6. Schematics of continuous process at a pilot scale

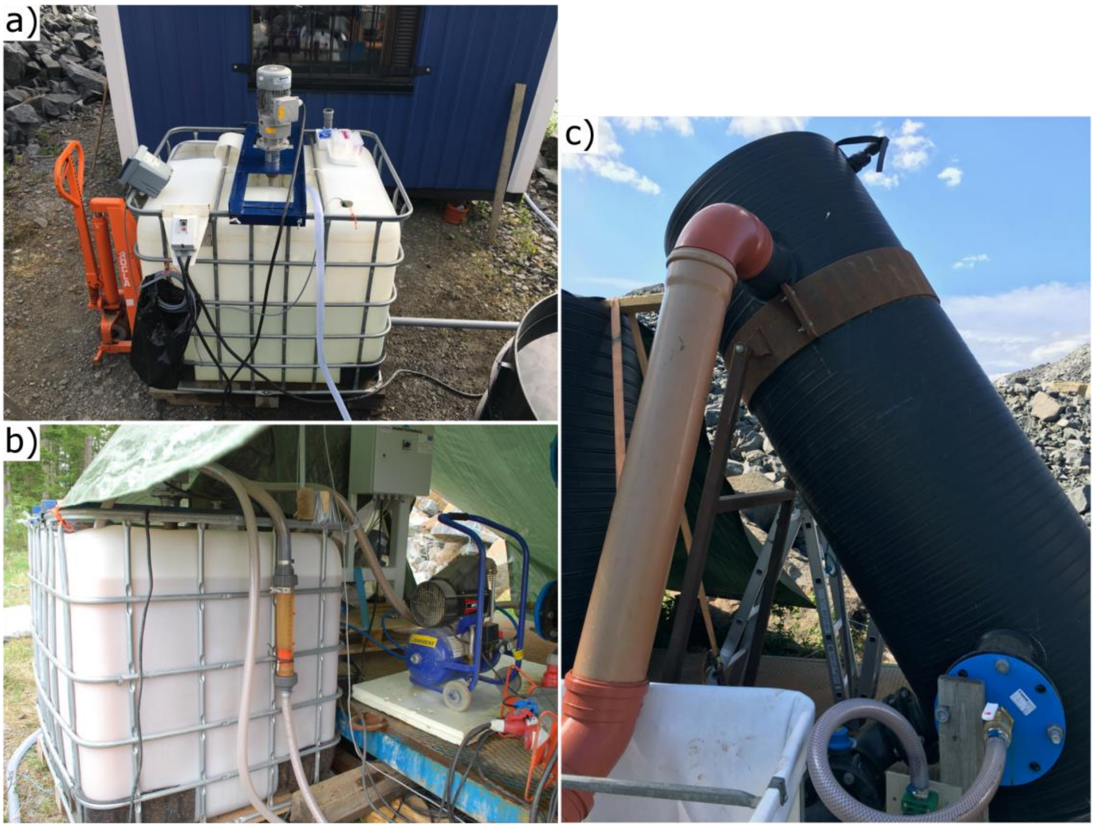


Figure 5.7. Batch (a), continuous process (b) and lamella clarifier (c) at the mine site

5.4 Results and discussion

5.4.1 Performance of IBS (ARM300 and GEH102) - preliminary tests

The tests were performed using: a) solutions only with As(III); b) solutions only with As(V) and c) solutions with both As(III) and As(V). The sorption isotherms presented in Figure 5.8 were obtained using flasks with 100 mL of a solution with an As concentration of 5 mg/L and adding different mass of sorbent. Control tests were simultaneously performed in the same way but without sorbent. The flasks were incubated in an orbital shaker (Ritabit, Selecta) during 24 hours. Next, the pH was measured and the content was filtered under pressure; a sample of 10 mL was collected from each flask and preserved by adding 100 µL of HCL at 37%. This procedure was used both for As(III) and As(V).

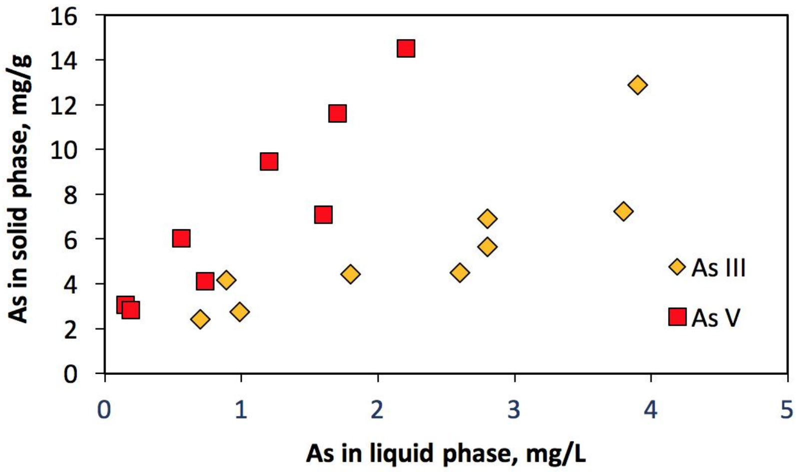


Figure 5.8. Sorption isotherms for As(III) and As(V) using ARM 300

The continuous tests through a fixed bed sorption column, filled with the reactive medium mixed with quartz sand, were programmed in order to quantify the influence of the interstitial water velocity through the pores. Three different flow rates were used 5, 10 and 20 mL/min corresponding respectively to interstitial velocities of 1.7E-04, 3.4E-04 and 5.1E-04 m/s. The last value was the highest that could be safely used taking into account the size and the characteristics of the column. The cumulative effluent volume was periodically measured and samples were collected for immediate measurement of pH and conductivity.

The general conclusions could be drawn from these experiments:

- The pH, starting from neutral water, decreases slightly with time,
- Hydrogen ions are generated as a consequence of the As sorption by the ARM 300; this proves that the sorption is not only of physical origin but there are also simultaneously chemical reactions involved.

Figure 5.9 represents the values for the As concentrations in the effluent normalized by the average initial concentration at the inlet, for different interstitial velocities for total As. The uptake capacities for the flow rates of 5 and 10 mL/min are similar with a value of 20 g As/kg of sorbent.

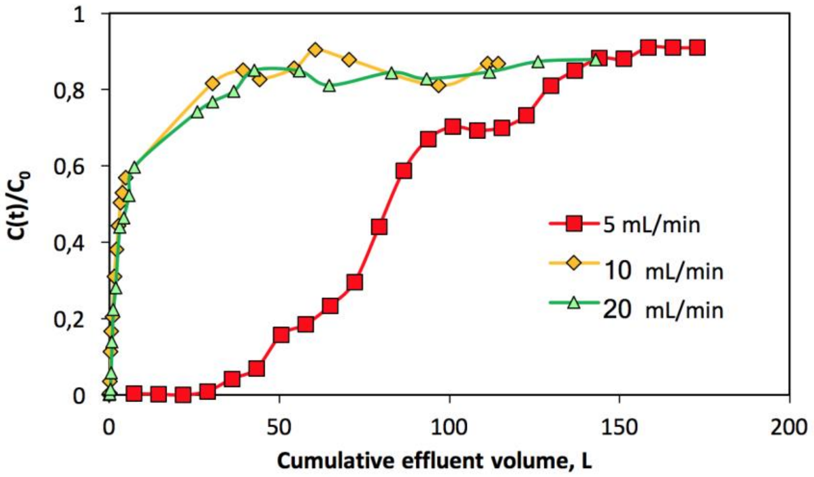


Figure 5.9. Total arsenic (As) breakthrough curves for different flow rates (GEH102)

5.4.2 Comparison tests between the IBS (ARM300 and GEH102)

Comparison tests between ARM 300 and GEH 102 were performed using two columns fed in parallel by the same As solution (around 1000 µg/L) using a multi-channel peristaltic pump. Tests were also performed for each sorbent using the same operating conditions: same amount of sorbent (1.5 g) and sand, and same flow rate (around 0.110 L/h). The procedures for collecting samples and measuring the cumulative effluent volumes were similar. Obtained results are presented in Figure 5.10.

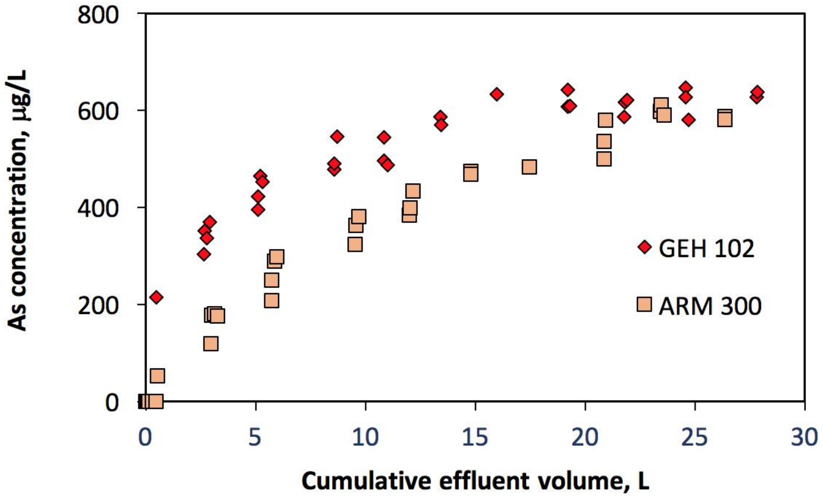


Figure 5.10. Comparison between ARM 300 and GEH 102

The most relevant conclusions are the following:

- ARM 300: The residence time was too short in relation to the kinetics demand. For this reason, not all the As had enough contact time to be adsorbed. This result was not expected because the water velocity used was lower than the recommended for operation in water treatment columns.
- GEH 102 demonstrates a slightly better performance.
- In both cases the saturation of the uptake capacity was not reached and the volume of water that passed through the column was insufficient.
- An extrapolation method was developed to estimate the uptake capacities of both sorbents and the following results were obtained: 20.6 g of As/kg sorbent for GEH 102 and 20.8 for ARM 300. In a previous study by Ipsen et al. (2005) an uptake capacity of 36 g As/kg for the GEH sorbent was found.
- In a potential field application, it would be required to build two permeable reactive columns, with a reasonable distance between them, so that the second barrier would allow the attainment of environmentally acceptable As concentrations.
- Alternatively, an excess of at least 100% of the sorbent in relation to the necessities estimated by the uptake capacity would be required.

5.4.3 Study of the sorption mechanisms using an Electron Microprobe Analyser (ARM300 and GEH102)

In order to better understand the mechanisms of sorption, samples of two sorbents were collected after their usage in fixed bed columns tests and analysed using an Electron Microprobe Analyser. Electron backscattered images were obtained from the sorbent particles.

The observation of Figure 5.11 allows us to conclude:

- ARM 300: The deposition of As was predominantly occurring at the lower face of the particle, indicating that it is a superficial reaction. Although the sorbent particle has several fractures, As has not penetrated into the inner part of the particle through those factures. It can be concluded that reaction occurs only in exposed surface in contact with the solution.
- GEH 102: As is captured around all the external surface of the sorbent particle constituting a layer with variable thickness.
- The increase in As concentrations coincides with a net depletion in oxygen.
- The same effect happens with Fe although the thickness of the depletion layer is thinner.

Quantitative analysis at selected points and all WDS X-ray intensity dot maps were obtained with the following operating conditions: 15kV, 60nA and 1µm beam diameter. A dwell time of 10ms was used for X-Ray dot maps.

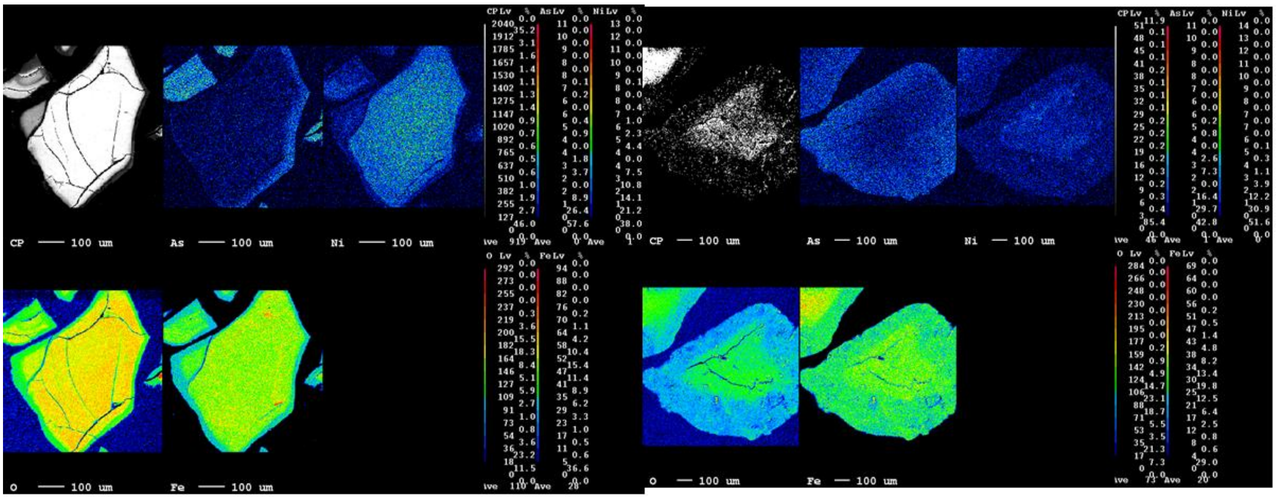


Figure 5.11. Mapping of concentrations in a particle of ARM300 (left) and a particle of GEH102 (right)

The observation of Figure 5.12 and Table 5.1 allows several conclusions:

- ARM 300: The concentration of adsorbed As is higher at the surface of the sorbent although As has apparently penetrated to the inner part of the particle, even if the particle as a large size (scale is indicated at the picture). Nevertheless, concentrations decrease from the outer to the inner side of the particle. Notice that the highest concentration in As coincide with the lowest concentration in Fe suggesting that part of the Fe is reduced to a soluble Fe(II) form. A reductive precipitation is possible and probably coexists with other removal mechanisms.
- GEH 102: There is no As in the inner part of the particle; the highest As concentration is found at point 10 and belongs to the external sorption layer. In the sorption layer located in the opposite side of the particle (points 6 and 7) concentrations are relatively homogeneous but lower than in the opposite face. This suggests that chemisorption prevails over the other possible precipitation mechanisms.

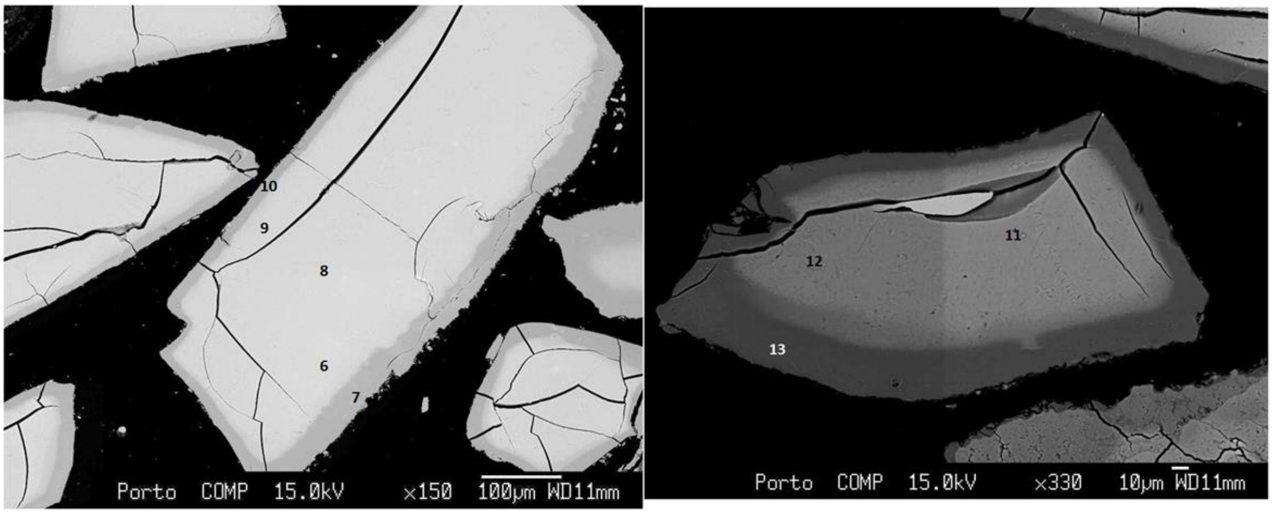


Figure 5.12. Points selected for chemical analysis in an ARM 300 particle (right) and GEH102 particle (left).

Table 5.1. Spatial distribution of concentrations in a particle of GEH 102 and a particle of ARM 300 (percentage)

Element	**ARM 300**			**GEH 12**			
	11	**12**	**13**	**6**	**7**	**9**	**10**
As_2O_5	2.82	3.07	3.59	1.08	0.97	1.92	2.47
FeO	64.51	64.91	54.84	64.08	51.01	67.16	56.78
SiO_2	1.38	1.14	0.68	1.80	0.99	1.52	0.84

5.4.4 Comparison tests between the IBS (ARM300 and GEH102) and nZVI

In order to compare the performance of IBS (ARM 300 and GEH 12) with nZVI we performed some tests with a suspension of this material, manufactured by Toda Kogyo Corporation (Japan). The particle size distribution of Toda nanoparticles is shown in Figure 5.13.

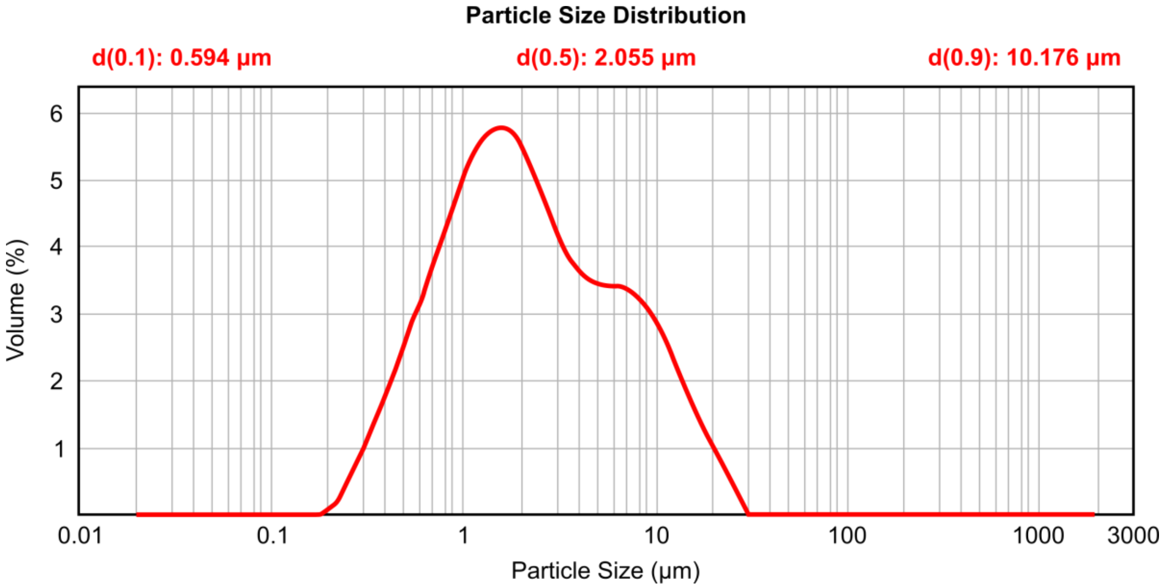


Figure 5.13. Particle size distribution of Toda nanoparticles

Kinetic tests were performed using flasks with 500 mL of a solution with a concentration in As of 1.1 mg/L and adding different masses of nZVI: 0.1, 0.2 and 0.55 g. The flasks were incubated in an orbital shaker during 48 hours. During this time 5 samples of 10 mL were collected from each flask and preserved by adding 100 µL of HCl at 37%.

The observation of Figure 5.14 allows several conclusions:

- As concentration decreases rapidly up to 4 hours. However, after 4 hours the sorption decreases;
- Test with 1 mL of nZVI: after 24 hours, the concentration of As stabilized at 270 µg/L. This may reveal that saturation of the uptake capacity was reached.
- Tests with 2 and 5 ml of nZVI: despite the occurrence of a drastic decrease in the sorption, in both cases the saturation of the uptake capacity was not reached.

This research proves that IBS may be used as reactive media in permeable barrier. The two commercial sorbents tested, ARM 300 and GEH 102, remove efficiently both As(III), As(V) and their mixtures. Breakthrough curves obtained in different operating conditions allowed comparison of both sorbents: the loading capacity is similar, around 20 g of As/ kg, and GEH has a slightly more favourable performance. Particles of the sorbents, after subjected to adsorption tests in fixed bed columns during 30 days, were consequently subjected to analysis using an electron microprobe analyser. Spatial mapping of the concentrations allows us to infer that the removal mechanisms are different: while for ARM 300 reductive precipitation is relevant for GEH 102 the adsorption mechanisms with complex formation are prevalent. Preliminary tests with nZVI show that this sorbent has a faster kinetics, mainly due to its high specific surface. Comparing both types of materials, nZVI evidences faster kinetics than IBS; nevertheless, the physical implementation of IBS in a permeable barrier is easier and the usages of polymers to fix nVZI probably reduces drastically its loading capacity.

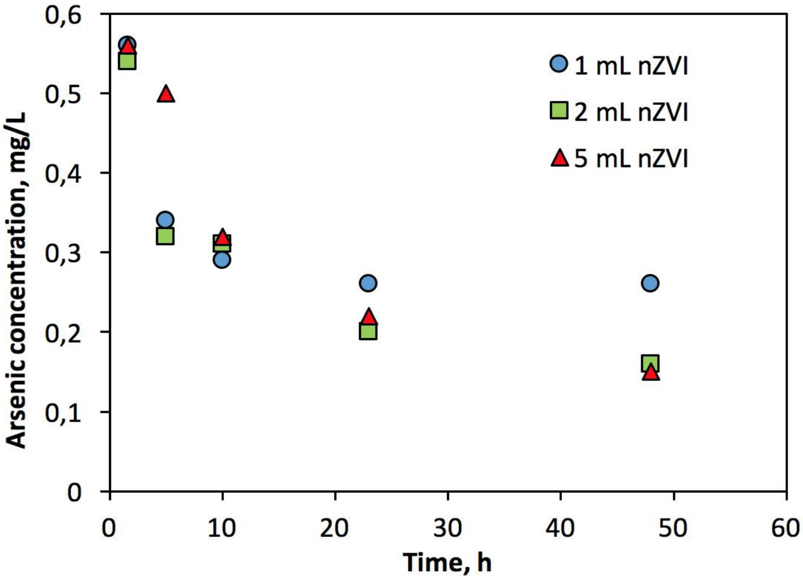


Figure 5.14. Time evolution of total Arsenic (As) concentrations using different mass of nZVI

5.4.5 Performance of “green” nZVI

The texture of the produced nanoparticles was characterized by its grain size distribution (Figure 5.15). The time evolution of the texture, without and with surfactants was also assessed. This data allowed for the selection of the most promising production methods.

Isotherms were determined both for As(III) and As(V) using artificially prepared solutions with reagent grade reactants. The results showed that “green” ZVI was not effective in removing As(III) but it was relatively effective in the removal of As(V).

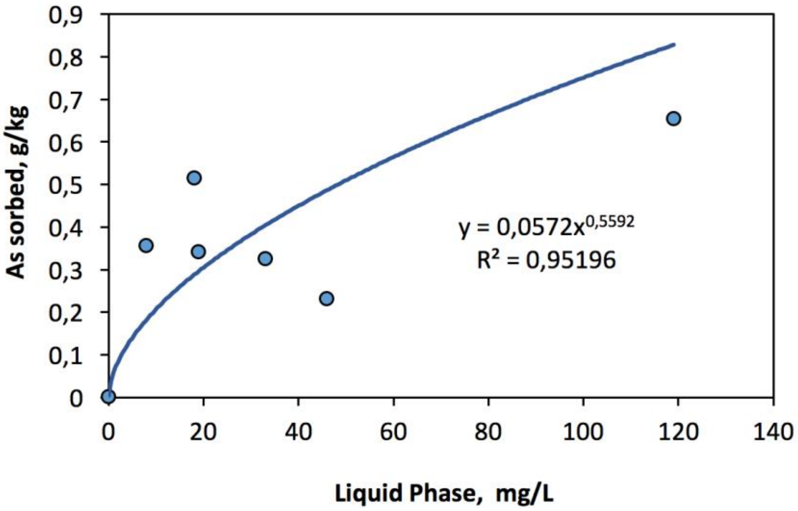


Figure 5.15. Sorption isotherms for As(V) using “green” nZVI

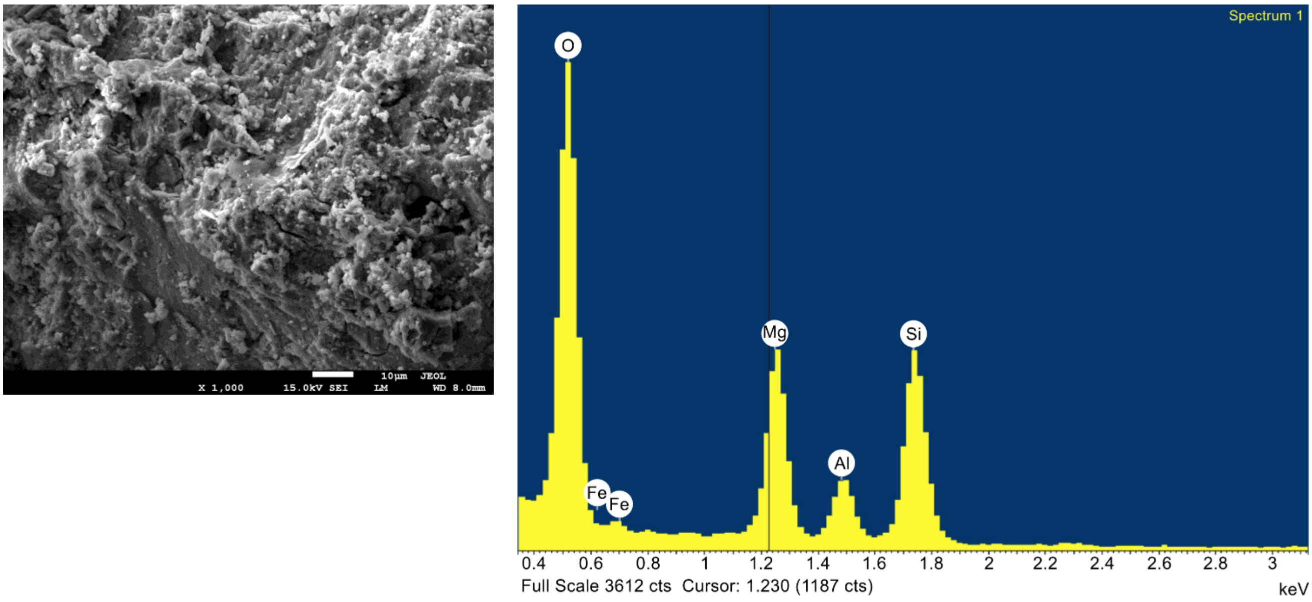
Another isotherm was determined using mining waste water with a total concentration in As of 261 µg/L. The efficiencies of removal did not exceed 50% in any case, which was a disappointing result.

For comparative results a new set of tests using industrial nZVI (Toda Kogyo Corporation, Japan) was performed. The industrial nanoparticles were able to decrease the As concentration continuously for 24 hours reaching a minimum value of 20 µg/L, corresponding to an efficiency of 92.3%.

The obtained results show that it is possible to produce nZVIs from natural materials. The best extractions were obtained with oak, strawberry and eucalyptus leaves. A short residence time of 5 minutes is sufficient for the reduction reaction to occur in full extent, producing the smaller nanoparticles. The conditions of production were optimized. The kinetics of aggregation was studied in detail. Over time nZVI particles have the tendency to aggregate and form clusters, reducing its surface area, decreasing its reactivity. The addition of Tween 80 stabilized the nanoparticles for longer periods of time. The removal of As(III) was not efficient while the removal of As(V) was slightly efficient. Calculation of the loading capacities are only possible, if based on the assumption that all the Fe that was added was transformed into nZVI. A final conclusion is that “green” nZVI is not an efficient As removal when compared to the crystalline nZVI produced by classical methods. The reason for such behaviour probably lies in its amorphous structure with incorporation of organic carbon, as it was observed by EDS analysis and SEM images.

5.4.6 Performance of IBS (CFH12) - synthetic waters

The granular material CFH12 based on ferric hydroxides was one of several materials used in the batch adsorption tests with synthetic waters. Adsorbent apart from As species, is able to remove other inorganic trace contaminants, such as phosphorus (P), Sb or Ni (Ilavský et al. 2015, Leiviskä et al. 2013, Ilavský & Barloková 2012). CFH12 is a media of porous morphology (Figure 5.16) with a specific surface area of 158 m^2/g (Figure 5.17). The CFH12 has brown and/or reddish brown colour granules with an average equivalent diameter d$_{50}$ of 1.4 mm. The Fe(III) content is up to 44%. CFH12 consist also magnesium (Mg), Al, silica (Si) or calcium (Ca) oxides (Szlachta & Wójtowicz 2016a, Szlachta & Wójtowicz 2016b).


a)

b)

Figure 5.16. SEM image (a) and EDS analysis (b) of the CFH12 material

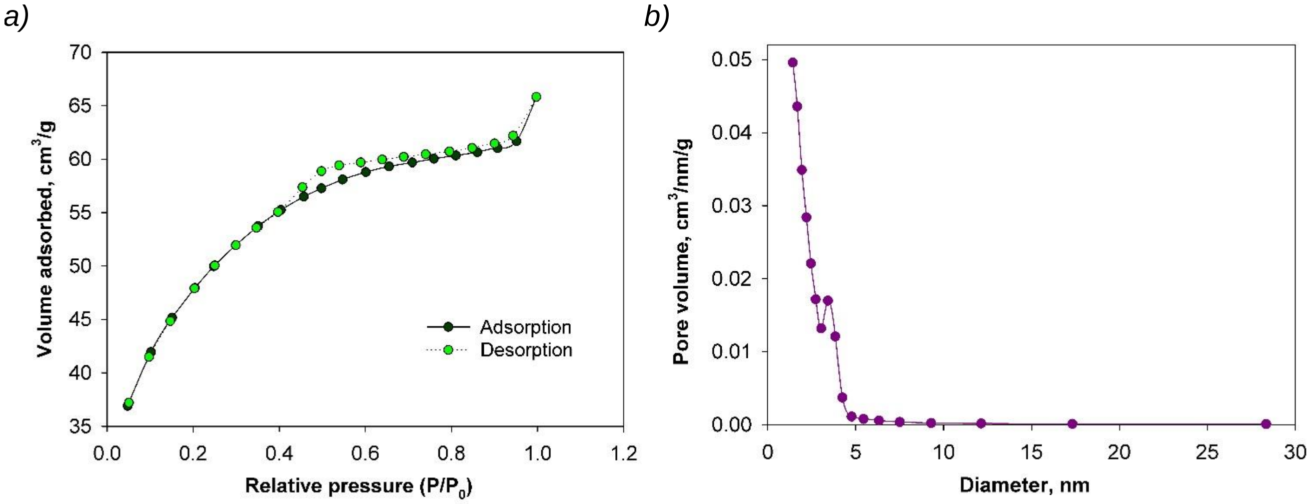


Figure 5.17. Nitrogen adsorption/desorption isotherms (a) and pore size distribution (b) of the CFH12

Kinetics study is particularly important in terms of proper assessment of performance of CFH12 in As removal as a function of time. In this study, the removal of As ions increases with contact time (Figure 5.18). After one hour of contact time, approximately 97.2% of As(V) is removed from the solution containing 1 mg/L, whereas the removal rate for As(III) is close to 45%. After five hours, uptake of As(V) is comparable (98.5%), but in the case of As(III), the increment is considerably higher, and the recorded maximum removal is 78.2%. The removal performance of CFH12 was tested also in extreme conditions, with very high concentration of As. It was observed that when As initial concentration of 20 mg/L is present in the synthetic water, after five hours of the process efficiency of As(III) and As(V) removal is approximately 50 and 85%, respectively.

The mechanism of the process involved as well as rate of adsorption was analysed on the basis of kinetic parameters. Two non-linear models were employed to describe the experimental data. The example of obtained results is shown in Figure 5.18, while the calculated parameters of kinetic models for 20 mg/L of As(III) and As(V) are presented in Table 5.2.

Both of applied models describe well As(III) and As(V) adsorption data. The pseudo-second-order kinetic equation gives slightly better fit due to the higher correlation coefficients. However, the adsorption capacity predicted by this model is not in good agreement with the experimental adsorption capacity determined for both examined systems. The difference between the experimental uptake capacity (q_{exp}) and predicted by the second-order model (q_2) is significantly higher than predicted by the first-order model (q_1). Thus, it can be assumed that the adsorption mechanism of As(III) and As(V) follows rather pseudo-first-order kinetic reaction than second-order.

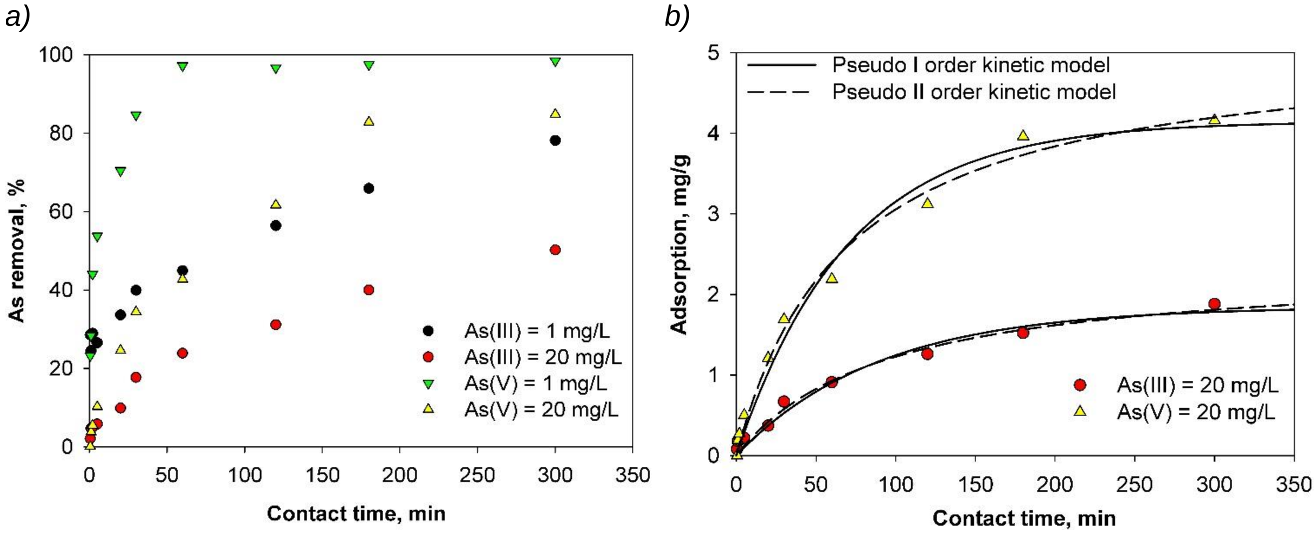


Figure 5.18. Sorption kinetics for As(III) and As(V). Percent of removed As (a) and the amount adsorbed (b) over time (CFH12)

Table 5.2. Parameters of adsorption kinetic models for 20 mg/L of As(III) and As(V) (CFH12). q_{exp} – experimental adsorption capacity; q_1, q_2 – predicted adsorption capacity; k_1, k_2 – rate constant of kinetic models; R^2 – correlation coefficient

Model	**Parameter**	**As(III)**	**As(V)**
	q_{exp} (mg/g)	1.88	4.16
Pseudo I order kinetic equation	k_1 (1/min)	0.011	0.014
	q_1 (mg/g)	1.85	4.15
	R^2	0.969	0.986
Pseudo II order kinetic equation	k_2 (g/mg min)	0.005	0.003
	q_2 (mg/g)	2.37	5.16
	R^2	0.978	0.991

Obtained equilibrium adsorption data are shown in Figure 5.19. As expected, both As(III) and As(V) adsorption is increased with increasing the concentration of As ions in the model solution at the equilibrium state. The nonlinear form of the Langmuir and Freundlich model was applied to fit the equilibrium data (Figure 5.19) and the calculated isotherm parameters along with the correlation coefficients are listed in the Table 5.3. High R^2 values indicate that both isotherm equations are in good agreement with the experimental results. However, for As(V), the Freundlich model provides slightly better fit, whereas the Langmuir model is more suitable for the description of As(III) adsorption onto CFH12. The maximum adsorption capacity calculated using the Langmuir equation is 44.04 mg/g for As(V) and 43.75 mg/g for As(III). It was observed that CFH12 exhibits higher affinity towards arsenate than arsenite since the calculated values of the Langmuir b parameter are nearly 4.5 times greater for As(V) compared to As(III).

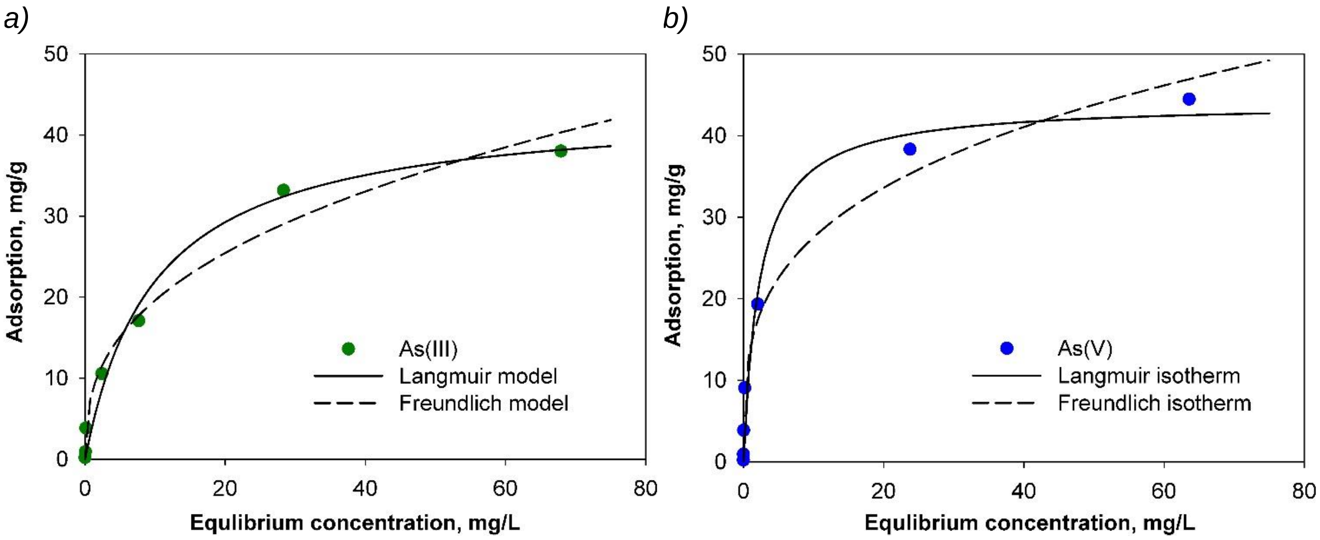


Figure 5.19. Sorption isotherms for As(III) (a) and As(V) (b) (CFH12)

Table 5.3. Parameters of Langmuir and Freundlich models for As(III) and As(V) (CFH12). qm –adsorption capacity; b – predicted adsorption capacity; K, n – rate constant of kinetic models; R2 – correlation coefficient

Model	**Parameter**	**As(III)**	**As(V)**
Langmuir isotherm	q_m, mg/g	43.75	44.04
	b, L/mg	0.101	0.439
	R^2	0.986	0.974
Freundlich isotherm	K, (mg/g) (L/mg)	8.24	14.17
	1/n	2.655	3.467
	R^2	0.980	0.981

In the study, it was observed that the process temperature has noticeable influence on CFH12 performance in As(III) removal, comparing to As(V) (Figure 5.20). Raising the solution temperature from 5 °C to 35 °C increased As(III) removal from approximately 80% to 92%, indicating endothermic nature of the process. The results show that the amount of As(V) removed by the CFH12 remained on the same level (99.0–99.7%) within the range of tested solution temperatures.

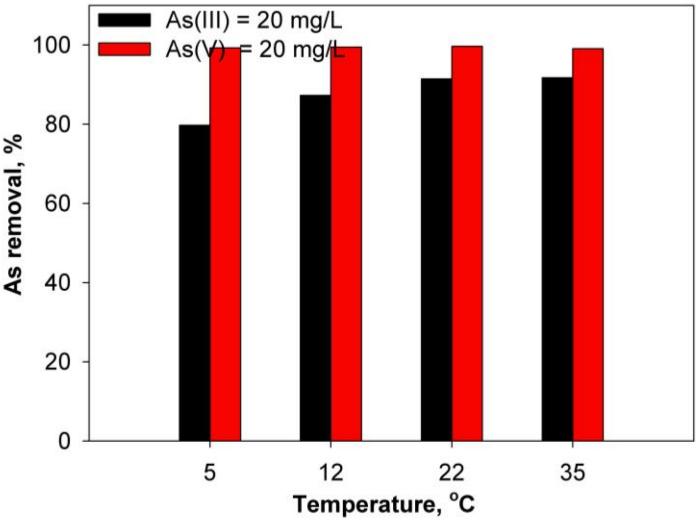


Figure 5.20. Effect of solution temperature on As(III) and As(V) removal (CFH12 dose of 5 g/L)

The granular Fe hydroxide CFH12 is a product developed to work under dynamic conditions. Therefore, the set of fixed-bed adsorption tests was run with the empty bed contact time (EBCT) of 23 minutes. This contact time between the solution with As initial concentration of 100 μg/L and adsorbent was sufficient enough to reach high removal rate of As(III) and As(V) for the very long period of time. The results from adsorption tests are illustrated in Figure 5.21. The curves represent the residual concentration of As in treated solution as a function of treated bed volumes (BV) as well as the changes of pH in columns' outlet as a function of treated bed volumes. As can be seen the adsorbent CFH12 performed well and the As concentration in the effluent remained below 10 µg/L (maximal permissible level in drinking water) up to about 15 000 bed volumes. After 15 000 BV the level of As(III) and (V) in treated solution gradually increased and reached 15 µg/L at approximately 20 000 BV.

The initial pH of model solutions was between 7.0 and 7.5. It was observed that at the beginning of the process, in case of both As(III) and As(V), the pH decreased rapidly to about 2.5. After 700 BV pH volume stabilized at the lever of 7.3–7.9 and doesn't change much during the process.

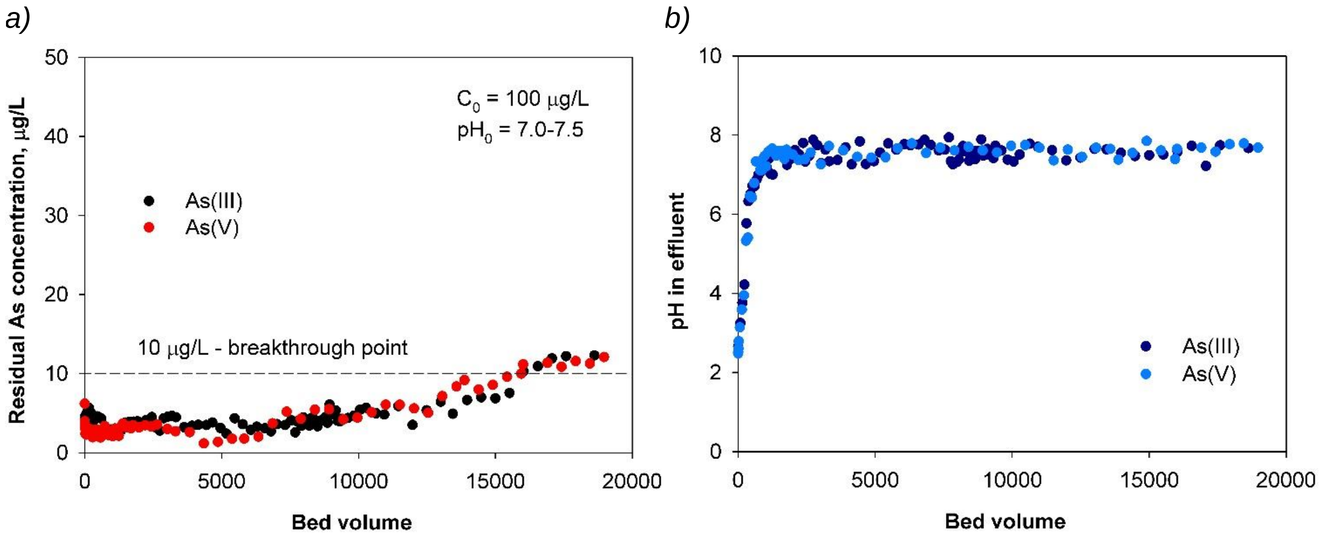


Figure 5.21. Breakthrough curves for sorption of arsenic (As) species onto CFH12 (a) and changes of pH in effluent (b)

Tested granular Fe hydroxides CFH-12 is a commercial sorbent and we have confirmed its great potential for adsorptive removal both form of As: As(III) and As(V) from aqueous solutions.

Batch adsorption experiments were performed and the maximal adsorption capacity of As(III) and As(V) calculated by the Langmuir equation was 43.75 mg/g and 44.04 mg/g, respectively. The adsorption test results under dynamic conditions demonstrated high adsorbent efficacy and stability over a long period of time. The As concentration in the effluent remained below the threshold of 10 µg/dm^3 during the column operation time corresponding to 15 000 bed volumes.

Hence, application of granular hydroxide to adsorptive treatment of As contaminated water and wastewater from mine industry should be regarded as a robust and effective solution. In practical application, it might be useful in protection of recipient against events of increased As concentration in mine effluents. The lifetime of adsorbent depends mainly on effluent chemistry, required flow rate and volume of water need to be treated. However, other factors like objectives of treatment, capital and operating costs, disposal of used material are the key elements in selection and design CFH-12 based treatment technology.

5.4.7 Performance of IBS (F7M/AQM) - real mine waters

The F7M/AQM is a material which can be utilized in a batch system followed by clarification or flotation. Sorbent is derived from natural minerals and consists mainly of Mg, Fe, Si, Ca and Al oxides/carbonates. Apart from As, the ion exchanger is able to effectively remove a wide range of elements including Cr, P, U, Ni, Cu, Pb, Zn, Mg and Cd. As presented in Figure 5.22, the surface of F7M/AQM exhibits smooth morphology with low porosity in the micrometre scale. The BET specific surface area of material was 11.9 m^2/g (Szlachta & Wójtowicz 2016c). The particle size distribution is illustrated in Figure 5.23 and an average equivalent diameter d_{50} of F7M/AQM was 0.9 mm.

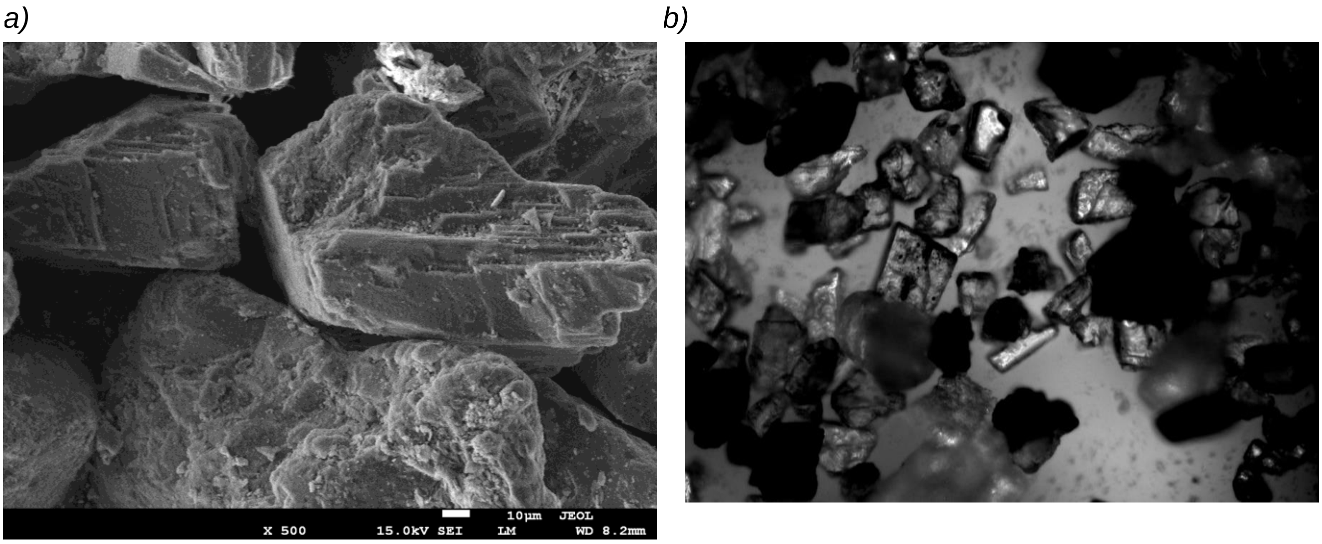


Figure 5.22. SEM (a) and optical microscope image (b) of the F7M material

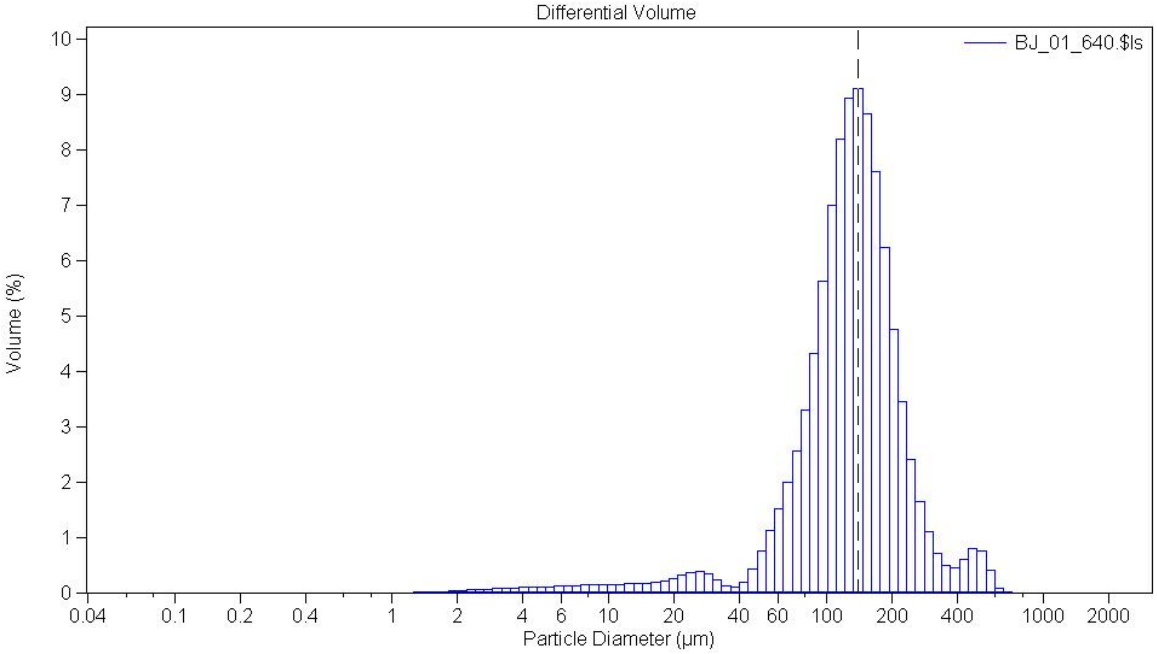


Figure 5.23. Particle size distribution of F7M

The As removal kinetics by F7M/AQM shown in Figure 5.24 indicates very fast initial uptake followed by a slower process. During the removal of Ni from Kittilä and Jokisivu mine water the similar trend was observed while the slower removal kinetics was observed in case of U and Sb.

For example, about of 75.5% of total As, 63.7% of Ni and 1.9% of Sb was removed from Kittilä mine water after 30 minutes of the process using 2 g/L of F7M/AQM. The percentage removal of As, Ni and Sb after one hour of contact time increased to 86%, 80% and 3.4%, respectively. The extension of contact time to five hours allows to reduce As, Ni and Sb concentration to approx. 10.5 µg/L, 16.9 µg/L and 302.1 µg/L, respectively. The performance of F7M/AQM (1 g/L) in treatment of water from Jokisivu mine resulted in maximum removal of 84.4% of total As, 100% of Ni and 88.1% of U after five hours of the process what corresponds to final concentration of 3.32 µg/L, 0 µg/L and 5.87 µg/L, respectively.

In case of water from Kittilä mine, the changes in removal percentage of As, Ni and Sb between 1 hour and 5 hours of the process were below 10%, so 60 minutes may be considered as the effective time for ion exchange adsorption. Eventually increment of dose of F7M/AQM may allow for shorten contact time with similar level of process efficiency. The difference between removal of As from Jokisivu mine water after 1 hour and 5 hours of the process was almost 25%, thus the application of much higher material dose and intense mixing may allow to reduce the contact time and receive satisfied level of effluents treatment.

In order to examine the mechanism of As removal from real mine waters kinetic models were used to fit experimental data (Figure 5.24). The calculated parameters of non-linear form of models are presented in Table 5.4.

The evaluation of the best models for describing the adsorption of As was made on the basis of correlation coefficient and agreement of predicted adsorption capacity with the experimental. Higher values of R^2 were observed for second-order equation for both treated mine waters. At the same time, better agreement in predicted and experimental uptake of As, comparing to first-order equation, was observed. Thus, the best fit and significant in describing the As removal process from Kittilä and Jokisivu mine water using F7M/AQM material is the second-order-kinetic model.

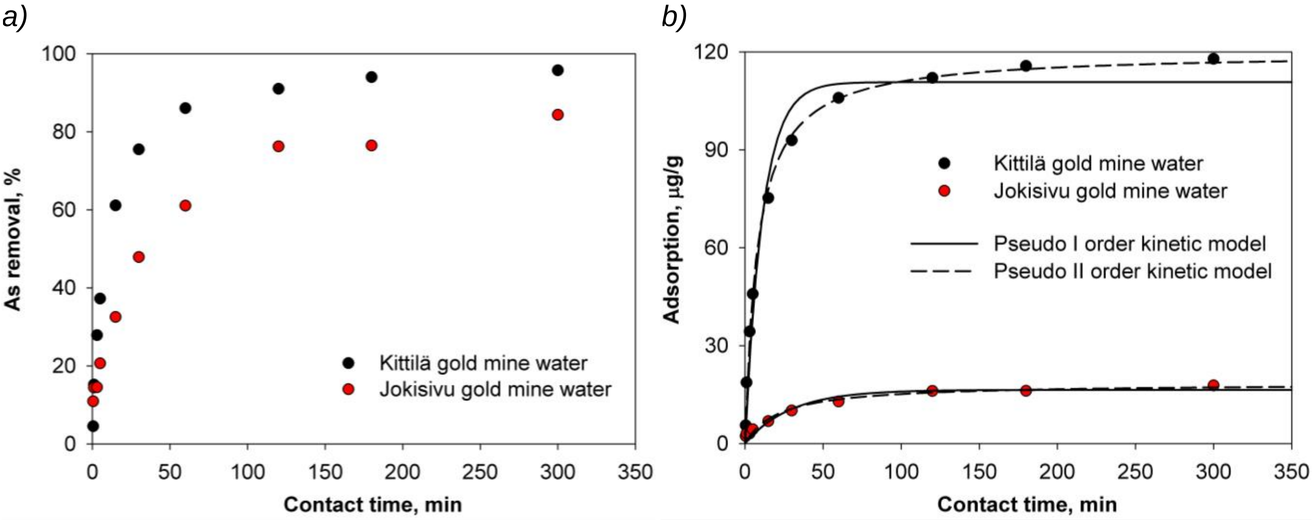


Figure 5.24. Adsorption kinetics for arsenic (As). Percent of removed As (a) and the amount adsorbed (b) over time (F7M/AQM dose 2 g/L for Kittilä mine water and 1 g/L for Jokisivu mine water)

Table 5.4. Parameters of adsorption kinetic models for of As (F7M/AQM)

Model	**Parameter**	**Kittilä mine water**	**Jokisivu mine water**
	q_{exp} (µg/g)	117.89	17.80
Pseudo I order kinetic equation	k_1 (1/min)	0.089	0.034
	q_1 (µg/g)	110.74	16.45
	R^2	0.974	0.941
Pseudo II order kinetic equation	k_2 (g/mg min)	0.001	0.002
	q_2 (µg/g)	119.86	18.45
	R^2	0.997	0.964

The removal of As from Kittilä and Jokisivu mine water using various doses of tested material is shown in Figure 5.25. It is evident that efficiency of the process increases with the increase of F7M/AQM dose used to treat both type of mine waters. In general, under applied experimental conditions we can observed substantial deference in process efficiency between every tested materials dose, regardless the treated mine water. In the study the optimum dose for removal of As species should be verified with higher amount then 3 g/L of tested material.

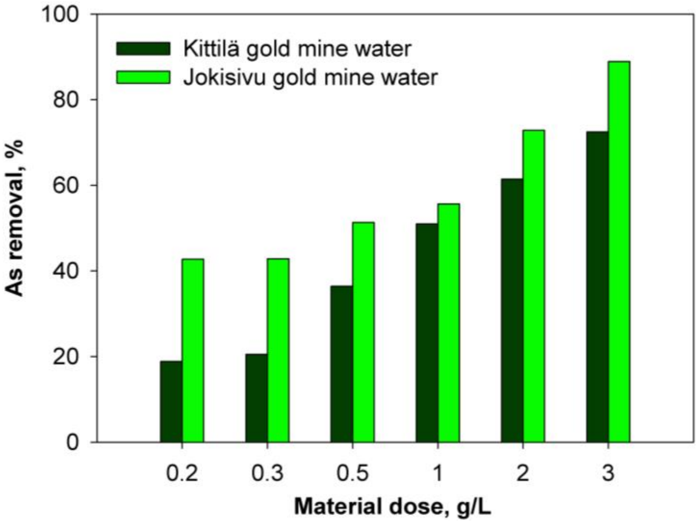


Figure 5.25. Effect of F7M/AQM dose on As removal from mine waters

The comparison of uptake of As ions from the synthetic solutions and real mine waters is presented in Table 5.5. The solutions were spiked with comparable amount of As (as total) to the initial concentration of this element measured in water from Kittilä and Jokisivu gold mine. The equilibrium adsorption data obtained for various scenarios - solution contains As(III) or As(V) or both As(III) and As(V), were used to calculate the adsorption capacity at equilibrium state. It can be seen, that the adsorption is comparable in case of treatment water from Jokisivu mine and synthetic waters, while the lower uptake of As in comparison to synthetic solutions, was recorded in tests with water from Kittilä gold mine.

Table 5.5. Comparison of uptake of arsenic (As) for synthetic and mine waters

Mine water vs synthetic solution	**As initial concentration, µgAs/L**	**Adsorption capacity, µgAs/g**
Kittilä gold mine	247	91.71
Solution As(III)	250	103.85
Solution As(V)	250	121.80
Solution As(III) + As(V)	250	119.86
Jokisivu gold mine	21	17.76
Solution As(III)	20	17.06
Solution As(V)	20	17.83
Solution As(III) + As(V)	20	17.16

5.4.8 Performance of IBS (F7M/AQM) – piloting test at mine site real mine water

The pilot scale adsorption tests were performed at the mine site of Jokisivu Gold Mine, Dragon Mining in Finland. Mineral-based adsorbent (F7M/AQM) provided for the pilot tests by Aquaminerals.

The material used at mine site was in the form of fine powder, and because of that it was utilized in a system with vigorous agitation, followed by clarification. After the process, sludge samples were collected for morphology study and EDS analysis. An example of obtained SEM images of the used adsorbent collected from lamella clarifier are shown in Figure 5.26.

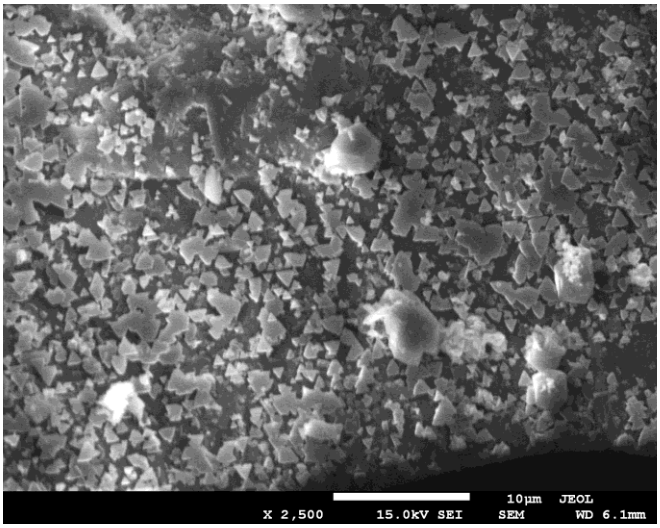


Figure 5.26. SEM image for material surface used in piloting tests - material collected from lamella clarifier

Selected results from batch adsorption tests are presented in Figure 5.27. The performance of F7M/AQM in treatment water from Jokisivu mine was satisfactory and the fast reaction time with high reduction rate was recorded. After 30 minutes of the process As, Ni and U was removed respectively with 83.3%, 100% and 96.5% efficiency, by applied material dose of 5 kg/m^3. In case of Ni and U there was no changes in removal efficiency after 30 minutes. The extension of contact time to five hours allows to reduce As concentration up to 91.7%. Reducing dosage to 1 kg/m^3 of F7M/AQM, resulted in maximum removal of 73.8% for total As, 82.7% for Ni and 95.6% for U.

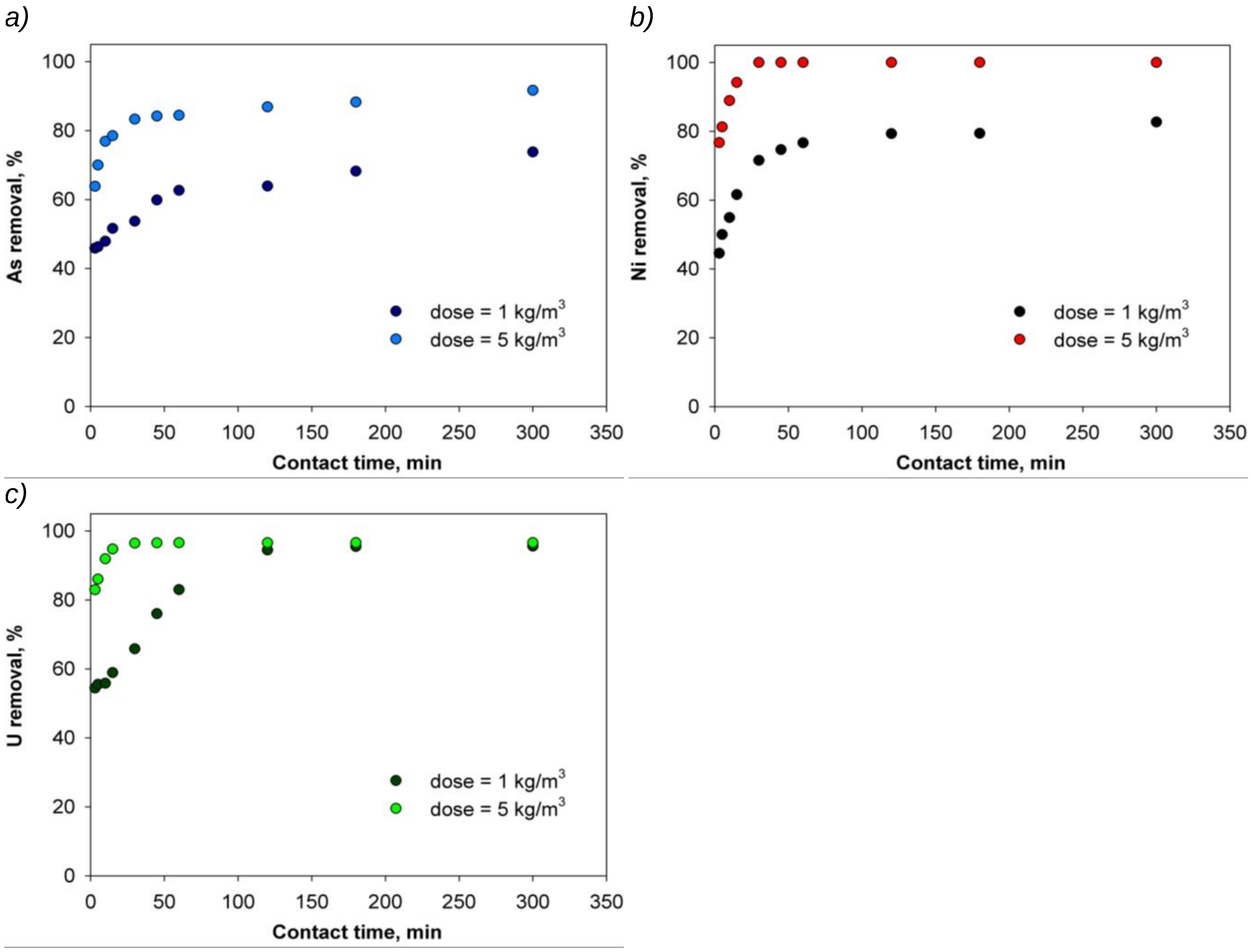


Figure 5.27. Performance of F7M/AQM in As (a), Ni (b) and U (c) removal from mine water – batch process at the pilot scale

The similar pattern was observed when adsorption tests were performed in a continuous mode, i.e. 1 kg/m^3 of material was less effective regardless the applied retention time (Figure 5.28). Furthermore, the longer contact time assure better treatment effect of As, Ni and U removal. For instance, incremental increase in process efficiency between tested RT of 15 minutes and 60 minutes was approx. 17%, 10% and 6.5% for As, Ni and U, respectively, when material dose of 5 kg/m^3 was applied.

The technological difference between batch and continuous mode system leads to various process efficiency. In batch mode, the concentration gradient between the adsorbed and the dissolved adsorbate decreases with longer contact time, while the driving adsorption force during the process carried out in continuous system remains constant. Thus, the greater adsorption can be observed when F7M/AQM was utilized in continuous mode (Figure 5.28). However, this pattern was evident for Ni and U but the efficiency of As removal was comparable for continues and batch system.

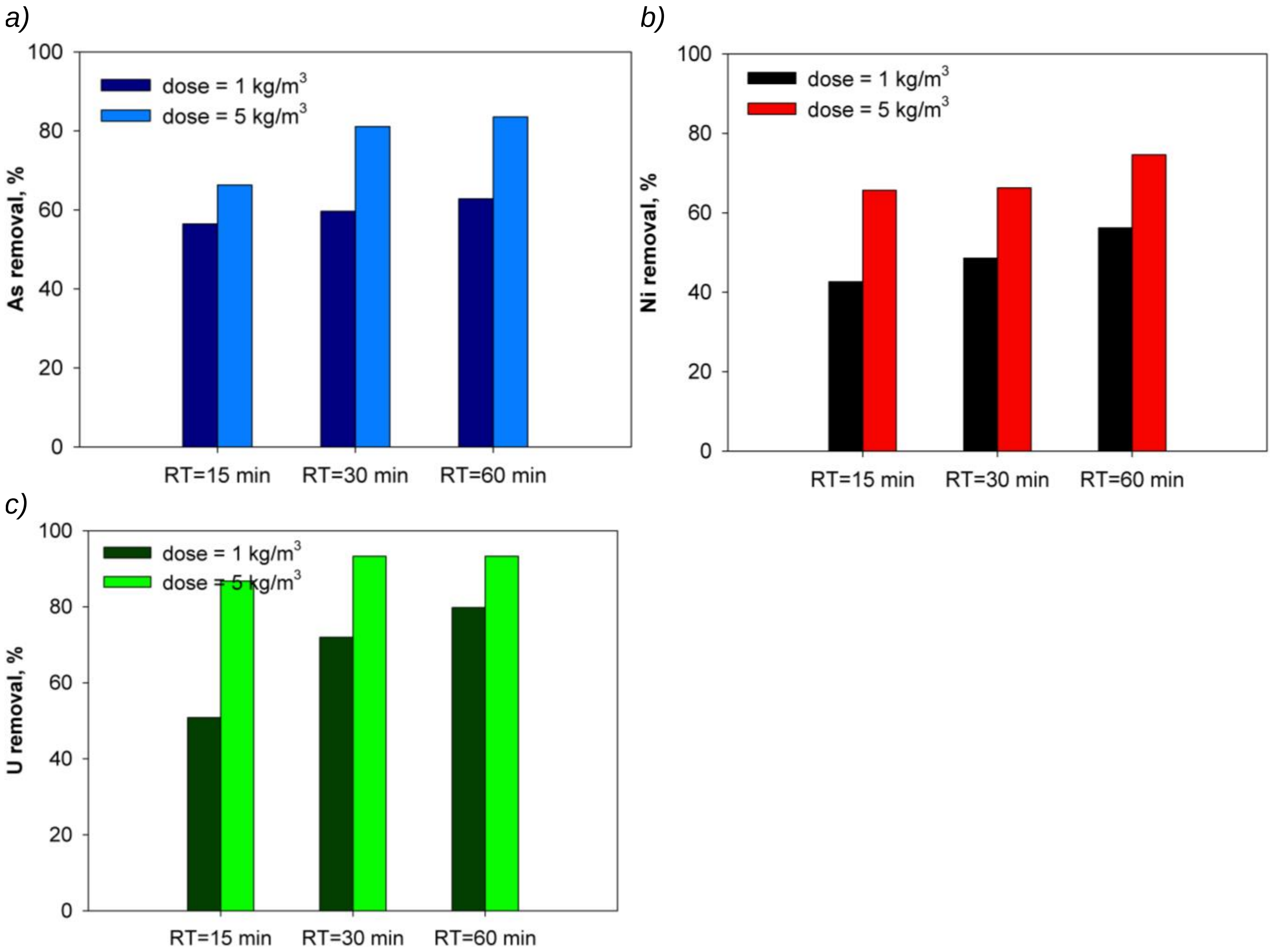


Figure 5.28. Performance of F7M/AQM in As (a), Ni (b) and U (c) removal from mine water – continuous process at pilot scale

5.5 Conclusions and recommendations

Material F7M/AQM is a commercial sorbent derived from modified natural minerals which proved to be successful in removing As, Ni and U from mine effluents. Biggest concern was how this material will perform throughout specific composition of mine waters. Tested sorbent was in a powder form and thus its performance was examined in batch adsorption system in the lab scale and batch and continuous mode in pilot scale. Series of tests confirmed high efficiency of F7M/AQM in As removal from mine effluents from two different gold mine in Finland. It was also confirmed that the efficiency of the process depends mainly on two operating parameters, such as contact time and material dose. F7M/AQM sorbent had significant effect on effluent pH, increasing its initial value from approximately 7.5 to final pH of about 10.0, after 5 hours of contact time. Thus, apart from toxic metals removal, the sorbent can be utilized for pH adjustment.

Overall, the application of F7M/AQM material to adsorptive treatment of As contaminated mine effluents may be considered as a good solution, especially that the F7M/AQM based technology is straightforward and easy to handle. However, as mentioned previously, several factors like objectives of treatment, capital and operating costs, sludge management issues need to be taken account in selection F7M/AQM material for regular (day-by-day) treatment of As-rich mine effluents. This material could be considered as an optional polishing step (depending on the presence of toxic elements) or used in case of emergency events to protect downstream aquatic environment.

5.6 References

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6 MINE WASTE MANAGEMENT

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6.1 Introduction

Gold is one of the rarest metals in the Earth. Its abundance is on the order of 0.002 g/t in the upper crust (Wedepohl 1995, Rudnick and Gao 2003) and 0.001 g/t in the mantle (McDonough and Sun 1995). The accumulations of economic interest should contain at least ca. 1 g/t gold, i.e. an enrichment factor of ca. 1,000 is needed to generate a gold deposit. The enrichment is commonly achieved by gold leaching from the rocks under the action of the hydrothermal solutions, followed by precipitation in certain conditions of temperature, pressure and chemistry of the solutions. The combined action of these factors determine the deposition of gold as native metal or as compounds with silver, tellurium, bismuth, sulphur, antimony, selenium, lead copper etc.

Gold is mined at very low grades (grams per ton), therefore, its extraction leaves large amounts of waste. The wastes of gold mining often contain sulphides and elevated concentrations of arsenic, mercury, cadmium, lead, zinc, thallium and copper. The impact of the mine waste resulted from gold mining includes the contamination of soil and water ± air, change of landscape, immobilisation of land, risk of catastrophic floods from tailings dam failure. The management of gold mining wastes addresses all these aspects.

The team from the Lulea University of Technology tested arsenic stabilization on the tailings from a gold mine at Svartliden, Sweden. Arsenopyrite is oxidized to arsenite and arsenate during cyanidation. The co-occurrence of these As-compounds and Fe- sulphides in tailings could pose great difficulties for remediation/treatment selection. Arsenites are soluble at a wide range of pH values and are less strongly adsorbed onto mineral surfaces than arsenates. A speciation of As-phases in ore and tailings suggested that As occurs dominantly as arsenopyrite in the ore, while most As in the tailings is associated with As-bearing Fe-hydrates. Leaching tests showed that As is stable in tailings at pH > 4.5 but its mobility is increased at pH < 3.5. Test of tailing conversion into Cemented Paste Backfill using cement and biofuel fly ash have been run. These showed that high saturation levels need to be kept in order to stabilize arsenic.

The study of acid drainage prevention in Castromil area (Portugal) has been undertaken by the University of Porto. The addition of low proportion of waste material from a pulp and paper industry (dregs) to make a paste proved to be efficient in neutralizing the potential acid generation and increased the material consistency.

In mine waste management, one effective approach can be the consumption of the wastes or the reduction of their volume by industrial use. On this purpose, the Geological Institute of Romania, investigated several waste rock dumps and tailings ponds in the Gold Quadrilateral of the Apuseni Mountains (Romania). The results are consistent with previous investigations showing the potential of some waste rock dumps and tailings ponds to be used as secondary gold resources or as raw materials in the manufacturing of cements, bricks and composite materials for construction, enamels, plastic materials and hydroisolation materials.

The efficient containment of mining wastes is a serious concern and measures are needed to be taken to minimize the risk of release of the waste in the environment by infiltration, erosion or dam failure. Examples of such incidents in Romania and methods of preventing further similar events were analysed by the geohazard team from the Geological Institute of Romania.

6.2 Stability of As in gold mine tailings – Svartliden gold mine, Sweden

6.2.1 Introduction

The Svartliden gold ore deposit is located along the so called Gold Line (Figure 6.1), southwest of the Skellefte ore district in northern Sweden. The operational time was 2005-2014 and until 2012, approx. 2.4 Mt of ore at a grade of 4.4 ppm Au was generated (Schlöglova et al. 2013). The Svartliden gold deposit is considered to be a structurally controlled epigenetic lode gold deposit (Hart et al. 1999, Bark and Weihed 2003, Bark and Weihed 2012) with key features resembling orogenic gold style mineralization. Gold is the only economic metal at Svartliden.

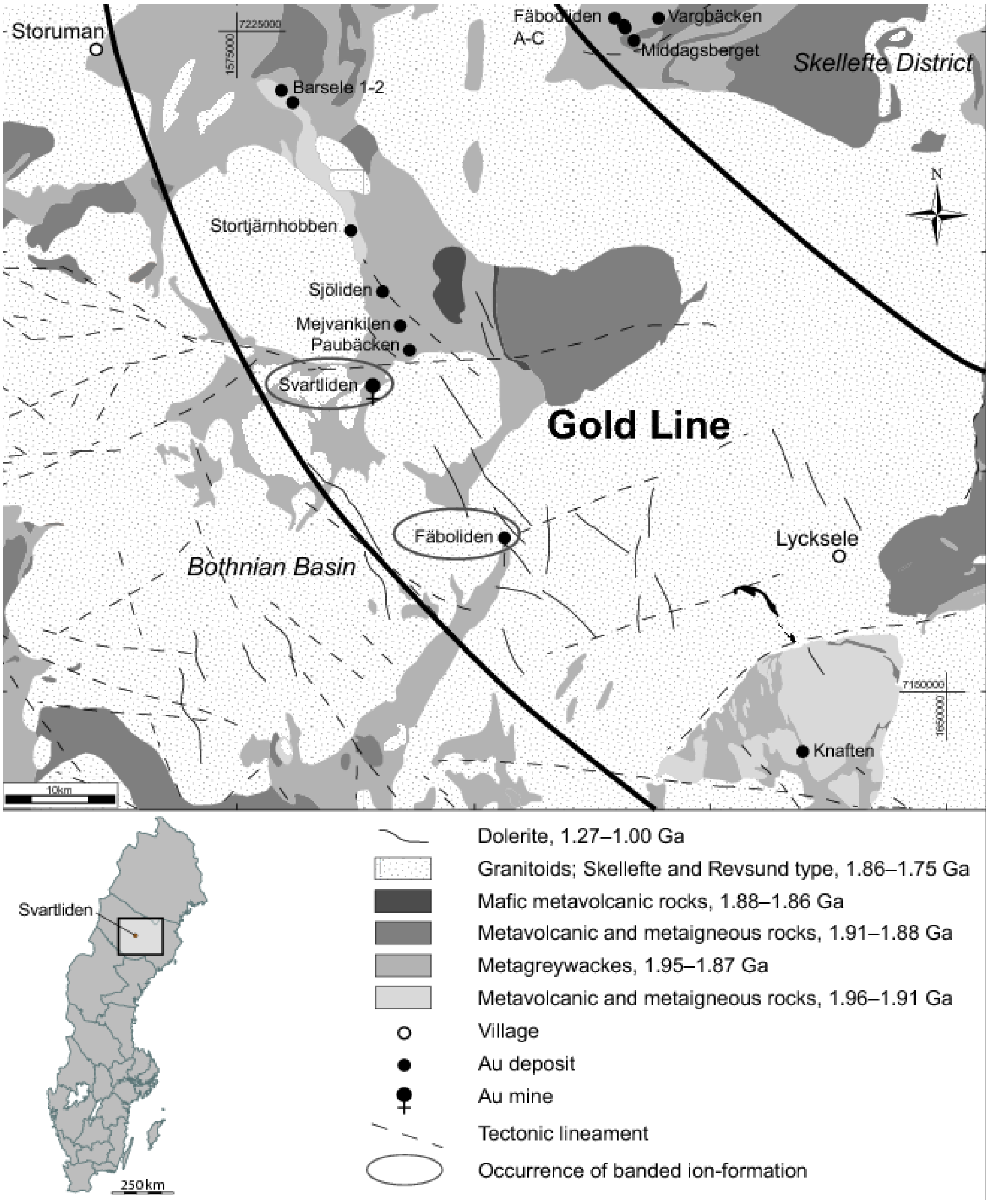

Figure 6.1. The gold ore deposit of Svartliden, mineralization of the "Gold Line" located in northern Sweden.

The mineralogy of the ore zone (including the banded iron-formation) constitutes mainly quartz, magnetite, diopside, hedenbergite, tremolite, grunerite, fayalite, pyrrhotite, arsenopyrite and löllingite (Sciuba 2013). Gold occurs as electrum (Au/Ag alloy). The gold grain size ranges between 5 and +100 μm with an average grain size of ca. 45 μm, and the gold occurs as inclusions in arsenopyrite-hosted löllingite, commonly at the grain boundary to arsenopyrite and within arsenopyrite. Gold grains are also found in the silicate matrix, commonly spatially related to arsenopyrite (Bark et al. 2013).

6.2.2 Characterization

In sulphide gold ores, fine gold particles mainly occur as inclusions in sulphide minerals such as pyrite, pyrrhotite and arsenopyrite. During the enrichment of gold, these minerals are dissolved in order to release the associated gold (Paktunc et al. 2004). Gold extraction processes most commonly includes the exposure of the crushed ore to a cyanide solution in alkaline conditions (pH 9-10). Arsenopyrite is oxidized to arsenite and arsenate during cyanidation and the effluents generated in this process need treatment before discharge into tailings facilities. The co-occurrence of these As-compounds and Fe- sulphides in tailings could pose large difficulties for remediation/treatment selection. Arsenites are soluble at a wide range of pH values and are less strongly adsorbed onto mineral surfaces than arsenates. Treatment of arsenic-rich tailings is, therefore, strongly enhanced if the majority of As is present as arsenates (As V). The evolution of pH in tailings is primarily governed by the oxidation of Fe- sulphide minerals which is considered to be an excessive acidifying process and the main cause for the generation of acid mine drainage (AMD) (INAP 2009). Management of As-rich sulphide mine tailings originating from a cyanidation process is hence a complex matter where stability of As-compounds and sulphide minerals must be considered. There are many methods for treating dissolved As in solution (Table 6.1), the most important of which were listed by Twidwell et al. (1994).

Table 6.1. Summary of arsenic removal processes (Twidwell et al. 1994).

Precipitation	Calcium arsenate Mineral-like arsenates Ferrous arsenates
Adsorption	Ferrihydrite Aluminium hydroxide Alumina Activated carbon Other sorbents
Ion Exchange/ Reverse Osmosis	Ion exchange Liquid ion exchange Reverse osmosis
Cementation Processes	Iron cementation

Co-precipitation of As with ferric salts is the preferred method for removing dissolved arsenic. The United States EPA has designated co-precipitation of As with ferric ions as “The Best Demonstrated Available Technology” (BDAT) for the removal of dissolved arsenic and it is widely used in the mining industry (Wilkie & Hering 1996, McNeill & Edwards 1997).

The unloaded arsenite produced by reaction (Equations 6.1 and 6.2) can be oxidized over days or months to arsenate.

$$H_3AsO_3(aq) + 0.5O_2 \rightarrow HAsO_4^{2-} + 2H^+ \qquad (6.1)$$

$$H_3AsO_3(aq) + 0.5O_2 \rightarrow H_2AsO_4^- + H^+ \qquad (6.2)$$

The rate of oxidation is increased by the addition of hydrogen peroxide during tailings treatment. This oxidation generates acidity but is essential for efficient co-precipitation of As (V) with Fe-hydrates. Arsenates in solution are present as anionic species such as $HAsO_4^{2-}$ or $H_2AsO_4^-$ (Blowes et al.1998). In general, arsenic bearing Fe-hydrates with a Fe/As-molar ratio of > 3 are stable in the pH range 4-8. If Fe/As-ratios > 8, the range of As-stability increases to a pH of 3-8. If conditions become more alkaline, increasing the Fe/As molar ratio will ensure the degree of stability (Riveros et al. 2001). In gold mining processes, $Fe_2(SO_4)_3$ is added aiming to form stable As-Fe-precipitates (Equation 6.3).

$$2H_3AsO_4 + Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2FeAsO_4(s) + 3CaSO_4(s) + 6H_2O \qquad (6.3)$$

Gold mine tailings slurries from As-enriched sulphide ores are often treated with lime and $Fe_2(SO_4)_3$ to promote the formation of stable Fe-As-precipitates and increase the pH to prevent AMD. The co-occurrence of pyritic minerals (i.e. pyrite, pyrrhotite) in these tailings increases the risk for a future generation of AMD and hence a destabilization of As. Gaining knowledge about the distribution and speciation of As in such tailings is essential for their future management. For that matter, a characterization is necessary.

6.2.3 Materials and Methods

At a mine in Svartliden, Sweden, gold was extracted by cyanidation from inclusions in arsenopyrite (FeAsS), which is predominantly associated with pyrrhotite (Bark and Weihed 2007). The major ore mineral assemblage in Svartliden consists of pyrrhotite, and arsenopyrite-loellingite. Chalcopyrite, pyrite, and localized traces of sphalerite are also present in small amounts. The arsenopyrite and pyrrhotite are primarily associated with silicates and magnetite (Sciuba 2013). Effluents from the enrichment process are treated with $Fe_2(SO_4)_3$, $CuSO_4$ and lime to immobilize As and destroy toxic cyanides. Tailings slurries are also pre-treated with H_2O_2 and O_2 to promote the oxidation of As (III) complexes into less mobile As (V) species. The pH of the outlet water is restricted to 8-8.5. $Fe_2(SO_4)_3$ is added to the effluent in order to form Fe-precipitates (FEP) that facilitate As-immobilization. Tailings were provided by the mining company Dragon Mining AB and was sampled from approximately ten different sites on the mine’s tailings dam and mixed to form a bulk sample.

A characterization of tailings from the Svartliden gold mine was conducted. Leaching tests (batch and weathering cell) were conducted to evaluate the behaviour of As in the tailings. These leaching tests were performed to determine the potential for As-leaching into ground and surface waters from the tailings. Weathering cell tests (WCT) and an Acid-Base-Accounting (ABA) test were conducted to simulate weathering reactions and predict the tailings’ potential for acid generation and metal release. In WCT, 70 g of tailings were placed on a paper filter in a Büchner-type funnel. The samples were leached by covering them with 50 ml of deionized Millipore®-quality water for approximately 2 h and then recovering the leachates by applying a vacuum to the funnel. The samples were exposed to weekly cycles involving one day of leaching, three days of ambient air exposure, a second day of leaching and finally two days of air exposure. Sequential leaching test was conducted to study As-phases in tailings and ore. Modelling studies were conducted using the PHREEQC program (Parkhurst & Appelo 2015) to verify the speciation of As and to estimate the extent of dissolution and precipitation of significant minerals during WCT. Arsenic speciation was assessed using the modified sequential extraction scheme described by Dold (2003). In each extraction sequence, 2 g of tailings was placed in an acid-washed round-bottomed centrifuge tube with a capacity of 60 ml and extracted with seven different solutions in succession as listed in Table 6.2. After each extraction, the suspensions were subjected to centrifugation at 1200 rpm for 15 min. The leachate was then filtered using a 0.45 µm syringe filter with an acetate cellulose membrane into acid-washed (60 ml) plastic bottles.

Table 6.2. Modified 7-step sequential extraction procedure for sulphide mine waste (Dold 2003).

Step	Chemical agent added to the solid sample	Duration	Target phase
1.	50 ml Milli-Q H_2O	1 h shaking	Water-extractable As
2.	50 ml 1 M NH_4 - acetate, pH 4.5	2 h shaking	Acid-Exchangeable (AEC) As
3.	50 ml 0.2 M NH_4 – oxalate, pH 3.0	1 h shaking in darkness	As bound to Fe (III) oxy-hydroxides
4.	50 ml 1 M NH_4 – oxalate, pH 3.0	2 h heating in water bath (80 °C)	As bound to Fe (III) oxides
5.	50 ml 35% hydrogen peroxide (H_2O_2)	1 h heating in water bath (85 °C)	Secondary sulphides
6.	Combination of $KClO_3$ and HCl, followed by 4 M HNO_3 boiling	20 min heating in water bath (90 °C)	Primary sulphides
7.	Aqua regia ($HCl:HNO_3 = 3:1$)		Residual fraction

6.2.4 Results

6.2.4.1 *Tailings and ore characteristics*

According to the XRD-analyses, the major tailings mineral assemblage in Svartliden consisted of quartz (SiO_2), tremolite ($Ca_2(Mg_{5-4.5},Fe_{0-2.5})[Si_8O_{22}](OH_2)$), albite ($NaAlSi_3O_8$) and microcline ($KAlSi_3O_8$). Jarosite ($KFe_3(SO_4)_2(OH)_6$) was present in small amounts and no crystalline phases of As were found. The relative proportions of the minerals were calculated from the peak heights of the XRD spectra. The dominant elements in the tailings and ore were Al, As, Ca, Si, Fe and S (Table 6.3). Both the tailings and ore had low contents of sulphide-associated elements such as Cu, Pb and Zn. The total sulphur contents of the tailings and ore were 2.1 ± 0.05 and 2.5 ± 0.23 wt. %, respectively. Low proportions of inorganic carbon (0.19 ± 0.03 wt. %, Table 6.3) and a net neutralization potential (NNP) less than -20 kg $CaCO_3$/ton (-60.8 ± 1.32), showed that tailings could be considered acid-generating. The As contents of the tailings and ore were 1070 ± 30 and 4703 ± 781 mg/kg, respectively (Table 6.3). According to a previous analysis (personal communication, Lars-Åke Lindahl, Dragon Mining AB), the As-content in the ore is highly variable (100-10 000 mg/kg).

Table 6.3. Chemical composition of the tailings and ore (n = 3, ± SD) for selected elements. Proportion of inorganic carbon (Cinorganic), Acid potential (AP), Neutralization Potential (NP), Net Neutralization Potential (NPP), Loss On Ignition (LOI)

Element	**Unit**	**Tailings**	**Ore**
Total Solids (TS)	%	89.0 ± 0.4	99.97 ± 0.06
SiO_2	% of TS	55.0 ± 4.9	30.3 ± 0.9
Al_2O_3	% of TS	4.69 ± 0.04	1.74 ± 0.07
CaO	% of TS	4.83 ± 0.25	4.26 ± 0.09
Fe_2O_3	% of TS	16.7 ± 0.6	12.6 ± 0.5
K_2O	% of TS	0.92 ± 0.03	0.32 ± 0.00
MgO	% of TS	3.24 ± 0.01	2.38 ± 0.07
MnO	% of TS	0.14 ± 0.01	0.15 ± 0.03
Na_2O	% of TS	0.82 ± 0.03	0.18 ± 0.01
P_2O_5	% of TS	0.24 ± 0.01	0.10 ± 0.00
TiO_2	% of TS	0.18 ± 0.00	0.09 ± 0.01
LOI (1000° C)	% of TS	1.83 ± 0.06	1.13 ± 0.01
As	mg/kg	1070 ± 30	4703 ± 781
Cr	mg/kg	166 ± 3	247 ± 45
Cu	mg/kg	147 ± 7	82.0 ± 12.5
Ni	mg/kg	63.8 ± 2.1	126 ± 12
Pb	mg/kg	4.56 ± 0.46	7.71 ± 2.58
S	mg/kg	20933 ± 493	25367 ± 2363
Zn	mg/kg	25.0 ± 0.4	10.6 ± 1.5
$C_{inorganic}$	%	0.19 ± 0.03	n.d.
AP		65.3 ± 4.3	n.d.
NP	kg/$CaCO_3$/t	4.43 ± 1.31	n.d.
NNP	kg/$CaCO_3$/t	-60.8 ± 1.32	n.d.

6.2.4.2 *Scanning electron microscopy*

Results from scanning electron microscopy (SEM) showed the occurrence of gold in ore samples and grains of arsenopyrite in tailings samples (Figure 6.2). No arsenic-bearing Fe-precipitates were detected, due to low content of As in tailings (less than 1 wt%). Indications of a hydrous ferric oxide (HFO)-rim enclosing As-sulphide grains could be detected (Figure 6.2).

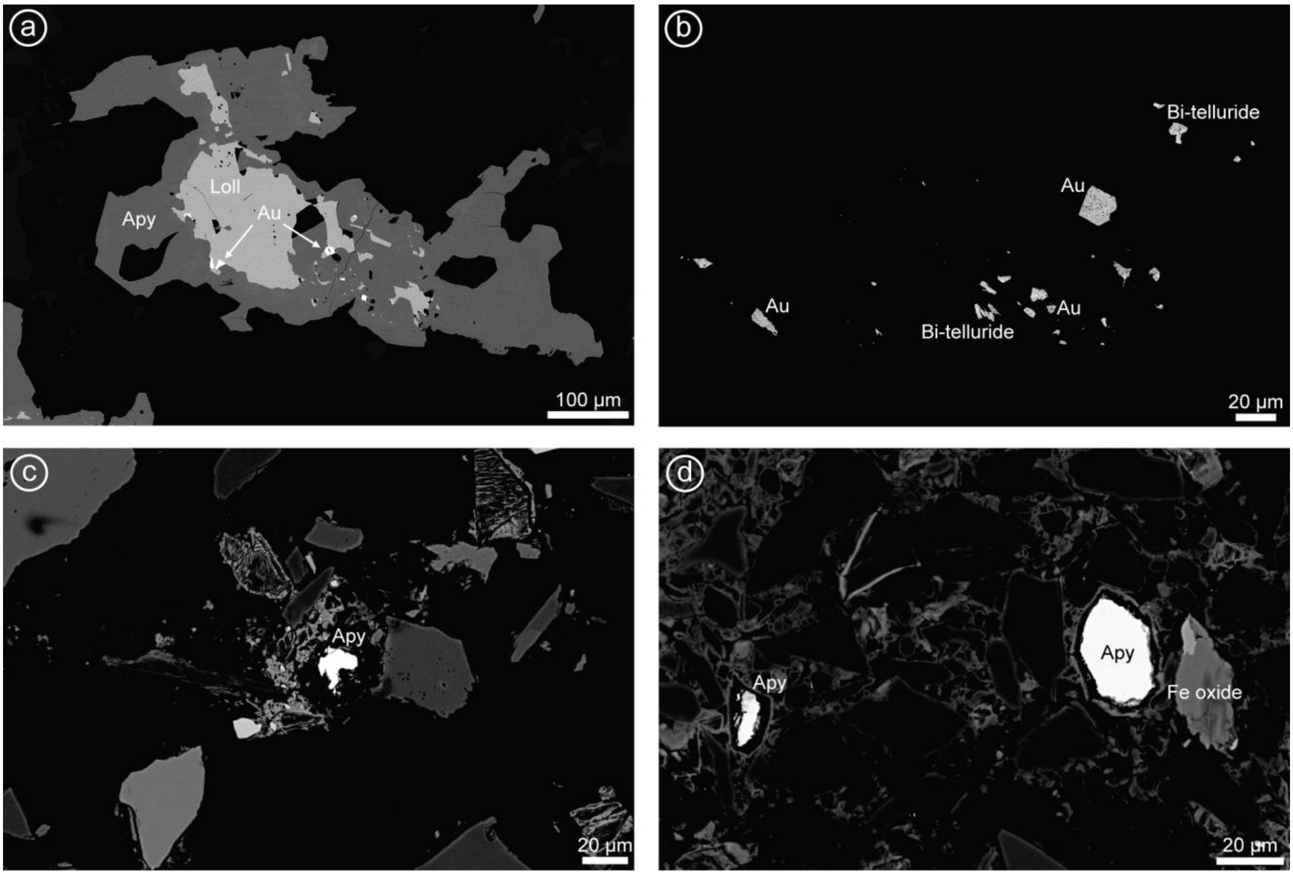

Figure 6.2. Mineralogical relationships of primary gold ore and tailings from the Svartliden gold deposit (backscattered images from scanning electron microscopy). a) Common mineral association in the primary ore, showing gold as inclusions at the boundaries between arsenopyrite and löllingite, which are hosted by silicate minerals. b) Gold together with Bi-tellurides scattered in the silicate matrix in the primary ore. c-d) Non-dissolved arsenopyrite grains in the tailings with indications of HFO-rims. Apy – arsenopyrite, Loll – löllingite, Au – gold.

6.2.4.3 *Sequential extraction tests*

Sequential extractions were conducted on tailings and ore samples in triplicate. In ore samples, analysed contents of As, Fe and Ca in each fraction deviated by less than 10% from the average. However, the standard deviation of S in each fraction was 12.6-33.8% (Figure 6.3), with the largest variation measured in the secondary sulphide fraction. Results (Figure 6.4) showed that most (98 wt. %) of the As in the ore was associated with the primary sulphide fraction and approx. 1 wt. % with the residual fraction (silicates). The majority (75 wt. %) of the Fe was associated with the residual fraction but lower (16.7 wt. %) quantities were associated with primary sulphides, Fe-oxides (5.6 wt. %) and the adsorbed-exchangeable-carbonate (AEC) fraction (1.8 wt. %). Most of the S (71 wt. %) was associated with the primary sulphide fraction, with smaller (15 wt. %) quantities associated with secondary sulphides and the residual fraction (12 wt. %). A small proportion (3.1 wt. %) of the Ca in the ore was associated with the AEC fraction and primary sulphides (2.8 wt. %), but the majority (93 wt. %) was associated with the residual fraction. Total contents of As and S differed (2654 and 10344 mg/kg) in these samples, indicating a large difference from the chemical composition analyses of the ore (Table 6.2). The non-existence of S-silicates and Ca-sulphides in natural environments implies that the sulphide fraction of S and silicate fraction of Ca were underestimated.

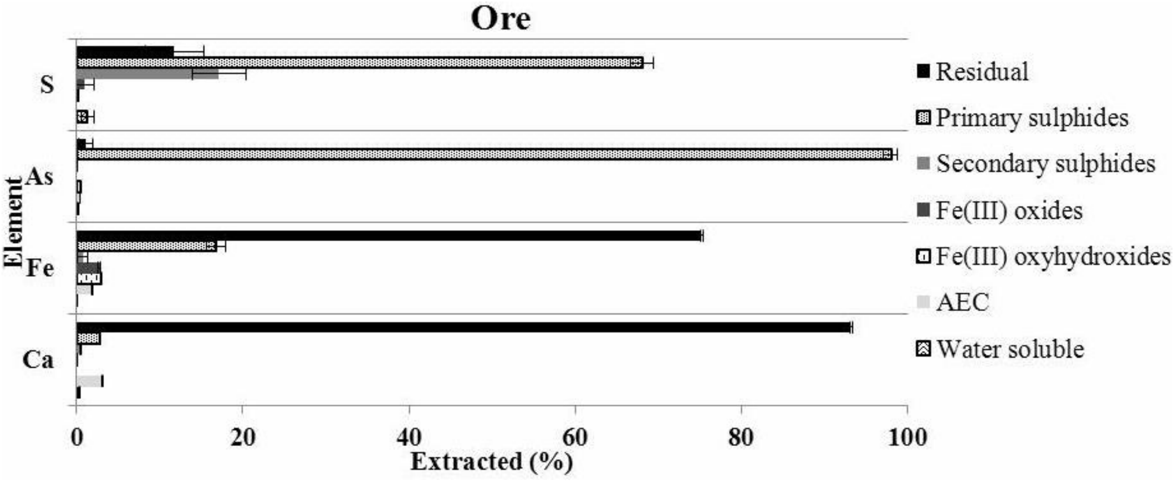

Figure 6.3. Distributions of elements across different phases in unprocessed ores from the Svartliden gold mine based on the results of sequential extraction tests (Error bars, n = 3, ± SD).

Results from the sequential extractions of tailings (Figure 6.4) suggested that the majority of As (94.6 wt. %) was co-precipitated with secondary Fe (III) minerals, whereas 2.5 ± 1.3 wt. % occurred as primary sulphides. A minor proportion of As (0.8 wt. %) was associated with the AEC fraction. The majority of Fe was associated with the residual fraction (61wt. %) and Fe (III) oxy-hydroxides (30 wt. %), but a smaller proportion was associated with primary sulphides (3.6 wt. %). Most of the S was associated with the primary sulphide fraction (37 wt. %) and water-soluble fraction (35 wt. %); smaller quantities were associated with the AEC (11 wt. %) and Fe (III) oxy-hydroxides (7.0 wt. %). The proportion of Ca in the residual fraction was (88 wt. %), whereas the rest was associated with the water-soluble fraction (7.4 wt. %) and primary sulphides (3.8 wt. %). The non-existence of Ca-sulphides in natural environments suggests that the silicate fraction of Ca was underestimated.

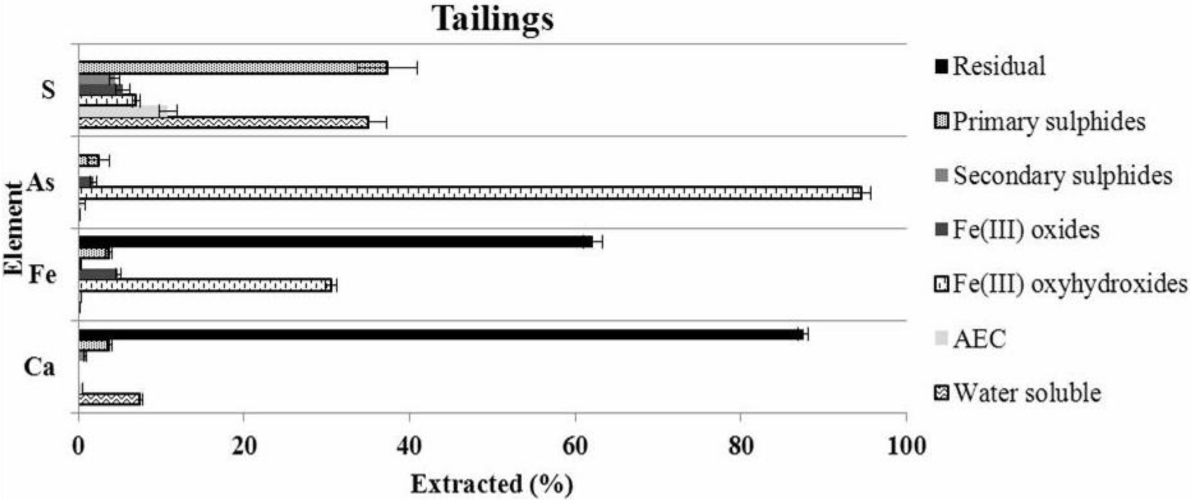

Figure 6.4. Distributions of elements across different phases in tailings from the Svartliden gold mine based on the results of sequential extraction tests (Error bars, n = 3, ± SD).

6.2.4.4 *Batch leaching tests*

The leachate from the batch leaching test (BLT) had an electrical conductivity (EC) of 2.86 mS/cm due to its high contents of S (532 mg/l), Ca (360 mg/l), Fe (650 mg/l), Mg (34.7 mg/l) and Al (60.3 mg/l). It was also quite highly oxidized (Eh: 347 ± 3 mV). The tailings leachate had a pH of approx. 3 and could be classified as acid mine drainage (AMD) according to INAP (2009) (Table 6.4).

Table 6.4. Batch leaching test results (L/S 10) (n = 3, ± SD) for the Svartliden tailings.

Element	**unit**		**Element**	**unit**	
Ca	mg/l	360 ± 12	Sr	mg/l	0.43 ± 0.02
Fe	mg/l	65.0 ± 4.1	As	µg/l	447 ± 13
K	mg/l	1.61 ± 0.11	Ba	µg/l	20.1 ± 1.6
Mg	mg/l	34.7 ± 0.9	Cd	µg/l	16.7 ± 0.5
Na	mg/l	2.35 ± 0.16	Co	µg/l	1004 ± 28
Si	mg/l	2.78 ± 0.28	Cr	µg/l	38.1 ± 7.0
Al	mg/l	60.3 ± 11.2	Cu	µg/l	838 ± 12
Ni	mg/l	4.78 ± 0.10	pH		3.07 ± 0.02
S	mg/l	532 ± 26	Eh	mV	347 ± 3
Mn	mg/l	4.59 ± 0.11	EC	mS/cm	2.86 ± 0.11
Zn	mg/l	0.97 ± 0.03			

The WCT of the tailings exhibited good reproducibility with only small differences between runs. The cumulative release of As from the tailings was 1.52 ± 0.06 mg/kg and the concentrations of As ranged from 22 to 554 µg/l. Similar trends were initially observed for the release of As, Fe, Ca and S: the concentrations of all four elements decreased gradually during the first few weeks of leaching. The concentrations of As, Fe and S subsequently increased but leaching of Ca remained low throughout the remainder of the leaching period. After 80 days, the release of As increased and concentrations of S and Fe increased in tandem once the pH fell below 4.5 (Figure 6.5).

6.2.4.5 *Weathering cell tests*

The dissolution of ferrihydrite was most extensive at the end of the WCT and coincided with increased leaching of As. Gypsum was the most dominant Ca-mineral and was under saturated during the WCT (Figure 6.5).

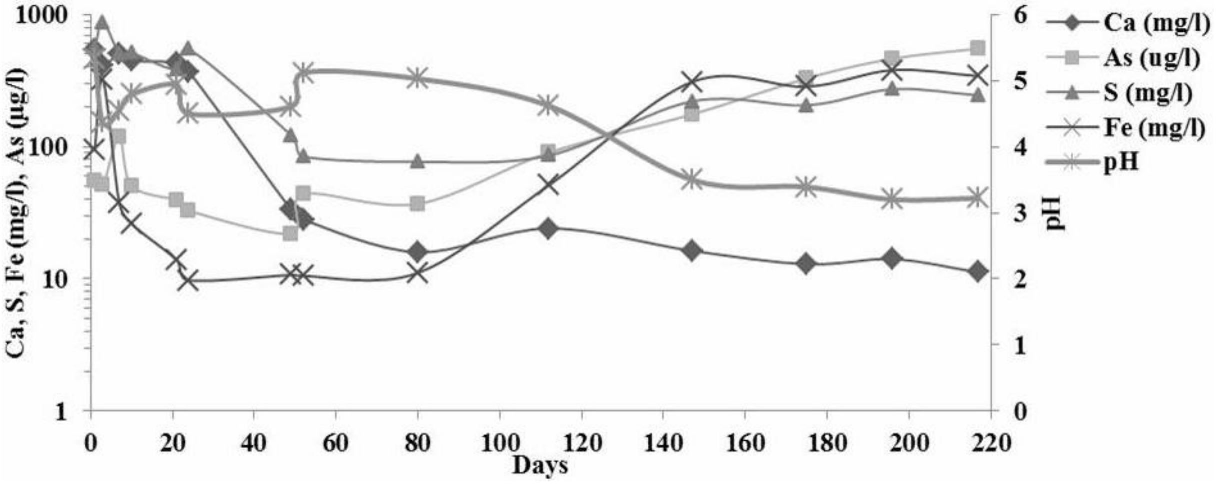

Figure 6.5. Evolution of pH and release of Ca, Fe, S and As from Svartliden gold mine tailings over time during the WCT.

6.2.4.6 *Modelling – PHREEQC*

Modelling in Phreeqc (Parkhurst & Appelo 2015) suggested that As-leaching increased while the stability of ferrihydrite and goethite decreased. Gypsum governed leaching of Ca and S throughout the WCT (Figure 6.6).

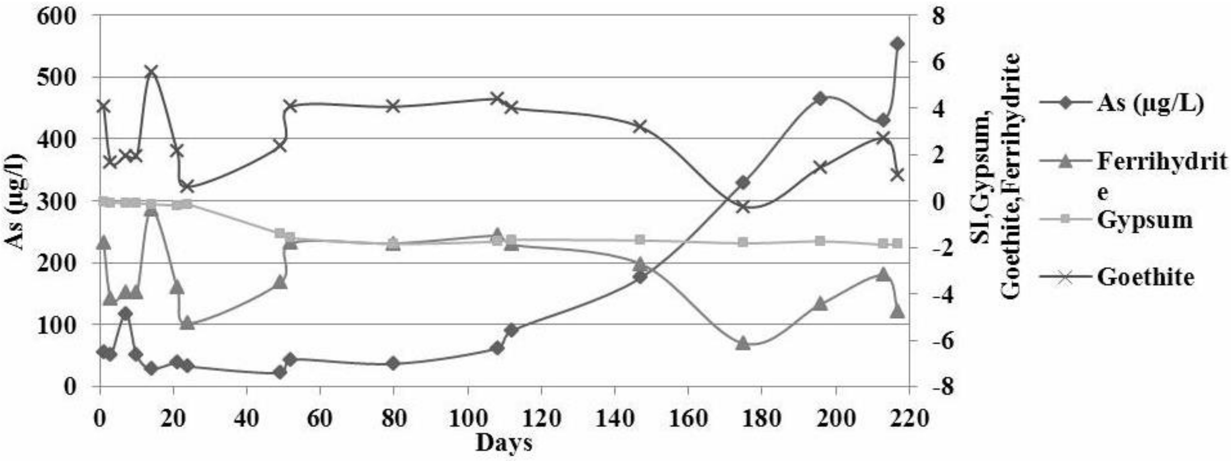

Figure 6.6. Evolution of As-release and Saturation Index (SI) of gypsum, goethite and ferrihydrite during the WCT.

6.3 Method of increasing the stability of As in tailings resulted from cyanidation

Speciation of As, Fe and S in tailings was assessed using the modified sequential extraction scheme described by Dold (2003) and suggested that a majority (approx. 95 wt. %) of As in the tailings of Svartliden was associated with the Fe (III) oxy-hydroxides-fraction as iron-arsenates (Fig 6.4). The majority of S was associated with the water-soluble fraction and the primary sulphides fraction. The sequential extraction tests suggested that the sulphide and sulphate contents of the tailings accounted for 42 % and 46 % of their total S, respectively (Figure 6.4). Speciation of Fe revealed that a significant proportion of Fe is present as sulphides assumed to be pyrrhotite (main Fe-sulphide in the ore assemblage). Results from previously conducted weathering cell tests (Figure 6.5) showed that the As-release increased as pH < 3.5 due to a more extensive pyrrhotite oxidation. Pyrrhotite is a highly reactive sulphide mineral which generates acid upon contact with water and air (INAP 2009). If Pyrrhotite is left in cyanidation tailings, further actions are needed to avoid acidic conditions and thereby preserve the stability of the iron-arsenates.

6.3.1 Cemented paste backfill

Methods for mining waste remediation often involve preventing oxygen from reaching the waste or the suppression of AMD formation, usually by treatment with lime or $CaCO_3$. Water or soil coverage (dry or wet cover) is widely used for remediation because oxygen is much less soluble and diffuses much more slowly in water than in air. Soil coverage often contains a liner with low hydraulic conductivity that becomes heavily waterlogged. Unfortunately, these approaches are not suitable for arsenic-containing mine waste because arsenic is more soluble in the reduced As(III) state than in the oxidized As (V) state. Consequently, other remediation options must be used. One method that has been suggested for the management of As-rich tailings is their conversion into a monolith using so-called “Cemented Paste Backfill” (CPB). A paste is defined as slurry that has been dewatered to the point that no water or solution will flow from the material. Paste formation is a method for the thickening and dewatering of tailings to reduce the risk of dam failures and the consumption of water in remediation applications. A paste can be pumped, if it contains more than 20% solids with a particle size less than 20 µm. CPB generally consisting of mine tailings, water and Portland cement (Benzaazoua et al. 1999). It is normally prepared from dilute slurries of tailings by dewatering it with conventional thickening or filtering.

Once formed, CPB can be backfilled into excavated underground areas. The aim of converting tailings into CPB is to minimize the amount of percolating water and decrease oxygen penetration through the material. The cement matrix of the CPB material helps to suppress oxidation due to its high degree of saturation. This in turn obstructs the oxidation of sulphide minerals. CPB can also serve as a geotechnical support for underground mine cavities, which increases its operational advantages in the mining (Coussy et al. 2011). The most common binder material used in CPB is cement, and the typical water content of CPB materials is 20 - 25%, which is required to enable its transport through pipes. Because mines can easily produce more than hundreds of thousands of tonnes of tailings, the cost of the cement required to form CPB can become very high. To reduce this cost, attempts have been made to replace some of the cement with cheaper materials that have similarly pozzolanic and alkaline properties such as granulated blast furnace slag (GBFS), biofuel fly ash (BFA) and cement kiln dust (CKD) (Tariq & Yanful 2013). These alkaline materials help to neutralize the acidity arising from the sulphide-rich tailings and prevent the spread of trace elements. However, increasing the alkalinity of the material may increase the risk of leaching for anionic trace elements such as arsenic.

6.3.2 Evaluation of the stability of As in cemented tailings

In this study, the use of cemented paste backfill (CPB) was evaluated for management of As-rich cyanided tailings. According to previously conducted studies (Benzaazoua et al. 2004, Coussy et al. 2011, Randall 2012, Coussy et al. 2012), proportions of 4-7 % CPB-mixtures (cement, fly ash, slags and tailings) are necessary to decrease the leaching of arsenic. Demands of strength in these mixtures were determined by the mine processor to maximize the amount of extracted ore. When less strength is needed in tailings management, lower proportions of binders could be added. This could, however, reduce the level of saturation within the CPB-materials increasing fluid transfer and weathering. However, CPB has also been evaluated as backfill of non-load bearing constructions or tailings dams (Deschamps et al. 2008, Deschamps et al. 2011, Yilmaz et al. 2014). In such cases the strength of the CPB-material is of less concern but aims to prevent the release of metal ions and minimize AMD still remains. So, when less strength is needed in the CPB-material, how does it affect the leaching of arsenic? A former study by Cruz et al. (2001) has shown that low proportions of binders could be insufficient to suppress the generation of acid mine drainage. It is therefore important to investigate the chemical stability of As-bearing FEP in CPB materials where iron sulphides are occurring. In this study, mine operators considered that a compressive strength of 200kPa was sufficient for the CPB-material. The compositions of CPB-materials are listed (in Table 6.5) and were also chosen by considering economic criteria minimizing the binder proportions. At lower strength demands, proportions of binders used in CPB materials could be reduced. The primary objective for this part of the study was to evaluate the effects of cementation on arsenic leaching. For cost-reduction, low proportions of cement and biofuel fly ash (1-3 wt. %) were used as amendments. The effect of cementation on As-leaching was evaluated by comparing CPB-materials and un-amended tailings. The specific aims of the study were to perform static and dynamic leaching tests to evaluate:

- The influence of weathering on the behaviour of As in CPB materials
- The effect of cementation on the stability of As

Moreover, at completely saturated conditions in the CPB-materials, sulphide oxidation is inhibited and sulphates affecting mechanical strength are mainly supposed to be those that were present in the initial tailings (pre-oxidized products) (Benzaazoua et al. 2004). In field conditions, more extended time periods are expected for the groundwater table to rise and flood the CPB-materials (INAP 2009). During that period of time, local desaturation in the CPB-monoliths is possible and this could increase the sulphide oxidation rate (Ouellet et al. 2006). It is therefore important to investigate the geochemical stability of As in CPB materials cured for extended time periods where unsaturated areas is present. For this reason, CPB-mixtures were studied with the specific objectives to:

- Assess the mobility of As in CPB-materials with low proportions of binders cured for an extended time period.
- Evaluate the effects of a delayed saturation (by flooding) on As-leaching in the CPB-materials.

6.3.3 Materials and Methods

In this study, leaching tests (tank, sequential and weathering cell) were conducted to evaluate the effects of cementation, delayed flooding and weathering of As-rich cyanided tailings. Cement (CE) and biofuel fly ash (FA) were mixed with tailings and cured for 31 days or 1 year forming a CPB-monolith, with the compositions of the studied mixtures being adjusted to achieve a hardened strength of 200 kPa while minimizing the amount of added binders. Two mixtures were examined: CE, which contained 1 wt. % of cement; and CE-FA, that contained 2 wt. % of cement and 1 wt. % of biofuel fly ash. The CE, CE-FA, and unmodified tailings were subjected to a tank leaching test (TLT) to examine their behaviour under simulated, flooded conditions. In TLT, CPB-monoliths were placed inside tanks on 2 cm tall plastic supports, after which the tanks were charged with distilled water until there was a 2 cm water head surrounding the CPB sample and a liquid/solid (L/S) ratio of 10 cm^3 of solution per cm^2 of exposed solid was established. Reference samples (tailings) were placed in paper filter bags with 1 µm pores inside nylon filters, which were hung from the lids of the tanks such that the tailings were fully immersed in the water. In WCT, crushed CE-FA and CE was used to evaluate the effect of the addition of binders in surficial environments. In addition, to simulate AMD production and the depletion of buffering minerals, acid was added to crushed CE-FA and CE in the later stages of WCT. Total contents of selected elements in cyanidation tailing, CE and FA are presented in Table 6.5.

Table 6.5. Selected element content in cyanided tailings, Portland Cement (CE) and Biofuel fly ash (FA) (n = 3, ± SD)

	Units	**Tailings**	**FA**	**CE**
Total Solids(TS)	%	89.0 ± 0.4	95.2 ± 0.7	99.4 ± 0.0
SiO_2	% of TS	55.0 ± 4.9	34.6 ± 1.3	20.6 ± 0.8
Al_2O_3	% of TS	4.69 ± 0.04	10.7 ± 0.6	5.61 ± 0.45
CaO	% of TS	4.83 ± 0.25	14.1 ± 1.0	50.3 ± 1.8
Fe_2O_3	% of TS	16.7 ± 0.6	13.9 ± 1.0	2.81 ± 0.05
K_2O	% of TS	0.92 ± 0.03	2.89 ± 0.08	0.83 ± 0.05
MgO	% of TS	3.24 ± 0.01	2.54 ± 0.08	4.00 ± 0.17
MnO	% of TS	0.14 ± 0.01	0.92 ± 0.03	0.10 ± 0.01
LOI 1000°C	% of TS	1.83 ± 0.06	4.93 ± 0.12	2.77 ± 0.12
As	mg/kg TS	1070 ± 30	124 ± 5	10.2 ± 0.2
Cd	mg/kg TS	0.27 ± 0.02	4.15 ± 0.08	0.10 ± 0.02
Co	mg/kg TS	13.2 ± 0.25	19.1 ± 1.2	21.0 ± 0.3
Cr	mg/kg TS	166 ± 3	132 ± 4	98.1 ± 4.4
Cu	mg/kg TS	147 ± 7	136 ± 10	86.2 ± 2.9
Ni	mg/kg TS	63.8 ± 2.1	114 ± 9	63.8 ± 1.3
Pb	mg/kg TS	4.56 ± 0.46	78.6 ± 1.1	8.46 ± 0.11
S	mg/kg TS	20933 ± 493	13700 ± 200	9960 ± 219
Zn	mg/kg TS	25.0 ± 0.42	374 ± 10	149 ± 3

The sequential extraction test adapted from Dold (2003) was conducted on crushed, CPB-materials (CE aged, CE-FA aged) to compare the proportion of As associated with certain target phases in aged CPB and unmodified tailings. Results from previously conducted sequential extraction test in Hamberg et al. (2015) conducted on unmodified tailings were used for comparison. Details about the preparation of the CPB-mixtures are described in Hamberg et al. (2015). The mixtures of CE and CE-FA were cured for 31days or 1 year. CPB-mixtures were kept in saturated, room tempered, dark conditions until the 31th day of curing. Thereafter, the CPB-mixtures were kept in dry, dark, room tempered conditions until one year of curing.

6.3.4 Results

In this study, cyanided tailings were solidified to form a monolithic CPB-mass. Cement and biofuel fly ash were mixed with the tailings and cured for 31 days or 1 year, with the compositions of the tested mixtures being adjusted to achieve a hardened strength of 200 kPa while minimizing the total load of binders. Two mixtures were examined: CE, which contained 1 wt. % of cement; and CE-FA, which contained 2 wt. % of cement and 1 wt. % of biofuel fly ash. Former, similar studies have shown that leaching of As could be decreased using CPB. These studies focused on the stability of arsenopyrite, scorodite or spiked As in natural or synthetic CPB with binder contents of 4-5 % (Benzaazoua et al. 2004, Coussy et al. 2011, Coussy et al. 2012, Randall 2012). Suggested mechanisms for As-leaching in a cementitious matrix are sorption onto C-S-H surfaces, As (V) replacing SO_4^{2-} in ettringite, and the formation of calcium–arsenic compounds (Phenrat et al. 2005). These processes all depend on the chemical and physical properties of the cementitious matrix. The aim when forming a CPB monolith is to increase the saturation of the material and thus reduce the intrusion of oxygen and water percolation. However, the WCT and TLT results indicated that the leaching of As from the CE and CE-FA materials, which contain relatively small quantities of binders (1-3wt. %), increased the leaching of As relative to that seen in unmodified tailings, especially when the pH was lowered from 10 to 8 (Figure 6.7). As-species adsorbed onto C-S-H and Ca-arsenates are only stable under alkaline conditions (pH<10), which may explain this increase in As-leaching.

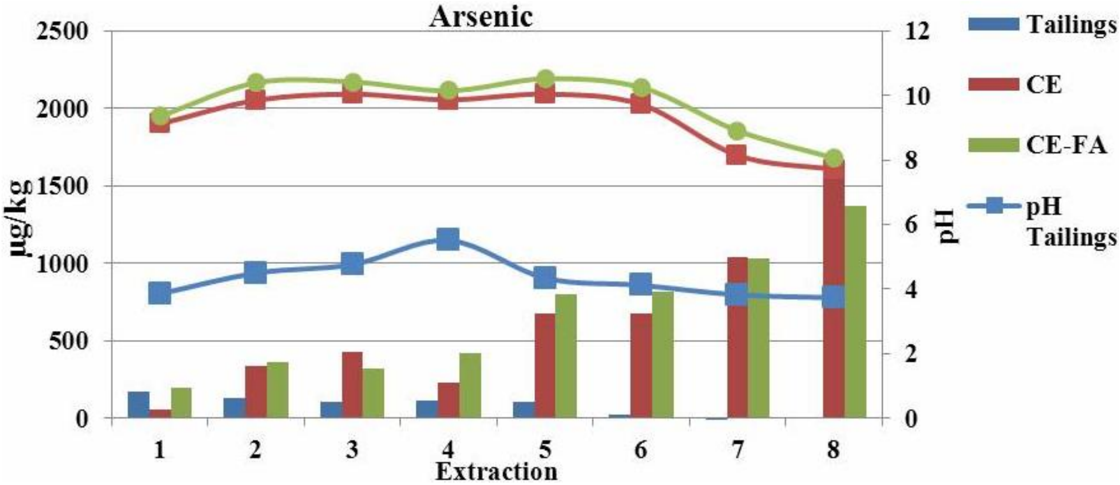

Figure 6.7. The evolution of As-leaching and pH in tailings, fresh CE, fresh CE-FA during TLT.

Calculations in accordance to the TLT-standard suggested that leaching of As in CE and CE-FA were predominately an effect of diffusion (Voglar and Leštan 2013). This means that the physical obstruction created by the cementitious materials was insufficient to encapsulate As. The increase in As-leaching was not correlated with the release of Fe. This implies that As-bearing Fe-hydrates were stable and that desorption of As from Fe-hydrates was the main mechanism for As-leaching. The point of zero charge (PZC) for Fe-hydrates generally occurs at a pH ≈ 8. At alkaline conditions, during leaching tests (WCT and TLT) of the CPB-materials, As adsorbed onto Fe-hydrates could desorb and enter into solution. Alkaline solutions originating from the dissolution of cementitious phases obstructed dissolved As to re-adsorb onto Fe-hydrates. Dissolved As formed less acid-tolerant As species, which subsequently dissolved during leaching. However, it should be noted that only a small proportion of the total As in the tailings was released during the leaching tests; the bulk of the As were retained in the CPB mixtures.

Previously conducted study of Jia & Demopoulos (2005) highlighted the importance of Ca ions for the stability of As in cementitious materials. The content of water -soluble Ca-phases in the tailings was primarily due to the presence of gypsum. Cementitious materials contain highly soluble Ca species whose dissolution may have raised the concentration of Ca ions in the leachates formed during the leaching tests. This dissolved Ca could increase the positive charge on the surfaces of Fe hydrates, especially under alkaline conditions, meaning that dissolved As could more easily re-adsorb onto their surfaces.

Acid (1M HCl) was added to consume the cementitious and buffering minerals in the crushed, cemented tailings. This increased leaching of Fe, Si and As, but had no significant effect on S-leaching (Figure 6.8). In alkaline, oxidized conditions, pyrrhotite oxidation is obstructed as dissolved iron from this process is at a higher degree precipitated on the surface of the sulphide grains. This in turn would make sulphide grains more acid-tolerant. Acid was added to the crushed CPB-samples to reach a pH of 4.5, this represents the average pH in tailings during the first stages of leaching. The addition of acid increased As-leaching most significantly in CE that had the lowest proportion of binders. The addition of binders increased the acid-neutralizing capacity of tailings and introduced more Ca ions and Fe-precipitates into the matrix. Higher proportions of Fe-hydrates could facilitate As-adsorption in a long term basis and decrease the sulphide oxidation rate.

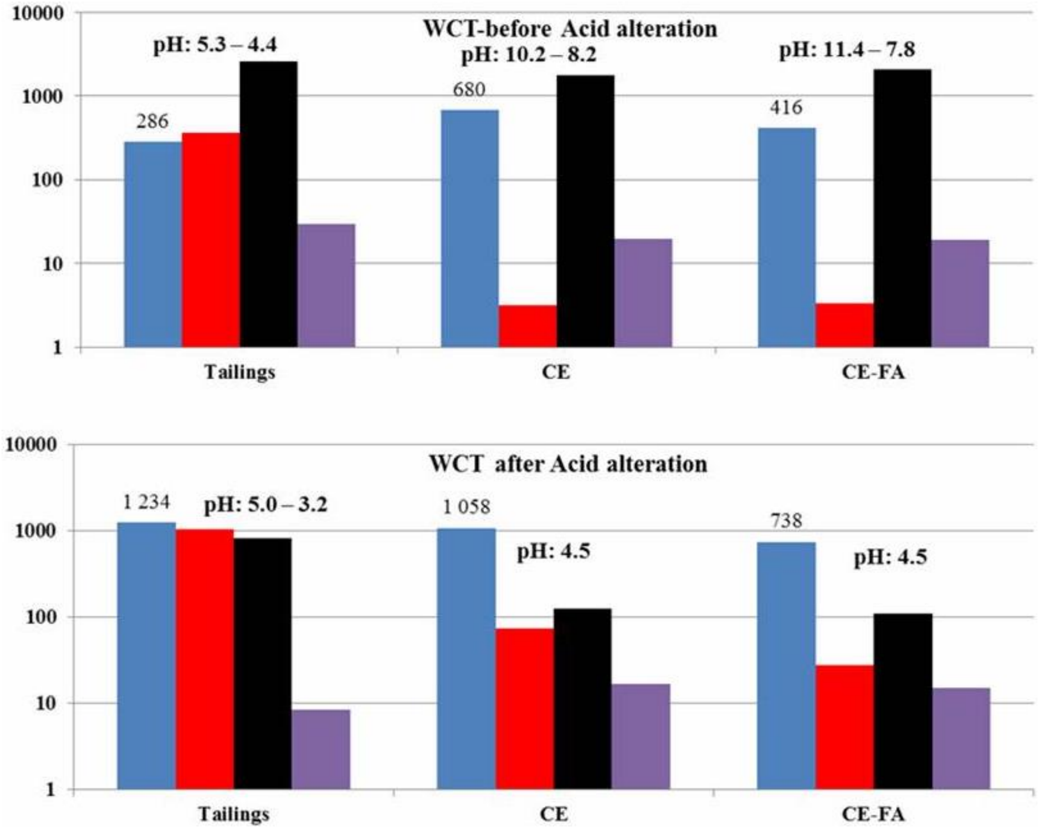

Figure 6.8. Cumulative leaching of Fe (red), Si (purple), As (blue) and S (black) before and after acid addition in CPB materials during the weathering cell test.

6.3.5 Effect of delayed saturation

The total release of As was more extensive in fresh CE-material (As fresh) compared to that in aged CE (As aged) (Figure 6.9), while the release of Si, Ca and S was more extensive in aged CE. The correlated release of S and Ca from tailings, CPB fresh and aged indicate dissolution of gypsum. The highest As concentrations released during the leachate renewal cycle were 32mg/m^2 observed for CE (fresh) at the 8th extraction and 6mg/m^2 for CE (aged) during the first extraction. This corresponds to 0.32 mg/l, 0.06 mg/l, respectively (L/S=10cm^3/cm^2). A low strength within the CE-material was observed while the monolith was disintegrated. As-release in fresh CE (As fresh) was lower compared to that in aged CE (As aged) at the beginning of the test but increased until the end of the test. The evolution of pH in aged CE had an opposite trend compared to that in fresh material with an initial low level (3.2) that rose to 6.2 in the last extraction (Figure 6.1). The evolution of pH in fresh CE-material started off at a high level (9.3) and decreased to 7.7 in the last extraction (Figure 6.9).

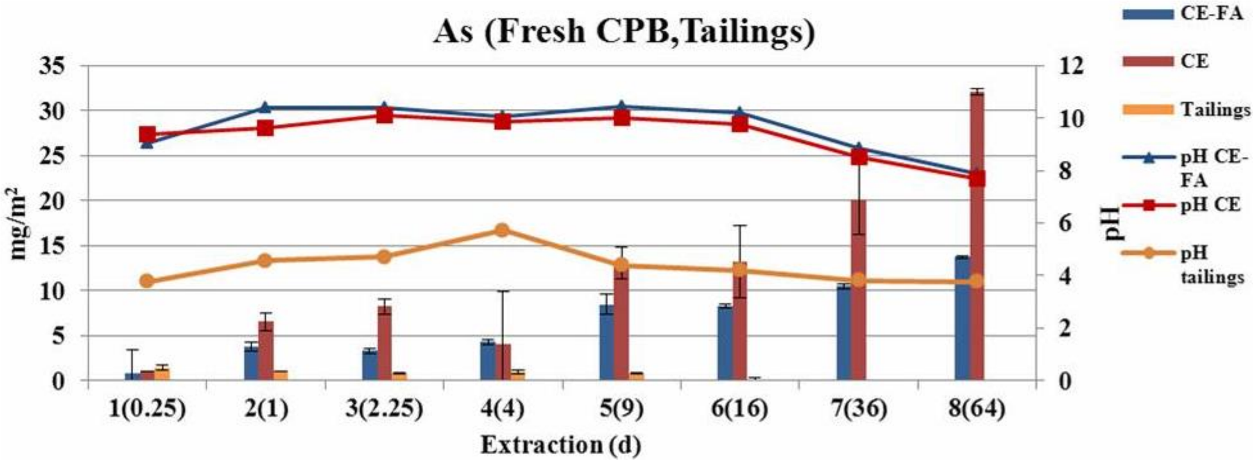

Figure 6.9. The evolution of As-release and pH during TLT (Fresh CPB-materials and tailings)

The highest As concentrations released during a leachate renewal cycle was 14mg/m^2 observed for CE-FA (fresh) and 12mg/m^2 for CE-FA (aged) at the 8th extraction. The evolution of pH in aged CE-FA had a similar trend compared to that in aged CE and started at 5.2 and increased to approx. 8 until the 7th extraction. In aged CPB-materials, the amount of As that leached from CE-FA during the tank leaching tests increased over time while CE decreased over time (Figure 6.10).

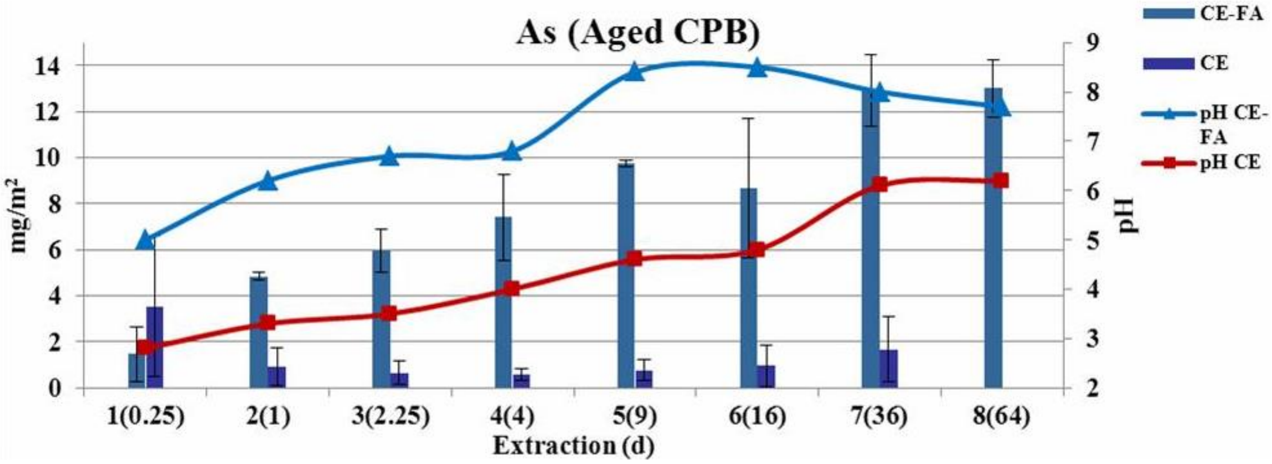

Figure 6.10. The evolution of As-release and pH during TLT (aged CPB-materials)

Crushing the aged CPB-materials before conducting the sequential leaching tests revealed that dry areas were present within the CPB-materials which indicated a low degree of water saturation. Results from the sequential extractions of CE and CE-FA (Figure 6.11) suggested that the addition of cementitious binders has modified the fractionation of As compared to the unmodified tailings. The proportion of As associated with amorphous Fe (III) oxy-hydroxides decreased in CE and CE-FA compared to that in unmodified tailings. Proportions (weight %) of As associated with the AEC fraction has increased in the cementitious mixtures, but most extensively in CE-FA. The proportion of As associated with Fe (III)-oxides has increased in CE but was unaltered in CE-FA compared to that in the unmodified tailings. The proportion of As associated with less soluble phases (sulphides, silicates) were unaltered in the CPB-materials compared to that in unmodified tailings.

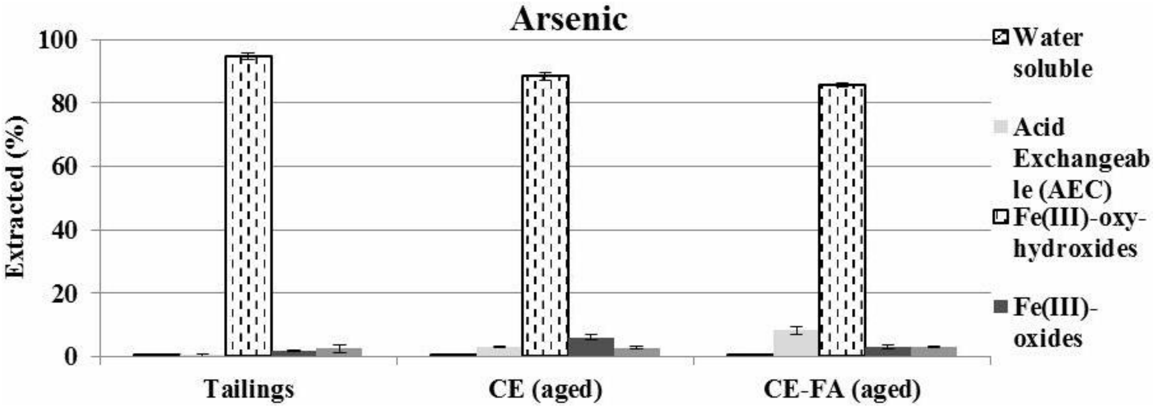

Figure 6.11. Fractionation of As in sequential leaching test of tailings, CE (aged), CE-FA (aged), (n=3, error bars ± SD)

6.4 Gold mine tailings disposal strategies - Castromil, Portugal

6.4.1 Introduction

Mine tailings management should be considered, in the design phase, for the all mine life cycle (exploration, feasibility, exploitation, ore processing, decommissioning, closure, post closure and relinquishment).

In the past, Castromil mine gold project in Portugal was not accepted by the government authorities due to environmental concerns. Currently, Castromil gold mine project is being reconsidered with alternative technological solutions less harmful for the environment.

Having in mind alternative strategies for the disposal of the tailings that will be generated in the near future, the following laboratory work was performed:

1. Selection of samples of tailings (natural and artificially prepared) from two different spots;
2. Characterization of the material before and after preparation to simulate tailings material (grain size distribution, main heavy metals and sulphur content);
3. Selection and characterization of industrial by-products considering co-disposal;
4. Artificial preparation of paste samples and its physical and chemical characterization;
5. Forecast of the Acid Generating capacity using static and kinetic tests: the acid base accounting method (ABA) and the static net acid generation (NAG) procedure, column tests;
6. Forecast of the metal leaching capacity.

6.4.2 Materials and Methods

Representative samples of Castromil gold ore were collected in a fresh slope and from an exploration gallery. A part of these samples was used in hydrometallurgical tests presented in Chapter 4. The remaining samples and the residues originated in beneficiation tests constitute the subject of this study: C1 (rock waste - original Castromil fresh slope), C2 (tailings from laboratory leaching tests - processed ore from Castromil fresh slope), C3 (tailings from laboratory leaching tests - Castromil's exploration gallery CSQ19). In order to study the feasibility of using alkaline by-products in gold mine tailings co-disposal, waste material from a pulp and paper industry (dregs) was used (DR sample).

All samples were characterized for particle size analysis and chemical composition. Particle size analysis were performed in standard sieve series and using a Laser Diffraction Granulometer – Malvern 2000. Chemical composition was determined by X ray dispersive energy fluorescence with an InovX portable equipment. Inorganic and total carbon were determined for samples C2 and C3 in a Shimadzu TOC-VCSN with a solids module SSM-5000A.Experimental Methodology

Static Net Acid Generation (NAG) tests were made according to the ARD Test Handbook procedure (Smart et al. 2002). Although the test is applicable to a single sample, these tests were applied to mixtures of sample C1 with dregs, varying the proportional quantity of these waste solids, in order to determine the amount of dregs needed to be added to waste mine rock in order to neutralize it.

Kinetic NAG tests are an improvement over the static tests as they allow to understand the kinetics of the oxidation reaction, the reaction’s sequence of the different minerals (Weber et al. 2004) and in certain cases it can be used to predict lag times in dynamic tests, like leach columns (Stewart et al. 2006) or humidity cells (Sapsford et al. 2008). Kinetic NAG tests do not have a protocol that define the test duration time. It depends on the sample and the purpose of the test. This test was only made to compare the kinetics of the dregs oxidation, to understand if they react faster than the mine waste and therefore one day was enough to obtain the necessary data. However, in some studies this test lasted 5 days in order to compare with the results from the humidity cell tests (Sapsford et al. 2008).

A dynamic leaching test was applied to sample C1 in a continuous stirring to understand if this sample produces acid mine drainage (AMD). This test was based on a test used in a study to evaluate behaviour of a sample to generate acidity (Nunes 2015).

Column tests were performed with samples C1, C2 and C3, varying the percolation conditions. A total of 10 column test were built and daily monitored by the measurement of the following parameters: pH, conductivity, salinity, total dissolved solids and total and inorganic carbon.

Lastly, consistency tests, also named as slump tests, were applied to paste materials and pulps to measure their consistency. The test’s procedure is standardized according to NP EN 12350-2. Sample C1 and a mixture of C1 with 7.8% of dregs (DR) were submitted to the consistency test.

6.4.3 Results

6.4.3.1 *Samples characterization*

The main parameters (d10 and d90) of particle size characterization for tailings and by-products samples are presented in Table 6.6.

Table 6.6. Particle size range of Castromil tailings samples and pulp paper industry by-products.

Sample ID	**Particle size range (µm)**	
	d10	**d90**
C1	220.0	17000.0
C2	76.2	833.7
C3	71.4	796.9
DR	2.5	487.2

The chemical analysis of the studied samples revealed high arsenic content in Castromil samples. In addition, dregs presented high concentration in manganese and calcium (Table 6.7).

Table 6.7. Chemical composition of C1, C2, C3 and DR samples (Fernandes 2016)

Element	**Sample C1**		**Sample C2**		**Sample C3**		**Sample DR**	
	Reading (ppm)	**+/- or n.d.**	**Reading (ppm)**	**+/- or n.d.**	**Reading (ppm)**	**+/- or n.d.**	**Reading (ppm)**	**+/- or n.d.**
S	48593	11918	>10%	7%	29096.5	n.d.	50947	9801
Cl	6959	n.d.	12954	n.d.	7879	n.d.	6409	n.d.
K	9027	n.d.	7697	n.d.	8031	n.d.	98245	5452
Ca	1481	n.d.	1766	n.d.	1323	n.d.	99479	4447
Ti	1493	419	2148	n.d.	2416	518	463	n.d.
Cr	148	n.d.	265	n.d.	227	n.d.	77	n.d.
Mn	196	n.d.	330	n.d.	243	n.d.	10934	479
Fe	>10%	1%	>10%	3%	>10%	1%	9362	411
Co	682	n.d.	3386	n.d.	1022	n.d.	128	n.d.
Ni	118	n.d.	489	n.d.	163	n.d.	481	35
Cu	162	22	741	77	264	30	163	19
Zn	41	n.d.	132	n.d.	45	n.d.	662	26
As	22795	445	93856	3384	13105	292	16	5
Se	27	n.d.	80	n.d.	32	n.d.	5	n.d.
Rb	81	5	31	8	79	6	196	7
Sr	9	n.d.	18	n.d.	12	n.d.	405	10
Zr	29	5	25	n.d.	35	5	29	5
Mo	17	n.d.	33	n.d.	70	7	39	5
Ag	196	24	809	55	208	27	60	n.d.
Cd	83	n.d.	156	n.d.	93	n.d.	66	n.d.
Sn	137	n.d.	261	n.d.	154	n.d.	103	n.d.
Sb	178	49	278	n.d.	164	n.d.	106	n.d.
I	985	n.d.	1637	n.d.	1140	n.d.	1615	n.d.
Ba	557	n.d.	973	n.d.	685	n.d.	197	n.d.
Hg	84	n.d.	245	n.d.	79	n.d.	12	n.d.
Pb	924	33	1766	93	7274	172	27	6

The results of carbon content analysis in samples C2, C3 and DR are presented in Table 6.8. The difference between Castromil samples and dregs is notable. Comparing the Castromil samples (C2, C3), their similar inorganic carbon content is coherent with the fact they have the same geological origin. The differences in total carbon content between samples C2 and C3 are related to previous hydrometallurgical tests (Chapter 4) in which different reagents were used.

Table 6.8. Carbon content of samples C2, C3 and DR (Fernandes 2016)

	Sample C2	**Sample C3**	**Sample DR**
Total carbon	1362	8565	369035
Inorganic carbon	182	171	32998
Organic carbon	1180	8394	336037

6.4.3.2 *Net Acid Generation Potential*

The most relevant results from potential acid drainage studies obtained through the following tests: a) Static Net Acid Generation, b) Kinetic Net Acid Generation, c) Maximum Potential Acidity; d) Acid Neutralizing Capacity by Lawrence's Method, e) Acid Neutralizing Capacity by Sobek's Method, f) Dynamic leaching and g) Column test, are shown in Table 6.9. The full results are presented in the Master's thesis by Fernandes (2016). It should be pointed out that all Castromil samples are potentially acid generating. However, C2 show to have a very high acid generation potential.

Table 6.9. Net Acid Generation (NAG) results for samples C1, C2, C3 and DR (Fernandes 2016)

		Sample C1	**Sample C2**	**Sample C3**	**Sample DR**
NAG pH		2.0	1.6	2.2	10.2
NAG value	pH = 4.5	55.2	256.9	26.2	0.0
(kg H2SO4/ton)	pH = 7	63.9	359.4	30.7	0.0

Net acid generation potential tests performed for the mixtures samples (C1 + DR) allowed to define the best proportions between Castromil samples and dregs that conduct to a neutral pH.

6.4.3.3 *Dynamic leaching and column tests*

The dynamic leaching was tested for sample C3 in duplicate. The results from the dynamic leaching (Figure 6.12) showed that sample C3 may generate acidity since the pH of the solutions decreased during the operation time.

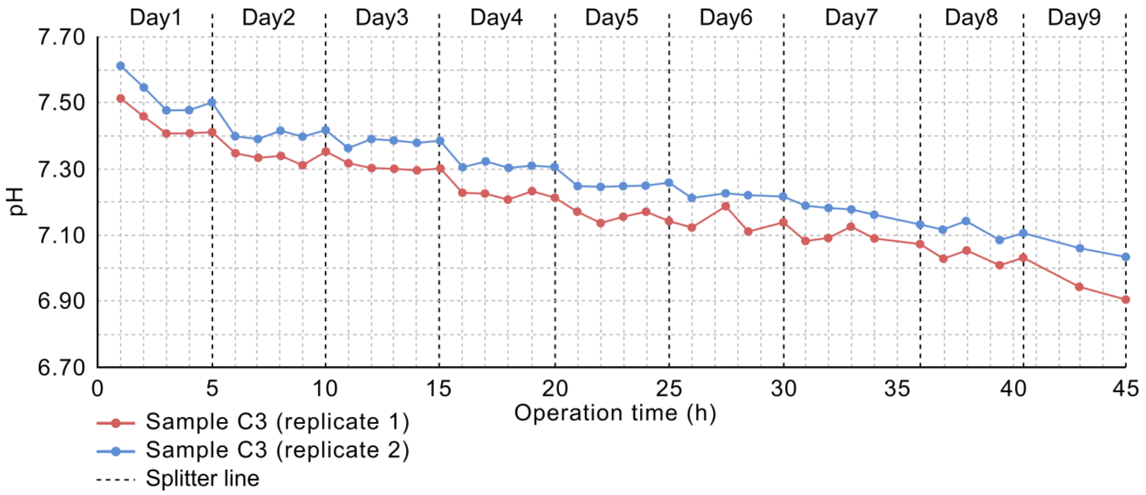

Figure 6.12. Observed pH during dynamic leaching tests for sample C3 (45 h operation time, total nine days).

Based on the results of column tests (Figure 6.13) it is possible to observe the benefits of the addition of by-products to the Castromil tailings.

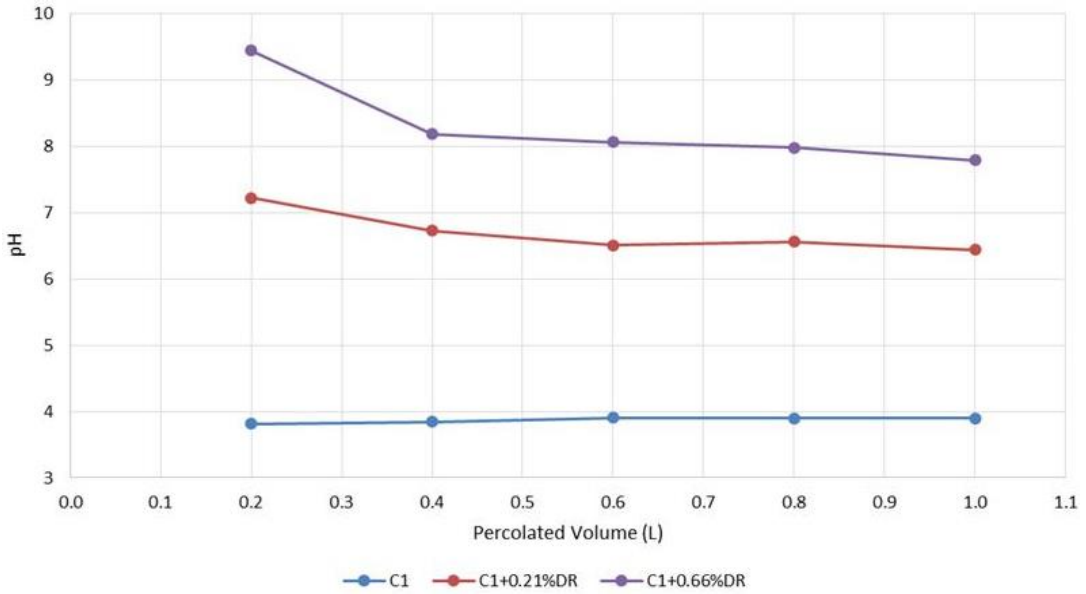

Figure 6.13. Effect on pH leachates of the addition of dregs to the Castromil tailings.

The pH of the distilled water that was added to all columns was between 6.2 and 6.8. For this reason, it was assumed that when the pH of the percolated fluid was below 6 the acid drainage occurred.

The concentration of some metals in the leachates was calculated based on the measured concentrations on the solid samples before and after distilled water percolation (Table 6.10). It should be noticed that arsenic and lead concentration exceeds the discharge limit values of 1.0 mg/L (Portuguese DL236/98).

Table 6.10. Chemical composition of C1, C2, C3 and DR samples (Fernandes 2016)

Sample	**As (mg/L)**	**Pb (mg/L)**
C1	3403.6	101.6
C1+0.21%DR	3149.0	80.8
C1+0.66%DR	2123.0	115.6

6.4.3.4 *Consistency tests*

The usage of dregs in sample C3 provided consistency to the mixture (Table 6.11).

Table 6.11. Results of the slump test (Fernandes 2016)

	0% DR	**7.8% DR**
Mass of sample C3 (g)	1751.8	1295.0
Mass of sample DR (g)	0.0	110.0
Added water (g)	425.0	420.0
Solids (%)	80.0	80.0
Slump (cm)	2.8	14.0

The addition of dregs increased the consistency of the mixture, as it is shown by the slump results: for the same solids percentage, when the quantity of dregs change from 0.0% to 7.8% the slump height moves from 2.8 cm to 14.0 of a maximum of 15.0 cm.

6.5 Gold mine tailings co-disposal strategies – Kittilä mine, Finland

6.5.1 Introduction

This chapter describes the study of paste tailings prepared in laboratory using gold tailings, produced in a Finnish gold mine (Kittilä) with the incorporation of coal ash. Natural leaching tests were conducted with the original materials (tailings, fly and bottom ashes) and also with paste mixtures that were prepared with different percentages of tailings and ashes. After leaching, the solid wastes were physically and chemically characterized and the results were compared to those selected as blank – the unleached samples. The tailings and the coal ash, as well as the prepared mixtures, were characterized, in addition to the textural parameters, by the following measurements: grain size distribution, chemical composition and pH. Mixtures were also tested in order to characterize their mechanical behaviour by measuring the flexural strength, the compressive strength and the consistency.

6.5.2 Materials and methods

The original materials used in this study were paste mine tailings and coal ash (fly ash and bottom ash). The paste tailings material were collected from Kittilä gold mine. Currently, the tailings from the leaching process are disposed on surface ponds after neutralization. The bottom ash was collected from the bottom of the furnace of a Portuguese thermal coal-fired power plant. The fly ash is from filtering system of the same coal-fired power plant.

The tailings paste sample was previously disaggregated in order to represent the original tailings (OT) from the mining operations. As the bottom ash have a coarser particle size it was necessary to grind. The resulting material is identified as bottom ash (BA) in the next sections.

The experimental stage comprised a previous characterization of all materials for particle size, chemical composition, pH, density, moisture and porosity. All materials were dried to constant mass at 110 ± 5 ºC for a minimum period of 16 h. pH was determined in an aqueous solution by two different methods, with distilled water in a 1:1 solid-liquid ratio and with 0.01 M $CaCl_2$ in a 1:2 solid-liquid solution ratio (Black 1965).

Slump testing was carried out for tailings to determine the best solids content (wt% solids) to be adopted for the paste preparation. The slump test followed the procedures given in the ASTM C143 standard. After this, a series of slump tests were performed to evaluate the consistency of the prepared mixtures.

Four mixtures of mine tailings and coal ash were prepared with different percentages of tailings, fly ash and bottom ash. The paste was moulded by adding tap water, according to a solids content of 77 % (best slump result). The composition of each mixture is presented in Table 6.12. The chemical composition was determined using X-ray florescence spectrometry (XRF).

Table 6.12. Composition of the prepared mixtures. (Dinis et al. 2016)

Materials	Mixture 1	Mixture 2	Mixture 3	Mixture 4
Tailings (g)	1600	1800	1600	1800
Fly ash (g)	133	66	0	0
Bottom ash (g)	266	133	400	200

The original tailings and the prepared mixtures were tested for flexural strength (ASTM C348), compressive strength (ASTM C109) and consistency (ASTM C143) in order to study the behaviour of the prepared paste tailings with and without coal ash. To produce the specimens to be tested, the mixtures were cast into three-gang prism moulds, each 40 x 40 x 160 according to ASTM C348. The flexural tests were carried out in duplicate, on a total of

10 prismatic specimen's, from each one of the mixtures and from the paste prepared only with tailings for a solids percentage of 77 %. One point load was applied according to ASTM C348. The compressive strength tests were conducted using 20 specimens obtained after the flexural strength test at a loading speed of 1 mm/min.

Natural leaching tests were conducted on the original materials (tailings, fly ash and bottom ash) as well as on the prepared mixtures. The leaching process was simulated with distilled water in batch cells with a constant stirring for a maximum period of 24 hours. The tests were stopped at each 1, 3, 12 and 24 h to measure the pH, dissolved oxygen, salinity, total dissolved solids, conductivity and temperature. The standard method DIN 38414-S4 was followed to set up the experimental phase in the laboratory.

The acid generation capacity was also tested through one of the possible acid generation prediction methods: the acid/base account (ABA) method. The procedure involves a laboratory static test that compares the maximum acid production potential (AP) of a sample with its maximum neutralization potential (NP). The acid-base accounting method was conducted only on the original materials (tailings and ashes).

6.5.3 Results and discussion

6.5.3.1 *Original tailings and mixtures solution's pH*

The results for the pH solutions of the original materials and the prepared mixtures, obtained by the two methods used, is presented in Figure 6.14. The difference in the results between the two methods is negligible.

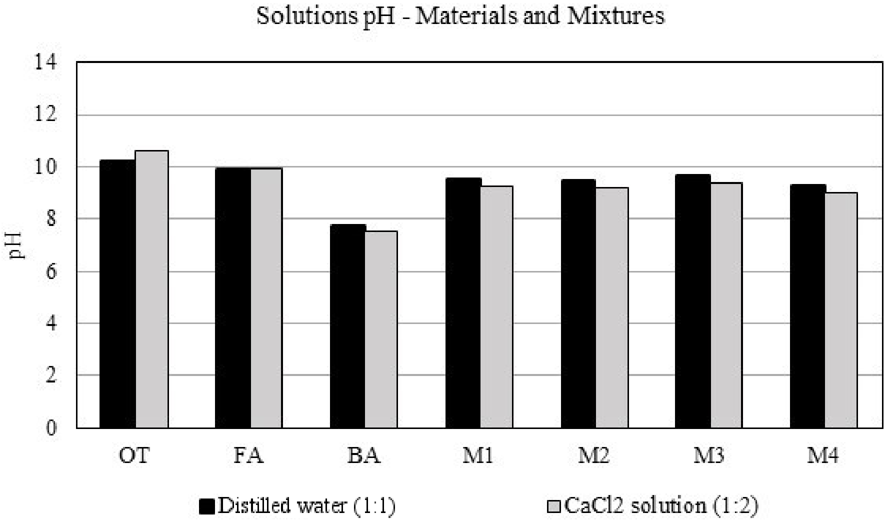

Figure 6.14. Solution pH of original materials and prepared mixtures (Dinis et al. 2016).

The pH of the original materials (OT, FA and BA) ranges between neutral and alkaline values. In particular, the original tailings samples present an alkaline pH related to the fact that during the processing stage these were previously submitted to pressure oxidation with destruction of the sulphides. For the prepared mixtures it was possible to observe that the addition of coal ashes allowed a more stable pH within the range of pH values of the original tailings and bottom ash.

6.5.3.2 *Density, moisture and porosity*

For coal ashes samples the bulk density ranged from 0.935 to 1.111 g/cm^3, the particles density ranged from 0.960 to 1.327 g/cm^3, the (gravimetric) moisture content varied from 2.74 to 4.17 % and the porosity ranged from 2.60 % (FA) to 18.52 % (BA).

The bulk density of the OT was 1.014 g/cm^3, the particles density was 0.852 g/cm^3, the (gravimetric) moisture content was 37.61 % and the porosity was 13.51 %.

Concerning the prepared mixtures (M1, M2, M3 and M4), the addition of coal ashes to the original tailings increased the porosity of the mixtures (range between 14.67 and 22.00 %) but decreased the moisture content (range between 27.20 and 31.60 %) while the density remained approximately the same.

6.5.3.3 *Particle size distribution*

The particle size distribution of both the materials (OT, FA and BA) and the obtained mixtures were determined. The results are presented in Figures 6.15 and 6.16, respectively.

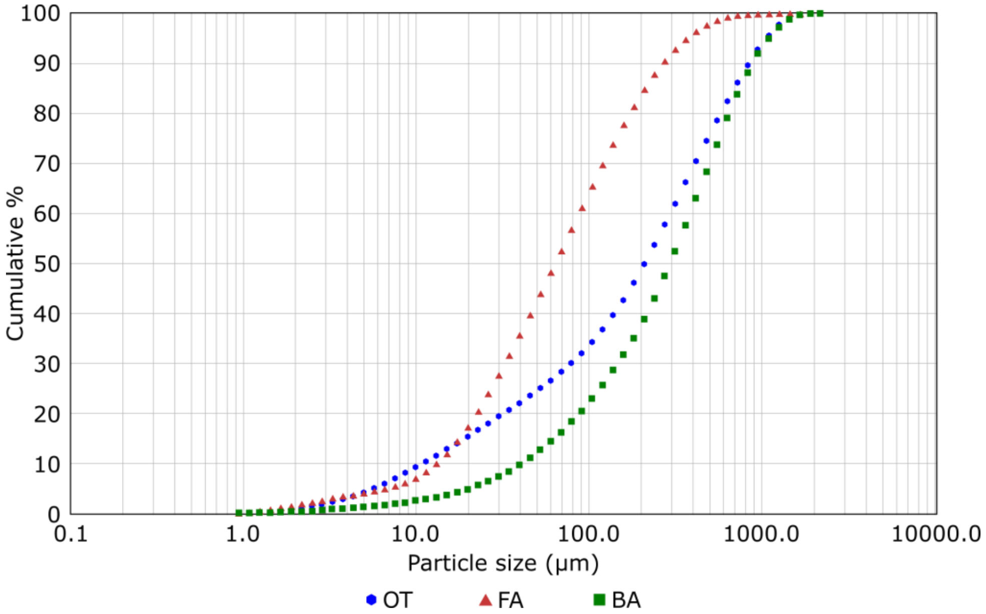

Figure 6.15. Particle size distribution of the materials (Dinis et al. 2016).

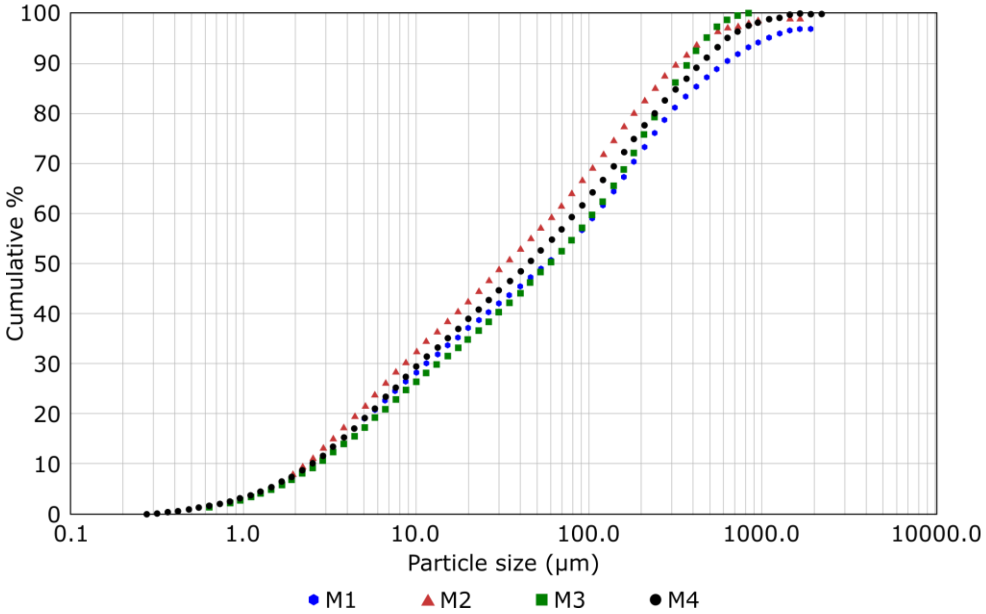

Figure 6.16. Particle size distribution of the prepared mixtures (Dinis et al. 2016).

In what concerns to the particle size distribution, both the OT and FA satisfy the minimum fine particle content for a stable paste production. However, BA alone does not accomplish the required minimum. For the prepared mixtures, the particle size distribution is similar for all ash percentages and all mixtures satisfy the minimum fine particle content for paste production.

6.5.3.4 *Elemental composition*

The chemical element composition for tailings, fly ash and bottom ash is presented in Figure 6.17.

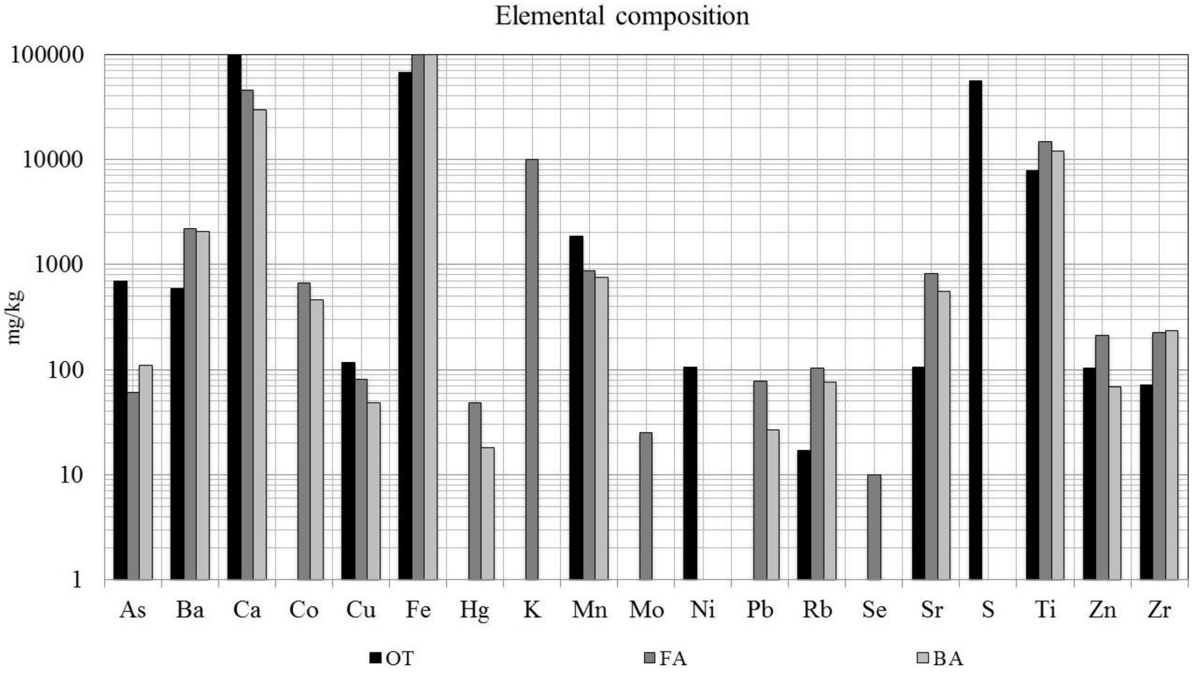

Figure 6.17. Chemical element composition of the studied materials (Dinis et al. 2016).

The tailings primarily consists of Ca and Fe but they also contain significant concentrations of heavy metals such as Ni, Ti, Mn, and Zn as well as S. The high concentration of Ca is a result of both the carbonate mineralization present in the tailings stream and liming, which is added to the acidic water and to the sulphur flotation tailings before disposal onto the tailing facility (Doucet et al. 2010). The high concentrations of S result from the sulphide mineral weathering (oxidation) process which may lead to the generation of AMD.

Fly and bottom ashes have similar elemental composition with the exceptions for K, Mo, and Se once these elements are present only in FA. The major composition of both type of ashes are Ca and Fe containing also significant concentrations of heavy metals such as Co, Hg and Pb but not present in the tailings. Therefore, the presence of Co, Hg and Pb should be looked into when considering to incorporate the coal ashes into the tailings. The presence of Ca provides a beneficial effect to control and mitigate the generation of AMD from the tailings as well as to enhance the stability of tailings. The element composition of the prepared mixtures is presented in Figure 6.18.

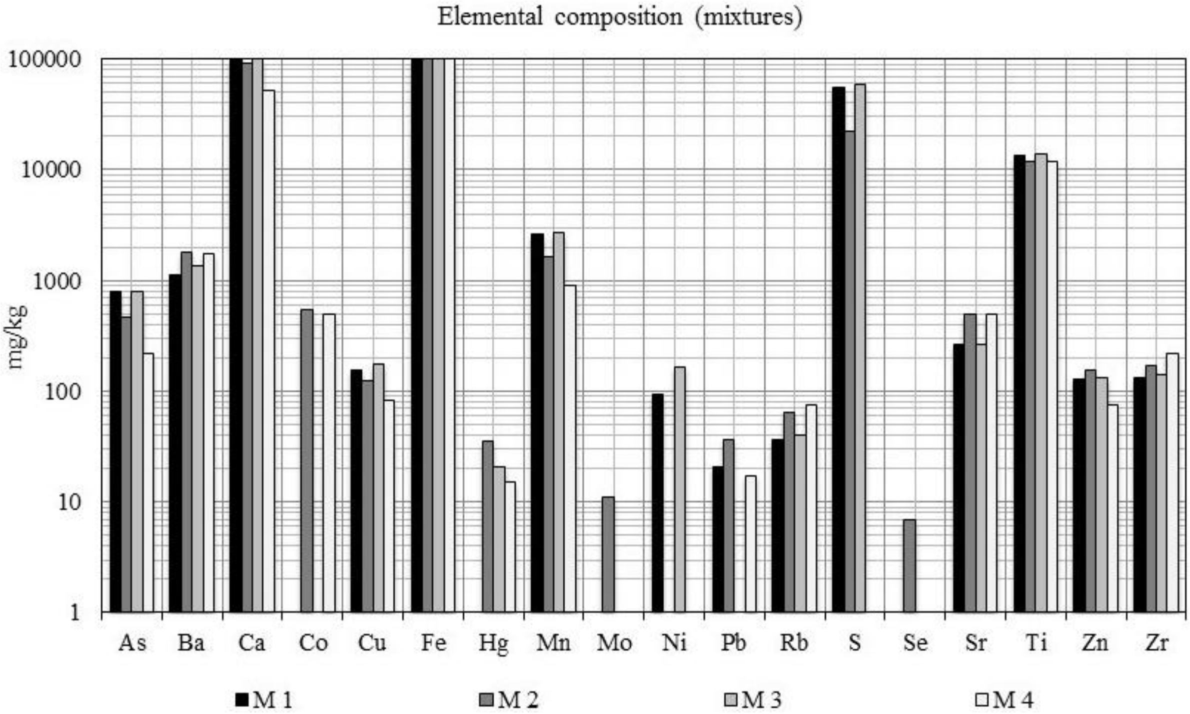

Figure 6.18. Chemical element composition of the prepared mixtures (Dinis et al. 2016).

As expectable, several elements occur both in the original materials and mixtures. It is the case mainly for the elements with higher concentration (*e.g.* Ca, Fe and Ti), but also for other elements such as As, Ba, Cu, Mn, Rb, Sr, Zn and Zr. However, there are still some differences that should be pointed out. Some elements are present only in the mixture M2 (Mo and Se) although they make part of the fly ash composition and therefore they should also be present in the mixture M1. The mixtures M2 and M4 are the only ones with Co, although this element is present in both fly and bottom ash and therefore it should be present in all mixtures. The same is verified for Hg which was not detected in mixture M1, for S which concentration is very high in the tailings but was not detected in mixture M4 and for Ni present in the tailings but not in the mixtures M1 and M4.

6.5.3.5 *Natural leaching tests*

The natural leaching tests were carried out as short-term extraction tests (24-hour batch extraction tests using distilled water). These tests provide information on the short term metal leaching potential although in natural conditions (under the influence of atmospheric conditions and the presence of microorganisms) there are several physical, chemical and biological processes that are not possible to reproduce in batch laboratory tests. The pH of the leachate solution as a function of weathering (leaching) time (hours) is presented in Figure 6.19.

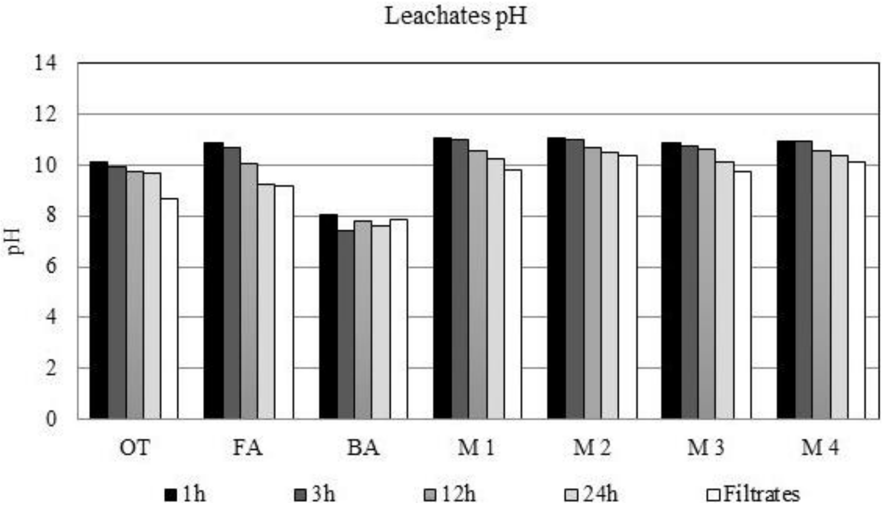

Figure 6.19. Variation of pH during the natural leaching tests (Dinis et al. 2016).

Based on the obtained results it is possible to observe a decrease on pH values for all materials and mixtures within the alkalinity range, with the exception of the bottom ashes, which show the lowest pH values, close to neutral (7.4-8.0).

The pH of the effluent from fly ash natural leaching test is generally higher than that of the control test, containing mine tailings only, indicating that addition of fly ash has contributed with some long-term alkalinity to the system. The measured values for salinity during the leaching test are presented in Figure 6.20.

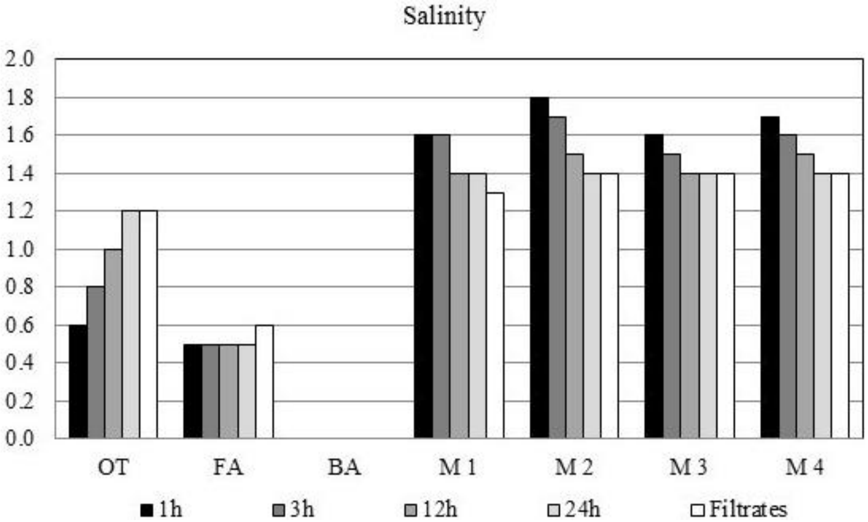

Figure 6.20. Variation of salinity during the natural leaching tests (Dinis et al. 2016).

The dynamics of salinity in tailings is very important in case of future re-vegetation of the disposed tailings. High salinity values are one of major constrains to re-vegetation in many tailings impoundments (Madsen & Mulligan 2006, Gozzard et al. 2009, Huang et al. 2012). In this study, while the salinity increases in the leachate of the OT, the leachates' mixtures show a continuous decrease over time. These behaviours need be analysed in a longer term testing.

In the early hours of the leaching test, both electrical conductivity (EC) and salinity from all samples show a similar behaviour. For the mixtures, the values decreased over time and it is expected that these values stabilize after a certain period of time. This is probably due to the dissolution of readily soluble salts present in the coal ashes and tailings materials.

For the OT, the behaviour was the reverse, with the increase of the EC over the considered period. The slight decrease in pH as well as the slight increase in electrical conductivity of the tailings materials could indicate a tailings oxidation activity.

6.5.3.6 *Acid generation capacity*

The acid-base accounting method was conducted on the original materials (OT, BA and FA) although these presented a pH within the alkaline range and therefore with no potential for acid generation.

The resulting pH from the acid generation tests (ABA method) is presented in Table 6.13. A decrease in the pH was observed for all materials tested, in particular for BA (from 7.77 to 5.04), although not enough to suggest having a potential for acid generation. Nevertheless, this should be looked out when selecting the proportion of coal ashes to be added to the tailings. Further tests will be needed to characterize the potential for acid generation of the mixtures as a function of the amount of FA and BA addition.

Table 6.13: Resulting pH from the acid generation test (ABA method) (Dinis et al., 2016)

Materials	pH
Original Tailings	8.75
Fly Ash	8.45
Bottom Ash	5.04

6.5.3.7 *Mechanical tests*

The results of the mechanical strength tests for the original tailings as well as for the prepared mixtures are presented in Figure 6.21. Although both tests, flexural and compressive, were performed the results of concern refers to the unconfined compressive test.

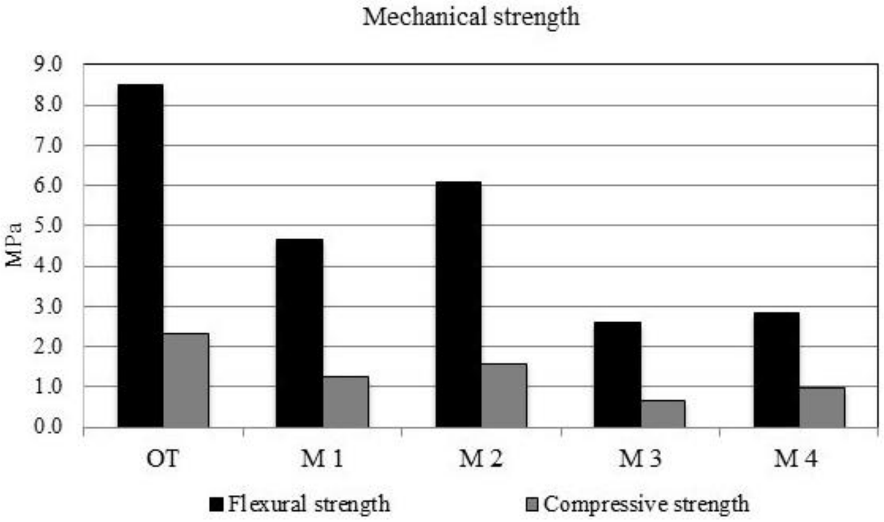

Figure 6.21. Flexural and compressive strength of the original tailings and the prepared mixtures (Dinis et al. 2016).

The compressive strength varies between 0.7 and 2.3 MPa, for M3 and the original tailings, respectively. Also, the compressive strength of the original tailings decreased with an increase in the replacement of coal ash. The mixtures without fly ash incorporated (M3 and M4) presented the lowest strength values. Also, within the mixtures, an incorporation of a blend of fly and bottom ash, up to a percentage of 10 % (M2), seems to be the best option in what concerns the mechanical strength.

6.5.3.8 *Slump tests*

The results of the slump test are presented in Figure 6.22 for the original tailings and for the prepared mixtures, for a solids percentage of 77 %.

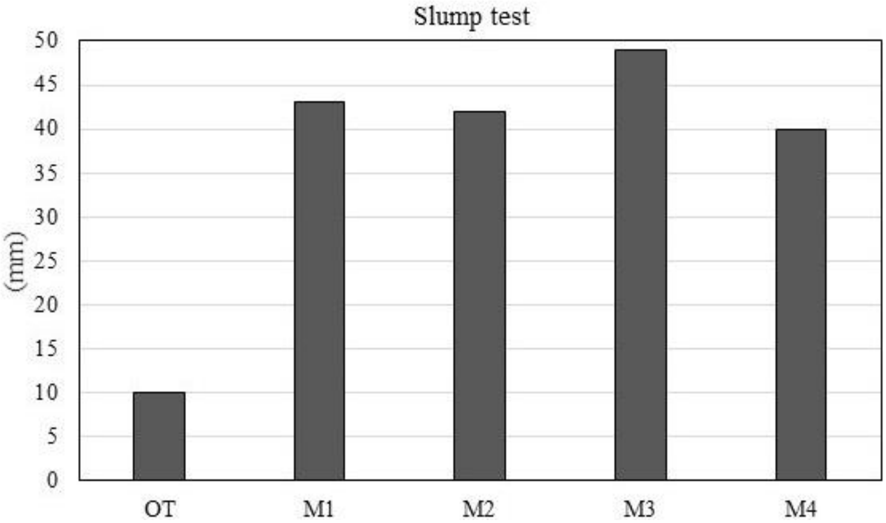

Figure 6.22. Slump test results for the original tailings and for mixtures (Dinis et al. 2016).

The results show that there are considerable differences between the original tailings and the prepared mixtures, with slumps ranging from 10 to 49 mm (OT and M3, respectively).

Concerning the mixtures, the lower consistency was obtained for mixture M3 (80 % OT + 20 % BA) and the highest consistency was obtained for mixture M4 (90 % OT + 10 % BA). These results can be explained by the coarser particle size distribution of BA making up these mixtures; slump vary considerably with particle size and size distribution where the presence of coarser particles will result in lower consistency (higher slump).

Between mixtures M1 and M2 there was no significant variation although being composed by different percentages of OT, FA and BA.

Comparing the results of mixtures M3 and M4, we can say that the incorporation of BA affect the consistency of the mixture. However, the incorporation of a blend of BA and FA into the OT (M1 and M2) allows to obtain a consistency closer to M4 mixture’s consistency.

The slump test provides a way of characterizing a material's consistency that can be related to transportability. A low-slump material will flow less easily than a high-slump material even if both are batched from the same material.

There has been also an attempt to accurately evaluate the yield stress of mineral suspensions by modifying the slump test as a way of simplifying yield stress measurements (Pashias et al. 1996, Schowalter & Christensen 1998, Boger et al. 2008).

6.6 Management of the waste resulted from gold mining in Romania

This chapter covers the activities undertaken by the research team from the Geological Institute of Romania in the years 2014-2016, with the following aims:

- Mineralogical and geochemical characterisation of the waste from gold mining in the Gold Quadrilateral of the Apuseni Mountains (Romania);
- possibilities of industrial use of gold mining waste in the Gold Quadrilateral of the Apuseni Mountains;
- Acquisition of data on the waste rock dumps structure and stability, using resistivity sections and terrestrial laser scanning.

- Documentation of the representative cases of incidents related to gold mining wastes in Romania and analysis of the technical and logistic measures for the minimization of the risk of such incidents.

6.6.1 Mineralogy, geochemistry and possibilities of industrial use of the gold mining wastes in the Gold Quadrilateral of the Apuseni Mountains (Romania)

Because gold is mined at very low grade (grams per ton), the ratio between the final product (refined gold) and the excavated rock can be higher than 600,000 (EPA 1994), which results in very large volumes of debris. These are stored mainly as waste rock dumps and tailings ponds

The concern for mining wastes is generated at least for two reasons: 1) Mining wastes can be considered as potential secondary mineral resources. 2) Mining wastes frequently have a harmful impact on the natural and social environment, mainly because gold mineralisation is commonly associated with sulphides that contain arsenic and heavy metals such as Hg, Pb, Cu, Zn, Cd, and Ni. The chemical composition of mining wastes is critical for their consideration as secondary resources and gives synthetic information on their potentially harmful effect on the environment.

The Gold Quadrilateral of the Apuseni Mountains (Romania) is a traditional gold mining area of ca. 900 km^2 (Figure 6.23), which contains historical mines and waste dumps, recently closed mines following the international procedures of mine closure and rehabilitation, and active mines. The metalliferous deposits are of epithermal type (Au+Ag, Pb+Zn+Cu+Au+Ag) and porphyry type (Cu-Au, Cu-Mo-Au, Au-Cu). Gold occurs mostly in metallic state, either as grains/foils in gangue minerals or as inclusions in sulphides (Figure 6.24).

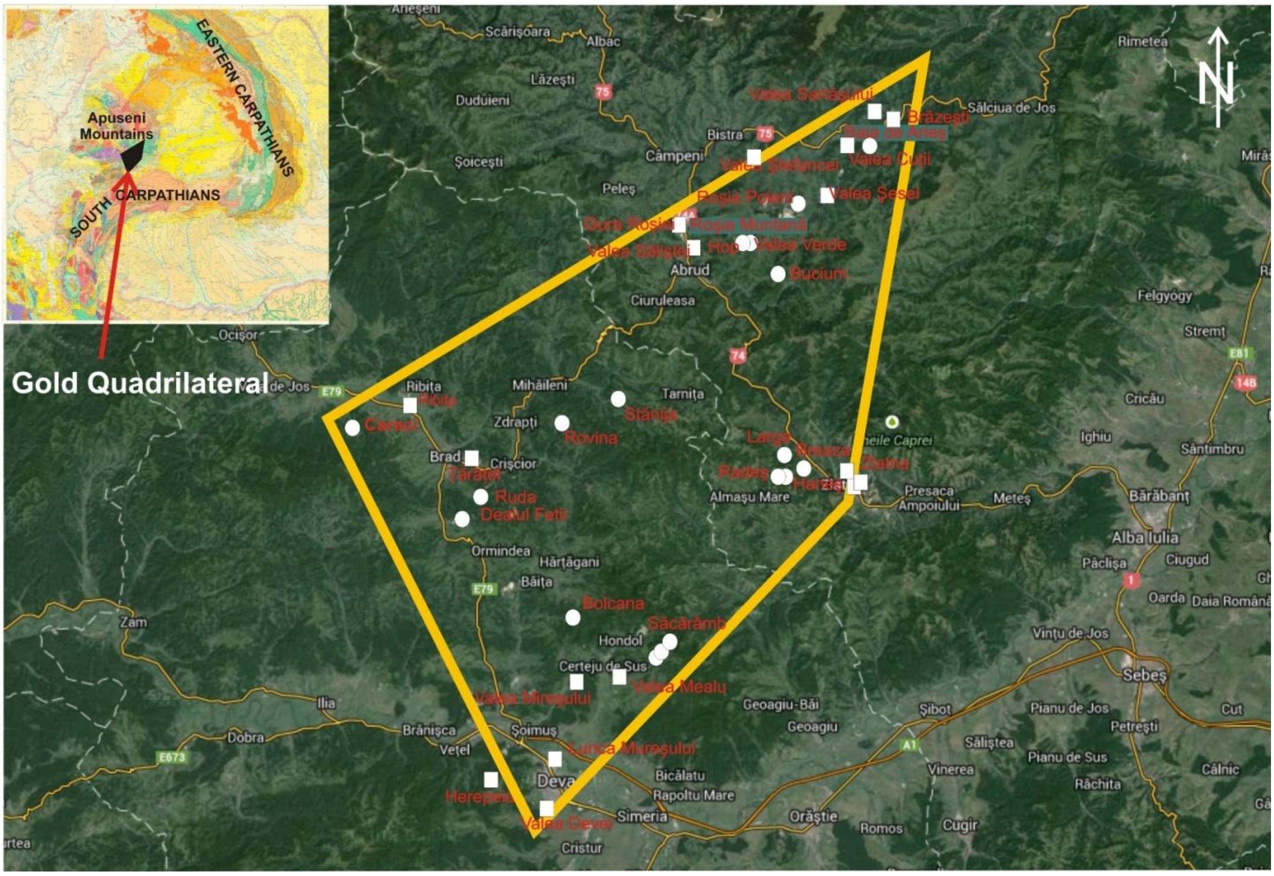

Figure 6.23 Location of the most recent waste rock dumps (circles) and tailings ponds (squares) in the Gold Quadrilateral.

6.6.1.1 *Mineralogy and geochemistry of the waste rocks in the Gold Quadrilateral*

In the Apuseni Mountains, gold is often associated with sulphides, the most widespread of these being pyrite, chalcopyrite, sphalerite, galena and arsenopyrite (Figure 6.24). The waste rock dumps in the Gold Quadrilateral were mostly generated by underground mining and represent sources of acid water and heavy metals because they contain various amounts of low-grade mineralization (below cut-off grade). Consequently, the areas around the mine waste dumps are commonly contaminated with heavy metals. For example, the soils near the waste dump of the mine Larga de Sus (Zlatna) contain ca. 146 ppm Pb, 0.5 ppm Cd, 300 ppm Zn and 42 ppm Cu (Keri et al. 2010). The waste rock dumps are highly inhomogeneous with respect to the size of the fragments (from dust to decimetric blocks) and to their composition (barren rocks and ore fragments). As an example, broad intervals of variation for the contents of heavy minerals (covering 2-3 orders of magnitude) have been reported from the Haneş waste rock dump (Zlatna mining field): 26-659 ppm Cu, 47-3,265 ppm Zn, 444-4,088 ppm Pb, 31-196 ppm Cr (Hulpoi 2008).

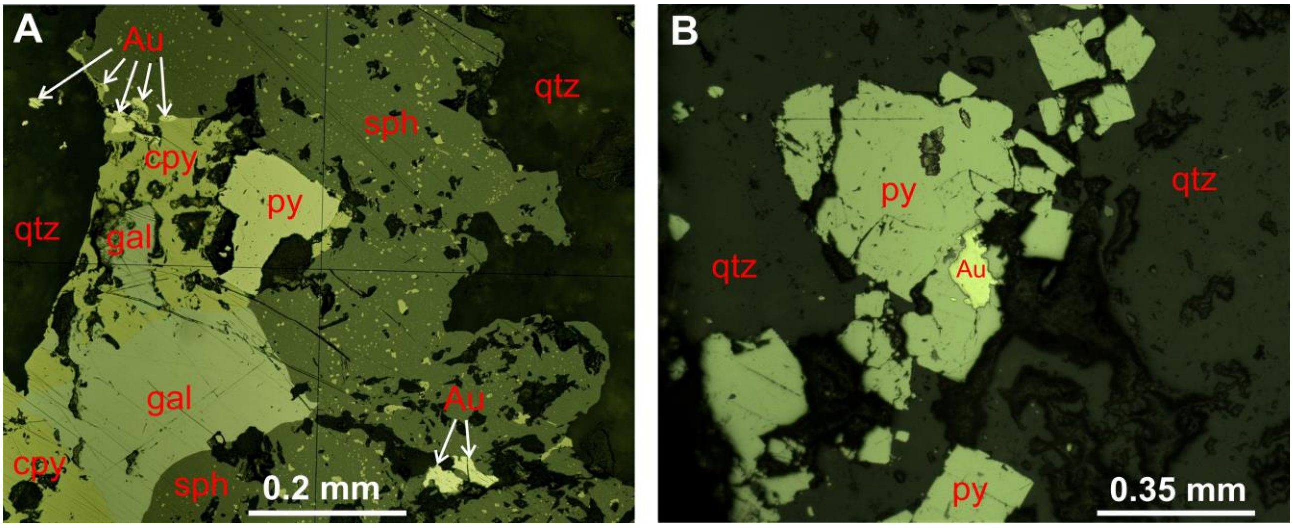

Figure 6.24. Gold-bearing mineral assemblages in the deposits from the Gold Quadrilateral of the Apuseni Mountains. A. Electrum in quartz, sphalerite and chalcopyrite at Roşia Montană. Reflected light. B. Electrum in pyrite at Larga, Zlatna mining field. Reflected light. Au = electrum; cpy = chalcopyrite; gal = galena; py = pyrite; qtz = quartz; sph = sphalerite.

Samples were collected from the waste rock dumps at Ruda Barza, Larga, Haneş, Radeş-Runcu, Dealul Fetii, Breaza-Valea Lungă and Caraci. The rock samples have been investigated for bulk rock chemistry, mineralogical composition and mineral chemistry of the ore minerals. Selected samples were investigated with the optical microscope (thin and polished sections), with the electron microprobe (EPMA) and with the scanning electron microscope having attached an energy dispersion spectrometer (SEM-EDS) at the Department of Geology, Rhodes University, Grahamstown, South Africa. Bulk rock chemistry was determined on a mix of rock fragments from each waste dump. The chemical analyses of bulk rock samples were performed in Bucharest by the company Prospectiuni S.A. The major elements (Si, Ti, Al, Fe, Mn, Ca, Mg, Na, K and P) were analysed by ICP-OES, sulphur content was determined by combustion, while the loss at ignition was determined gravimetric, most trace elements were measured by ICP-MS, mercury was measured using atomic absorption spectrometry, gold was determined by atomic absorption spectrometry after pre-concentration by fire assay with lead oxide.

The analytical data are shown in Table 6.14. Sulphur contents can reach high values, especially at Haneş and Larga, which were mining the same vein system. Mercury shows the most elevated values (close to 0.8 ppm) at Ruda Barza and Haneş. Cu and Zn have contents of tens to hundreds ppm, while Pb can reach thousands ppm (close to 8,000 ppm at Haneş). Arsenic shows variable contents (from 30 to ca. 300 ppm). Gold contents are within 0.2-0.8 g/t.

Table 6.14. Compositions of waste rock samples from several mines that extracted epithermal ore in the Gold Quadrangle.

Element	**Unit**	**Caraci**	**Ruda**	**Dealul Fetii**	**Larga Horea adit**	**Larga adit**	**Larga Petru şi Pavel adit**	**Breaza-Valea Lungă**	**Radeş-Runcu**	**Haneş**
SiO_2	%	58.77	67.78	56.6	70.82	67.08	63.25	61.4	72.32	63.71
Al_2O_3	%	16.63	18.53	16.14	11.19	9.91	12.29	15.22	9.35	6.62
Fe_2O_3	%	4.88	1.69	5.98	5.15	7.15	9.42	5.54	3.3	10.16
TiO_2	%	0.64	0.71	0.64	0.56	0.56	0.61	0.58	0.57	0.25
Na_2O	%	1.69	0.31	0.81	0.12	0.22	0.09	0.5	0.06	0.13
K_2O	%	2.18	3.79	2.64	2.68	2.38	3.16	3.52	2.23	2.01
CaO	%	5.55	0.17	3.96	0.82	0.94	0.07	4.28	1.99	0.51
MgO	%	2	0.72	2.29	0.41	0.38	0.42	0.87	0.43	0.27
MnO	%	0.23	0.02	0.15	0.03	0.02	0.01	0.47	0.03	0.02
P_2O_5	%	0.18	0.14	0.14	0.05	0.05	<0.001	0.14	0.05	<0.01
PC	%	6.75	4.85	6.72	5.38	7.41	8.43	5.58	4.8	10.9
SO_3	%	<0.02	0.85	3.38	2.22	2.77	1.44	1.23	4.08	3.97
S	%	0.62	0.34	1.92	2.13	5.73	5.79	2.08	1.61	7.04
Hg	g/t	0.33	0.79	0.32	0.25	0.28	0.46	0.27	0.76	0.7
Cu	g/t	66.4	10.6	126.1	124.1	81.4	992	36.5	36.9	179.4
Zn	g/t	436.6	19.7	512	58.6	367.6	45.5	453.6	98.2	266.2
Ge	g/t	6.78	1.82	4.86	4.67	6	9.41	3.5	2.94	6.87
As	g/t	8	31.5	168.1	80.4	182	155.8	284	143.9	157.8
Se	g/t	4.9	4.2	8.1	26.2	17.7	47.1	3.5	9.5	4.7
Ag	g/t	1	5.6	1.4	3.6	11	22.8	1.7	6.9	16.5
Cd	g/t	2.38	0.17	3.29	0.28	1.85	0.22	1	0.45	0.95
Sb	g/t	1.6	8.2	7	8.2	16	41.5	172.9	23.9	305.3
Te	g/t	0.11	1.65	0.99	1.59	1.41	2.08	0.45	1.05	0.24
Ba	g/t	311	1042	518	314	327	408	499	210	192
Tl	g/t	0.81	2.05	1.35	0.97	0.85	1.64	5.71	1.35	4.69
Pb	g/t	149.9	34	244.4	636	5028	1816	522	2464	7796
Bi	g/t	0.15	2.18	3.31	8.2	1.49	15	0.28	2.85	0.39
Au	g/t	0.04	0.15	0.14	0.5	0.3	0.3	0.6	0.8	0.2

The waste rock dumps related to the porphyry-type deposits are more uniform than in the case of epithermal deposits with regard to the distribution of ore minerals and chemical composition. Bulk rock analyses on samples from the waste rock dumps at Bolcana, Bucium, Rovina and Stănija (Runcu valley) and from the open pits from Roşia Poieni and Valea Arsului showed contents of 0.1-1.3 g/t Au, 0.2-8.5 g/t Ag, 4-278 g/t Pb, 0.2-105 g/t Te, 1.6-7.7 g/t Se and 0.2-10.5 g/t Cd (Cioacă et al. 2014). Noteworthy, the arsenic contents are remarkably uniform, in the range of 20-26 g/t, with the exception of Bolcana deposit, which showed some higher contents.

The ore minerals are dominated by pyrite, chalcopyrite, sphalerite and galena ± arsenopyrite. Other minerals such as tellurides and sulphosalts can also be present in subordinate amounts. The observations with the electron microprobe indicated that pyrite often contains arsenic, which is frequently on the order of thousands ppm but can exceed 3 wt% in some samples. Pyrite composition is significant because most fragments of barren rocks in the waste dumps contain disseminated pyrite (*e.g.* Ruda Barza, Caraci, Bucium, Haneş, Larga, Stănija). The main chemical and mineralogical transformations in the waste dumps are the oxidation of pyrite to sulphates (mostly jarosite) and the argillization of feldspars.

6.6.1.2 *Mineralogy and geochemistry of the tailings in the Gold Quadrilateral*

The tailings ponds in the Gold Quadrilateral are located close to the (former) ore processing facilities from Baia de Arieş, Roşia Poieni, Roşia Montană, Brad-Barza, Zlatna, Certej-Săcărâmb and Deva. The data on the chemical composition of the waste in the tailings ponds are scarce and inhomogeneous with respect to the analysed elements. The major and trace elements were analysed on samples from the tailing ponds Ţărăţel-Rovina (Barza-Brad mining field), Valea Săliştei (Roşia Montană) and Ribiţa (Brad and Valea Arsului mining fields). The material in these ponds has a prevalently sandy grain size. The mineralogical composition of the tailings, determined by X-ray diffraction, at the Geological Institute of Romania, indicated quartz and feldspars as dominant phases with subordinate sericite, clay minerals and sulphides ± sulphosalts ± chlorite ± carbonate ± amphiboles.

The compositions shown in Table 6.15, indicate Hg, Cu, Zn, As, Te and Bi contents one order of magnitude higher at Ribiţa and Ţărăţel (Brad-Barza mining field) than they are at Valea Săliştei (Roşia Montană deposit). The gold content at Valea Săliştei (0.4 g/t) is similar with the gold content at Gura Roşiei, both tailings ponds containing material from Roşia Montană deposit. The high potassium content is also a common feature of the Gura Roşiei and Valea Săliştei ponds. The analytical results on a sulphide concentrate on the tailings from the processing facility at Bucium (Table 6.15, epithermal gold ore from the Arama vein), which were piled on the right hand side of the river Izbita, show high tellurium contents, hundreds of grams per tonne.

Table 6.15. Composition of the tailings samples from Ribiţa, Ţărăţel, Gura Roşiei, Valea Săliştei and Bucium. The composition for Gura Roşiei pond are taken from Ene et al. (1996).

Component	**Unit**	**Ribiţa**	**Ţărăţel**	**Valea Săliştei**	**Gura Roşiei**	**Bucium**
SiO_2	%	57.02	63.48	70.78	68.4	
Al_2O_3	%	12.29	13.02	15.22	13.6	
Fe_2O_3	%	7.92	6.28	1.25	2.15	
TiO_2	%	0.62	0.58	0.37	0.2	
Na_2O	%	0.92	0.69	0.26	0.2	
K_2O	%	2.28	2.45	9.12	10.4	
CaO	%	2.35	3.05	0.04	0.1	
MgO	%	1.41	1.33	0.17	0.3	
MnO	%	0.07	0.24	0.02	0.08	
P_2O_5	%	0.09	0.14	0.05	0.1	
PC	%	9.17	5.75	1.75	2.5	
S	%	2.43	1.72	0.21	1.3	
Hg	g/t	0.67	0.72	0.17		
Cu	g/t	198	213	15		359
Zn	g/t	259	660	45		1050
Ge	g/t	7.5	3.3	2.1		1.9
As	g/t	148	210	34		47
Se	g/t	12	5.9	2.2		17
Ag	g/t	2.2	1.4	3.8	8	4.3
Cd	g/t	0.8	3.9	0.2		7
Sb	g/t	10.9	8.4	3.6		9
Te	g/t	0.7	0.75	0.02		264
Ba	g/t	1112	974	748		454
Tl	g/t	1.2	2.4	8		0.9
Pb	g/t	337	356	120		537
Bi	g/t	3.27	1.94	0.08		6.0
Au	g/t	0.8	0.3	0.4	0.4	0.1

6.6.1.3 *Possibilities of industrial use of mine waste in the Gold Quadrilateral*

Mine waste can be re-mined as secondary mineral resources, when more efficient methods of extraction are available than in original ore beneficiation. Waste rocks and tailings can be used as materials for *e.g.* construction, backfill or landscaping, substrate for re-vegetation, asphalt component, additive to agricultural soils and raw materials for cements, bricks, ceramics and glass.

The waste rock dumps in the Gold Quadrilateral, especially the oldest ones, can contain elevated contents of Au. Several old waste rock dumps have been mined as secondary resources in recent periods (*e.g.* Săcărâmb, Dealul Fetii), sometimes being considered as ore stockpiles and used to complete the production when technical problems interrupted the extraction from the active mines. Based on the analyses of 62 samples, Popescu et al. (2013) indicated that all waste rock dumps from Săcărâmb contain high concentrations of Au (1-12 ppm), Ag (1-13 ppm), Te (1.3-13.3 ppm), Se (4.9-16.8 ppm) and Cd (0.5-13.3 ppm). Udubaşa (2004) estimated an amount of ca. 60 t tellurium contained in the waste rock dumps from Săcărâmb. The analyses of the tailings from different ponds produced a wide range of Au and Ag contents (Table 6.16). Popescu et al. (2013) indicated an average content of 1.1 g/t Au and 4.5 g/t Te in the damaged tailings pond from Săcărâmb, which was in use until 1971. Gravitational concentration of the tailings from the Ţărăţel-Rovina (Brad) pond produced *ca*. 5 kg of gold concentrate with 63.6 g/t Au from ca. 600 kg of tailings (Eco-Tailing 2010).

Table 6.16. Volume and precious metal contents in several tailings ponds from the Gold Quadrilateral of the Apuseni Mountains.

Tailings pond	Mining area/type of deposit	Volume	Au (g/t)	Ag (g/t)
Zlatna 2	Zlatna/epithermal	1.18 mil m^3[@]	0.11[*]	0.8[*]
Zlatna 1	Zlatna/epithermal	2.3 mil m^3[^]	0.25[*]	1[*]
Lunca Mureşului	Deva/porphyry	4 mil m^3[^]	0.1[*]	0.5[*]
Ribiţa	Brad/epithermal	9.4 mil m^3[@]	0.22[*], 0.8[#]	0.1[*], 2.2[#]
Valea Mealu	Certej/epithermal	5.8 mil m^3[@]	1.15[*]	10.4[*]
Ţărăţel-Rovina	Brad/epithermal+porphyry	11 mil m^3[@]	1.75[*], 0.2[#]	5.95[*], 1.4[#]
Valea Cuţii	Baia de Arieş/epithermal	1.62 mil m^3[^]	1.32[*]	12.5[*]
Gura Roşiei	Roşia Montană/epithermal	5.8 mil m^3[^]	1.78[*]	7.53[*]
Valea Săliştei	Roşia Montană/epithermal	6.6 mil m^3[^]	0.4[#]	3.8[#]

Source of data: [*] = Eco-Tailings (2010), [@] = Răducă (2010), ^ = MMPA (2009), [#] = SUSMIN.

The research done in SUSMIN -project on the tailings ponds Ribiţa, Zlatna 1, Zlatna 2 and Zlatna 3 (Table 6.17) indicated that Au contents are higher in the finest fraction of the tailings (<0.07 mm) than in the coarser fractions. This is in agreement with previous research done on Gura Roşiei tailings pond (Ene et al. 1996) and would suggest that a combination of milling, sieving and gravitational concentration could be used efficiently in gold recovery from the tailings.

Table 6.17. Gold contents in the tailings from Ribiţa (Brad mining field), Zlatna 1, Zlatna 2 and Zlatna 3 ponds (determined by atomic absorption spectrometry after preconcentration by lead collection fire assay).

No.	Sample name	Name of tailings pond	Au (g/t)
1	RBT-11-E (0.070-0.2 mm)	Ribiţa	0.34
2	RBT-11-F (< 0.070 mm)	Ribiţa	2.08
3	PTR-1-E (0.070-0.2 mm)	Zlatna 1	1.33
4	PTR-1-F (< 0.070 mm)	Zlatna 1	1.65
5	PTR-3 (not sieved)	Zlatna 2	0.49
6	PTR-4 (not sieved)	Zlatna 1	0.34
7	PTR-5 (not sieved)	Zlatna 1	0.46
8	PTR-7 (not sieved)	Zlatna 3	0.80

The use of tailings from the pond Zlatna 1 as silica corrector in the fabrication of cements resulted in the production of high-quality clinker and Portland cement (Fechet et al. 2010a, Fechet et al. 2010b, Eco-Tailing 2010). The possibility of using gold ore tailings for production of bricks and other composite materials for construction industry was successfully tested (Eco-Tailing 2010). Unpublished research done by the Geological Institute of

Romania during the 1990s (Ene et al. 1996) suggests that the tailings from Gura Roşiei can be used as secondary resources of gold and feldspar.

Despite the mentioned results, the tailings from gold extraction in the Gold Quadrilateral of the Apuseni Mountains were not used in industry, so far. Nevertheless, the tailings from Baia Mare (northern Romania), resulted from gold deposits similar to those in the Apuseni Mountains, have been mined for gold extraction.

6.6.2 Structure and stability of waste rock dumps

6.6.2.1 *Materials and methods*

Electrometric profiles with the length of 315 m each have been done on Dealul Fetii waste rock dump (Brad-Barza mining field), using a Wenner/IP equipment. The results are shown in Figure 6.25. Dealul Fetii waste rock dump was also scanned with a V-Line 3D Terrestrial Laser Scanner RIEGL VZ-1000, in 2015 and will be scanned periodically to monitor any change in topography that might be related to instability phenomena.

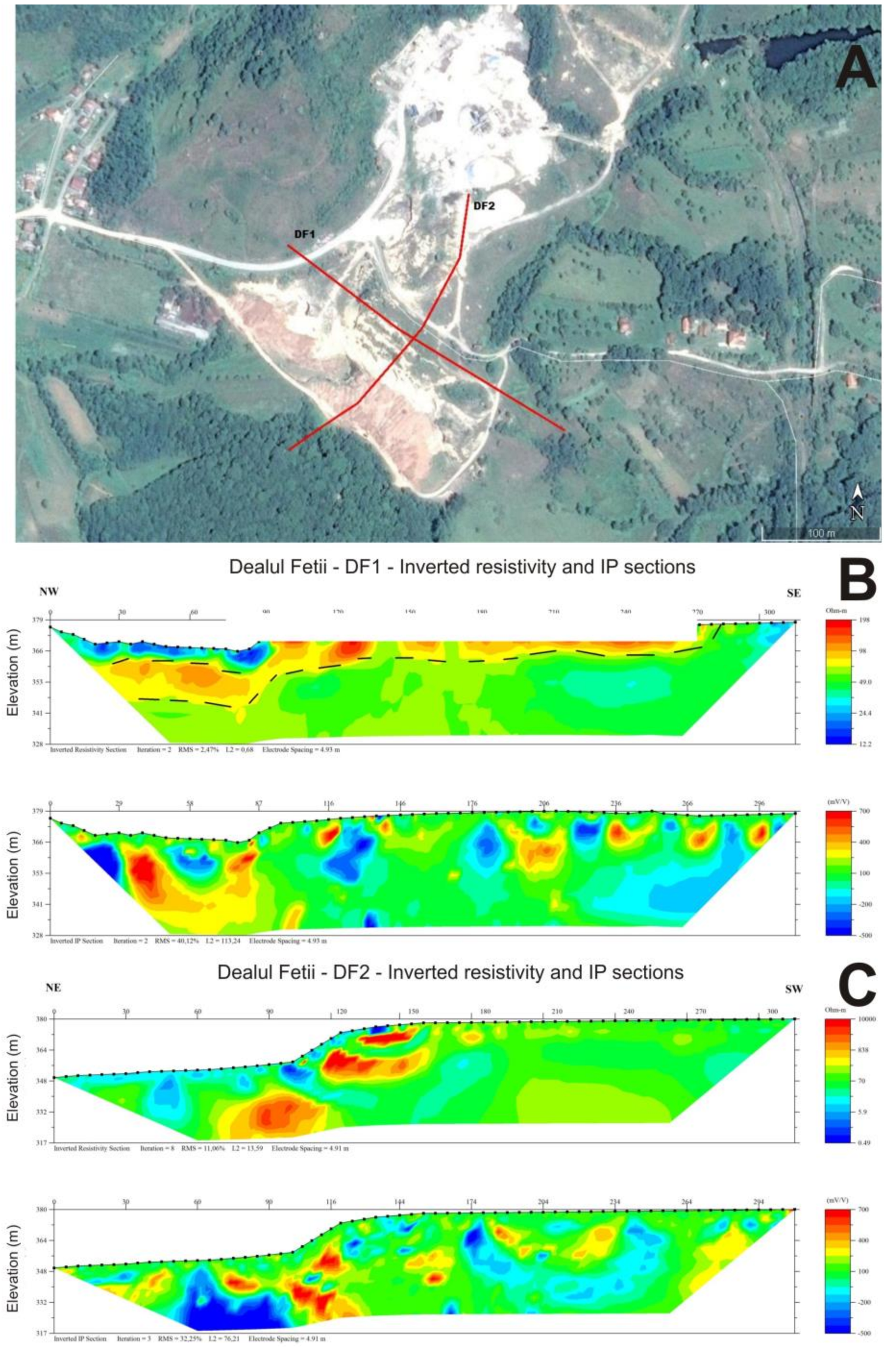

Figure 6.25. A) Location of the electrometric profiles at Dealul Fetii waste rock dump. B) Inverted resistivity and IP sections resulted from profile DF1. C) Inverted resistivity and IP sections resulted from profile DF2.

6.6.2.2 *Results*

In profile DF1, there is a clear distinction between the waste rocks from the mine, characterized by lower resistivity (ρ =30-70 Ωm) because of their low-grade mineralisation, and the sedimentary rocks ($\rho \geq 75$ Ωm) used to cover the mineralised ones. The masses with minimum resistivity correspond to areas with moisture and vegetation.

6.6.3 Long-term stability of tailings

Tailings are waste products that have no financial gain to a mine operator at a particular moment. Dams, embankments and other types of surface impoundments are the most common storage methods used today. It concerns fine-grained waste and slurries such as mill tailings. The principle of tailings dams (or ponds) is to dispose of the tailings in an accessible condition that provides for their future reprocessing, when technology is improved or a significant increase of price makes it profitable. The vast majority of tailings facilities are designed as permanent disposal facilities.

Operating activities and exploitation of mineral deposits in Romania occupy an area of over 8200 hectares. Part of this area (about 46%) is used for carrying out production activities and the remainder, amounting to 54% is occupied by rock dumps and tailings ponds (Fodor et al. 2001, Fodor 2015). In Romania, there are more than 550 waste rock dumps with total area of approximately 800 ha and a volume of waste rock that exceeds 200 million m^3; additionally, 64 tailings ponds were made, with a cumulated area of nearly 1350 hectares and a volume of >350 million m^3 of tailings (www.agir.ro). The tailings ponds resulted from the preparation of metalliferous ores in Apuseni Mountains, Maramureş and Banat are usually located along river banks in the area, heights of 20-30 m or higher and occupy dozens of hectares each.

Most of the tailings ponds in Romania are dried, which increases their stability. However, erosional phenomena can release the tailings in the neighbouring areas. In a tailings pond from Băiuţ mining area, a high degree of degradation of the protective slopes, dams and exhaust system can be remarked (Figure 6.26). In the area where this system exists, it is easy to remark a high risk of erosion of the structural integrity of the tailings by deepening of the trenches, where some of the surface water resulted from rainfall created an outlet area by gravity flow to the collector. Thus, in time, some low stability places were highlighted as subsidence funnels and discharge paths through slopes. In addition, on the side facing the road, there is a rupture of slope protection with traces of discharge and degradation that led to the dispersal of tailings into the environment, constituting a factor of high risk for local flora and fauna, but especially for the population, by the spreading of pollutants (reagents, heavy metal ions, or colloidal solids, etc.) and the degradation of the local transport infrastructure.

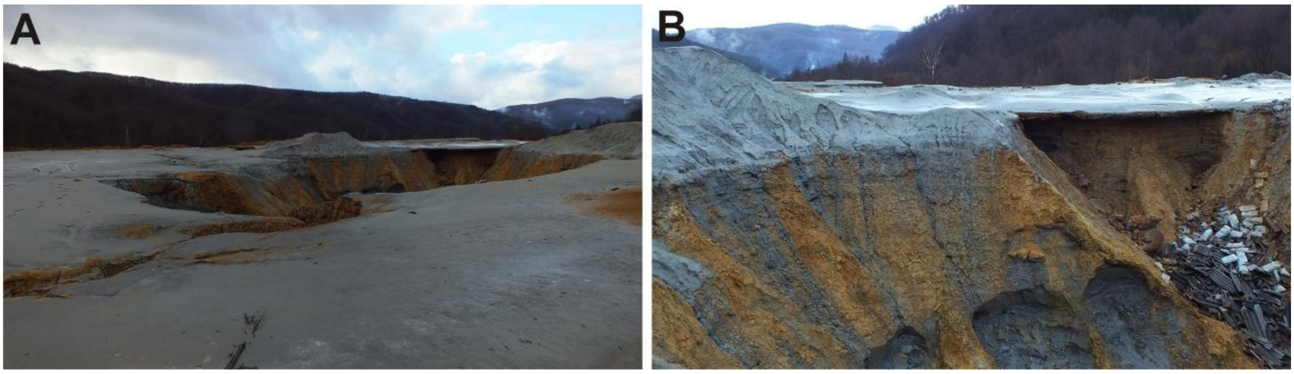

Figure 6.26. Erosion effects on tailings from Băiuţ-Bloaja Vechi pond.

An example of accidental massive tailings spillage is related to the re-mining of the tailings from gold mining in the Baia Mare area. The tailings dam was part of an operation of retreatment of gold tailings from the old Meda tailings pond, originally containing 4.43 million tonnes of solids, with a recoverable gold grade of 0.6 grams per ton. The tailings were pumped from the Meda pond to the Aurul S.A. processing plant, where sodium cyanide was added for the recovery of gold. After gold and silver extraction, the tailings were pumped over a distance of 6.5 km to a new tailings pond (ca. 93 ha) lined with a plastic membrane. The embankments of this pond consist of small starter dams which, during the filling process, were sequentially raised from the coarse fraction of the tailings. The slimes fraction was deposited in the impoundment. In the year 2000, the tailings dam failure resulted from an overflow of the ponding liquid, caused from heavy rain and snow melting. At the time of the failure, there obviously was insufficient storage capacity in the impoundment for the water influx occurring at that time. The dam crest was washed away over a length of 25 meters.

After the accident was reported to the site management the plant stopped operations and the central and local authorities were notified. Sediments from a nearby tailing deposit were used to seal the breach, which was partially closed within 5 hours after being reported. A controlled discharge of 40-50 l/s continued to flow from the dam, being neutralized with sodium hypochlorite till the breach was completely sealed.

Subsequent investigations concluded that the accident was caused by the inappropriately designed tailings dams, the inadequate monitoring of the construction and operation of those dams and by severe (though not exceptional) weather conditions.

Another example refers to the slurry flood in Certej mining area (ca. 10 km away from Deva city). In 1971, a dam failure resulted in the flow of 300,000 cubic meters of slurry that flooded Certeju de Sus, resulting in the death of 89 people.

The tailings dam collapse and the flood of the village represent Romania’s worst peacetime tragedy: six buildings with 25 apartments each, a hostel with 30 rooms, seven individual houses and 24 households were destroyed or damaged. The scale of the disaster was kept secret at the time by the communist authorities. Several possible causes were considered, including ground hogs and tectonic movements. Nevertheless, the stability loss of the tailing pond was most likely caused by the increase of the dam beyond the safety limits.

Nowadays, a new gold mining project is planned at Certej (Alexander et al. 2014). The project is going to have a duration of 15 years and will produce 56 million m^3 of tailings (30 million m^3 of flotation tailings and 26 million m^3 of neutralization residue tailings). The tailings will be treated in a detoxification circuit to lower the levels of residual cyanide to below legislated values. Initial stages of embankments construction will be for a starter dam. The embankments will subsequently be raised to their final elevation by lifts throughout the life of the project using mine waste rock. A 2 mm thick high density polyethylene liner will be installed initially on the starter dams to minimize seepage through the upstream face of the embankments. To minimize the seepage leaks on subsequent lifts, a tailings beach will be generated against the embankment. The liner will be anchored on the starter dam crest, valley sides and floor, and lie against the fine filter material. Beneath every raise for the embankments, a layer of heavy duty geotextile will be placed on top of the tailings and will extend horizontally to the downstream side of the raise. Seepage will be collected in a seepage collection sump and re-circulated via pumps back to the tailings pond.

6.6.4 Methods of increasing the stability of tailings

The main objectives of a stability analysis are:

- Slip phenomenon assessment for the slope
- Evaluating the stability of different types of artificial embankments in various stress conditions or stages of construction
- Sliding body stability analysis, in order to understand the mechanisms that led to slope failure (retroanalysis)
- The effects on the stability modelling work
- Dynamic loading effects, such as those performed by an earthquake;
- Understanding the evolution of morphological analyses highlighted by natural forms.

The slope stability analysis methods are grouped into two categories:

Methods that take into account the equilibrium state limit in a given area. In this case the sliding mass is considered rigid and the interaction between it and the rest of the massive is carried out through the forces manifested on the sliding surface. In most cases, it is considered that slopes slid on a cylindrical-circular surface, but it must be taken into account specific cases that relate to the existence of pre-existing slip surfaces, such as areas of weakness.

- Methods that are based on the measurement and analysis of the deformation (forces) acting in the slope, in comparison with the force of resistance along the critical slip surface Such methods can model to some extent the massive behaviour and can highlight, if necessary, the dangerous areas where plastic disposal processes can begin.

The most used method for analysing slope stability are methods that take into account the steady state limit on a sliding surface and have a long period of application and verification in practice. Depending on the sliding mass, these methods can be grouped as follows:

- Methods that consider sliding as a whole (plane surfaces sliding methods, friction circle method, logarithmic spiral method) (Murthy 2002)
- Methods that supports dividing the mass sliding in vertical strips, which allows consideration of various geometries and complex conditions (Fellenius's methods, Maslov-Berer, Janbu, Bishop, etc.) (Thiel 1989)

In Romania, the risk assessment for tailing ponds associated with mining activities is determined through the program promoted by the Mining Strategy for the period 2004-2010, approved by Government Decision no. 615/2004. The institutions which oversee the tailing dams situation in Romania are Supervisory Commission for tailing ponds in the mining industry (COSIDIM) functioning, under the coordination of Ministry of Economy, and National Commission for Dams Safety and hydraulic works (CONSIB), besides the Central public authority in waters sector.

The actions necessary to ensure stability and re-vegetation of the ponds:

- Adjustment of the upstream catchment areas
- Rehabilitation or restoration of dam water diversion and drainage systems
- Restoration or construction of guard ditches and drains water from the slopes
- Draining and reshaping platform pond and downstream slope, vegetation surfaces
- Rehabilitation or construction of a new drainage system of the pond

Pollution assessment of soil and subsoil, to determine the possibilities of migration of pollutants in soil, subsoil and groundwater, is achieved by investigating the geological environment, mainly the soil lithology, to determine the structure, texture, permeability, geo-chemical characteristics, namely the ability to interact with pollutants generated from mining waste.

The type of dam embankment, to some extent, dictates the tailings discharge management to be adopted. For example, embankments that are designed as water retention structures are made of low-permeability materials and tailings are discharged well upstream of the embankment.

Foundation conditions (rock or sediment type, compaction rate, etc.) are important in terms of safety, environmental protection, reducing risks of groundwater pollution. It is important that impoundment is designed with future mine closure in mind, so that it will remain stable, secure and virtually pollution free, with little maintenance required. Standards should be laid down to ensure the safe management of tailing dams.

The design of the tailings dams and the prediction of their stability should also consider the specific conditions of the site, such as:

- The topography of the geographic sector in which the site is located: *e.g.* in a valley or on a slope
- Groundwater flow direction and speed
- Presence of groundwater catchworks, locally altering the flows,
- Rainfall and seasonal fluctuations in the aquifer.

The measures used to control instability from tailings dams recommended by Ministry of Industry and Resources (2001) include:

- Controlled placement of tailings - the most cost-effective method of controlling. Provided that the tailings are of low permeability they will form a cohesive system
- Foundation grouting - involves the injection of fluidised material and could not be effective unless there is high permeability rock beneath the impoundment or where there are high permeability zones in the rock
- Foundation cut-offs - necessary when soil foundations are sand or sand and gravel. A significant reduction in seepage may be achieved by construction of an earth fill cut-off or a slurry trench cut-off wall. They may be applied to extremely weathered rock such as laterite or other highly permeable rock
- Clay liners - can be effective in areas where the storage is located in an area of high permeability. They are susceptible to cracking on exposure to the heat (by sun),which can increase permeability
- Under drains and toe drains - to attract the water and discharge it to a collector system, ideally for recycling to the process plant. Some methods of collecting and treating this seepage are required, such as:
    - Toe drains
    - Pump wells
    - Seepage collection
    - Artificial wetlands
- Artificial liners - used to line waste disposal facilities, often with provision for drainage layers beneath the membranes to collect any leachate, which leaks past the first. However, these liners do not seem to be always appropriate for all tailings disposal situations (such as in case the underground water is confined and spouting.

6.7 Conclusions

At Svartliden gold mine (Sweden), the addition of low proportions of binders to tailings increased As leaching due to the relocation of desorbed As from FEPs into less acid-tolerant species such as Ca-arsenates and cementitious As-phases. Compared to CE-FA, CE contained lower levels of binders and Ca ions in its cementitious matrix. Consequently, it may have had a lower positive charge density on its FEP and C-S-H surfaces, reducing their capacity for As adsorption. Unmodified tailings generated an acidic environment in which As-bearing FEPs were stable. A crust of Fe-oxides enclosing the unmodified tailings was formed during flooded conditions, which decreased the surface area susceptible for oxidation. In the Cemented Paste Backfill (CPB) mixtures, small (> 1%) proportions of the total As in the solid material was released.

A scenario where flooding of CPB-materials occurs within 1 year of curing, revealed that time has a positive effect on As-leaching, while cementitious phases of As has dissolved during pyrrhotite oxidation facilitated in unsaturated conditions. In cases where cementitious phase of As still exist after 1 year of curing, no positive effect is noticed. Decreased saturation levels have caused sulphide oxidation and dissolution of cementitious phases in CPB-materials cured for 1 year. This scenario has caused less acid tolerant species of As to be formed in the CPB-materials. Increasing the amount of binders added could add more Ca ions to the As-Fe-precipitates formed in unmodified tailings and thereby destabilize As, especially in the acidic range. Increasing the amount of binders in CPB-mixtures based on tailings with high proportions of As associated with amorphous Fe-hydrates, will increase the importance to maintain high saturation levels within these mixtures. However, As-release from cementitious phases in CPB-materials corresponds to a minor proportion of the total As-content. Instead, the addition of binders has relocated a significant proportion of arsenic into less acid tolerant species such as Ca-arsenates or Ca-Fe-arsenates. This underlines the necessity of maintaining high saturation levels in CPB-materials to prevent acidic conditions.

Cyanidation tailings from a gold mine in the north of Sweden was characterized and subsequently managed with CPB method. The release of arsenic from unmodified tailings was low as pH > 3.5. As pH was lowered due to a more extensive pyrrhotite oxidation, the release of arsenic increased while iron-arsenates were destabilized. This underlines the necessity of treating these tailings. In the present study, CPB was made using low proportions (1-3 weight %) of binders mixed with cyanidation tailings, containing iron-arsenates and pyrrhotite. Managing cyanidation tailings with the use of CPB generally increased the mobility of arsenic. The As-increase was most extensive on a short term basis while soluble cementitious As-phases have formed. If unsaturated conditions occur within these CPB-monoliths, pyrrhotite oxidation will generate acid. This acid could dissolve As-phases in the CPB-monoliths that are considered to be less acid-tolerant than the originally formed iron-arsenates. Therefore, if CPB is going to be used as a management method for these cyanidation tailings, maintaining high saturation levels is the key to prevent acidic conditions and thereby stabilize As. If these CPB-monoliths cannot maintain high saturation levels, other options for treatment must be considered.

The study of acid drainage prevention in Castromil area (Portugal), motivated by the interest in resuming mining activities, showed that the addition of low proportions of waste material from pulp and paper industry (dregs) is efficient in neutralizing the potential acid generation. Another value obtained from this waste management strategy is the improvement of paste behaviour given by the increase of material consistency.

At Kittilä mine (Finland), the addition of coal ash to the tailings resulted in a more stable final product in what concerns to pH, electrical conductivity and salinity.

The potential for acid generation of the mixtures, as a function of flying ash and bottom ash (BA) addition to the tailings, will need to be studied in order to interpret the pH variation and determine the fractional composition of fly and bottom ashes that still allow to obtain a non-acid-generating mixture.

Paste reactivity was affected mostly by the bottom ash: tailings blended with bottom ash presented lower mechanical strength than when blended with a combination of fly and bottom ash. On the contrary, a better slump was obtained for a mixture with the incorporation of bottom ash alone (M4).

Although relevant results were obtained with the mixtures prepared with bottom ashes, not only at operational level but also with economic and environmental benefits (every ton of bottom ash used beneficially is one not disposed in a landfill) a higher percentage of solids, between 77 % and 82 %, should be tested and the mixtures studied through all the process. The incorporation of bottom ash with the minimum need to reduce particle size should also be tested.

The technical methods outlined in this study provide the basis for a comprehensive characterization of the paste tailings production which is essential to all segments of the process. These should be integrated when evaluating the paste production to meet the necessary (rheological) requirements at the “end of the pipe”.

Research done on the tailings from the gold mining in Romania indicated that waste rock dumps and tailings ponds could be used as secondary Au resources. Au extraction can be locally combined with the separation of other commodities (*e.g.* feldspar), which can raise the economic efficiency of the operation. Tailings from gold mining can be used as silica corrector in the fabrication of cements or as raw materials in the manufacturing of bricks and other composite materials for construction industry.

Mining activities in Romania include accidents related to tailings dam stabilities, the most known examples being the collapse of the tailings dam at Certej/Săcărâmb mine in 1971 and the tailings spill from Baia Mare in 2000. In order to prevent such accidents, regulations have been enforced to ensure tailings ponds stability. Their application is monitored by institutions belonging to Ministry of Economy and Ministry of Environment. Analytical methods based on steady-state limit require verifying stability conditions for the masses constitute as a slope, in particular for the balance of forces and moments. Methods based on similar criteria provide broadly analysed slope modelling, defining state of charge and adopting a breaking criterion. Consequently, these analyses depend on the model adopted and on the assigned physical-mechanical properties of the materials.

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7 ENVIRONMENTAL MONITORING, MODELING AND RISK ASSESSMENT

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7.1 Introduction

The abundance of metallic minerals in rocks in specific areas, such as mine sites, may give an increased background of heavy metals and other harmful substances in soil as well as in surface water and groundwater. Mining tends to increase, especially airborne and water related emissions of possibly harmful elements to the environment and humans. Therefore, it is important to estimate the effects of mining activity and compare it with the natural background when assessing the long term environmental impacts. Fortunately, the best practises in environmental and social management have been recently recognized within the mining companies. However, the monitoring and sampling campaigns conducted at the mine sites have not always been effective enough to assess the actual impacts. Thus reliable measurements are needed to understand contaminant sources and seasonal variation in mixing and dilution processes controlling the water quality in the river system.

The present study provides perspectives from three European gold mine sites: the Kittilä mine in Finland, and two mining areas in Romania, Roșia Montană and Zlatna. A new approach of geochemical and isotope methods for investigation and monitoring of migration of possibly harmful substances from mining sites and mining waste deposition areas was carried out at case study sites. In addition, new water quality monitoring and field measurement equipment was also tested during the project. The ecological risk assessment was carried out by comparing the values obtained in field sampling with various ecological benchmark values as well as local background concentrations and baseline values obtained in earlier studies.

Table 7.1. Summary of environmental and historical mine site conditions at the three study sites (Papp et al. 2018).

	Kittilä mine, Finland	**Roșia Montană mine, Romania**	**Zlatna mining area, Romania**
Average annual temperature	-1.3 °C	7.4°C	10.5 °C
Average annual precipitation/ evaporation	Precipitation: 55 cm/yr Evaporation: 25 cm/yr	Precipitation: 74.5 cm/yr	60 cm/yr 45 cm/yr
Vegetation	Northern boreal vegetation	Nemoral formations (temperate forest – deciduous and coniferous)	Nemoral formations (temperate forest – deciduous and coniferous)
Proximity to residential areas	50 km northeast of Kittilä, Finland (population: 6 421 (2017), municipality of Kittilä 2018)	5 km northeast from Abrud, Romania (population 5000)	4-5 km NW of Zlatna 2-3 km N of Almașul Mare 1-2 km N of Techereu
Economic mineralization	Refractory gold (Au) within arsenopyrite and pyrite	Native gold, electrum gold (gold-silver) associated with sulphides (predominantly pyrite)	Au-Ag and Au-Ag-Pb-Zn-Cu mineralizations
Host rock	hydrothermally altered meta-oceanic sediments with 10% sulphides within tholeiitic basalt (Proterozoic Kittilä group)	Neogene maar-diatreme volcanic complex intruding Cretaceous detrital sediments	ophiolite, conglomerate, sandstones and clays, andesites
Underground workings	exist beneath open pits and are being actively expanded	140 km of underground workings	underground workings 2 mines: Haneș and Stănija
Open pits	2 open pits totalling 35 ha	2 open pits totaling 24.95 ha	no open pits
Mining operation dates	production began in 2009 and projected to continue to 2037	>2,000 years bp to 2006	>2,000 years bp to 2007
Current mining activity	Underground mining ongoing with planned expansion	No current mining, but mining permit being sought by Roșia Montană Gold Corporation	mining activities were abandoned in 2007 without planned reopening

7.2 Objectives

The purpose of mining environmental research in SUSMIN -project was to evaluate and test new methods for environmental monitoring, modelling and risk assessment. This task pursued to enhance environmentally sustainable mining by characterizing and evaluating the anthropogenic emissions compared to the geogenic background, modelling reactions and pathways of contaminants, and assessing the environmental risks. One target was to test suitability of hydrological and flow rate profiling equipment in studying mixing and dilution of the mine waters in recipient river systems. Additionally, isotopic analysis was used to provide supplemental insight to geochemical characterization. Further, the benefits and limitations of the studied multi-isotope application for the specific case study sites and to general mine-site environmental monitoring applications were assessed. The integrated risk assessment tools were used to evaluate ecological and health risks based on the geochemical characteristics and bioavailability of metals and metalloids in recipient waters at all the study sites and also in soils in Rosia Montana study site. This complex approach allows a detailed insight in the generation of acid waters, their underground flow paths, and the migration of harmful substances in the environment. The environmental research was conducted in close cooperation between GTK, UBB and GIR.

7.3 Case study sites

7.3.1 Kittilä mine

The Kittilä mine, located in Finnish Lapland, is currently the largest operating gold mine in Europe. The mine site is located in the 307 km^2 Seurujoki River catchment, and the surrounding terrain is peat wetland in which 1 to 2 m of peat overlays 3 to 6 m of low permeability glacial moraine deposits (Figure 7.1). There are no significant alluvial or glaciofluvial groundwater deposits in the vicinity of the mine (AVI 2013).

At the Kittilä site a Proterozoic orogenic gold deposit which occurs along the Kiistala shear zone within the Kittilä group of the Central Lapland Greenstone Belt (CLGB) is being mined. The mineralization is associated with amorphous carbon, graphite, silica, albite alteration and carbonate alteration of meta- sedimentary and volcanoclastic rocks within the Kittilä group (Figure 7.1) (Wyche et al. 2015, Lehtonen et al. 1998). The gold is predominantly refractory within the lattice structures of arsenopyrite and pyrite, and the host rock sulphide content is from 2 to 30% (Doucet et al. 2010). The mineral processing at the Kittilä mine consists of crushing, grinding, flotation, autoclave oxidation and cyanide leaching.

For mineral beneficiation approximately 1.1 Mm^3 of water is diverted annually from the river Seurujoki, while the remaining 65% of water used for processing is recycled between tailings ponds and the beneficiation plant (AVI 2013). The waste stream from the flotation step of processing is neutralized and stored in tailings impoundment NP3 (MWPW pond) before being discharged to the 60 ha open fen-type treatment wetland 4 (TW4) (Figure 7.1 and Figure 7.2) (Doucet et al. 2010). Discharge to TW4 began in 2010 (Pöyry 2012). 1.1 Mm^3 of process effluent was discharged to Seurujoki River during 2015. Cyanide treated tailings undergo cyanide destruction and are kept in a closed circuit between the mill and carbon-in-leach (CIL) tailings ponds. Mine dewatering and waste rock drainage waters are managed separately from process waters. Underground mine dewatering water is pumped to the MK pond (MWDW pond), treated with PIX (ferrisulphate) coagulant, and discharged to the 5.5 ha treatment wetland 3 (TW3), from which it flows to a second 17 ha treatment wetland (TW1) that drains to the Seurujoki River (Figure 7.1 and Figure 7.2). Discharge of underground mine dewatering water to TW3 began in 2006. Altogether 3.4 million m^3 of dewatering water was discharged to Seurujoki River during 2015. Suurikuusikko open pit dewatering water from the LO2 storage pond was discharged to TW3 until May, 2013, after which it has been recycled back to the process and/or stored on site for later use.

Map ID.	Site Name
1	SWUS Suasjärvi
2	SWUS Nuutijoki
3	SWUS Tuonkasomma
4	SWUS Hakokodanmaa
5	SWUS Talvitienmukka
6	SWUS Kolvakoski
7	SWDS PumpingStation
8	SWDS Välikoski
9	SWDS Rossimukka
10	SWDS Konikoski
11	SWDS Lintula
12	SWDS Mesiniemi
13	SWDS Vientola
14	SWDS Loukinen
15	GW Köngäs
16	GW Kuotko KUG15
17	GW Kuotko KUG2
18	MWPW (Rimmi Stream)
19	MWPW (Rimmi Pond)
20	MWDW (MK Pond)
21	MWDW (TW3 Discharge)
22	MWPW (TW4 Discharge)
23	MWDW (TW1 Discharge)
24	MWDW (Open PIt)

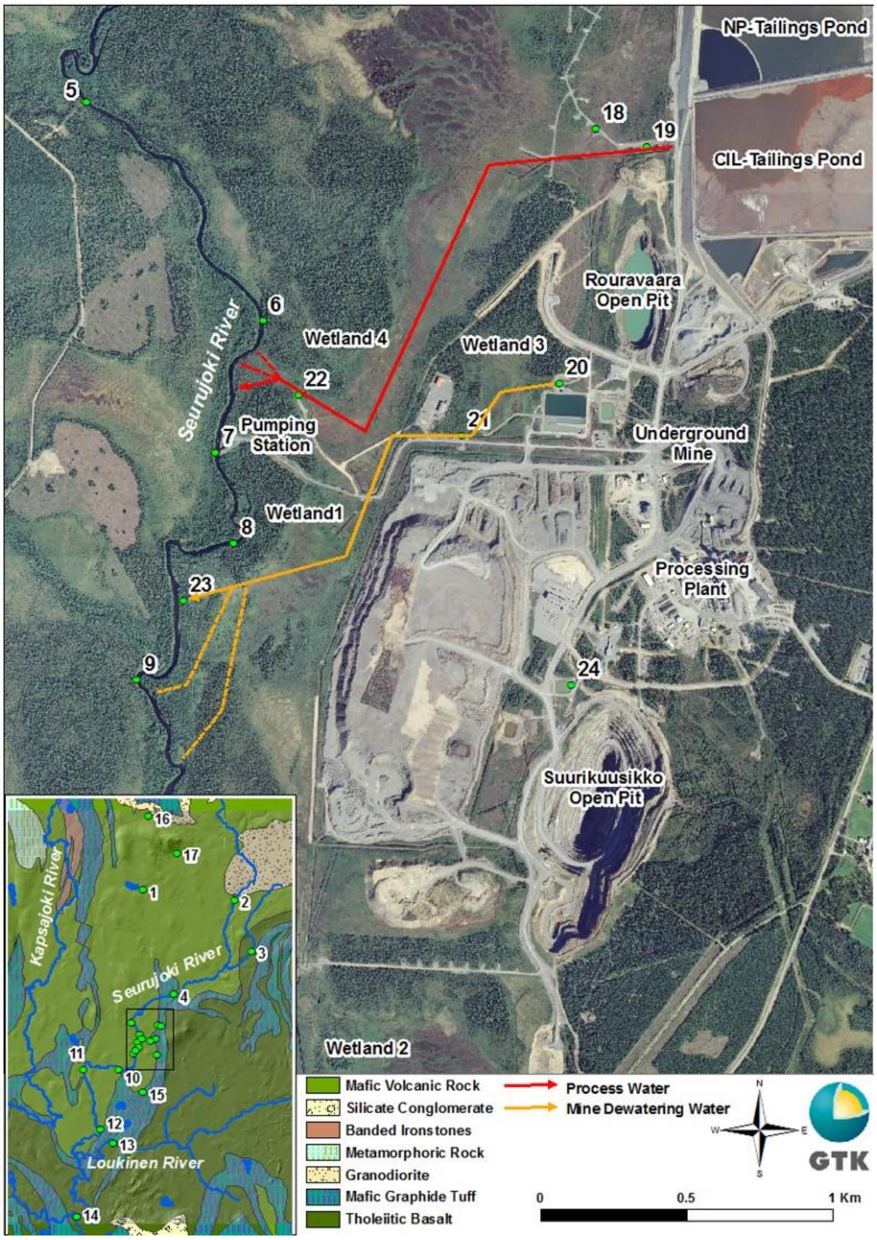

Figure 7.1. Kittilä mine site, local bedrock and the location of isotope and geochemical sampling sites. Water sample sources: surface water from upstream of mine site discharge (SWUS), surface water downstream of mine water discharge points (SWDS), groundwater wells (GW), mine water dewatering water (MWDW) and process water (MWPW) from the holding ponds and discharged from treatment wetlands.

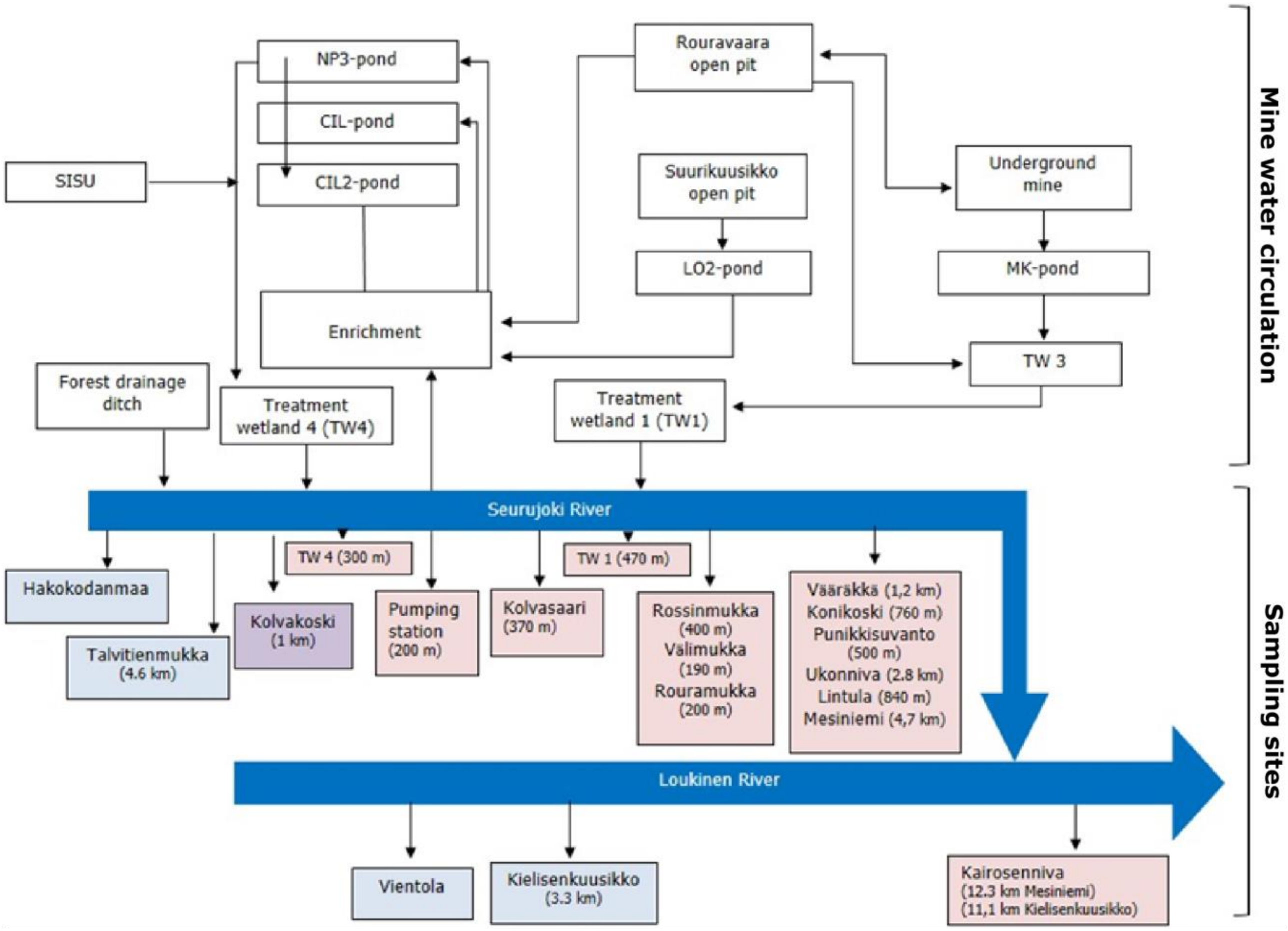

Figure 7.2. Chart of mine water circulation in Kittilä mine and sampling points in recipient Seurujoki and Loukinen Rivers. The distance to previous sampling point in Seurujoki and Loukinen Rivers is presented in brackets. The total distance from Hakokodanmaa to Kairosenniva is approx. 31km. (Modified from Hämäläinen E. 2015 and Malinen 2016).

7.3.2 Roșia Montană

Rosia Montana is located in the Southern Apuseni Mountains in Western Romania and belongs to the Golden Quadrilateral, one of the most important gold areas in Europe. The region hosts gold-, silver-, and copper-bearing deposits, which are related to three approximately parallel belts of Neogene volcanism, Rosia Montana being part of the northernmost belt. The Rosia Montana volcanogenic complex is a maar-diatreme structure, which intersects Cretaceous fine-grained sediments (black shales) with intercalations of sandstones and conglomerates. This structure includes distinct types of breccias (*e.g.* phreatomagmatic breccias) and volcaniclastics. Two dacitic bodies, named Cetate Dacite and Carnic Dacite, have played an essential role in the mineralization process, generating the gold and silver bearing deposit (Tamas 2007).

Several studies have been conducted in order to track the potential pollutant loads, especially of heavy metals in soil (*e.g.* Lăcătuşu et al. 2009, Lazăr et al. 2014). According to these studies, apart from some areas in the proximity of the mining workings, the heavy metal contents in the topsoil are generally low, in the range of normal concentrations, as defined by the national environmental regulations. Actually, the acid mine drainage (AMD) and the related transfer of heavy metals from the old mining sites represents the main pollutant factor that affects the environment in this mining area. The acid runoff dissolves trace metals such as Pb, Zn, Ni, Cu, Fe, contaminating the groundwater and the main water courses in the region. High concentrations of harmful elements are present also in stream sediments, disturbing the aquatic environment (Florea et al. 2005, Bird et al. 2005).

Arieș River is the most important watercourse in the Apuseni Mountains, and flows at about 10 km north of Rosia Montana, collecting water from various tributaries. Rosia Montana is crossed by Rosia stream which flows to Abrud River (Figure 7.3). Roșia and Corna Valleys collect the runoff and mine waters coming from adits, open pits, waste dumps and gallery outlets within the Roșia Montană mining area. Saliste stream flows approximately parallel to Rosia Valley, and collects mine waters leaking from Săliște tailings impoundment. Several artificial lakes (Taul Mare, Taul Brazi, Taul Corna, etc.) have been used in the past for storing the necessary water for the ore washing.

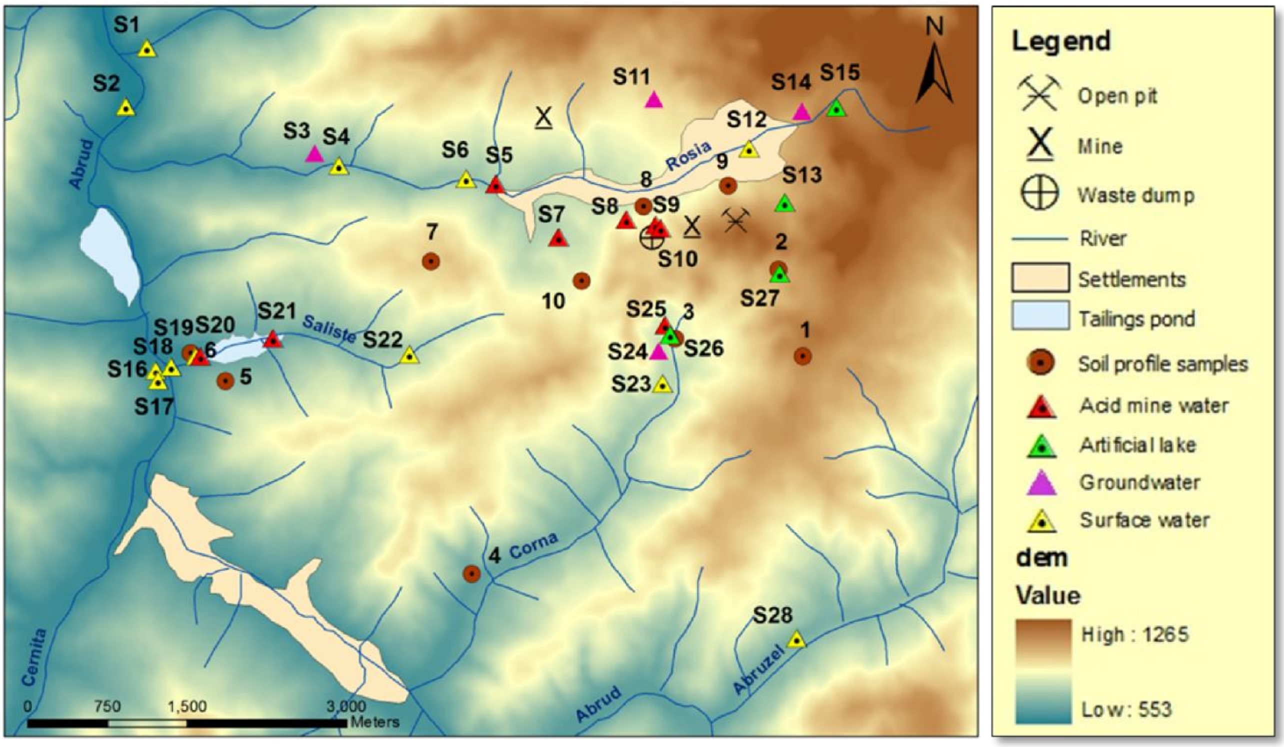

Figure 7.3. Rosia Montana site and the location of isotope and geochemical sampling sites.

7.3.3 Zlatna mining area

Zlatna gold mining area (approx. 40 km^2) is located in the Metaliferi Mountains of the South Apuseni mountain range (Romania) approximately 24 km south of Roșia Montană (Figure 7.4). It also belongs to the ’Golden Quadrilateral’ mining district. The Zlatna mining group includes three mines: Haneş, Almaș and Stănija. The Almaș mine was closed during the Second World War, and at present the amount of drainage water from the Almaș mine is insignificant. The mining operations at the Haneș and Stănija mines ceased in 2007. Currently, the mine openings are secured, but significant flow of acid mine water continues to discharge into the river system.

The basement in the area is made up of Jurassic ophiolites. The sedimentary cover, with a thickness of several hundred meters, consists of Late Jurassic – Hauterivian reef limestones, followed by a suite of detrital formations, Cenomanian - Early Turonian in age and Late Cretaceous molasses.

The Neogene volcanic activity had two peaks at 14.6 - 10.8 Ma and 9.3 - 7.4 Ma, ending 1.6 Ma ago (Roșu et al. 2004). Quartz andesite with amphibole and pyroxene, and quartz andesite with amphibole and biotite are the main petrographic types. Three types of polymetallic mineralization occur: (1) porphyry type (with or without veins at the upper part); (2) vein type, and (3) breccia pipe type with transitional forms generated by remobilization. All mineralizations contain Au ± Ag, Cu, Pb, and Zn in various proportions.

The Zlatna mining area shares the same environmental concerns as the majority of gold ore and complex, sulphide ore mining areas. The opening of mineralized magmatic bodies by mining workings, the extraction of ores and then the cessation of operation results in the formation of AMD by allowing infiltrating water to come into contact with reactive minerals.

In most cases, mine water infiltrates into the waste rock pile located in front of the mine adits, before it discharges into the river system. Waste rock piles may contain large amounts of trace metals and metalloids (*e.g.* Pb, Zn, Ni, Al, Cu, Mn, Fe and As) which add to the initial load of mine water, as well as sulphate (SO_4^{2-}) which causes a drop in the water pH.

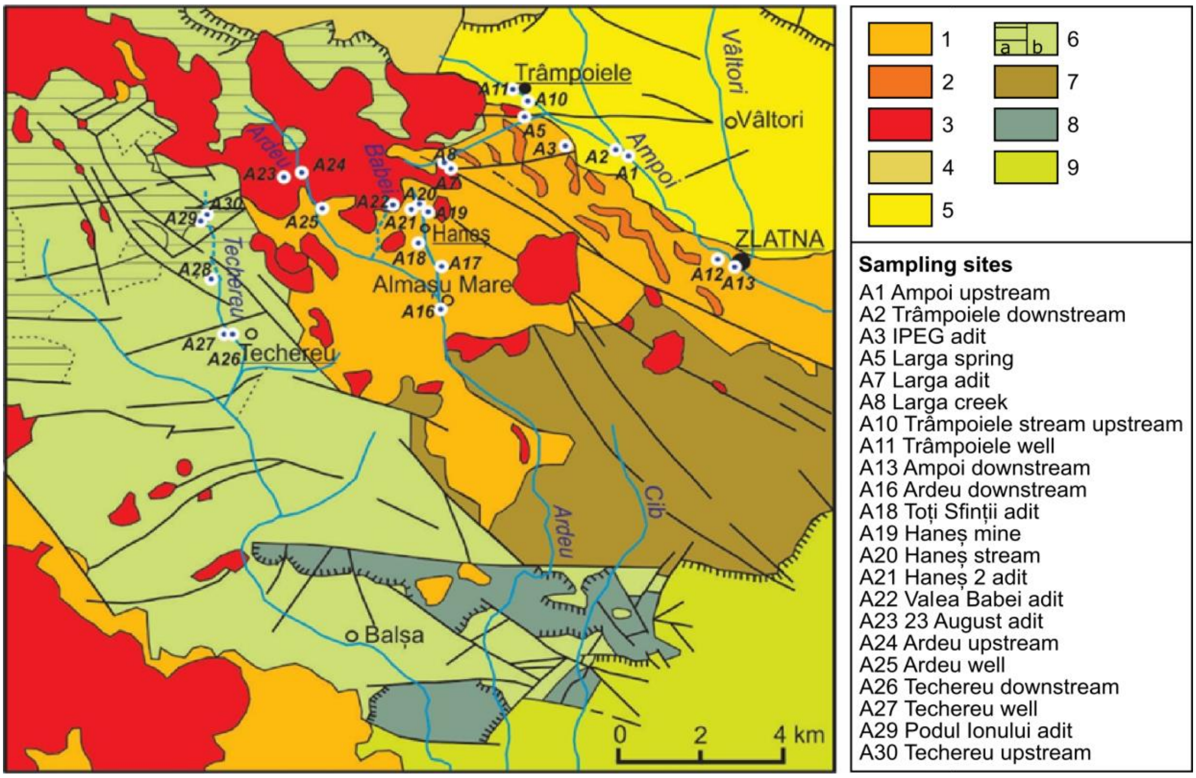

Figure 7.4. Geological sketch map of the Zlatna mining area showing the location of isotope, geochemical and biomonitoring sampling sites. (redrawn after the Geological map of Romania scale 1:50,000, sheet 74C-Zlatna; 1 – Neogene molasse; 2 – Neogene magmatites stage II; 3 – Neogene magmatites stage I; 4 – Early Cretaceous – Middle Jurassic flysch, Bucium Unit; 5 - Early Cretaceous – Late Cretaceous flysch, Feneș Unit; 6a – Early Cretaceous – Turonian flysch, Techereu Unit; 6b – Late Jurassic ophiolites; 7 – Late Cretaceous wildflysch, Galda Unit; 8 – Jurassic – Early Cretaceous reef limestones, Ardeu Unit; 9 – Senonian – Maastrichtian flysch, Bozeș Unit).

7.4 Use of geochemical characteristics and isotopic methods for assessing contaminant migration

7.4.1 Materials and methods

Water samples were collected for isotopic analysis of $^{18}O/^{16}O$, $^{2}H/^{1}H$, $^{87}Sr/^{86}Sr$, $^{34}S/^{32}S$ of SO_4, $^{7}Li/^{6}Li$, and $^{26}Mg/^{24}Mg$, as well as major and trace element analysis at and around the **Kittilä mine** site in June 2013, March 2015, and June 2015. Water sample sources included surface water from upstream of mine site discharge (SWUS), surface water downstream of mine water discharge points (SWDS), groundwater wells upgradient of mine impacted waters (GWBG), mine water dewatering water (MWDW) and process water (MWPW) from the holding ponds and discharged from treatment wetlands, as well as groundwater from bore holes and seeps within the underground mine (MWGW) (Larkins et al. 2018). Figure 7.1 shows the surface sample locations of Kittilä site in a map view.

Chemical analysis of water samples was conducted by Labtium Oy. Dissolved metals and metalloids were analysed by ICP-MS or ICP-OES and anions by IC techniques. All elemental purification and isotopic analyses were conducted at the GTK Research Laboratory in Espoo, Finland, as summarized in Table 7.2. Detailed description of the analysis and pretreatment procedures can be found in Larkins *et al.* 2018.

Table 7.2. Solute separation method, analytical method and analytical precision for isotopic analyses.

Sampling	**$^{87}Sr/^{86}Sr$**	**$^{7}Li/^{6}Li$**	**$^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$**	**$^{34}S/^{32}S$ - SO_4^{2-}**	**$^{18}O/^{16}O$ and $^{2}H/^{1}H$**
Standards	NBS987	LSVEC	DSM-3	VCDT	VSMOW
Error (2σ)	<0.00003	<1.1‰	<1.06	<1‰	<0.1‰δ^{18}O;<0.5‰δ^{2}H
Separation	IC	CC	IC	CC	n.a.
Analysis	MC-ICPMS[1]	MC-ICPMS	MC-ICPMS[2]	MC-ICPMS	CRDS

CC is conventional column, IC is ion chromatograph, MC-ICPMS is Nu Instruments™ Multi-Collector Inductively Coupled Plasma Mass Spectrometer, CRDS is cavity ring down spectroscopy, and na is not applicable. Standards were used for quality control during separation and analysis, correcting for instrumental fractionation, and for delta-notation reporting. Error is analytical precision reported as 2σ of repeatability.

[1] March of 2015 Sr isotopes analysed by Thermal Ion Mass Spectrometry (TIMS)

[2] Mg isotopes not analysed in June 2013

In **Roșia Montană** area, water samples for major ions and trace elements analysis and isotopic measurements ($^{18}O/^{16}O$, $^{2}H/^{1}H$), were collected in the period January 2014 – August 2015. In order to draw the local meteoric water line, monthly cumulative samples of precipitations have been collected from two sampling stations in Roșia Montană and Cluj-Napoca, using the IAEA standardized methodology (August 2014 – August 2015),In addition, one-time isotopic analyses of strontium ($^{87}Sr/^{86}Sr$) and sulphur from sulphate ($^{34}S/^{32}S$ -SO_4) isotopes were conducted in May 2015 by GTK.

The water sampling network initially consisted of 28 sampling points: 12 streams, 4 lake, 4 groundwater (dug wells and springs) and 8 mine water points. After obtaining the preliminary results, the network was reconfigured to 24 sampling points, considered the most representative.

For each water source the following parameters: pH, EC, T, salinity, TDS, DO, redox potential, and turbidity, were measured directly in the field by using a WTW Multi 350i portable multimeter, and a portable WTW Turb 430IR turbidity meter, respectively.

Chemical and isotopic analyses of water samples were conducted in the laboratories of Babeș-Bolyai University. Metal concentrations (Ni, Cu, Zn, Cr, Cd, Pb and Fe) were determined by using an atomic absorption spectrometer (AAS), ZEEnit 700 type, and the major ions were measured by ion exchange chromatography. Oxygen and hydrogen stable isotopes in water were analyzed by laser (IR) based cavity ring-down spectroscopy (CRDS) using a Picarro L2130-I isotopic water analyser. The precision of the δ^{18}O and δ^{2}H (δD) measurements was ±0.12‰ and ±0.8‰, respectively. All isotopic data are expressed in conventional δ notation as per mille deviation of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios with respect to the V-SMOW standard (Larkins et al. 2018).

In addition to water samples, soil samples were collected in order to assess the potential soil acidification and contaminant load.Samples from 10 soil profiles (100 cm deep) were collectedin 2014, and the pH and heavy metal contents in soil were measured.

At the **Zlatna** site, water samples were collected on a monthly basis from January 2015 to December 2015 for isotopic analysis of $^{18}O/^{16}O$, $^{2}H/^{1}H$, and major and trace element analysis.

The sampling scheme included 25 sites (Figure 7.4), of which samples were collected from: 8 sources of mine water (collected at mine openings), 10 sources of running water, 4 springs, and 3 domestic wells. Sampled mine water is drained from the Haneș mine (adits: Larga, Haneș, Haneș 2, and Toți Sfinții) and the Stănija mine (adits: Podul Ionului and 23 August), as well as from a mining exploration adit (IPEG). The main water courses (Ampoi Valley, Trâmpoiele stream, Ardeu stream, Techereu stream) were sampled both upstream and downstream of the discharge point of mine water.

For each water source, the following parameters were determined in the field: pH, temperature, DO, TDS, and conductivity, using a Hanna HI9828 (Hanna Instruments Inc. 2008) portable multimeter. The isotope and chemical analyses were performed at "Babeș-Bolyai" University, following the same procedures as for the water samples from Roșia Montana site.

7.4.2 Results and discussion

7.4.2.1 *Kittilä case*

Each water type exhibited distinct chemical characteristics. Average concentrations of selected major ions and trace elements are shown in Figure 7.5. The lowest TDS concentrations were in samples from upstream of Seurujoki River (SWUS), which were compositionally similar to background groundwater sample (GWBG) and are therefore grouped together in Figure 7.5. The highest single TDS concentration was analysed from a deep groundwater sample from underground mine (MWGW), collected from 863 m below the ground surface (bgs), and exhibited extremely high Cl and Na concentrations, while shallower deep groundwater samples had lower TDS concentrations with SO_4 as the most concentrated solute. The highest average TDS concentrations were in mine process water (MWPW), which were 2 to 3 orders of magnitude greater than in upstream waters of Seurujoki River, and characterized by high proportions of SO_4, Mg, K, Na, Li and Mn. Mine dewatering waters (MWDW) exhibited average TDS concentrations 1 to 2 orders of magnitude higher than in upstream, and were characterized by high proportions of SO_4, Ca, Cl and NO_3. Dewatering waters also exhibited high concentrations of Ni, Sb, and As. In downstream of mine discharge in Seurujoki River, SO_4 was over an order of magnitude higher than in upstream, while most other major and trace element characteristics of mine waters were elevated downstream of mine discharge, but to a lesser degree. (Larkins et al. 2018)

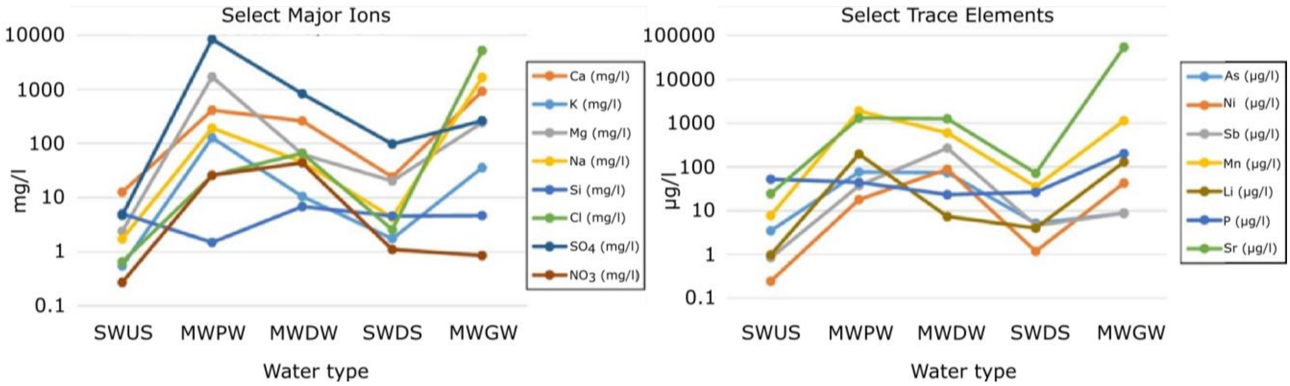

Figure 7.5. Average concentrations of selected major ions and trace elements in water samples of Kittilä mine. Water sample sources: surface water from upstream of mine site discharge (SWUS), surface water downstream of mine water discharge points (SWDS), mine water dewatering water (MWDW) and process water (MWPW) from the holding ponds and discharged from treatment wetlands, as well as groundwater from bore holes and seeps within the underground mine (MWGW).

Hydrological and geochemical relationships in mine and surface waters are illustrated in Figure 7.6. In dewatering waters a notable increase in Cl from 2013 to 2015 sample events was interpreted to reflect increasing contribution of deep saline brine waters to dewatering water as mining progressed deeper. Increased Cl to SO_4 ratio in dewatering waters was also reflected in river downstream results from 2013 to 2015, as indicated by the arrow in Figure 7.6. The 2015 downstream samples at lower Cl to SO_4 are those collected upstream of dewatering discharge, but downstream of process water discharge. (Larkins et al. 2018)

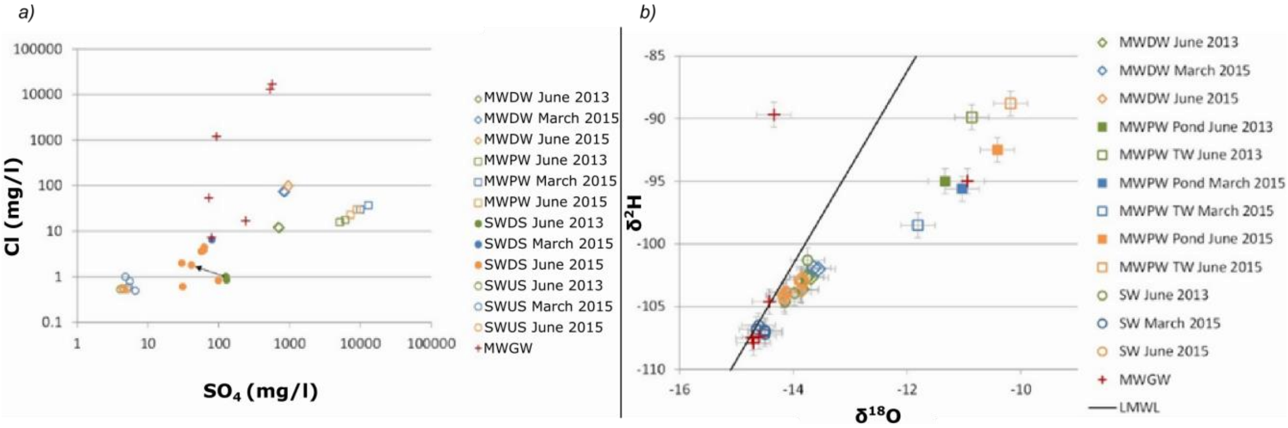

Figure 7.6. a) Ratio of sulphate and chloride and b) Ratio of $\delta^{18}O$ and $\delta^{2}H$ in water samples from Kittilä mine. Water sample sources: surface water from upstream of mine site discharge (SWUS), surface water downstream of mine water discharge points (SWDS), mine water dewatering water (MWDW) and process water (MWPW) from the holding ponds and discharged from treatment wetlands, as well as groundwater from bore holes and seeps within the underground mine (MWGW).

Four distinct water isotope ($\delta^{18}O$ and $\delta^{2}H$) compositions were identified in site waters (Figure 7.6). Process water is enriched in heavy water isotopes with characteristic negative d-excess values. The deep saline groundwater from 863 m bgs had a distinctively high d-excess (+25), which is similar to other Finnish cratonic brine waters, and has been attributed to water-rock interactions (Kietäväinen et al. 2013). The three shallowest groundwater samples from underground mine coincide with the March 2015 surface waters, which were depleted in heavy water isotopes relative to June 2013 surface waters reflecting snow melt runoff. The dewatering water, on the other hand, consistently coincides with June surface waters, and does not show seasonal variation, indicating it is primarily of modern meteoric water origins, despite indication of increasing contribution of formation water from Cl concentration. Further, the similarity in the shallow groundwater samples from underground mine and contemporaneous surface water provides evidence for rapid surface water capture to the underground mine at 390 and 625 m bgs. However, because $\delta^{18}O$ and $\delta^{2}H$ of deep groundwater likely varies with depth, similarity between these and seasonally depleted surface waters may be coincidental, and could be clarified with additional sampling. (Larkins et al. 2018)

Sr isotopic compositions were distinct between different water sources and also varied with distance downstream in the Seurujoki River. Decreasing $^{87}Sr/^{86}Sr$ in the downstream direction from Tuonkasomma to Talvitiemukka was attributed to a change from granodiorite bedrock upstream to mafic tuff and tholeitic basalt bedrock downstream. Sr isotopes and Cl concentrations were applied separately in sequential two-part mixing calculations to allocate contributions from process and dewatering waters to the Seurujoki River. Both tracers provided similar estimates for source water contribution, which also aligned reasonably with monthly monitoring data (Table 7.3). (Larkins et al. 2018)

Table 7.3. Mine water contribution to Seurujoki River water estimated from end member mixing using Cl concentration and Sr isotope composition

Analyte	**June 2013**			**June 2015**		
	Process water at pumping station	**Dewatering water at Lintula**	**Total mine water input**	**Process water at pumping station**	**Dewatering water at Lintula**	**Total mine input**
Cl conc.[1]	2.09%	1.43%	3.51%	1.34%	2.81%	4.14%
$^{87}Sr/^{86}Sr$	1.89%	1.82%	3.71%	1.54%	2.80%	4.09%
Mean monthly discharge	0.58%	1.53%	2.1%	1.49%[1]	3.35%[1]	4.84%[1]

[1] These values are based on June 2014 monitoring results, as June 2015 results were not available at the time of writing.

Li and SO_4 exhibited non-conservative behaviour in the Seurujoki River downstream of mine discharge based on mine water contribution estimates shown in Figure 7.7. Li in solution was enriched by 2.76 to 2.94‰ relative to projections by conservative mixing, and attributed to Li precipitation and re-dissolution at different reaches in the Seurujoki downstream of discharge. In June 2015 SO_4 was attenuated from solution by over 50% and depleted in $^{34}S_{SO4}$ by up to 0.86‰ relative to conservative mixing projections. The depletion of $^{34}S_{SO4}$ indicated that bacterial sulphate reduction was not the attenuation mechanisms, as this attenuation mechanism results in $^{34}S_{SO4}$ enrichment in solution due to the preferential reduction of the lighter ^{32}S isotope. Subsequently, SO_4 attenuation within the Seurujoki can be attributed to precipitation of sulfate salts and/or hydroxide minerals. (Larkins et al. 2018)

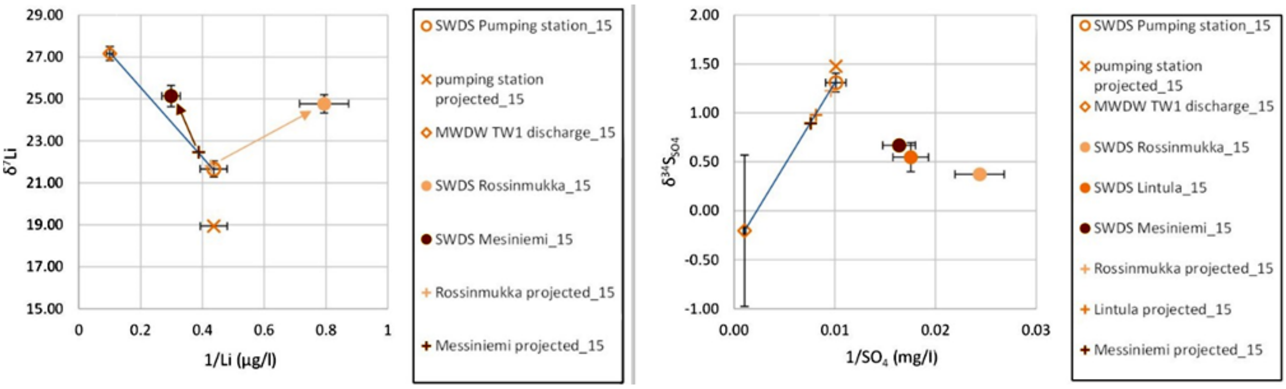

Figure 7.7. a) Ratio of 1/Li and δ^7*Li and b) Ratio of 1/SO4 and* $\delta^{34}S_{SO4}$ *in water samples from Kittilä mine. Water sample sources: surface water from upstream of mine site discharge (SWUS), surface water downstream of mine water discharge points (SWDS), mine water dewatering water (MWDW) and process water (MWPW) from the holding ponds and discharged from treatment wetlands, as well as groundwater from boreholes and seeps within the underground mine (MWGW).*

Non-conservative fractionation of Li and S also provided insight to solute source and mobility within the treatment wetlands. Deep groundwater samples from underground mine exhibited two distinct $^{34}S_{SO4}$ compositions indicating spatial heterogeneity in the $\delta^{34}S$ of mineralization within the mine. The increase in dewatering water $^{34}S_{SO4}$ from 2013 to 2015 suggests increasing influence from the more ^{34}S enriched mineralization over time. Increase in SO_4 concentration and $^{34}S_{SO4}$ from process water pond to treatment wetland 4 (TW4) suggests leaching of SO_4 form the wetland, specifically from sources other than secondary sulphides, such as sulphate salts and/or hydroxides (Figure 7.7). Contribution of solute to TW4 discharge from a solid phase source in March 2014 was further supported by an increase in Li concentration and δ^7Li observed from the process water pond to TW4 during this sample event. (Larkins et al. 2018)

7.4.2.2 *Roșia Montană case*

Soil

Most of the soil samples in Roșia Montană area were classified as weakly acidic soils (according to the Romanian legislation – RMO 278/2011), and most of the heavy metal concentrations fall in the range of the normal values, or between normal threshold and alert threshold. This indicates that in most cases, heavy metal concentrations correspond to the geological setting of the area. In agreement to the previous studies, the highest concentrations of metals (Zn, Pb, and Cu) were recorded close to the former mining area, near Tăul Cartuş (profile 3), Cetate dump (profile 10), and Cetate Adit (profile 8) (Figure 7.3), indicating the impact of mining. Close to Sălişte TMF, high concentrations of nickel were recorded in the case of two soil profiles (profiles 5 and 6).

The variation of metal concentrations was studied in relation with depth. The concetrations of zinc and lead tend to decrease on most of the soil profiles, while for the other elements differences are quite minor at various depths. Near the mining areas, a slight increase with depth of zinc, cadmium, and copper concentrations was noticed, which indicates the influence of the mineralized rock bodies on the soil quality.

A factor analysis between trace elements suggests an association between Cd, Zn and Cu on one hand, and Cr, Ni and Pb on the other (Table 7.4). A principal component analysis confirmed these two associations, which were related to the potential origin of the elements. In accordance with the geochemical characteristics of these elements, the association between Cd, Zn, and Cu is normal, as well as between Cr and Ni. It is less expected to find Pb in connection with the latter group. Higher concentrations of lead were observed at the base of Sălişte TMF, where higher values were recorded at a depth of 30cm. This area is heavily influenced by the presence of the tailings that severely modify the concentration of metals in soils.

Table 7.4. The factor analysis between trace elements in the investigated soil profiles in Roșia Montană area (Eigenvectors F1 and F2 after Varimax rotation)

Elements	Factor - 1	Factor - 2
Cd	**0.936424**	-0.198692
Zn	**0.961572**	0.132132
Pb	0.262632	**0.834835**
Cu	**0.986610**	-0.006424
Ni	-0.130750	**0.946925**
Cr	-0.082583	**0.962575**
Expl.Var	2.867803	2.577146
Prp.Totl	0.477967	0.429524

Water

One of the main goals of our study was to assess the impact of the past mining activity on the water resources from Roșia Montană area. Most of the local geological formations, as the magmatic rocks and the Cretaceous sediments, show low permeability, although some thin detrital intercalations are present. Therefore, the geological structure does not support the occurrence of significant aquifers. However, the dense network of underground mining workings provides artificial pathways for the water flow in the underground space. The open pits favour infiltration of rainwater, that reaches the galleries, and after a longer or shorter pathway in the underground, is discharged to the surface, mainly through adits. The water circulating through the mining workings is affected by AMD, which severely modifies their hydrochemical original features. Similar effects are produced in the case of rock waste dumps and tailings dumps. The AMD diminishes pH to very low values, making the water very aggressive against rocks. The content of disolved solids increases, and sulphate becomes the dominant anion, eventually reaching extremely high concentrations. The content of the other major ions also increases. The acid water mobilizes important amounts of heavy metals, thus increasing its toxicity.

Although all the waters in the study area share the same meteoric origin (Figure 7.8), intense mixing processes between different hydrochemical types occur. The influence of evaporation on the isotopic ratios is visible in the case of lakes. The load of heavy metals depends on the water pH (Figure 7.9). The low pH of the mining influenced waters is always a prerequisite of the high concentration of metals. The most important ion that shows the influence of AMD is sulphate (Figure 7.10), which replaces bicarbonate as a consequence of the increased acidity.

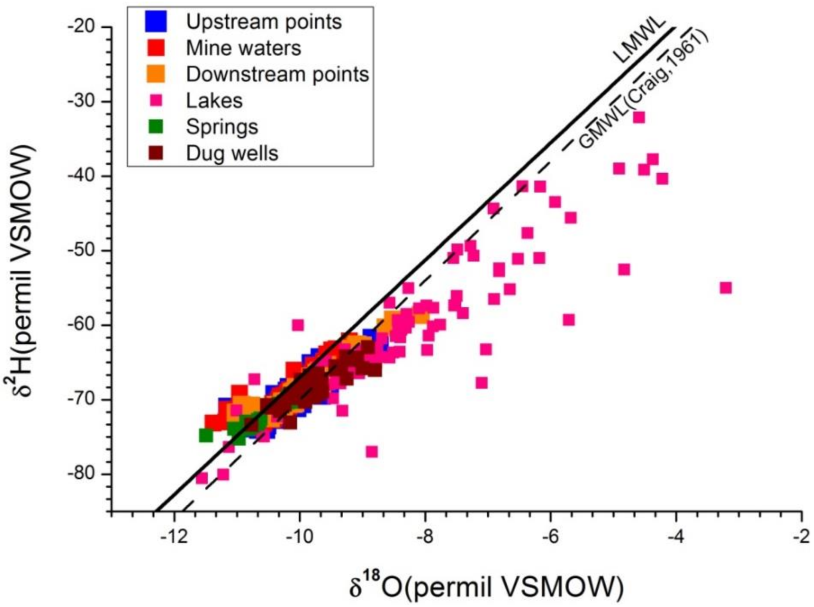

Figure 7.8. Stable isotopic composition of different categories of water sampled in Rosia Montana study area.

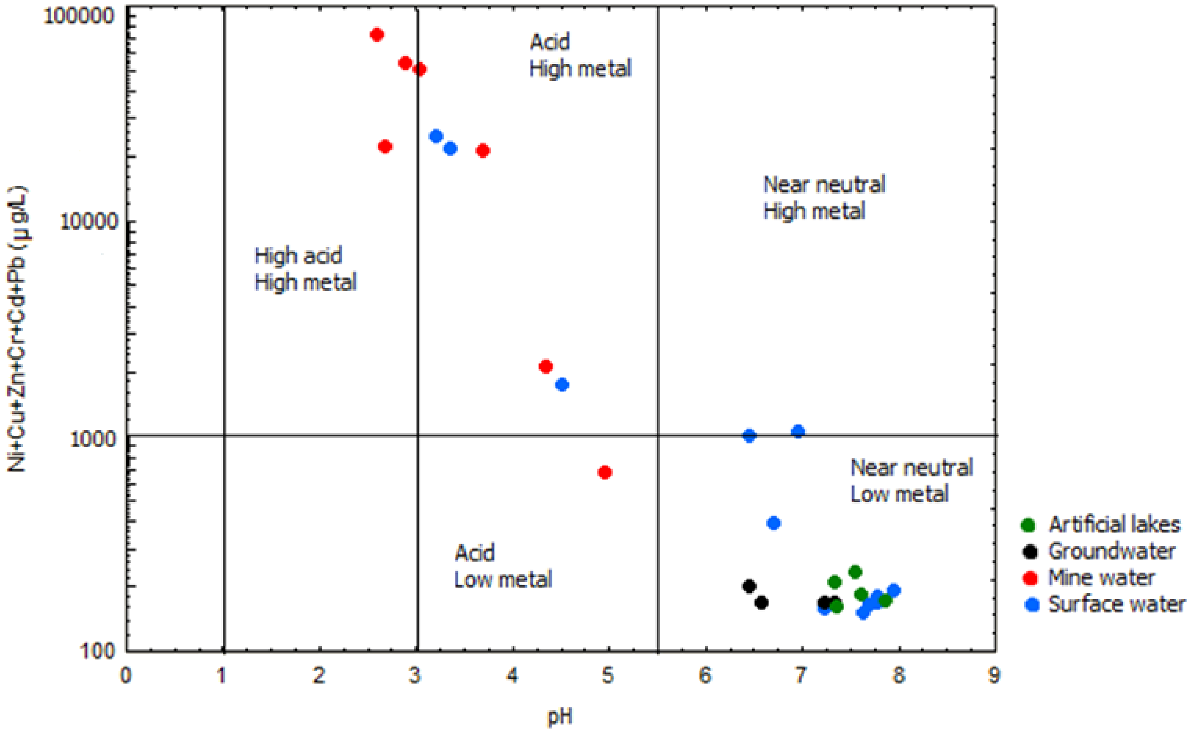

Figure 7.9. Ficklin diagram of water samples showing the sum of heavy metal concentrations vs. pH (averaged data Jan. 2014 - Aug. 2015)

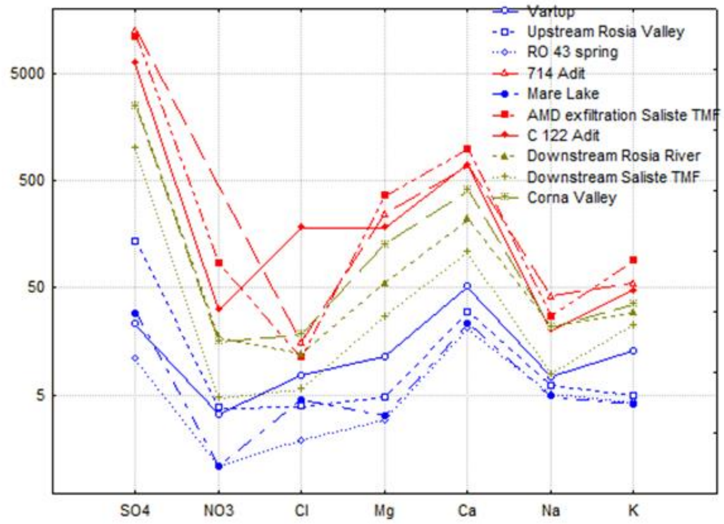

Figure 7.10. Major ion concentrations (mg/L) in surface water (upstream and downstream points), ground water and artificial lake sampling points compared to underground mine waters (averaged concentrations Jan. 2014 – Aug. 2015).

Roşia and Corna Streams exhibit the highest concentrations of contaminants, which far exceed the national quality standards for surface water. Beyond Roşia Montană area, mining workings belonging to the Bucium area occur in the south-eastern part of the area of interest, strongly impacting the local streams. Low pH and high concentrations of sulphates, Ni, Cu, Zn Cd and Pb were found in the samples collected downstream of the mining area (*e.g.* S2, S4, S6, and S28). These values are illustrative for the bad state of the mining impacted surface waters, that are included in the 4th and 5th class (very poor quality), according to RMO 161/2006. The high metal and dissolved solids concentrations in Roşia Stream is a consequence of the numerous mine water discharges from Cetate and Cârnic open pits, from the numerous waste rock piles of various sizes, and also from the underground workings. The differences in the water quality between the upstream and downstream points are obvious, the dissolved content in the downstream points being significantly higher than upstream of the mining area (Figure 7.11).

Corna Stream is the second most polluted watercourse in Roşia Montană area, due to the mine waters released from the waste dumps located upstream the valley. In this case the flow rate is very low and the SO_4 content is higher compared to Roşia Valley.

On Sălişte Stream, the water leaking from the tailings is mixed with the relatively clean water conveyed along Sălişte diverting gallery (S19), this way diminishing the pollutant load. High concentration of sulphates, Ni, Zn, Cd, and Pb were recorded in the case of points S18, on Saliste Valley, and S23, on Corna Valley. Similar trends concerning the difference beween the upstream and downstream points (Figure 7.11), as in the case of Rosia Stream, were noticed.

Although it is the main collector of the adjacent streams, Abrud River has the lowest SO_4 content, electric conductivity, as well as heavy metal concentrations, due to its high flow rate and consequent dilution.

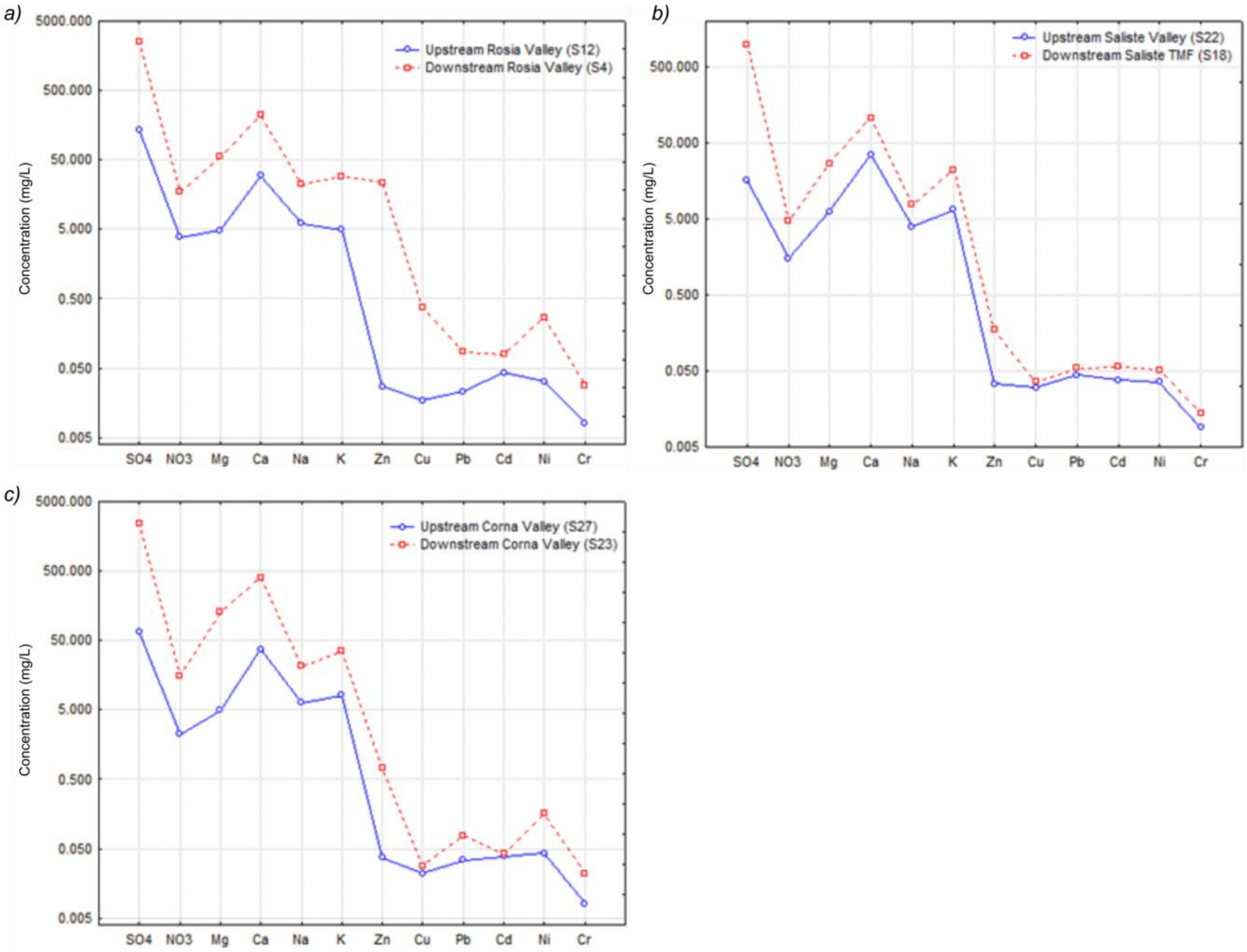

Figure 7.11. Major ions and heavy metals average concentrations (mg/L) in surface water (upstream and downstream points) on (a) Roşia Valley, (b) Sălişte Valley, and (c) Corna Valley.

The waters inside the former mining area and downstream of it show low pH and high content of heavy metals and dissolved solids, related to the acid mine drainage process. Upstream of the settlements and former mining activities, and also on Vârtop River (S1) (which is considered as a background water quality site), the water quality is good. The water in artificial lakes, used in historical periods as reservoirs for storing water for washing the ore, is also of good quality. With some exceptions, the springs and dug wells used as domestic water supplies, meet the standards for drinking water.

7.4.2.3 *Zlatna case*

A summary of the distribution of the parameters measured in the field (temperature, pH, TDS), as well as the δ^{18}O and δ^{2}H values for different water sources are shown in Table 7.5.

Table 7.5. Summary of the distribution of t, pH, TDS, $\delta^{18}O$, $\delta^{2}H$ of waters from Zlatna mining area

	t (°C)	**pH**	**TDS (mg/l)**	**$\delta^{18}O$ (‰)**	**$\delta^{2}H$ (‰)**
Surface water *(no. of obs. 10)*					
Mean value	10.9	7.1	296	-9.9	-67.2
Min. value	9.4	3.9	68	-10.2	-69.4
Max. value	11.8	8.1	792	-9.6	-64.9
Std. Dev.	0.8	1.4	243	0.2	1.4
Domestic well (no. of obs. 3)					
Mean value	10.2	7.3	283	-9.9	-68.0
Min. value	9.0	7.0	174	-10.2	-69.4
Max. value	10.8	7.6	429	-9.6	-65.9
Std. Dev.	1.0	0.3	132	0.3	1.9
Spring (no. of obs. 4)					
Mean value	10.2	7.5	219	-9.5	-66.3
Min. value	9.2	7.2	104	-10.1	-69.3
Max. value	11.1	7.8	336	-8.9	-60.6
Std. Dev.	0.8	0.2	97	0.5	3.9
Mine water (no. of obs. 8)					
Mean value	11.0	5.6	1404	-10.6	-72.6
Min. value	8.3	4	316	-11.0	-75.7
Max. value	14.6	8	3122	-10.3	-70.0
Std. Dev.	2.2	1.6	1132	0.3	1.9

Surface water and groundwater samples display similar $\delta^{2}H$ and $\delta^{18}O$ values, neutral pH, and total dissolved solids (TDS) values. In contrast, mine water is characterized by lower $\delta^{2}H$ and $\delta^{18}O$ values, and displays high variability in TDS and compared to other types of waters. Two distinct groups of mine water could be distinguished: mine water showing TDS values similar to other underground water and surface water sources (IPEG, Toți Sfinții, 23 August, Larga, Podul Ionului, Figure 7.12) and mine waters with much higher salts content (Haneș, Haneș 2, and Valea Babei). The majority of mine water sources display pH values between 4 and 5 (Figure 7.12). Mine water discharged from the Podul Ionului adit, displays slightly higher pH values (~ 6). This could be due to the interaction with the ophiolitic rocks through which the adit crosses and which have high pH buffering capacity. The mine water with neutral pH (~7) does not come into direct contact with the mineralization, either because it is discharged from an exploration adit (IPEG) or because of the depletion of pyrite and other sulphides exposed to weathering in old abandoned mining workings (Toți Sfinții, 23 August).

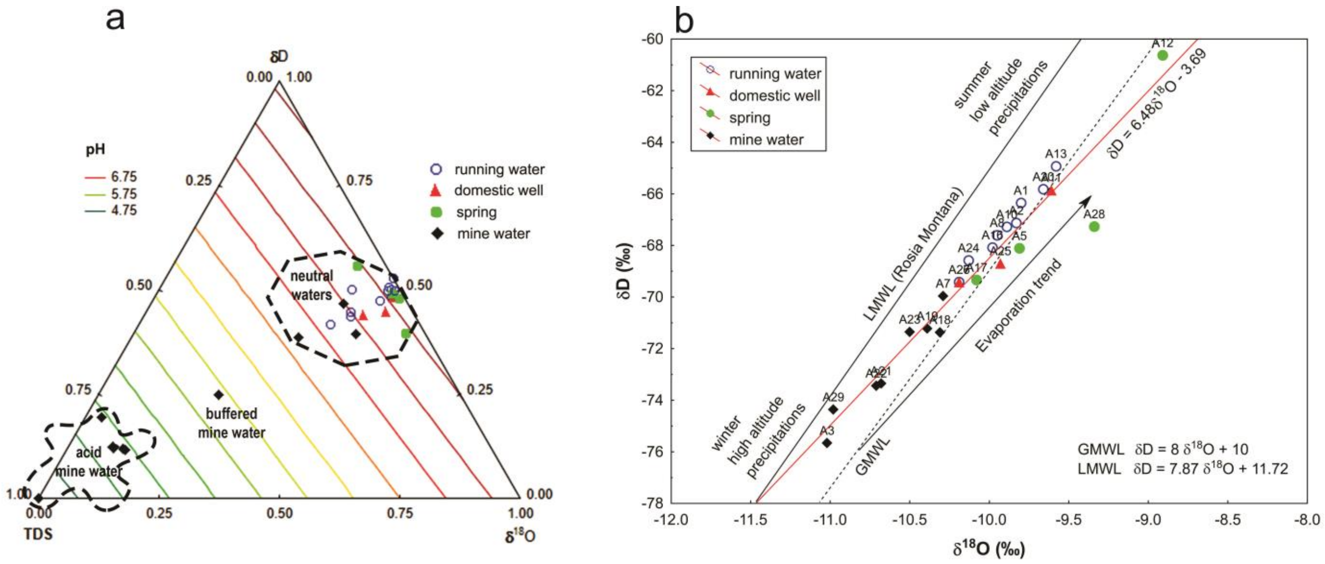

Figure 7.12. a) δ^2H and δ^{18}O values and TDS versus b) linear correlation between δ^2H and δ^{18}O values

Mine water, surface water and groundwater are all Ca-dominant type waters, indicating the same mechanisms of mineralization. Mine water from Podul Ionului adit contains more Mg relative to other mine waters. This is due to weathering of ferromagnesian minerals contained in the basic ophiolites crossed by the adit. The Larga spring and the Techereu spring have a distinct position, showing no dominant cation.

All mine waters have very high SO_4^- concentrations (up to 67,541 mg/l) and are classified as SO_4-type waters. Lower SO_4^- concentration was found in mine water from the 23 August adit (< 370 mg/l). Surface and groundwater sources are classified either as SO4 -type or HCO3 -type waters.

Distribution of heavy metal concentrations (Cr, Pb, Cu, Ni, Zn, Fe and Cd) differs from one water source type to another. In surface water, mine water and groundwater Fe is the dominant metal. As expected, the highest concentration was found in mine water (up to 3100 mg/l), except the mine water drained from the Toți Sfinții adit which shows very low Fe concentration (average 0.3 mg/l). Mine water also shows the highest concentrations of Zn (up to 108 mg/l), Pb, Ni and Cd. The highest concentration of Cu was found in running water from the Larga creek (0.338 mg/l). High concentrations were also found in mine water discharged from the Haneș and Larga adit (up to 0.11 mg/l). Running water also displays elevated concentrations of Ni (up to 0.13 mg/l) and Pb (up to 0.074 mg/l). In domestic well water, the dominating metals are Zn (up to 0.180 mg/l) and Fe (up to 0.035 mg/l). Concerningly, elevated concentrations of Pb were also found in well water (up to 0.059 mg/l in Techereu well). Lead concentration of spring water was also high (up to 0.057 mg/l in Larga spring). The lowest concentration of Pb was found in Ardeu stream upstream (0.024 mg/l) and the highest in Haneș 2 mine water (0.266 mg/l).

Linear correlation between δ^2H and δ^{18}O values (Figure 7.12) indicates that all water sources belong to the meteoric cycle. Low δ^2H and δ^{18}O values of mine water suggest snowmelt and high altitude precipitation as the main source of recharge.

For waters belonging to the meteoric cycle, temperature variations are the essential factor which controls their isotopic composition. Both surface water and groundwater (springs, domestic wells) show seasonal variation of the studied parameters, but the variation patterns are different from one source to another. The influence of snow melt manifests both in surface water and underground water. The surface waters from the Ampoi River and Trâmpoiele stream show a minimum in salt content and δ^2H, and δ^{18}O in June, as the result of snow melt. For other surface waters (Ardeu stream and Techereu stream) the influence of snow melt is less obvious. At these sites evaporation during summer months substantially changes both the salt content and isotopic composition of waters. Such variation patterns are distinct within each hydrologic basin.

Underground water (springs, domestic wells) show seasonal variation similar, but with delay to the surface water. Seasonal variations of TDS and isotopic composition of underground water, as compared to surface water, provided information on recharge zone and underground dynamics. As an example, the Zlatna spring has genetic relationships with the phreatic water in the vicinity of the Ampoi Stream and relatively fast underground circulation was estimated for this spring. For the Techereu spring the seasonal variation of the δ^2H is V-shaped with the lowest value recorded in May, which reflects influences of snow-melt. The seasonal variation of TDS and isotopic composition of the Haneș spring suggested a slow flow recharge pathway.

In groundwater, Zn and Fe concentration do not exceed the standard values for drinking water. The Pb and Ni concentration exceed these standards by less than 1%. Elevated concentration of Cd was recorded in all water sources. In groundwater, Cd concentration is up to 6 times higher than the quality standard for drinking water. However, such elevated concentration could be due to elevated geochemical background in the area.

Mine water is less affected by the seasonal variation of temperature. A slight increase of the pH values occurs during warm seasons when the infiltration of surface water increases. In most cases the variations in isotopic composition are within narrow limits (less than 1‰ for both δ^2H and δ^{18}O). The highest TDS values are recorded during winter months when the contribution of precipitation and infiltration water is diminished. During springtime (March – April) the infiltration of surface waters intensifies due to snow melting, and as a result, the dilution of mine water increases. A delay of 2 - 3 months could be observed in the variation sequences of TDS and δ^2H for these mine waters. An exception is the Larga mine adit, for which the seasonal variation in isotopic composition is larger. An increasing trend in the δ^2H values, along with a decreasing trend in the TDS values was recorded from March to September, suggesting a continuous dilution of the mine water with surface water directly derived from precipitation.

Due to flooding of mine workings after mine closure, favourable conditions for mixing are created and therefore seasonal variations in the chemical and isotopic composition of mine waters are smaller. Where there is a lack of mining works below, adits may act like rapid drainage pathways for infiltration water, not allowing underground mixing. In such cases, larger seasonal variations occur as in Larga adit. For the watercourses, the seasonal variation patterns of all studied parameters are comparable downstream and upstream, but in most cases, the variation range is larger downstream than upstream (Figure 7.13).

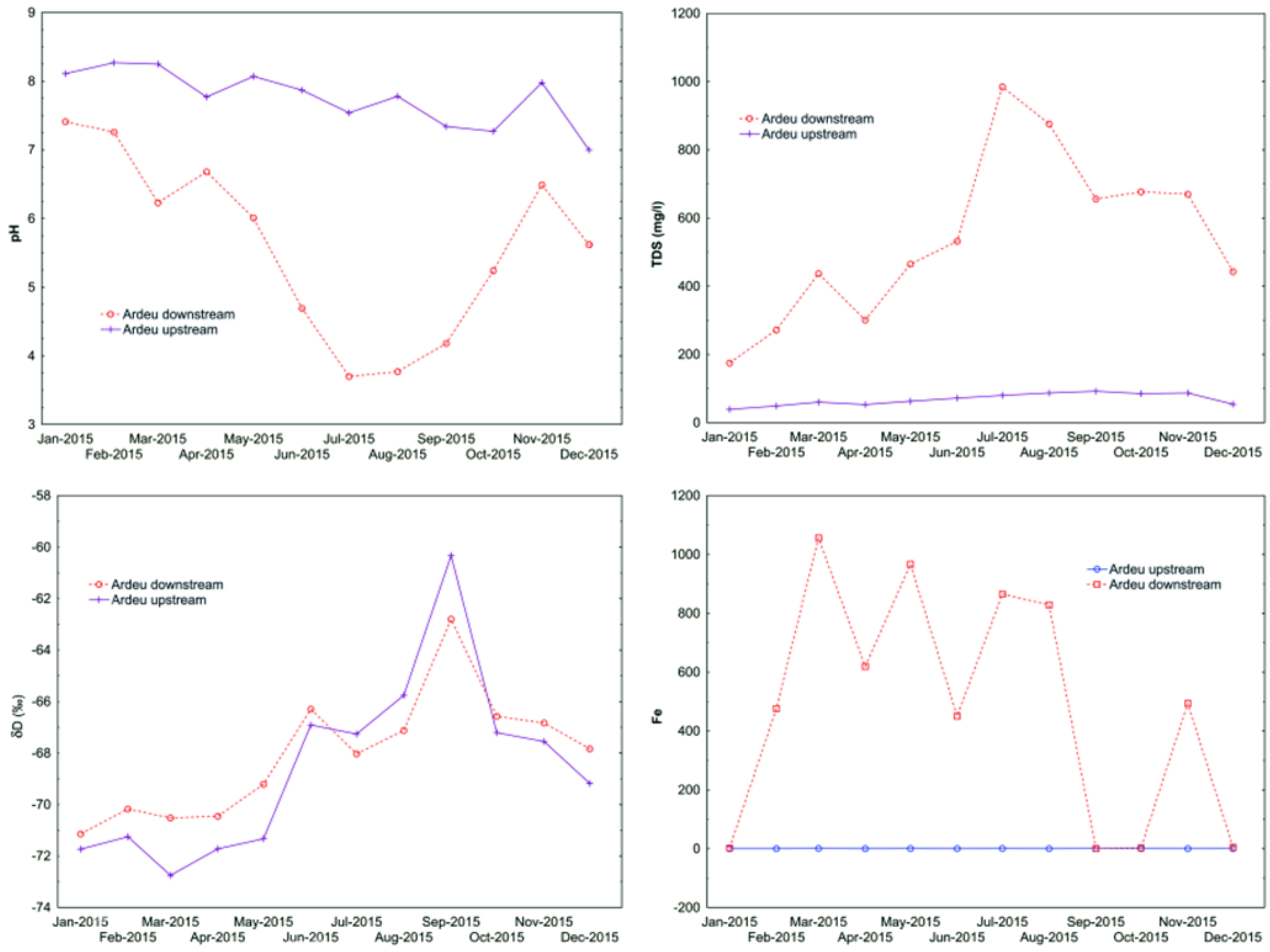

Figure 7.13. Seasonal variations of pH, TDS, δ^2H and Fe values along the Ardeu stream

The pH values are lower downstream because of the acid mine drainage. The difference is more pronounced in the summer months when the water flow decreases. The TDS values increase toward downstream. The δ^2H and δ^{18}O values also increase along the watercourses as effect of evaporation.

For the study area, no relevant contamination of springs and phreatic water by mine water could be revealed. This suggests different underground pathways for the two types of water. Conversely, surface water is contaminated by mine water and the negative effects of acid mine drainage occur mainly in the summer months. This is due to extreme evaporation and desorption of the acid iron hydroxide precipitate from the bottom of stream, in very low flow conditions.

The most affected watercourses are the Ardeu stream, the Techereu stream and the Larga creek, downstream of water mine discharge. For the Ardeu stream, the drop of the pH values correlates with the increase of the total dissolved solids, SO_4 content, as well as the heavy metal concentrations. The sulphate, nitrate, Fe and Zn concentrations far exceed the national quality standard for surface water. The highest concentration of contaminants was found in the Larga creek. However, its negative impact on the environment is less important due to low flow throughout the year. Both the Ardeu stream downstream (pH = 5.6) and the Larga creek (pH = 3.9) are more acidic than the quality limit (pH > 6.5).

The Ampoi River and the Trâmpoiele stream, which show high flow rates throughout the year, have the ability to collect contaminated water from the mine adits without recording radical changes of composition and acidity.

7.5 Use of environmental monitoring to predict contaminant behaviour in recipient rivers

7.5.1 Materials and methods

Long term environmental impacts of gold mining and the suitability of new field equipment to monitor contaminant behaviour were studied near the Kittilä mine during the summer of 2014 and in Rosia Montana site in May 2015. CastAway CTD (SonTek 2012) was used to measure electric conductivity (EC) vertically along the river as well as horizontally from river cross-sections at both sites.

In Kittilä mine the aim of the study was to understand how the dewatering and process waters from the Kittilä mine are mixed and diluted in the river Seurujoki and to provide information on how mine dewatering and process waters should be discharged to minimize environmental impacts of the mine. In addition to EC monitoring with Cast Away flow monitoring devices, River Surveyor M9 and Flow Tracker, were used to create the flow profiles on different parts of the river. The study included defining the suitability of different monitoring devices for environmental impact assessment of gold mining. In addition to EC and flow profiling, continuous water quality monitoring devides were installed in the vicinity of Kittilä mine site. Two YSI EXO2 – multiparameter sondes (YSI incorporated 2009) measuring dissolved oxygen, temperature, pH, redox-potential, EC, turbidity and nitrate were installed into the dewatering and process water discharge points of the mine (Figure 7.1 and Figure 7.2). Also Oneset HOBO® U24-001 Conductivity Loggers (Onset 2010) that measure both EC and temperature were installed into two locations in River Seurujoki, one upstream- and one downstream from the mine. These locations were chosen in order to both gain baseline values and to detect the possible environmental influences of the mine at the same time.

Electrical conductivity (EC) is a general measure of total dissolved solids (*e.g.* salts, alkalis, chlorides, sulphides and carbonate compounds) in water and usually higher conductivities indicate higher mineralisation and pollution. Moreover, since EC is rather quick and easy to measure it was chosen as the single most significant variable to be monitored.

A Cast Away CTD (conductivity, temperature and depth) - hydrographic instrument was used to measure a 14 km section of the river once a month on 16.6., 22.7., 26.–27.8 and 17.9.2014 (Hämäläinen E. 2015).

Along with the on-site measurements water samples were taken from the Seurujoki and the mine discharge waters in June and August 2014. The variables analyzed were Ag, Al, As, B, Ba, Bi, Cd, Co, Cr, Cu, I, K, Li, Mn, Mo, Ni, P, Pb, Rb, Sb, Se, Sr, Th, Tl, U, V, Zn, Ca, Fe, Mg, Na, Si, S, DOC, Br, Cl, F, SO_4, NO_3 and NO_2.

Cast Away CTD was used while rendering the horizontal electrical conductivity cross sections. Measurements were done cross stream, in one continuous sweep, with 5 measurements per second interval. The device was hoisted into a long handle and was held upstream from the measurer, flow-through cell of the device parallel to the stream. The profiles were done following the shapes of the river bottom but without the device touching it. The device has been designed for vertical EC profile measurements and it hasn't been applied to horizontal cross river measurements before. The variables measured were temperature corrected electrical conductivity, salinity, acoustic velocity and depth (Hämäläinen E. 2015). The measurements with the Cast Away CTD were conducted along the same cross-section as the flow rate measurements, which allowed correlation of EC profile with flow rate profile (Hämäläinen, E. 2015, Hämäläinen, M. 2015).

Long term environmental impacts of the acid mine drainage from former Rosia Montana goldmine on recipient river system were studied in May 2015. The field work was conducted by GTK and UBB in 26-31 of May 2015 and the risk assessment itself was done for the SUSMIN -project as a part of an environmental engineering course by the students from the

Savonia University of Applied Sciences. The assessment was based on 24 water samples, 36 EC measurements done with CastAway CTD and three flow rate measurements conducted during the field work (Savolainen et al. 2016). Along with the estimation of environmental impacts, one goal was to evaluate the usefulness and accuracy of the CastAway CTD in mine environment studies together with similar studies conducted at the Kittilä gold mine (see above). This was done by comparing the temperature compensated EC results from the device to EC results from the samples analysed at a laboratory.

7.5.2 Results and discussion

7.5.2.1 *Kittilä case*

The pH values of the discharge waters were observed to be close to neutral during the whole measurement period. This was expected as the mine regulates the pH before releasing it to the Seurujoki River (Agnico Eagle Finland Oy 2015). The redox-potential measured with YSI EXO2s were observed to be between 180–350 mV during the whole measurement period, with process waters having slightly higher values on average (Hämäläinen E. 2015). According to Evangelou (1998) this makes the waters mildly oxidizing. The dissolved oxygen, also monitored with the YSI EXO2s, varied between 3.6 mg/l and 12.4 mg/l. The DO values varied considerably more in process water compared to mine dewatering water. (Hämäläinen E. 2015).

Upstream from the mine the highest EC values occurred near the surface of the river. Horizontally across the river variation in the electrical conductivity was not significant. The natural electrical conductivity of the Seurujoki was between 54-102 µS/cm and the mine discharge increased the EC in downstream to a level of 180-230 µS/cm (Table 7.6). Vertically, the highest EC values were found near the river bottom. Moreover, the high conductivity correlates well with concentrations of different metals, magnesium, potassium, sodium, calcium, and sulphate (Figure 7.14). This can be explained by the heavier, dissolved solids settling to the bottom of the river after discharging from the treatment wetlands. (Hämäläinen E. 2015)

Table 7.6. Electrical conductivity of the mine discharge and EC values from Seurujoki up- and downstream from the discharge release sites. (Hämäläinen E. 2015)

Month	**Upstream from the discharge location (µS/cm)**	**Mine discharge (µS/cm)**	**Downstream from the discharge location (µS/cm)**
June	54	3894	181
July	86	1191	141
August	82	1580	230
September	102	856	116

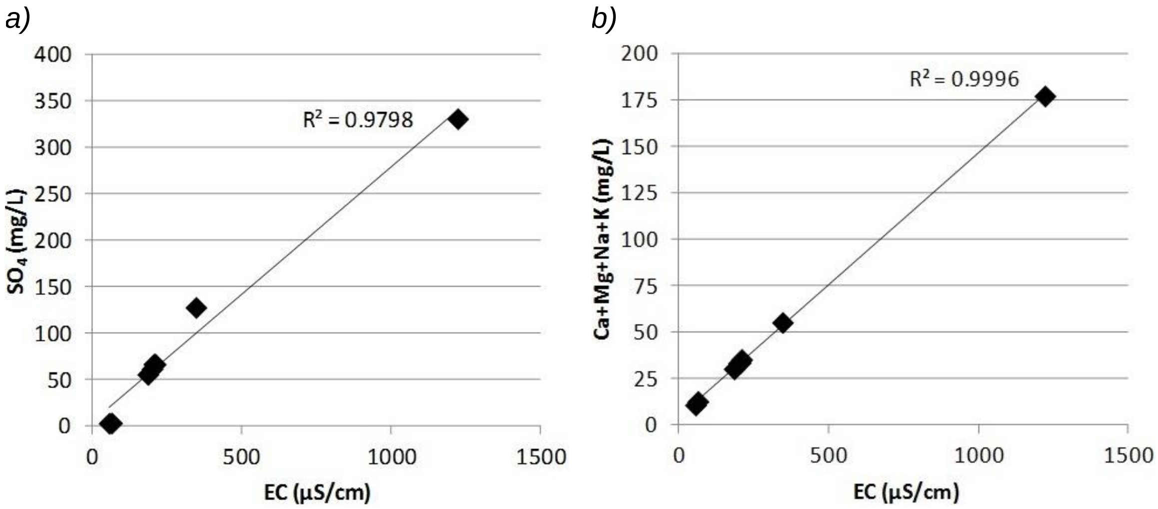

Figure 7.14. a) The correlation between SO4 and EC, b) The correlation between alkali and earth alkali metals and EC

The dilution and mixing of dewatering waters in the river is slow in comparison to process waters. It takes approximately 300 meters downstream from the process water discharge site for the EC to level out across the whole river (Figure 7.15). For dewatering waters this takes up to 9 kilometres. Of course the higher background values caused by the process water discharge might further hinder the dilution and mixing of the dewatering waters, but the most substantial reasons for the difference were observed to be *(1.)* the amount of water discharged, *(2.)* the differences in the river flow rates at the discharge sites and *(3.)* the different methods for discharging the waters:

1. The amount of discharged dewatering waters was approximately five times the amount of process waters. Even if the EC values of process waters are considerably higher in comparison to dewatering waters, the larger volumes of dewatering water pose a bigger impact on the river water quality.
2. Dewatering waters are being discharged into the river at places where the flow rate is naturally low (20% lower than at the process water discharge site). Lower river flow rates were observed to hinder the mixing and dilution of mine waters significantly. By discharging at a location where the river flow rate is naturally higher, the mixing and dilution could be enhanced.

At the process water discharge site the highest river flow rates occur at the mines side of the river which further increases the mixing of process waters. Thus, it is also important to consider the differences in the river flow across the horizontal profile of the stream.

3. Dewatering waters are discharged through multiple small ditches, while process waters are led through one channel. The dilution and mixing of dewatering waters could be enhanced if they were discharged through one clear channel as well. (Hämäläinen E. 2015, Hämäläinen M. 2015).

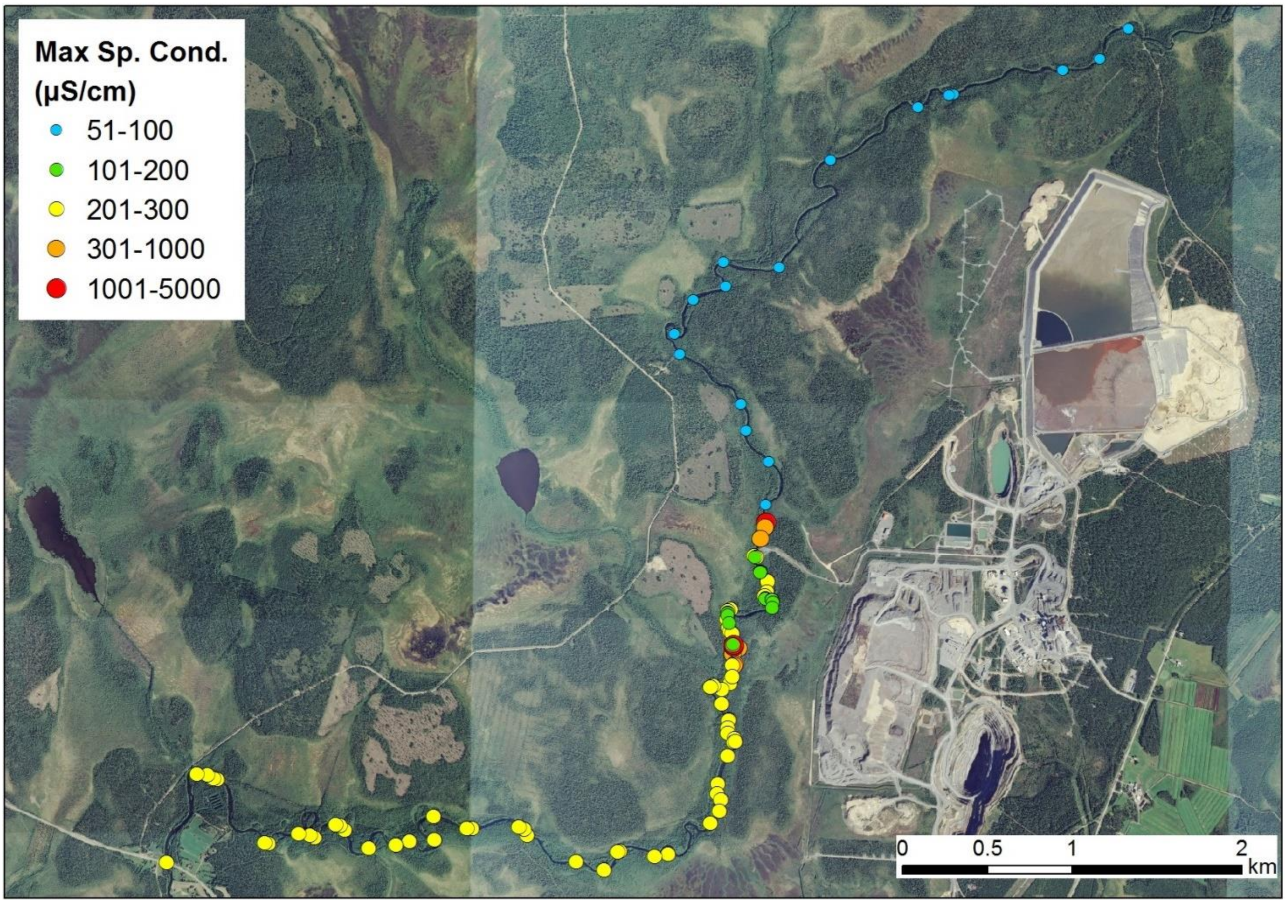

Figure 7.15. EC values across the River Seurujoki before and after the mine water discharge points. For the process waters it takes about 300 metres, and for the dewatering water up to 9 kilometers to mix and dilute close to natural background level.

Due to the low flow rates of the discharge waters, the plume of high EC values (originating from the mine discharge) stays on the mine's side of the river. Currently the mine takes the freshwater it needs from the same side and from the stretch between the two discharge sites. The freshwater quality at the mine could be improved if the mine would take the water it needed from the opposite side of the river. Also, the mining company monitors the river water quality only on the western side of the river. It would be advisable to monitor the water quality also on the mine's side (east side), due to the heterogeneity in the EC values. (Hämäläinen M. 2015).

The water flow of a river can be expected to increase downstream. This is due to the drainage basin of the river getting larger as the river progresses (Leopold 1953). At Seurujoki this is true only upstream from the process water discharge site but at the vicinity of the mine the claim is no longer valid even when the water intake and discharge of the mine are taken into account (Figure 7.16). This indicates that part of the water must enter a natural reservoir. This reservoir was observed to intake water in average at a rate of 0.44 m^3/s during September, which accounts for approximately 15% of the total flow of the river (Hämäläinen M. 2015).

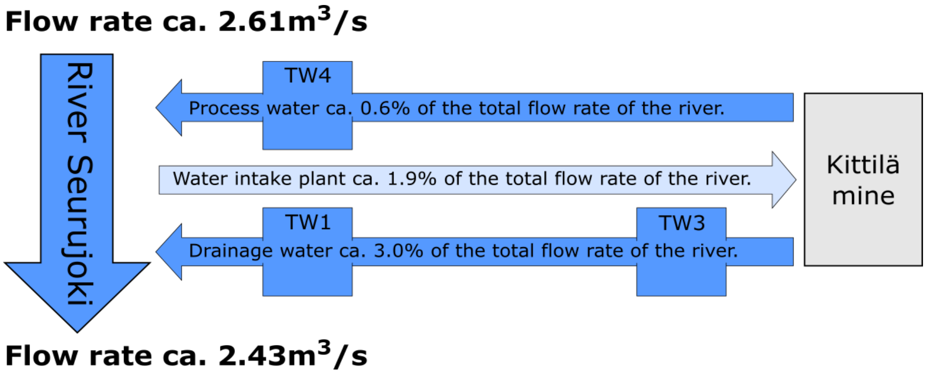

Figure 7.16. Water balance of the Kittilä mine. Total flow of the river Seurujoki decreases downstream from the mine, while the opposite is normally true. According to Hämäläinen M. (2015), this indicates an existence of a natural reservoir intaking approximately 15% of the total river flow. TW = Treatment wetland.

Measurements with RiverSurveyor M9 were found to be challenging to conduct at Seurujoki. The gradient of the river varies, the shape of the riverbed is un-uniform, the river is often very shallow and on some sites the river bottom is densely vegetated. Finding locations that filled at least the basic requirements for accurate measurements was hard and some of the measuring locations that were planned beforehand were deemed unsuitable and had to be abandoned or relocated. (Hämäläinen M. 2015).

The device was also observed to slightly exaggerate the flow rates. When comparing results from the M9 with results from Talvitiemukka fixed measurement station operated by the ELY –center, the results were 37% higher in August and 11% in September. On the other hand the flow rate results of M9 and the measurements done by the very accurate permanent ultrasound flow rate measuring station of the mine were similar, which adds some reassurance on the accuracy of M9. (Hämäläinen M. 2015).

The Cast Away CTD was found, along with normal EC measurements, to be technically applicable to horizontal measurements in a stream, as long as the orientation of the device is being considered. The axis of the device must be parallel to the stream so that water can freely flow through the flow-through cell of the device. The measurement should be conducted close to the river bottom, following the profile of the bottom. Water depth proved to be the limiting factor for the measurements. Parts of the river where the water level was less than 10 cm couldn't be measured due to the size of the device. Overall the device was noted to be very functional due to its small size, low weight and quick measurements. (Hämäläinen E. 2015).

The operation of the continuous measurement instruments proved to be problematic. The Oneset HOBO U24-001 loggers had to be taken out of the water in order to export the recorded data. For an unknown reason this caused inaccurate measurements after the device was submerged again and the data collected after 28.8.2014 had to be discarded. With the YSI EXO2's, the nitrate results differed from the laboratory results. The device wasn't designed to be used in mine water environments which might explain the inaccuracy with the nitrate results. (Hämäläinen E. 2015).

7.5.2.2 *Roșia Montană case*

In Figure 7.17, EC values measured with CastAway CTD are shown along with laboratory measured values. The laboratory samples indicate that high EC values originating from the mine are caused by a combination SO_4, different metals, alkaline earth metals and alkali metals (Figure 7.18). (Savolainen et al. 2016).

Considering human health, the most substantial contaminants at the site are lead and nickel. Additionally the concentrations of zinc and fluoride exceed the Canadian Water Quality

Guidelines for the Protection of Aquatic Life (CCME 1999) and might pose a risk to aquatic organisms in River Abrud and near the river confluence. However, the concentrations are elevated also in river Aries upstream, indicating high natural background values. Upstream of the River Abrud, all contaminants have concentrations above 1000 µg/l. After the relatively small River Abrud (0.81 m^3/s) mixes with the considerably larger River Aries (5.49 m^3/s), concentrations of all contaminants quickly dilute to levels below 100 µg/l. The quick dilution is also visible in the EC measurements (Figure 7.17) (Savolainen et al. 2016).

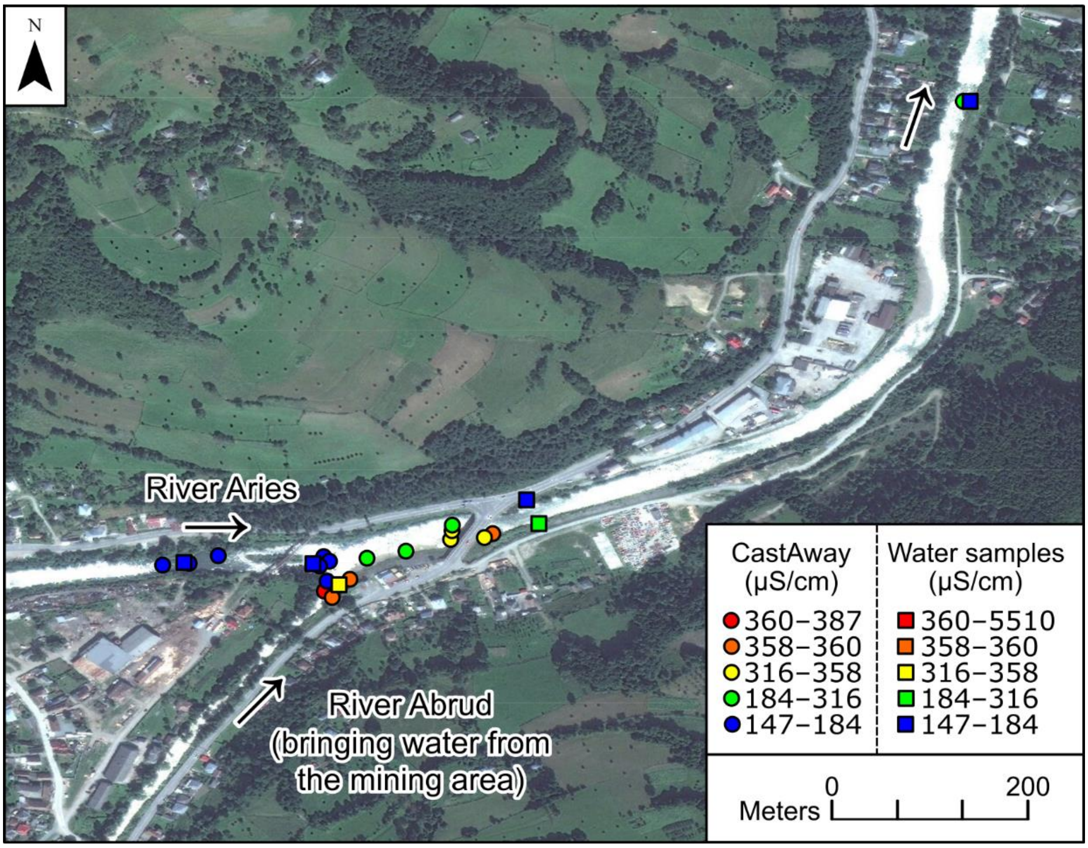

Figure 7.17. Electrical conductivity measurements and water sample locations near the confluence of Aries and Abrud Rivers.

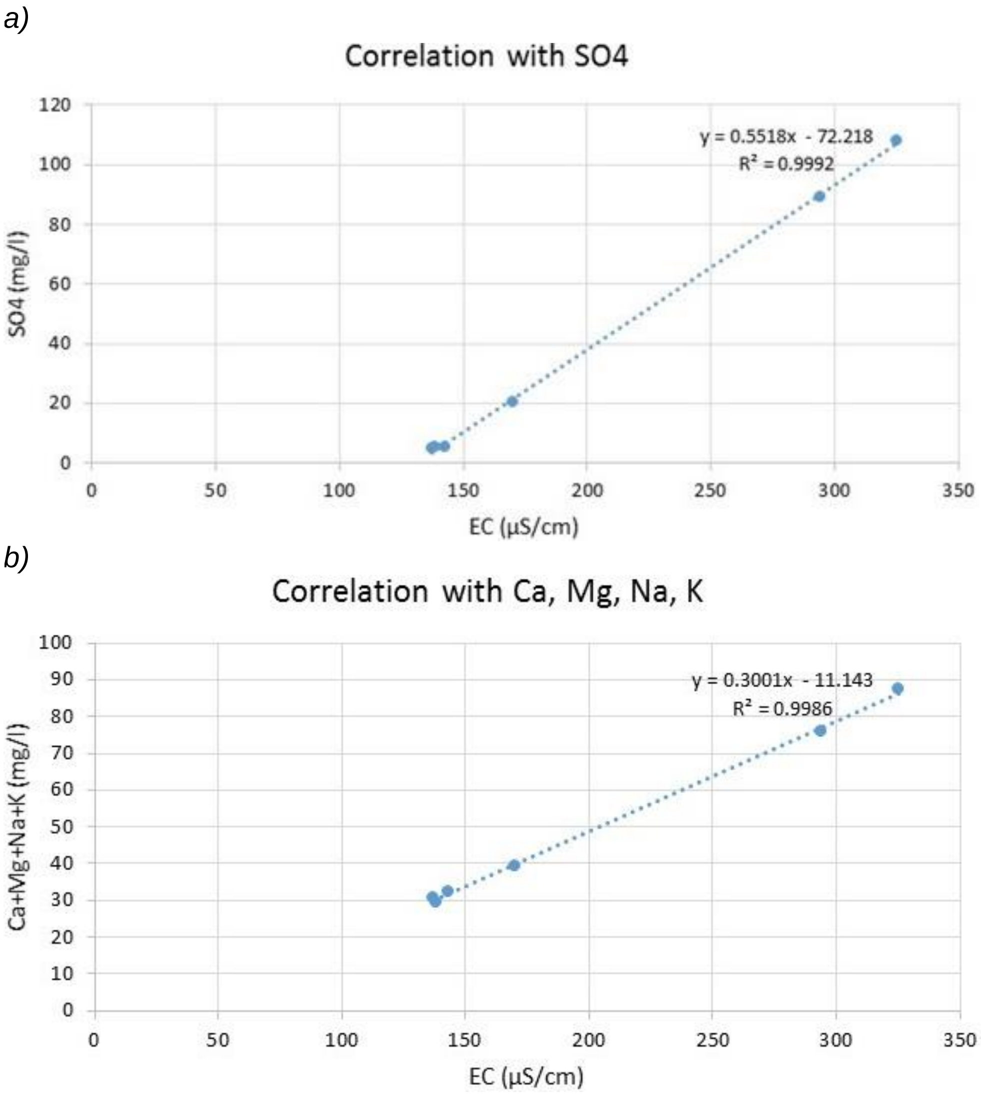

Figure 7.18. a) The correlation between SO4 and EC, b) The correlation between alkali and earth alkali metals and EC in Aries and Abrud Rivers

A deviation was observed when comparing EC results from the CastAway CTD with the laboratory results. The deviation varied between 7.8 – 22.2%, with CastAway showing higher values than the lab results. The deviation was also observed to non-linearly increase with the EC values. Reasons for the deviation are unknown, but small differences in sampling and measurement time, location and depth might explain some of the variation. The samples and CastAway measurements were conducted simultaneously only on six locations, making the comparison of values also fairly un-comprehensive. (Savolainen et al. 2016)

7.6 Environmental risk assessment practices and applications for gold mines in EU

7.6.1 Materials and methods

The aim of the ecological research in Kittilä mine was to assess the usability of ecological risk assessment for improving water management strategies in gold mining.The ecological risk assessment was carried out in order to evaluate the possible ecological impacts of the mine discharge waters on the receiving rivers. The study also evaluated the usability of the risk assessment in predicting the possible impacts of the upcoming mine expansion on the rivers. The hypothesis was that the results of ecological risk assessment could be used by environmental authorities in setting permit regulations, and on the other hand by the mining companies in planning and improving water management (Malinen 2016).

The data applied in this study included the already existing monitoring data obtained from the Agnico Eagle Finland Oy mining company (AEF) and data gained through sampling in SUSMIN -project in July 2015. The existing data comprised the annual environmental reports of water discharge and benthic fauna observation reporting done approximately every two years by various consult companies between years 2006-2014 (Lapin Vesitutkimus Oy 2007, Pöyry 2008, 2009, 2011, 2012 and 2013, WSP Environmental 2010 and Ramboll 2014 and 2015). All together the environmental sampling conducted for this study included 15 water, 10 benthic fauna and 9 sediment samples that were taken from Seurujoki River, upstream and downstream from the mine site, and its recipient Loukinen River. To be comparable with already existing data, the samples collected for the SUSMIN -project were located as close as possible to the previous monitoring sites of the mining company. However, since the river basin is mainly stony and fine sediments exist only locally, the sediment and benthos sampling points were located where sediment was available and thus there might be slight variation in the exact sampling sites. Figure 7.19 shows water and benthos sampling points from the water monitoring of AEF and the sampling done by GTK due to changing location of the sedimentation (Malinen 2016).

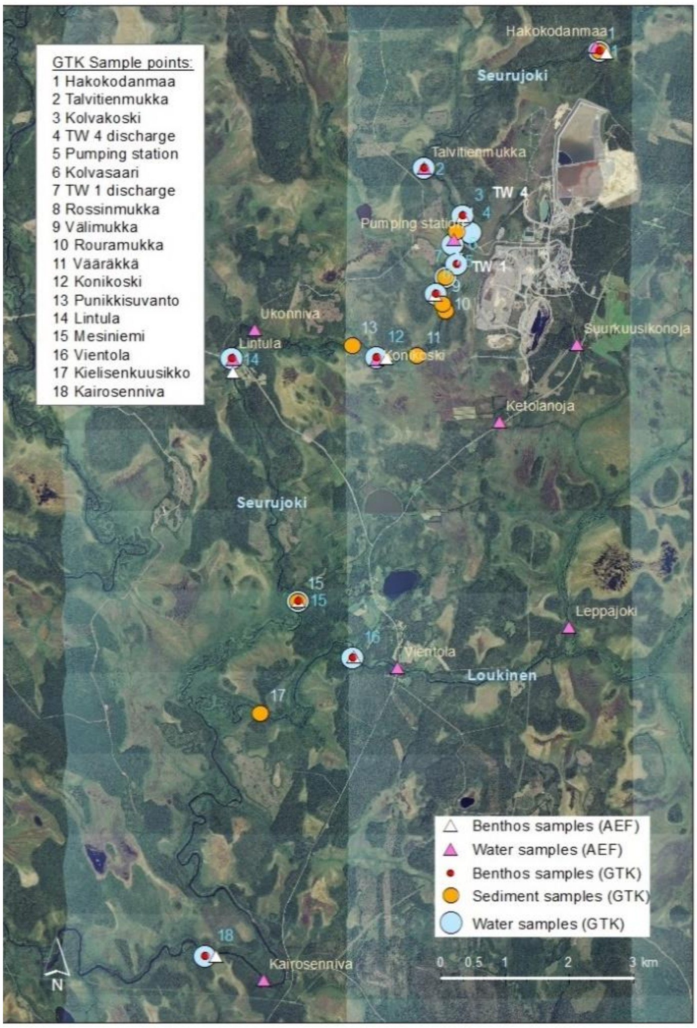

Figure 7.19. The benthos, water and sediment sampling locations in Seurujoki and Loukinen Rivers. GTK refers to the samples taken in this study, AEF refers to the samples taken by the mining company for surveillance of which the data was used as a part of the ecolological risk assessment in this study.

The benthic fauna sampling was carried out according to a guide by Meissner et al. (2013), which applies the standard SFS 5077. The samples were collected from riffles in Seurujoki River. Since most of the benthos species mature during summer months, leaving the river basin, the sampling date was not the best for collecting benthos samples. Usually the sampling is done during spring or autumn to have maximum diversity of species. Four samples were collected from each sampling point with a net. To have the total diversity for the whole width of the river present, the samples from one sampling point were taken as varying river bed type as possible (*e.g.* varying size of rocks, sediment type), and the results of all four samples are presented combined. The benthic fauna samples were analysed by Probenthos Oy laboratory.

The sediment and water samples were analysed in an accredited laboratory, Labtium Oy. The bioavailable concentrations of elements in sediment samples were analysed using acetic acid extraction according to Heikkinen and Räisänen (2008) method for sediment samples. The total concentrations were analysed using nitric acid digestion in microwave oven according to Niskavaara (1995). The concentrations of dissolved metal and metalloid in water samples were analysed using ICP-MS or ICP-OES – method and anions by using IC-technique, according to standard SFS-EN-ISO 10304. Physico-chemical parameters (temperature, dissolved oxygen, pH, redox potential and electrical conductivity) were measured at field with YSI Professional Plus meter (YSI Incorporated 2009) in pursuance of the water sampling, alongside with alkalinity measurement by titration (Malinen 2016).

The ecological risk assessment of Kittilä gold mine focused on selected potentially harmful substances elevated in mine waters. The selection was based on the previous studies and the monitoring data from the mining company, which indicated higher concentrations of SO4, Cl, NO_2, NO_3, Ni, As, Sb, Fe and Al in Seurujoki and Loukinen rivers. For the ecological risk assessment the elemental concentrations in river waters were compared to national and international guidelines and Predicted No Effect Concentrations (PNECs), which are derived from the Species Sensitivity Distributions (SSDs) drawn according to data from U.S. EPA Ecotox database (U.S. EPA 2015). To be able to create a representative SSDs for elements of interest in Kittilä mine environment, the chemical speciation of the elements was needed. The speciation in river water samples was modelled with PhreeqC modelling software (Parkhurst and Appelo 2015). For benthos the study used the EPT and Shannon-Wiener diversity indices which both describe the species richness and evenness (Shannon and Weaver 1949 and Lenat 1988). The EPT index is based on the presumption that higher water quality means higher species richness, reflected by a higher value of the index. In EPT index only certain fly species are taken into account since they are known to be sensitive for contamination. Shannon-Wiener index is based on the proportional abundance of species and assess the current conditions. The reference Shannon-Wiener's diversity index value for Northern boreal geographic region is 2.65 (Swedish EPA 2000).

In **Rosia Montana** area, 16 sampling sites were chosen for the ecological risk assessment on Abrud River, upstream and downstream the confluence with tributaries polluted with mine waters, and on tributaries that flow from the mining area. The samples were collected during spring, summer and autumn campaigns (Figure 7.20). Epilithic diatom samples were collected and processed following European standards EN 13946/2003 and EN 14407/2004. Epilithon was sampled on submerged stones in the flow, euphotic zone of each stream, using a toothbrush, and preserved in 4% v/v formaldehyde. Clean frustule suspensions were obtained by oxidizing organic matter with hot hydrogen peroxide 30% v/v. Carbonate inclusions were removed adding a few drops of hydrochloric acid. Permanent microscopic slides were mounted using a refractive resin. Species identification was carried out according to usual taxonomic references, using an optical microscope (Hofmann et al. 2011).

Biofilms have been widely used for bio-monitoring in rivers due to their rapid response to environmental changes which makes them suitable as early warning systems for toxicity evaluation (Sabater et al. 2007). Biofilms constitute an integrative indicator of metal exposure occurring over a period of days or weeks (Ancion et al. 2010), supporting their use as metal pollution indicators (Mages et al. 2004 and Ancion et al. 2010). However, relationships between metal toxicity and biofilm responses may differ depending on metal dose and exposure time.

Diatom community often represents the major autotrophic proportion of biofilms (Navarro et al. 2002, McClellan et al. 2008, Morin et al. 2010). They are the most common and diverse group of algae in many rivers and streams and thus are important components of these ecosystems (Round 1981). As the diatom communities of a river ecosystem integrate the variability of the habitat, species may present certain combinations of adaptations related to survival; biological attributes may reflect environmental conditions (Townsend 1989). In lotic habitats, diatom communities' structure and dynamics are influenced by a number of external factors as light, salinity, temperature, concentration of inorganic nutrients, dissolved oxygen, and the nature of the substrate. Some diatoms can tolerate a small range of environmental conditions, and are used as indicators of physico-chemical characteristics of water (Pârvu, 2003). In this context, the main objective of our study was to observe the effects caused by the environmental conditions and by the high concentration of heavy metals on benthic diatom communities.

The values of the pH showed that most waters in the study area had an acidic character that affected the diatom communities on Corna, Săliște, and Roșia streams and Abrud River, downstream the discharges of mine waters. At the same time, there were sampling points with pH values that indicated a neutral character of the waters. The values of the conductivity of water and of the EC suggested a high content of chemical elements in most of the sampling sites. It was observed that this is one of the reasons for the presence of the teratological individuals on Abrud River and even for disappearance of the diatom communities in some sampling points situated on Abrud River, Corna, Săliște and Roșia streams. It could be also seen that in spring and autumn waters contained more dissolved oxygen, due to the lower temperature. Meanwhile, O_2 concentration was determined by the features of the talweg of the water courses and by the presence of mine water in the study area. Oxygen concentrations measured in the collection points indicated the presence of water falling in all classes of surface water quality, from very good to poor (RMO 161/2006). It was observed that the high concentration of these heavy metals had a big influence on the appereance of abnormal individuals on Abrud River. In addition, the high concentration of Ni, Fe and SO_4^{2-} had led to the disappareance of the algal assemblages in the sampling sites that were mencioned before. On the contrary, the relative contribution of other parameters such as O_2 and Pb concentrations or water temperature was negligible. Also, it was observed that the concentration of heavy metals increased considerably in autumn in comparison with the other seasons. This variation of the physico-chemical characteristics could be explained by the combination of several factors, such as dilution after rainfall episodes.

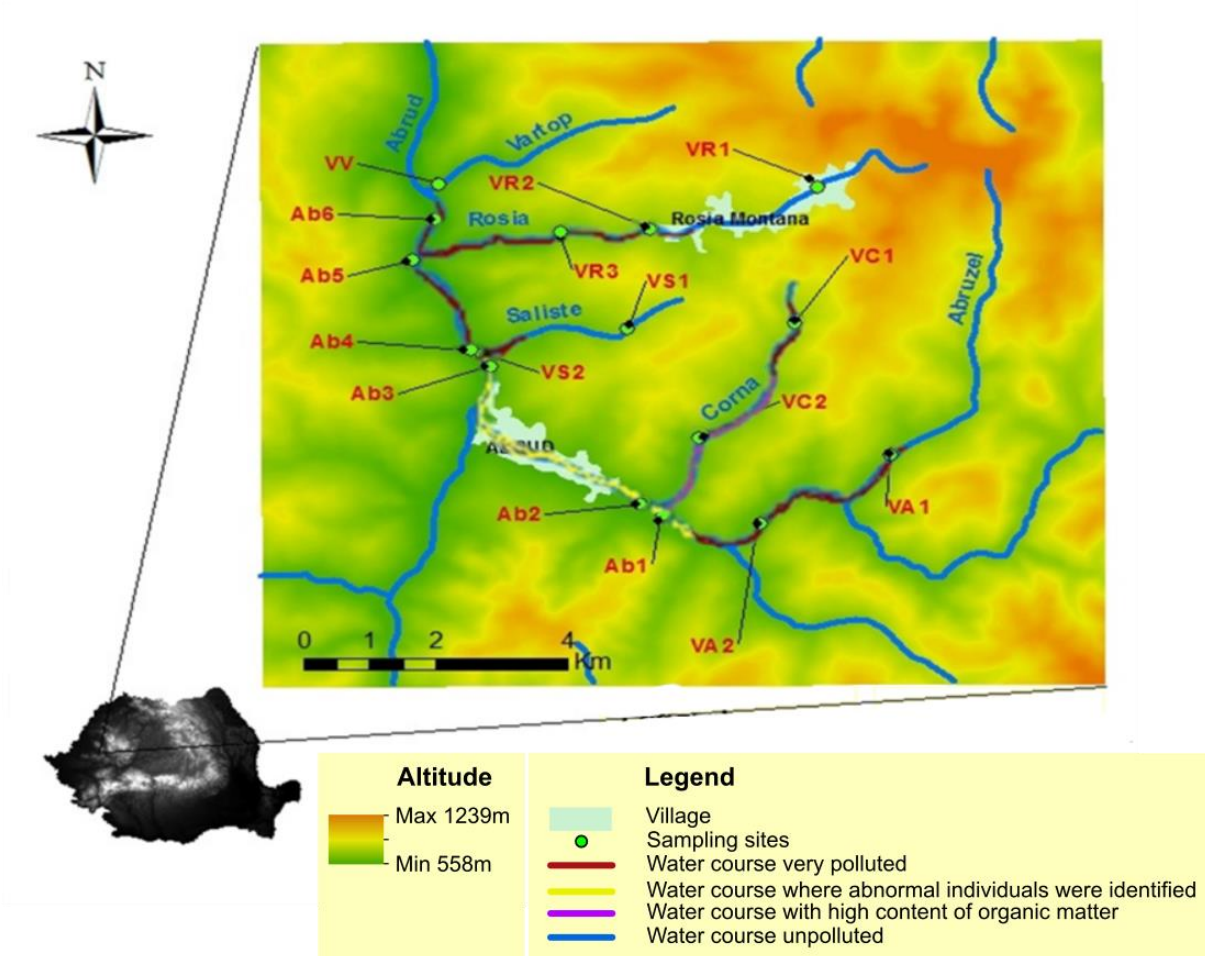

Figure 7.20. Map of the Rosia Montana ecological risks study area with the diatom community sampling points

Many species that presented abnormal individuals and a seasonal dynamic of the benthic diatom communities were observed in Abrud River, not only regarding the number of species or their relative abundance, but also regarding the type of teratology. In some seasons we found only individuals that presented deformed valve outlines, but in other seasons we found also individuals that presented other types of deformed valves, modification of the raphe canal system (displaced fibulae) or abnormal central area location and irregular striation. The presence of teratological individuals indicates that the diatom communities were strongly affected by acid mine waters (Olenici et al. 2017). The diatom taxa that presented a high abundance of deformed individuals were *Achnanthidium minutissimum* (Figure 7.21) and *Achnanthidium macrocephalum*. The maximal abundance of abnormal individuals of both species of *Achnanthidium* was identified in summer, where the concentrations of the heavy metals and the ions are lower in comparison with other sampling points. Another taxon that was very affected by the presence of AMD in the study area was *Fragilaria rumpens* (Kützing) (Carlson 1913) (Figure 7.22). More than 90% of the identified valves were deformed. Teratological individuals of *Fragilaria vaucheriae* (Kützing) (Petersen 1938), *Diatoma moniliformis* Kützing ssp. moniliformis, *Fragilaria recapitellata* (Lange-Bertalot & Metzeltin 2009) and *Nitzschia linearis* (Agardh) (Smith 1853), were also observed, with low relative abundances (Olenici et al. 2017).

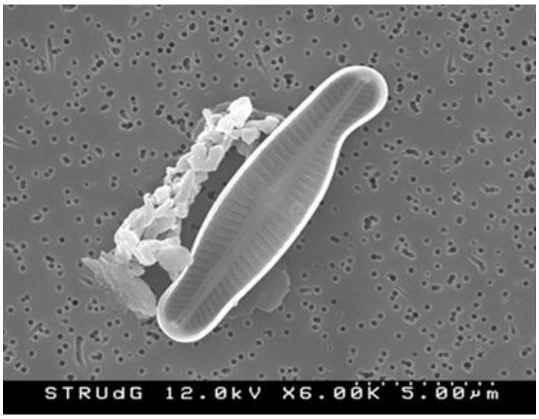

Figure 7.21. Achnanthidium minutissimum

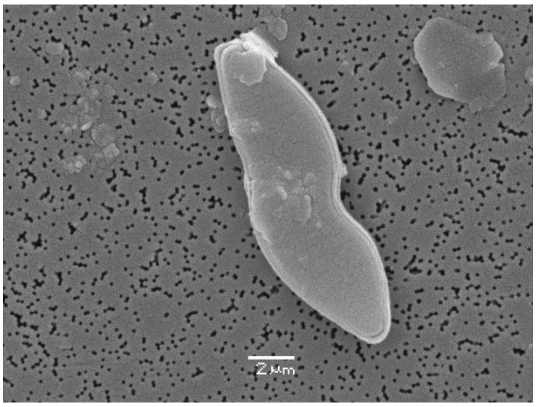

Figure 7.22. Fragilaria rumpens

The high values of conductivity, sulphates and heavy metal concentrations affected the diatom communities, having as a result a very low relative abundance, the presence of the teratological individuals and even the disappearance of the algal communities. Additionaly, in 3 sampling points on Vârtop, Roșia and Săliște streams, upstream the mine waters discharge to the watercourses, high diversity of the diatom communities was observed. As the values of the physico-chemical parameters were normal, the influence of the AMD in the mining affected water on the algal assemblages was confirmed. As mentioned before, the number of diatom species exhibited significant variation among sampling sites, and the most important factors that control the characteristics of the algal assemblages are the Zn and Cu concentrations and the high conductivity. It is possible that other unmeasured factors had affected the diatom communities in the study area (Olenici et al. 2017). For the samples where teratological forms were identified, the geometric morphometry was used to assess the degree of valve deformation in the studied *Achnanthidium* populations. A total of 543 individuals were photographed using an Olympus BX60 optic microscope equipped with an Optikam B9 digital camera and OptikView7 software: 348 *A. macrocephalum* and 195 *A. minutissimum* individuals both normal and teratologic. Valve morphology was modelled as a geometric configuration of pseudolandmarks or reliably identifiable points in the investigated set of specimens (Olenici et al. 2017). Approximately 40 pseudolandmarks were placed at regularly-spaced points along the valve outline and digitized using CLIC software (Dujardin et al. 2010). The Cartesian coordinates of the pseudolandmarks were aligned (translated, rotated and scaled) by the Procrustes generalized orthogonal least-squared superimposition procedure (Rohlf and Slice 1990). Resulting data were subsequently analysed by means of multivariate analysis to test for significant differences between pre-established groups, using a non-metric multidimensional scaling (NMDS) analysis in Past v. 2.17 software (Hammer et al. 2001). In order to visualize the size and shape of the scatterplot for each predefined group, confidence ellipses were added in the resulting graph (Figure 7.23 and Figure 7.24).

In order to test the null hypothesis of no differences in shape between these populations, a nonmetric analysis of similarity (ANOSIM) was performed between the Cartesian coordinates of resulting groups in the NMDS using the Euclidean distance measure (Figure 7.23 and Figure 7.24).

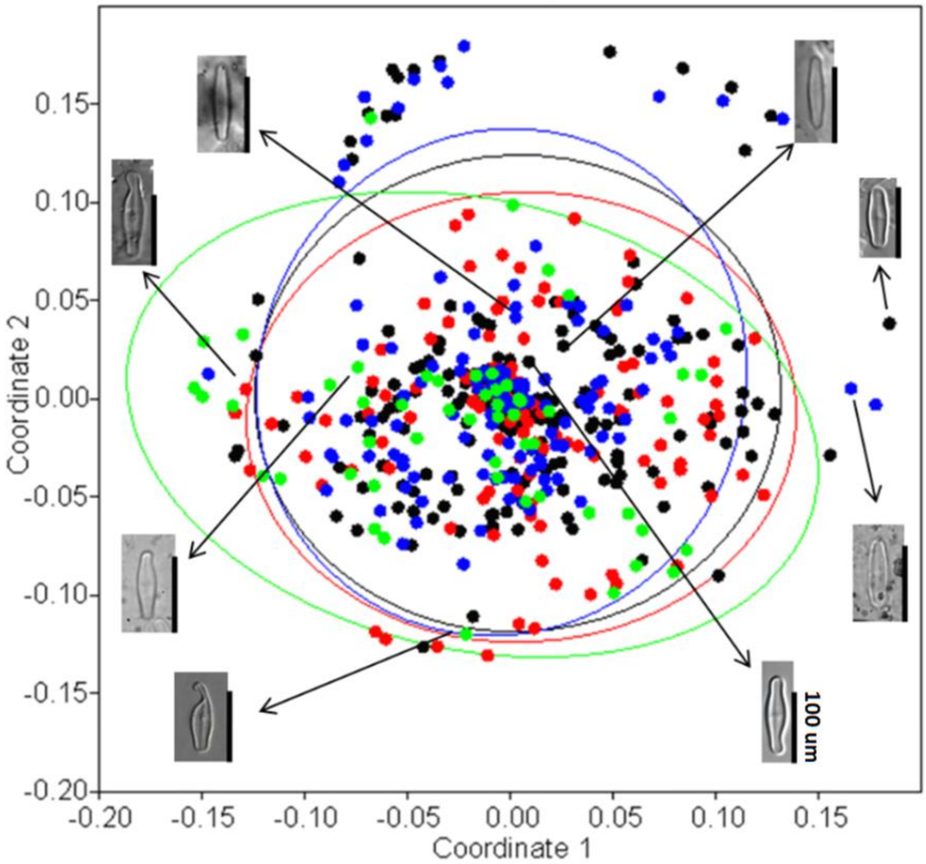

Figure 7.23. Nonparametric multidimensional scaling plot of normalized coordinates for the morphological pseudolandmarks digitized on LM images of selected populations of Achnanthidium macrocephalum and A. minutissimum (black = A. macrocephalum, red = A. macrocephalum teratologic, blue = A. minutissimum, green = A. minutissimum teratologic).

In order to assess the major environmental drivers causing valve deformations, a two-block partial least squares analysis was performed using the outline coordinates and the environmental data matrices as inputs. As described by Rohlf & Corti (2000), this method is used to determine the combinations of variables in the two matrices that account for most of the covariation present between the variable sets. The method is based on the singular value decomposition of the correlation matrix between the variable matrices which are treated symmetrically. It can be noticed that the conductivity and the concentration of Zn and Cu were the main factors that affect diatom communities and cause the appearance of teratological forms in the study area (Olenici et al. 2017).

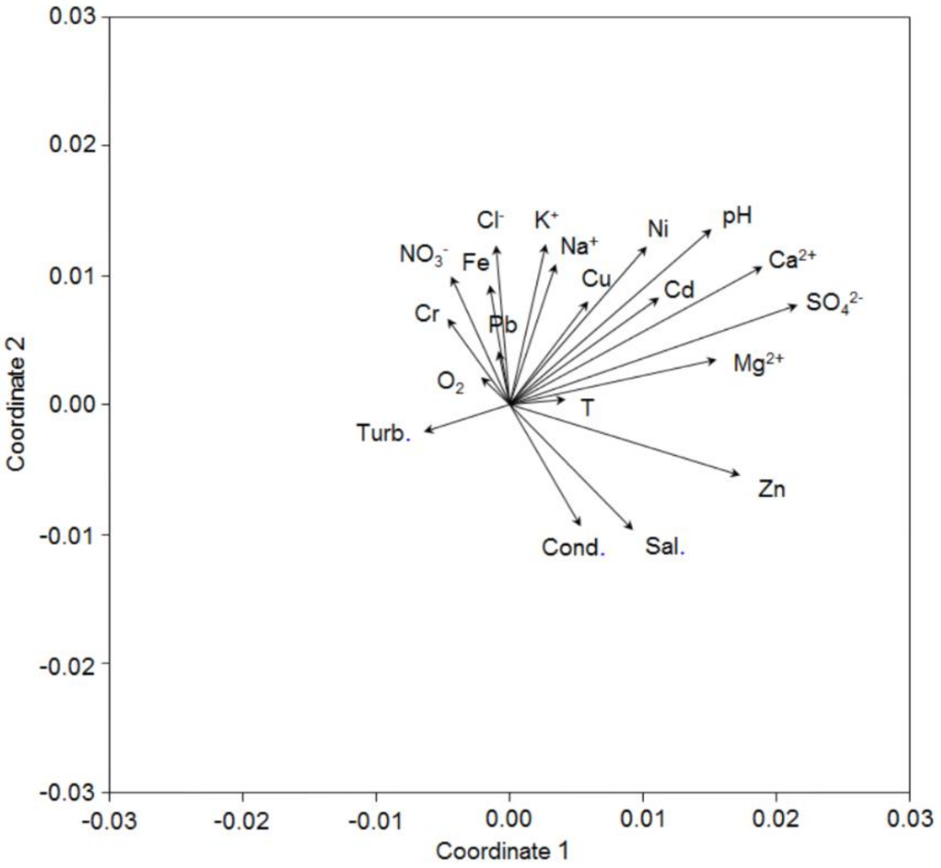

Figure 7.24. NMDS plot of environmental variables from analysed sampling sites

At **Zlatna site**, biological monitoring (micro-organisms and invertebrates) was seasonally conducted (May, August, October and December) to assess the risks of the mining pollution on water habitat. Water sample sources considered for monitoring corresponds to the water sample sources presented in the paragraph 7.4.1., with the exception of sources A12, A17, A28 which were not taken into consideration for this study. The study site and the sample locations are presented in Figure 7.4 in paragraph 7.3.3.

The presence of microbes and their quantitative evaluation represent an indirect way to assess the risk of pollution by exploring the life-support in mine, groundwaters and surface waters from the mining areas. Besides these, aquatic invertebrates that spend most of their life cycle in water are extremely important in maintaining the health of aquatic ecosystems and also represent a very useful instrument for rapidly assessing the pollutants' risk.

Two types of sanitation tests were used (RIDA®COUNT, R-BIOPHARM AG, Germany) for monitoring the microbial concentration in mine, groundwater and surface waters: RIDA®COUNT TOTAL (TC) for quantitative determination of total aerobic bacteria, and RIDA®COUNT YEAST&MOLD (YM) for quantitative determination of yeast and mold. RIDA®COUNT ready-to-use compact dry plates represent a simple and safe method for determination and quantification of different microorganisms from the environment. The test is based on specific chromogenic substrates which are converted into colored products by the metabolism of microorganisms. In microbial monitoring, 1 ml water was directly applied on the plates, right after sampling, transforming the dry medium into a nutrient gel. After inoculation the TC plates were placed in a portable incubator at 36 °C for 48 hours, and the YM plates were stored at 25-30 °C for 120 hours in dark conditions. The red colonies of TC, the blue colonies of yeast and the specific colored colonies of molds were counted in order to determine the viable microbial concentration (CFU/ml) in mine drainages, ground waters and surface waters.

Water invertebrates were sampled by qualitative filtration of the water sources in August, October and December of 2015. Fauna were collected from a 100 µm mesh-sized hand net. Animals were fixed in 70% ethanol, counted and sorted to different taxonomic levels, using a stereomicroscope Optika SZR-10.

7.6.2 Results and discussion

7.6.2.1 *Kittilä case*

The PNEC values are presented in Table 7.7, excluding nitrogen and aluminium which could not be drawn due to lack of data and solely the existing guideline concentrations are used as PNECs. Moreover, some of the guideline and PNEC values differ a lot and there were not enough data for reliable SSD and thus the SSD derived PNEC values should be considered as general toxicity threshold values, not site-specific guidelines. Figure 7.25 shows the water chemistry and Table 7.7 the maximum concentrations in sediments around Kittilä mine. (Malinen 2016).

According to our results, SO_4, Sb and Ni are the most significant elements elevating the potential of ecological risk in recipient aquatic systems. However, although some higher contaminant concentrations have been occasionally detected in 2006–2015 in Seurujoki River water, on average only the concentration of Sb constantly exceeds the set guideline values (Figure 7.25) and the overall ecological state of the Seurujoki and Loukinen Rivers was good. Also, the concentrations in sediments are mostly within the common concentrations range of Finnish stream sediments (Lahermo et al. 1996) and exceed some of the set guideline values only locally (Table 7.7). The exceeding concentrations tend to focus near mine water discharge points, but they were observed also in background sampling points. Also, the exceeding contaminants differ between these points. For instance, As concentrations are the highest in background point and do not dilute as well as other concentrations towards downstream, which is most likely due to natural geogenic background derived from arsenopyrite rich bedrock and tills. In contrast, on average the NO2 and NO3 concentrations are above 10 mg/l in treatment wetland discharge points, which might pose a risk to aquatic life (CCME 2014). However, as already mentioned in previous chapter 7.5.2.1., the dilution in the Seurujoki and Loukinen Rivers seem to be quite efficient and the fast decrease of NO2 and NO3 concentrations in the river might imply that the nitrogen is taken up by the aquatic organisms. (Malinen 2016)

Table 7.7. The maximum of total and bioavailable concentrations in sample points for selected elements. Also the common concentrations in Finnish stream sediments and Guideline values for ecological risk assessment if available.

Contaminant	Common total concentration (90%) in Finnish stream sediments (mg/kg)	Guideline value (mg/kg), if available	Maximum concentration of sample points, total concentration (mg/kg)	Maximum concentration of sample points, bioavailable concentration (mg/kg)
Arsenic	0.8–15	10–30 (Swedish EPA, class 3)	308	15.7
Antimony	0.009–0.13	25 (WNR, probable effects)	35.6	14.8
Iron	10 000-75 000		117 000	16 900
Nickel	6–40	15–50 (Swedish EPA, class 3)	25.3	5.3
Aluminum	7 000–30 000		17 100	553
Calcium	3 000–10 000		8 910	7 450
Magnesium	1 400–9 000		13 100	11 300
Sodium	130–550		1 210	1 140
Potassium	500–7 000		1 180	804

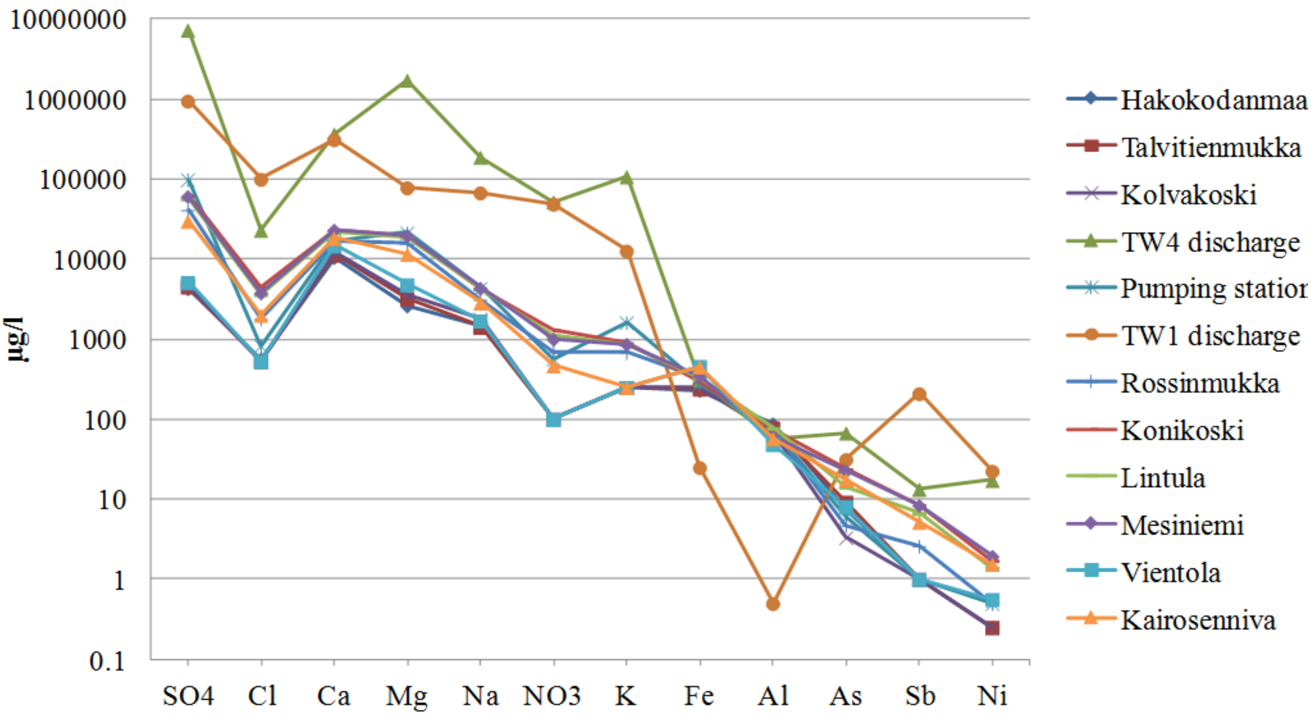

Figure 7.25. The concentrations of different elements in different sample points (in June 2015).

The benthos results are slightly contradictory since the high ratio of the sensitive EPT species in the benthic community would indicate a very good state of the rivers (Figure 7.26) (Hickey and Clements 1998), but on the other hand locally distributed decrease in benthos diversity in water and sediment would indicate a decline in the rivers' ecological state (Figure 7.26 and Figure 7.27) (Swedish EPA 2000). As with the concentrations, the decline in diversity is seen not only at the points near mine water discharge, but also in Seurujoki River upstream, which could indicate an increased load on the whole river, *e.g.* due to forestry. However, the lower EPT index in background point and higher in mine water discharge points could also indicate the natural nutrient level of the river being low, and thus the mine waters would actually increase the nutrient load to the river. Hence, the natural load of Al, Ni, Fe, and As might have altered the community by favouring the more tolerant individuals to survive. (Malinen 2016)

The upcoming mine expansion, having a new environmental permit with a limit set also for SO_4 concentration, could improve the quality of the discharged waters. However, based on the scenarios of TW retention capacities and dilution rates calculated for recipient river systems in this study, the safe guideline-based levels of mine discharge for Sb would be lower than the proposed permit limits. Also, based on water quality guidelines and calculated PNECs, the proposed future environmental permit limits would allow higher discharge concentrations of As, Sb and SO_4, than would be safe towards the aquatic ecosystem. However, the interpretation of this study and the proposed permit limits are based on the results of a single year (2014) and implementing site-specific guideline concentrations would require more data (*e.g.* on toxicity) to model such a complex system. (Malinen 2016)

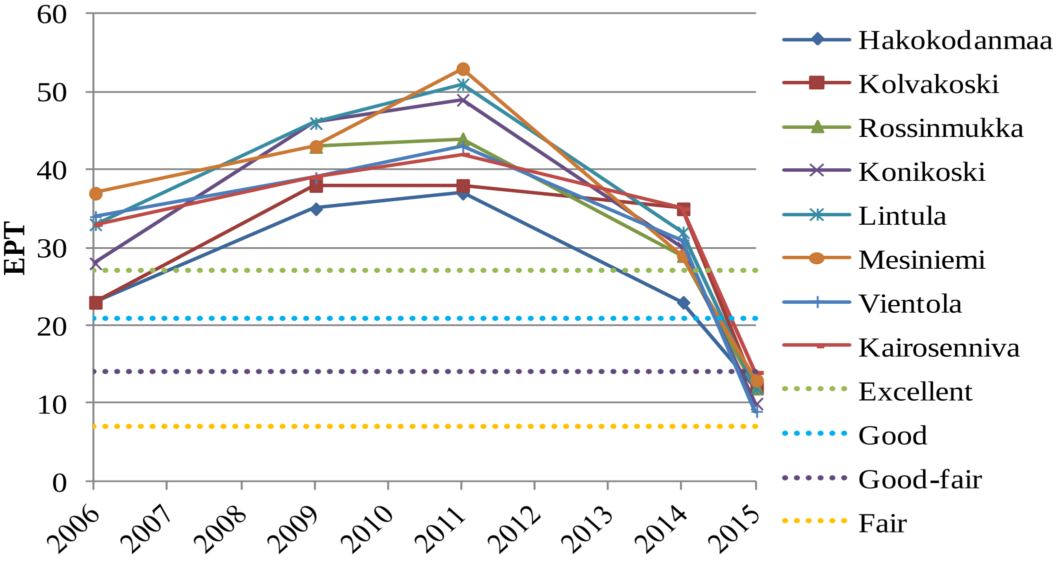

Figure 7.26. The EPT index value at different sample points in 2006–2015. The 2015 sampling was done during June, while others in September.

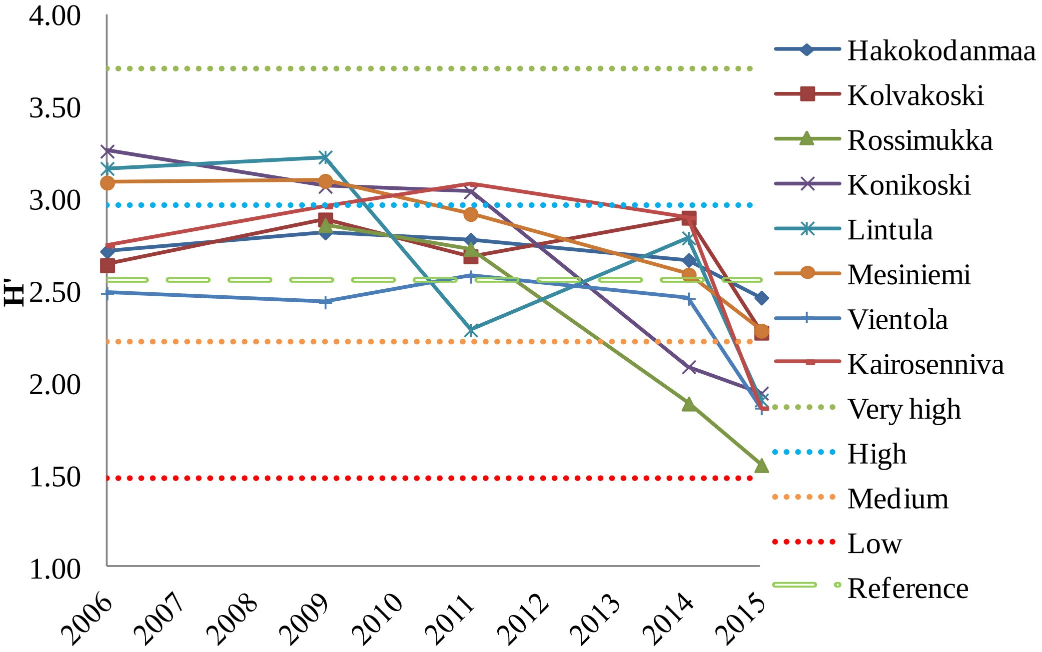

Figure 7.27. The Shannon-Wiener biodiversity index value at different sample points in 2006–2015. The 2015 sampling was done during June and others in September. The interpretation is according to Swedish guidelines (Swedish EPA 2000).

7.6.2.2 *Roșia Montană case*

Evidence of heavy-metal toxicity on freshwater diatom communities from previous studies suggests that morphological traits may be informative for investigating the relationship between metal pollution and organism response. In this regard, it has been widely reported that diatoms respond to chemical stress not only at the community level through shifts in dominant taxa and diversity patterns (structural endpoints), but also at the individual level, with increasing occurrence of frustule deformities or decrease in cell size of the community or within specific taxa (morphological endpoints) (Morin et al. 2007 and Falasco et al. 2009). Cell deformities affecting general cell shape and/or valve ornamentations have been observed under metal stress, and are suspected to be an indicator of such pollution (Dickman 1998; Torres et al. 2000 and Gómez & Licursi 2003). Many environmental stresses seem to be responsible for teratological diatom cell development and the recording of abnormal cells in a diatom population or community can give both a temporal and quantitative indication of the stress (Falasco et al. 2009). Several studies report morphological abnormalities in diatoms under metal stress (Falasco et al. 2009) and therefore there is good opportunity of using the frequency of deformed diatom frustules as a parameter for biomonitoring of metal contaminants (Morin et al. 2012). The presence of abnormal diatom individuals in our study area, confirmed the results of these previous studies. According to Cattaneo et al. (2004) and Smol and Carraballo (2008), diatom morphological alterations could prove to be an useful tool for monitoring environmental changes, but their potential remains largely unexplored (Cantonati et al. 2014). A correspondence between a certain environmental stress and a defined morphological alteration such as outline deformations has not been demonstrated yet (Falasco et al. 2009).

Qualitatively, in our study area, the number of diatom species exhibited significant variation among sampling sites, also suggesting seasonal dynamics. For instance, in some sampling sites, algal assemblages were absent, as diatom communities were strongly affected by acid mine waters, released from old mining workings and waste rock dumps. This fact could be also attributed to the large amount of suspended matter recorded in the main river and in some tributaries, displaying an orange-brownish color.

Trophicity of the water is determined by the concentration of nutrients and electrolytes. Depending on the preferences of each species of diatoms to this level, this may indicate (tolerate) oligotrophic, oligo-mesotrophic, mesotrophic, meso-eutrophic, eutrophic and hypertrophic waters, this signifying a level of nutrients from low, moderate to high and very high (van Dam et al. 1994). In the study area we identified dominant species that indicate waters of a trophicity level form mesotrophic to hypertrophic.

Regarding saprobity conditions in the studied communities, the saprobity system developed by Sladeček (1973) was used. Saprobity spectrum in this system is composed of 8 categories which correspond to four quality classes and each taxon is characterized by a value indicator for each degree of saprobity (Table 7.8, Figure 7.28). Based on this system, the Saprobic Index can be calculated, that indicates also the quality classes of waters occurring in the study area. Thus, in particular the dominating species identified in the sampling points may indicate a certain level of saprobity of the waters.

Most of the dominant species in the study area indicate a β-mezosaprobic level of the waters. But, some dominant taxa from Abrud River and its tributaries have been observed as well, suggesting critical saprobic levels This indicates a large amount of organic matter, originating from untreated urban sewage, that together with the high concentrations of NO_3^-, draw attention to the low quality of water.

Table 7.8. Saprobity categories system developed by Sladecek (1973)

Nr.	Saprobity level	Quality class
1.	xenosaprobic	I
2.	oligosaprobic	I
3.	oligo-/β-mezosaprobic	I-II
4.	β-mezosaprobic	II
5.	β-α-mezosaprobic	II-III
6.	α-mezosaprobic	III
7.	α-mezo-/polysaprobic	III-IV
8.	polysaprobic	IV

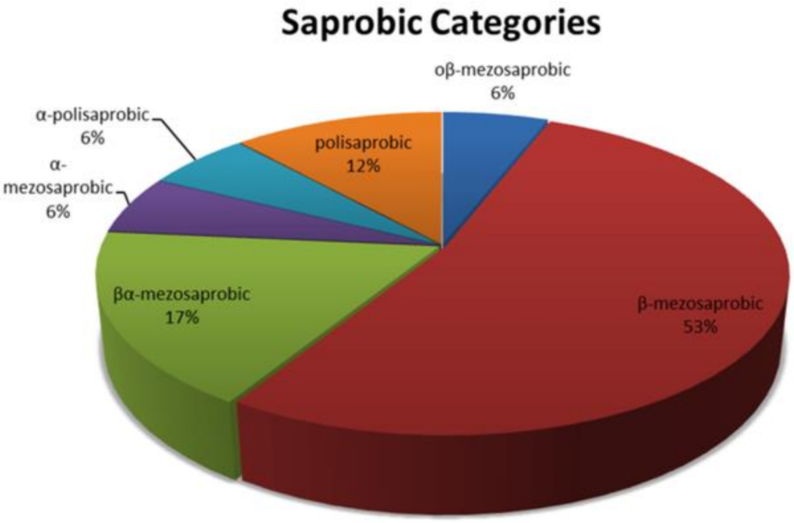

Figure 7.28. The percentage of saprobity indicator dominant diatom species in the study area

The floristic similarity was calculated using the Jaccard index (Jaccard 1901) and, as it was expected, the values of floristic similarity were low between the communities identified in sampling sites that weren't affected by the discharged AMD and the ones identified in sampling points affected by this. Additionally, the values of floristic similarity suggested the presence of multiannual dynamics. At the same time, a high level of floristic similarity exists between the communities identified in the sampling sites affected by the acid mine waters (Figure 7.29). The integrity of the diatom communities is reflected in their specific diversity. Species diversity is influenced by two components: the number of taxa (richness) and the degree of uniformity of distribution of individuals between taxa (equitability). In undisturbed natural waters, both the number of species and equitability is high, versus the polluted waters that show decreased specific diversity, as in our study area.

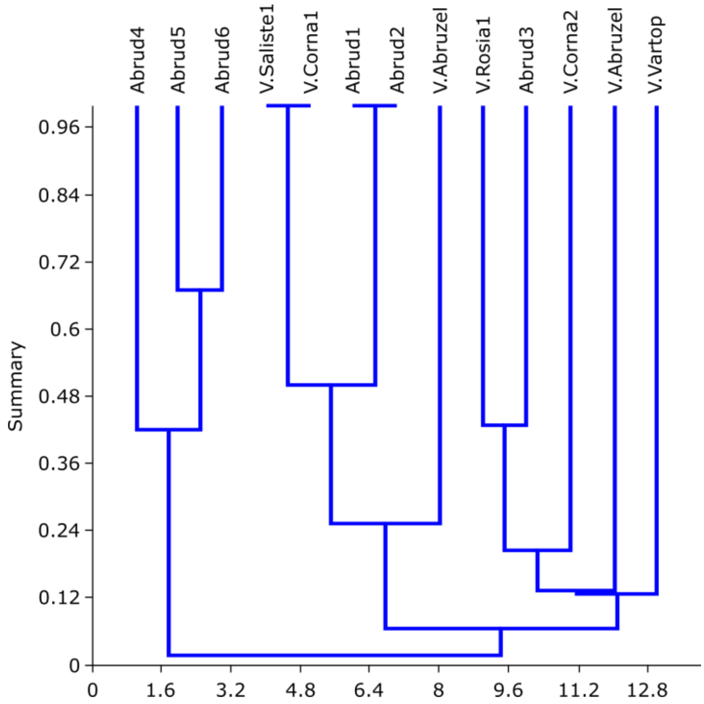

Figure 7.29. The floristic affinity relationships between diatom communities sampled regarding the dominant species

Diatoms are an important component of aquatic ecosystems and constitute a mean of monitoring water quality and evaluating the environmental risk, with a primary objective to either measure the water quality in general, or on specific components (*e.g.* eutrophication, acidification, saprobity, etc.) (Stoermer and Smol 1999).

Concerning Rosia Montana area, some conclusions can be drawn:

- Qualitatively, the number of diatom species exhibited significant variation among sampling sites, also suggesting seasonal dynamics.
- In some sampling sites teratological forms were identified, or algal assemblages were absent, as diatom communities were strongly affected by acid mine waters.
- The richness of the diatom communities is uneven between sampling sites.
- Some dominant taxa have been observed as well, suggesting organic pollution in the study area.
- The presence of deformed individuals within the diatom communities could be explained by the strong effect of the acid mine waters released from old mining workings and waste rock depots.

7.6.2.3 *Zlatna case*

The microbial analysis of water samples from the Zlatna mining area shows lower bacterial load in mine drainage than in groundwaters and surface waters, more than half of drainage waters being inadequate for supporting the survival and multiplication of the aerobic mesophilic bacteria (Table 7.9). The drainage water from the Haneş Mine (A19) and from the Haneş 2 adit (A21) were sterile in all seasons and the Valea Babei adit (A22) and the Podul Ionului adit (A29) showed only few viable microorganisms (1-2 CFU/ ml). The IPEG (A3), Larga (A7) and Toţi Sfinţii (A18) adits showed a low concentration of aerobic bacteria (0-99 CFU/mL), but the 23 August adit (A23) indicated medium microbial growth (100-199 CFU/mL), similar with the surface waters.

In most of the surface waters, the total aerobic count had medium values, showing a concentration of more than 100 CFU/ml, whereas in the Ampoi stream upstream (A1), the Ardeu stream upstream (A24) and the Techereu stream A30 and A26) the total count of aerobic bacteria was over 300 CFU/ml. The highest concentration of aerobic bacteria was recorded in the Haneş stream (A20) (522 CFU/ml) and the lowest (<100 CFU/mL) in downstream of the running waters (Larga Creek (A8) and Ardeu stream (A16)).

The groundwaters (draw-wells and springs) from the mining areas indicated reduced concentration of aerobic bacteria with less than 100 CFU/ml in the Larga spring (A5), medium values (100-200 CFU/ml) in the Trâmpoiele draw-well (A11), as well as high concentrations (>300 CFU/ml) in the draw-wells from the Techereu (A27) and Ardeu streams (A25) (Table 7.9).

Table 7.9. The microorganisms and invertebrates monitored in mining drainages, groundwaters and running surface waters from the Zlatna mining area.

Site	**Type of water**	**Total count of aerobic bacteria (CFU/48 ore/mL)**				**Yeast&Molds (CFU/96 ore/mL)**				**Aquatic invertebrates (no of taxa)**			
		May	**Aug.**	**Oct.**	**Dec.**	**May**	**Aug.**	**Oct.**	**Dec.**	**May**	**Aug.**	**Oct.**	**Dec.**
A1 Ampoi upstream	rw	155	>300	110	246	4	34	2	1		1	3	1
A2 Trâmpoiele downstream	rw	138	157	114	2	44	13	1	1		3	0	2
A3 IPEG adit	mw	98	4	22	3	0	1	0	0		4	0	0
A5 Larga spring	gw	75	13	76	66	91	5	3	1		0	13	1
A7 Larga adit	mw	0	4	17	0	1	1	0	0		16	29	0
A8 Larga creek	rw	3	22	5	49	0	2	3	0		4	29	4
A10 Trâmpoiele stream upstream	rw	59	189	121	138	12	>300	9	11		10	1	0
A11 Trâmpoiele well	gw	28	sec	152	36	6	sec	1	3		sec	sec	1
A13 Ampoi downstream	rw	115	174	81	133	39	26	7	7		4	0	2
A16 Ardeu downstream	rw	99	55	35	90	3	22	0	4		2	2	0
A18 Toți Sfinții adit	mw	7	46	20	63	2	20	8	0		4	4	2
A19 Haneș mine	mw	0		0	0	0	0	0	0		0	0	0
A20 Haneș stream	rw	522	>300	123	67	46	37	3	30		11	4	8
A21 Haneș 2 adit	mw	0	0		0	0	0		0		0	-	0
A22 Valea Babei adit	mw	0	1		0	0	0		0		4	-	0
A23 23 August adit	mw	167	63	28	9	30	13	0	0		7	13	3
A24 Ardeu upstream	rw	108	>300	100	73	30	>300	3	1		10	2	0
A25 Ardeu well	well	68	>300		53	33	17		2		88	-	2
A26 Techereu downstream	rw	-	>300	75	279	67	>300	3	0		0	0	0
A27 Techereu well	well	352	93	89	99	176	1	9	5		62	4	9
A29 Podul Ionului adit	mw	0	0	2	1	0	0	0	0		0	1	0
A30 Techereu upstream	rw	65	227	20	0	11	1	0	0		1	6	0
Total no. of individuals		2059	2553	1190	1407	595	1096	52	66		231	111	36

rw – running water; mw – mine water; gw – groundwater (springs and wells)

Fungi (yeast and mold) show a similar pattern, but with a lower concentration of viable cells than bacteria. Thus, the mine drainage comprised the lowest number of fungi, with a maximum (2 – 30 CFU/ml) observed in Toţi Sfinţii (A18) and 23 August adits (A23). The acid waters of four mines (Podul Ionului adit (A29), Valea Babei adit (A22), Haneş Mine (A19), and Haneş 2 adit (A21)) did not contain any viable fungi in any season, and the IPEG (A3) and Larga adits (A7) showed only one colony growth on the nutrient medium during warm season. In winter, the mine drainage did not contain any viable yeast or mold. The running waters show the highest number of fungi (>300 CFU/ml), whereas the groundwaters had medium content in yeast and mold (1-176 CFU/ml).

The absence of aquatic invertebrates was observed in the Haneş Mine and the Haneş 2 adit, the surface waters of the Ardeu stream (A16) downstream of the Haneş Mine, as well as in the Techereu stream (A26) downstream of the Podul Ionului adit, although running waters had an elevated microbial content. In the IPEG, Valea Babei and Podul Ionului mine drainage less than five invertebrates were recorded, and only during warm seasons. The last category of mine waters, represented by the Larga, 23 August and Toţi Sfinţii adits were distinguished by a large number of aquatic invertebrates, like the surface waters. The running surface waters generally had less abundant invertebrate fauna, similar to the mine waters' mean invertebrate counts, whereas groundwaters showed the most abundant aquatic fauna, with a total of 150 invertebrates recorded during summer (Table 7.9).

In terms of taxonomic diversity, 13 groups of aquatic invertebrates were found in warm seasons, compared to 9 groups recorded in winter. In surface waters the most abundant invertebrates were insects, represented by *Diptera* larvae, however in groundwaters copepods (*Copepoda* and *Harpacticoida*) were the most abundant. Comparing the three types of analysed waters, the mine drainages, groundwaters and running surface waters, it is evident that surface waters had the highest concentration of microorganisms, followed by groundwaters. The mine drainages were either sterile or showed low concentration of bacteria and fungi (Figure 7.30). In all types of analysed waters the aerobic bacteria were higher than fungi. The running surface waters exhibited a reduced concentration of bacteria and fungi downstream compared to those situated by the main drainages upstream. A constant exception was the Techereu Valley, where the distance from the two sampling points was greater (about 6 km), including a village, which contributed to the increase of microorganism content.

The seasonal variation of aquatic organisms reveals the fundamental role of temperature for the microorganism viability and growth, but also for invertebrate development. The most favorable seasons were spring and summer, as demonstrated by a greater number of organisms sampled from the mine drainage and surface water. In groundwaters the seasonal influence on organism populations was not so evident for aerobic bacteria, as their concentration was rather uniform. However, the fungi concentration and the aquatic invertebrates followed the seasonal pattern of surface water, being more abundant and diverse in the warm seasons. Thus, the summer samples indicated the highest number of aquatic invertebrates (228 individuals), followed by autumn (109 individuals), and winter season had the fewest animals (36 individuals) (Figure 7.30).

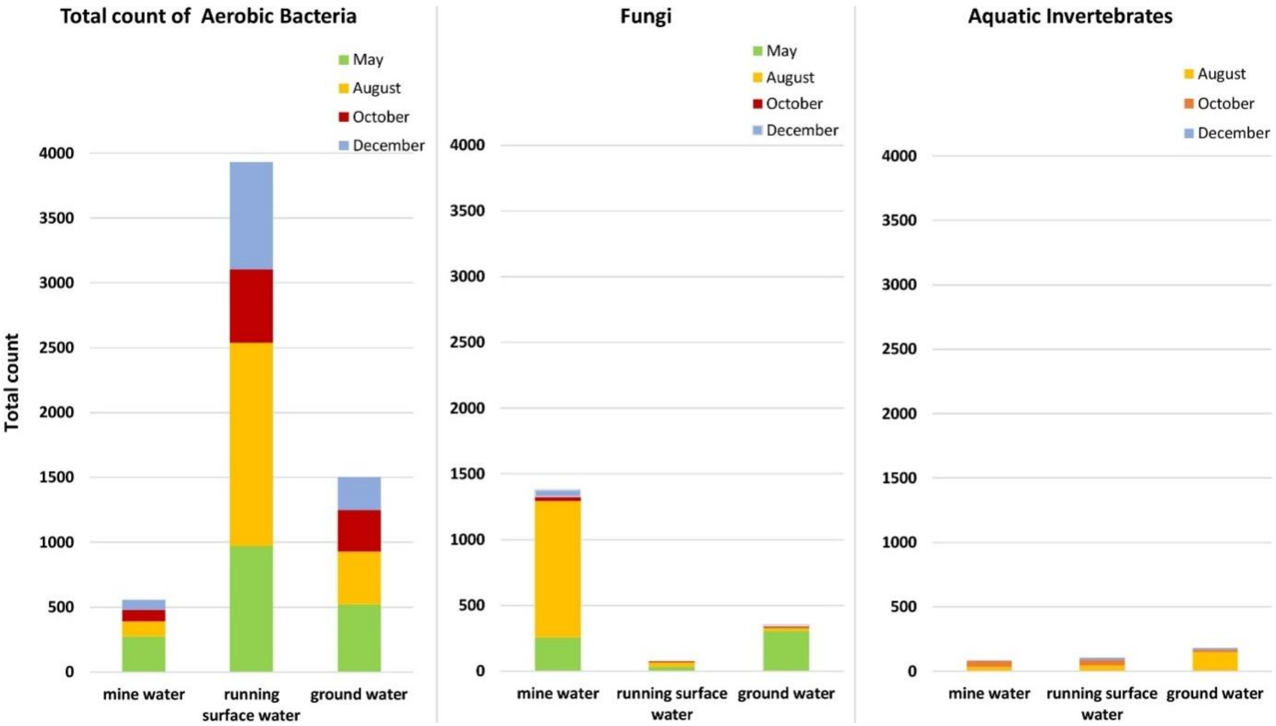

Figure 7.30. The aquatic organisms seasonally monitored in mine water, groundwater and surface water from the Zlatna mining area.

The results of the biomonitoring of mine drainages, groundwaters and running surface waters from the Zlatna mining area showed that: (1) the mine drainages were inadequate for supporting life, or exhibited a low concentration of mesophilic aerobic bacteria, yeast and molds, and aquatic invertebrates; (2) the running surface waters had the highest concentration of microorganisms and invertebrates, the upstream areas being richer in aquatic organisms than those located downstream the mines; (3) the groundwater showed an intermediate pattern of microorganism content, but were the richest in aquatic invertebrates.

7.7 Conclusions and recommendations

Testing of new geochemical and isotope methods carried out in this research proved to be a useful tool for investigation and monitoring of migration of harmful substances from mine waste areas. However, for the regular supervision of environmental impacts for a mining company the geochemical and isotope methods are laborious, span over a long period of time and require a large volume of samples to be collected and analysed. Furthermore taking water samples represent always only the current time, location and conditions, which fluctuate especially in flowing waters such as rivers. Certainly, taking water samples cannot be totally discarded, especially since there is not yet reliable equipment to detect elemental concentrations, but realtime monitoring for certain parameters such as EC in water allows faster response to react if any disturbance in water quality or quantity occurs. This information can be then used to improve water sampling procedures for more representative sampling as well as for planning continuous monitoring locations to be able to act in case of a spill or other accident. Nevertheless the selection of monitoring water sources and area has to be carefully chosen so that all important sources that might interact are taken into consideration. This requires comprehensive knowledge on natural baseline concentrations, ecology as well as the hydrological characters around the mining site.

The stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ (δD) were particularly useful for assessing hydrologic connectivity and mixing, as they are the only truly conservative tracers of water. These isotopes provided important evidence of groundwater relation to meteoric water, and provided unique indication of water subject to industrial processes, whereas the conservative behaviour of $^{87}Sr/^{86}Sr$ in solution allowed delineation of water pathways and estimates of water mixing. However, the accuracy of these estimates is dependent on accurate end-member characterization. $\delta^{34}S\text{-}SO_4$ showed variability across site waters that suggests it may provide a valuable tracer of sulphate origin and transport between different waters. $\delta^{7}Li$ was consistently distinct within different mine water types, though evidence of its non-conservative behaviour in solution suggests it may provide a more practical tracer of solute attenuation processes than of solute source and mixing at the mine site and river reach scale. $^{26}Mg/^{24}Mg$ was not found to provide additional insight into water mixing due to lack of isotopic variability between different samples. Further, the controls on isotopic variation in Mg are not well constrained, complicating interpretation of these results in a field setting.

Using different bioindicators is the only way to measure the true impact on fauna and flora around the mine site. One of the aims of this study was to evaluate usefulness of ecological risk assessment tools in estimating the safe discharge levels of different elements in a certain environment. Combining the geochemical and microbiological data was successfully used to assess mining effects on groundwater and surface water. With the ecological risk assessment and better knowledge of geochemical characters of the contaminants in wastes and mine waters, the mining companies are able to predict and to prevent the impacts to the surrounding environment. The results obtained from monitoring campaigns revealed new information on mixing and dilution processes of contaminants in recipient river systems, whereas the ecological survey revealed the impact on fauna. Moreover, in Kittilä the monitoring of water flow in Seurujoki River revealed that the way of discharging is crucial for diminishing environmental effects of mine drainage. Thus, this kind of monitoring study could be useful when designing and optimising discharging methods.

This type of a modelling method could be best when applying an Environmental Impact Assessment (EIA), which is the foundation of setting the environmental permit. Furthermore, ecological risk assessment would help monitoring the efficiency of the water treatment and management methods during mine operations. However, when implementing site-specific guideline concentrations for example by the use of SSD would require more precise information on *e.g.* the river characteristics, toxicity data and geochemical modelling of the behaviour of different mine water constituents in the environment after discharge.

Ecological risk assessment tools appeared to be useful in supporting water management strategies. However, ecological risk assessment alone would be too simple to model such a complex system as mine environment and more defined modelling of the water flows and reactions could give more robust results. Moreover, since there was not enough toxicity data available to allocate PNEC to a specific environment, PNECs was not seen to be very practical tool for setting environmental permit limits without conducting toxicological tests.

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8 SOCIO-ECONOMIC IMPACT OF MINING

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8.1 Introduction

Over recent decades, the social and environmental impacts of mining have become an increasingly important subject of public discussion in many countries. At present the operators are expected to be able to control the socio-economic and environmental themes covering the whole lifespan of the mine from exploration to closure. In addition, the mining and environmental administrations are expected to know how to thoroughly monitor mining operations, recognize the possible problems of individual mining projects, and require solutions for the detected problems, avoiding any conflict with social, economic or environmental values.

The social impacts of mining are not simply negative or positive; they are always inter-related, mutually dependent and cumulative. Mining affects to a variable extent the environment and the social interactions, no matter where it occurs. The main challenge is to ensure that mining communities benefit from the presence of mining companies and that the negative effects of mining are reduced as much as possible. This, in recent years, has been termed responsible mining which includes respecting the rights of all stakeholders, informing and including local communities into decision making, being environmentally friendly, having no negative effects on human health, respecting local rules and law and contributing sustainably to the benefit of the nation and local communities.

Responsible mining is a challenging goal and risks cannot be ignored when it comes to the large changes that a mining project will bring into the local community and environment. Klinke & Renn (2001) proposed a general definition, in which risk is seen as “the possibility that human actions or events lead to consequences that harm aspects of what humans’ value”. When these consequences are labelled as harmful or negative – depending on how people asses them (*e.g.* their health, their well-being, their values and their social status), the only way they can be altered is by changing the initiating activity or event, or by reducing the impacts to human beings. The public authorities, policy makers and professional community should strive to keep risks under control, avoid or reduce them, as they are perceived as undesirable for society. When it comes to the mining activity, both the government and mining companies should put measures in place to ensure that there will be advantages for both mining companies and their host communities, and that the risks related to mining will be minimised.

Acquiring and maintaining a social license to operate (SLO) is the key to success of any mining company. The term SLO emerged in the mid-1990s from within the mining industry as a response to social risk. Since then, it has been adopted by a wide range of operators in the resources sector, including mining companies, civil society and non-governmental organizations, research institutions, governments and consultants. A SLO refers to the ongoing acceptance and approval of a mining development by local community members and other stakeholders (Prno & Slocombe 2012, Boutilier & Thomson 2011). Research and theory suggest that upholding basic human rights, avoiding bribery and corruption, and working to minimize harm to the environment, define the minimum standards and licensing requirements for SLOs. The notion of a SLO is also tightly linked to the concept of sustainable development. Mining companies should relate their sustainable development practices to maintenance of their social license to operate, and vice-versa.

Gold mining has some common features with the other mining sectors, but it also has some unique characteristics, that should be taken into account. Gold is a symbol of wealth, and the community perceives a gold deposit as a latent reserve for its future prosperity. The style of mining is changing as large-scale mining techniques are introduced, and in many cases, small operations are no longer viable. Traditionally, the lifespan of a mine was not precisely determined beforehand, giving the impression that the mining activity will continue for an undefined period of time. More accurate geological investigations and large-scale extraction techniques are shortening the lifetime of mines. The community is interested in how their lives will proceed, and what will take the place of the mine after its closure. In most of the cases, it is difficult for the involved parties to imagine how the area will look like after the mine has closed. What will be the alternative to mining when the operation ends? How could the community benefit from the existence of the mine for a certain period? What should they request from the mining company? How should the corporate social responsibility be directed? It is clear that a strategy should exist from the beginning of a mining project, and part of the resources generated by the mine should be used for building the economic and social life in the area after the mine closes. A new mining project has the potential to bring economic and social benefits to the community, but it could also produce negative effects like environmental pollution, change in land-use, contrasting opinions between different members of the community, etc. The state of the environment after mine closure is a major concern for the stakeholders. The territory affected by the mining operation should be “liveable” and adaptable to new land uses. The landscape degradation and the soil and water pollution are the main physical damages induced by mining. If not properly addressed, they may persist for centuries. Innovative technical solutions are needed in order to restore the functions of the ecosystems and the general state of the environment to an acceptable level.

A detailed socio-economic study is a useful approach in order to accomplish several objectives: to improve the sustainability and long-term development of the mining areas; to identify the nature of conflicts, solutions, and ways to increase the level of mutual confidence and acceptance, and provide benefits to the community and stakeholders; to develop the mechanisms of corporate social responsibility (CSR), community engagement and management of the relations with the stakeholders; to better design the post-operational development of the mining sites and identify the opportunities for the further socio-economic development.

8.1.1 Study sites

The selected study sites are in different stages of mines’ life cycle (mining began a few years ago in Finland, and has not yet started in Romania). The local socio-economic and environmental conditions are also very different.

The Kittilä gold mine is located in Finnish Lapland, 900 km to the north of the Finnish capital Helsinki. It was constructed in 2006. Named after the community that resides nearby, the mine is one of the largest gold-producing mines in Europe. Its commercial production began in May 2009, four months after the first gold bar was poured (January 2009). The mine is operated by Agnico-Eagle Mines Ltd. It has an estimated lifespan of 15 years (2009-2024), but further exploration is being made in the mine and in surrounding areas. The mining started open-cast, and advanced to underground after few years.

Rovina site in Romania was the main area of socio-economic investigation in this study. SAMAX Romania is the mining company currently responsible for the exploration and preparation for operation of the site. Significant resources of gold and copper are confirmed, equal to about 120 tons of gold and 100000 tons of copper. The potential mining site is located in the southern part of the Apuseni Mountains, belonging to the “Golden Quadrilateral” mining district, about 20 km south-west from Rosia Montana, and it is expected to become one of the biggest mining areas in Romania. It is worth mentioning that for the first time in Romania, the government offered the license for utilizing the resource without the implication of some state-owned national company.

8.2 A quantitative and qualitative study on the social licence to operate in Rovina, Romania

In order to assess the situation of the company intending to develop mining operations in Rovina area and to understand the community perception about it, several research objectives were proposed:

- To analyse the public perception on the dynamics of mining in the area – descriptive insights on the impact of the mining activity: perceived fears, risks, problems, positive aspects.
- To examine the relationship with the stakeholders.
- To identify the way the mining project responds to the expectations and needs of the community

A sociologic survey, consisting of a qualitative and a quantitative part, was conducted in Criscior – Bucuresci – Rovina area in 2015. Although Rovina is a relatively small village, as it is the centre of interest for the mining project, we will include in the so called Rovina area also the neighbouring localities, which could be directly influenced by the mining operations. The target group consisted of the general population in the mining area, communities, community leaders, local authority representatives, the mining company, non-mining companies, and contractors.

The quantitative survey was carried out on representative samples of respondents; 400 questionnaires were distributed in the study area. The sampling was random, but stratified on gender and territorial administrative units. The sample is representative for the population in the area, with a maximum sampling error of 5% at a confidence level of 95%. The questionnaires were completed “face to face”, at the respondents’ home.

The qualitative survey consisted of 13 individual semi-structured interviews with representatives of key stakeholders and community. Among the respondents, there were business representatives, local authority representatives, local community informal leaders, community representatives, and one representative of the mining company.

The following topics were addressed by the research instruments: region/community infrastructure and resources, access to public services as health care and education, health issues, alcoholism and drugs, positive and negative effects of the mining project, benefits and costs of the mining project, mitigation actions to the negative effects of mining, community values, land-use and ownership in the mining area, employment status, employment conditions and practices, individual and household income, human rights violations and community tensions, migration and labour fluctuation, corruption, and attitudes towards the mining operations in the area.

8.2.1 Social profile of the surveyed community and general aspects

The gender distribution was almost equally balanced within the sample population (48% females and 52% males). The average age was 57, which shows that the population in the area is quite aged (Figure 8.1).

Age	Male	Female	Total
18-24	4	11	15 (3.8%)
25-34	20	18	38 (9.5%)
35-44	36	32	68 (17.0%)
45-54	45	38	83 (20.8%)
55-64	50	50	100 (25.0%)
65 +	53	42	95 (23.9%)
Total	208	192	400 (100%)

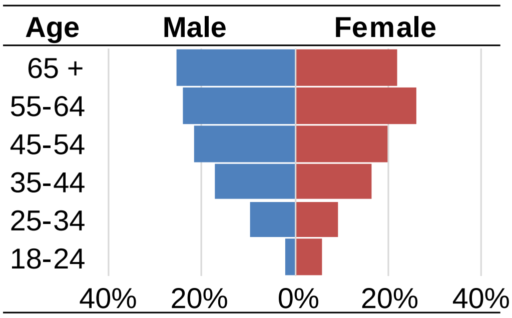

Figure 8.1. Age and gender distribution of the sample population in Rovina area

The level of education is average, a high percentage of the population having completed high school studies (33.5%). A quarter of those interviewed (25.5%) has completed some high school, 15% has completed the primary school, and 20.5% of them have graduated from higher education (Table 8.1).

When it comes to the main economic activity, the figures show that most of the population is retired (45.6%), mainly from other sectors (28.3%) than mining (17.3%) (Table 8.1). Still, the number of those who used to work in the mining sector is high as compared to the overall population, showing that this activity used to prevail in the area. More than 15% of the answerers are unemployed or housewives, indicating a lack of employment options in the community. Only 37.1% of those interviewed are working, showing again a significant shortage of working places in the area and a community where the elderly people are predominant.

About 80% of the interviewed population has total household income smaller than 2500 RON (about €550), and only 18.6% of the households receive more than 2500 RON per month. Less than 1% reported to have no income, denoting that people have some form of income, despite the fact that a large number of people are currently not working. The average amount of income might be increased by the pensions of those who are retired.

Table 8.1. Social profile of the community in Rovina area

Variable	***n***	**Percentage**
Sex		
Female	193	48.0
Male	208	52.0
Level of education		
Some primary school	20	5.0
Completed primary school	60	15.0
Some high school	102	25.5
Completed high school	134	33.5
Technical or university studies	82	20.5
NA	2	0.5
Main economic activity		
Employer/ Business owner	11	2.8
Freelancer	7	1.8
Professional services/ Intellectuals	20	5.0
Non-professional services	80	20.0
Agriculture	10	2.5
Student	4	1.0
Retired (from the mining sector)	69	17.3
Retired (other sectors)	113	28.3
Unemployed	13	3.3
Housewife	47	11.8
Other occupations	22	5.5
NA	4	1.0
Total household income (per month, RON)		
0-1000	154	38.5
1001-2500	166	41.5
2501-4500	59	14.8
4501-6000	11	2.8
6000 +	4	1.0
No income	3	0.8
NA	3	0.8
Average age		
	57.0	

Most of the respondents felt somehow unpleased with their way of living. More specific, if the categories ‘not pleased at all’ and ‘not too pleased’ are summed up, the result would be 61.75%, compared to 38.25% for ‘quite pleased’ and ‘very pleased’. The tendency to be less satisfied increases with age, and despite the gender balance in the sample, men declare to be more satisfied with their lives than women. The level of satisfaction seems to be influenced by the level of education, in the sense that those who are more educated tend to be more satisfied and their level of satisfaction is less affected by their employment status.

Even though 20% of the respondents declared that their lives are somehow worse than a year before and 5.5% of them say it is much worse, the highest percentage agree on the fact that things have not changed much as compared to the previous year, remaining almost the same (57.75%). A proportion of 14.25% say their lives are better now, but only 1.5% feel a significant improvement. This variable is correlated with some socio-demographics such as gender and occupation.

People seem to be quite pessimistic with regard to the improvements that may occur in their lives. The greatest percentage of respondents (37.5%) feel that nothing will change the following year, and they will keep being unpleased or unsatisfied with their lives. A significant number of those interviewed actually think that their life will turn slightly worse than now (22.75%), or worse (6.50%). A percentage of 21.25% feel they will live better and only 2% of the population consider that there will be some improvements and will have a much better life. Age does not matter much when it comes to this kind of pessimism. All age-groups showed similar lack of confidence regarding any improvements for the following year, with the mention that the number of cases is quite low for a proper comparison. Still, gender does make a difference in the sense that younger men are more optimistic than women that their lives will be better (62.4% vs. 37.6%) or much better (5 cases vs. 3). Also, those who are more educated feel that some improvements will happen in their way of living during the next year.

8.2.2 Community infrastructure and resources

When asked about various aspects that characterize their community and their way of living, a large percentage of the respondents (39.6%) scored the lack of workplaces as being one of the biggest sources of dissatisfaction (Figure 8.2). Some of them also feel unpleased by the quality of the roads, lack of open spaces for leisure, lack of possibilities for recreational activities or sports and condition of the local transportation system. The medical and the educational services are rated quite well on the Likert Scale, as well as the local public institutions, the quality of the potable water and the communal safety (characterized by reduced cases of crime or delinquency). This shows that the area ensures the basic infrastructure and resources which humans need in order to make them feel comfortable and pleased with their lives. An important aspect which needs to be mentioned is the one related to the level of pollution. Even though the area has a history of mining since ancient times, and despite the general fears related to the negative effects of mining – especially those related to pollution – more than half of the respondents in Rovina area feel pleased or very pleased with the overall level of pollution and do not find it as a threat to their health.

	1	2	3	4	5	6	7	8	9	10
Work places	39.6	12.4	6.6	8.2	16.2	5.5	5.8	3.3	0.8	1.4
Transportation	12.1	6.5	5.9	7.6	15.5	7.9	11	17.5	9.6	6.2
Food supply	5.2	3	1.9	2.7	9	6	10.6	27.5	14.2	19.6
Locality cleaness	8.3	6.5	3.2	7.3	12.6	9.1	9.1	21.8	11	10.8
Medical services	5	3	3.3	3.9	10.2	6.9	9.1	22.1	17.4	18.8
Education services	4.4	1.6	1.9	3.1	10	10.3	10.9	24	15	18.7
Crime/ deliquency	4.3	2.4	1.5	4	9.2	4.9	11.9	20.2	19	22.3
Local institution functioning	6.4	1.7	2.2	3.3	8.3	4.1	13.8	24.9	18.2	17.1
Open spaces for leasure	15.6	5.3	3.8	6.2	10.6	8.3	11.8	12.1	11.5	14.7
The quality of drinking water	3.8	2.2	1.9	0.8	6.3	3.3	8.5	18.3	18.9	35.8
Roads	15.8	7.5	4.8	7	9.1	8.3	7.8	12.8	12	15
Level of pollution	5.8	5.2	3.4	4	8	7.1	9.2	21.5	16	19.9

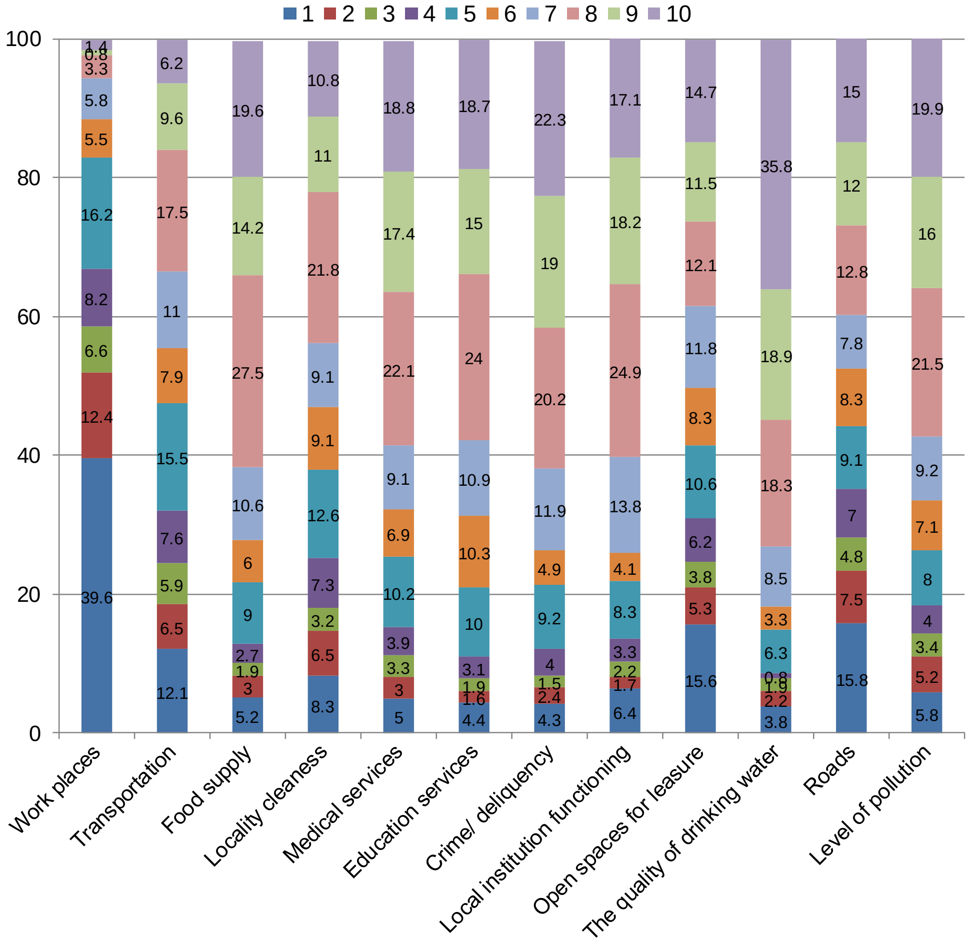

Figure 8.2. Level of satisfaction of the community related to general aspects of life in Rovina area; 1 = "totally unpleased", 10 = "totally pleased"

When asked to compare the current year's situation with that from previous year, respondents did not point to any significant improvements on the aspects related to local infrastructure and resources. Everything seems to have remained the same, except for some small changes on dimensions such as the roads' quality, the level of crime/delinquency, the medical services and the food supply, showing that a small part of the inhabitants feel that there is some progress going on in the community and the local institutions work for a better life within the area.

At the open-question "*In your opinion, which are the two most important problems of the community?*", high percentage of the respondents (45%) mentioned the lack of working places as one of the most important problems affecting the community, followed by a bad infrastructure (15.8%). Other problems included an unsatisfactory system of water supply, lack of a sewerage system and bad quality of the services offered by the local council.

8.2.3 Individual and community values

When asked about the level of trust towards others, most of the respondents say it is better to be on guard (85.8%), and only some of them (13.8%) feel that they can trust the people around them without any fears.

Going more specific with the level of trust within the community, the balance remains inclined in the same direction, which recommends being cautious when dealing with the others. Almost 50% of the inhabitants totally agree with the statement that one has to be careful so that they would not get aggrieved by others, and 18.5% rather agree on that. Still, it seems that respondents feel that most people in the locality are willing to help (22.3% rather agree; 43.5% totally agree), and that one can trust them when it comes to lending money (17.3% rather agree; 48.8% totally agree).

Even though the level of trust to others seems to be rather low, interesting positioning appears in the relationship with the representatives of the mining company (Figure 8.3). A rather high percentage of the respondents declared to trust them (36.8%), pointing to some indications of the fact that the mining representatives are welcomed in the community and there is a positive bond between the locals and the company.

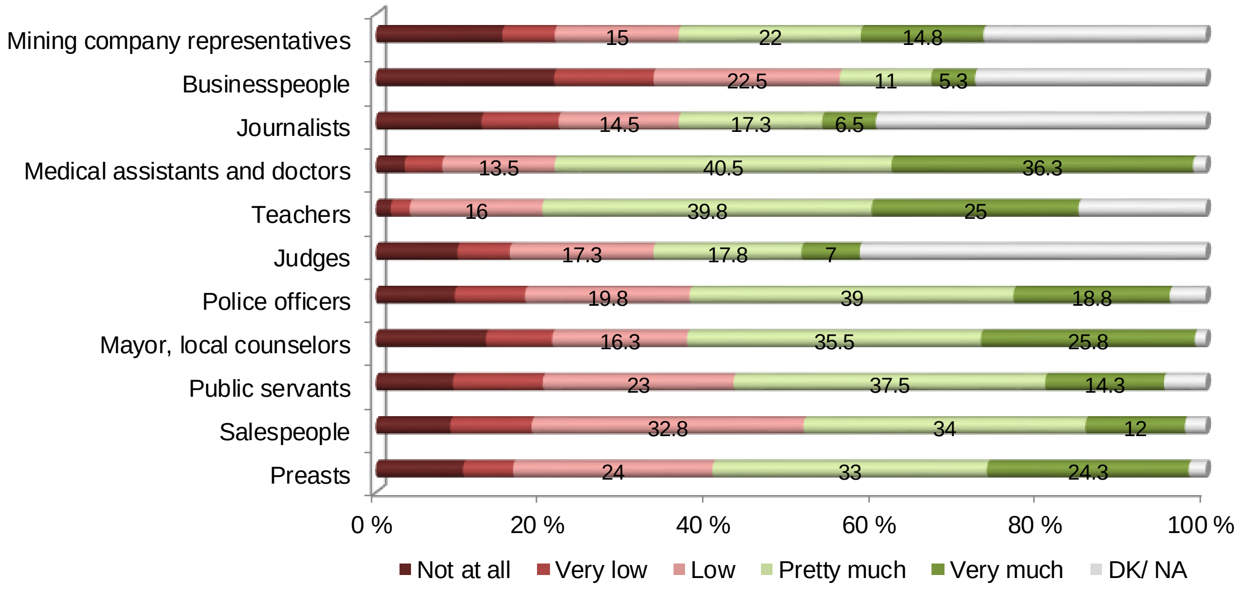

Figure 8.3. Community's level of trust in persons and institutions

Regarding various forms of protest, it appears that generally the inhabitants do not take such action towards the situations that bother them. A small percentage of them declare to have signed a petition (9%), attended legal demonstrations (8.5%), or refused to attend public activities (5.3%). They agree though, to have into consideration the possibility to sign a petition in the future (43.3%) or attend legal demonstrations (43.5%).

Most of the respondents within the surveyed area do not agree with the statements related to some common situations. Almost all of them (93.3%) say it is never justified to accept privileges or undeserved benefits during the mandate/ working position. Also, another large percentage (95%) of those interviewed declare it is not justified to buy things which you know were stolen. Still, there are some who say that sometimes and very rarely, one can choose to avoid paying taxes (9.3%), travelling without a ticket in public transportation (11.8%), or asking for benefits from the state to which they are not entitled (13.3%). This last aspect might show a position of dissatisfaction towards the local and/or national public services towards which they feel one can react from time to time by not committing to the general accepted rules.

Despite the fact that the lack of work places stands as a concern for a significant number of the population in Rovina area, when asked about the most important aspect which matters when searching for a job, more than half of the respondents (52.88%) declared to be looking for stability rather than financial aspects or personal/professional improvement. They would choose a safe job which should offer them the long-term comfort of not changing or concluding their professional activity. A proportion of 22.81% confessed to be looking for a good income, and some 11.78% declared to be interested in having a job which should make them feel like doing something that matters for them. Less than 10% feel it is important to work close to their acquaintances or relatives.

Regarding the health status of the 400 interviewed inhabitants in Rovina area, it generally appears to be not good, nor bad (35.3%). This might be an indicator of the rather advanced age of the respondents. A total of 48.5% declare to have a good and quite good health, while a total of 16% confess to feel quite bad or bad in this regard. Going further with the questions on this topic, out of those who are currently affected by a sort of disease, infirmity or mental problem, 15.3% say they are very affected by this in their daily activities, and 21.6% say that their daily routines are somehow affected. About 63% of the interviewed population declares to have no serious health problems that would affect their daily lives.

According to respondents' answers to a set of questions related to discrimination, violation of human rights and community conflicts, almost all of them (a proportion between 88 and 99.5%) say they did not encounter any of the situations presented. Some of them confessed though to have encountered problems on employment due to gender, age, political view, religion, ethnicity, or health problems. A percentage of 12.2% declared to have been badly paid due to the above characteristics, and 9% complained about receiving too many tasks at work.

8.2.4 Relation with the mining company

When asked to mention some of the companies within a 20-40 km distance for which they would like to work, the mining company was the first on the top of respondents' priorities, summing up a total of 16.5% of votes. It was followed by a company that produces car accessories, which is indeed the largest employer of the area (5.5%). The other two options of the respondents were again connected to the mining sector. They would wish that the mine from Barza reopens (3.8%), otherwise they would move to Rosia Montana to work in the new mining project, provided it will start soon (5%). Still, on the top of their preferences was the mining company if they were to choose only one company to work for. About 15% of the respondents voted this as the best option for them. A large portion of population (86.25%) seems to atleast have heard of the mining company. This might show that this company is engaged in the life of the community through various activities/ actions, and that the inhabitants are looking for a new investor in the area, which could offer them professional opportunities and financial stability.

Out of those who have heard of the mining company, a total of 81% think that its presence in the area would bring benefits to the community (24.1% consider there would be some benefits, 34.8% – quite many benefits, and 22.1% – a lot of benefits). A proportion of only 8% of the respondents estimate that the mining operation would bring no benefits at all, and 8.3% of them think that there would be extremely few benefits for the inhabitants.

Among the benefits that the interviewed population bears in mind, on the top of their list is the opportunity to find work (60.8%). Another perceived benefit is financial-related, meaning that respondents hope they will have again money to spend (14.8%), which eventually would bring personal stability/security (2.5%), economic development, community development, improvement of the living conditions, etc. Respondants also felt that the mine would improve public services (60.5%), raise salaries compared to other parts of the country (69.9%), and that vulnerable groups will have a chance to get a job (69.5%).

When asked about the problems which the mining operation might cause to the inhabitants of Rovina area, most of the respondents did not find the mining activity as a threat for the community. A total of 46.7% of those interviewed think that there will be no problems, or very few. A portion of 25.8% feel that there will be some problems, and 19.5% of them think that there will be quite many, or a lot of negative consequences.

Among the problems that the inhabitants had in mind, the most important was pollution (34%), which they feared would affect their lifestyles on a long-term. They feared that pollution would affect the local infrastructure and agriculture, or that there would be expropriations, increased radioactivity or some other bad consequences for the environment.

Among other negative impacts of the mining operation that respondents fear are those related to the financial aspects which will put the area on a disadvantaged position as compared to its investors (Figure 8.4). Most of the inhabitants (72%) feel that the largest part of the benefits will go to the mining company rather than to the community, and that actions of corruption and bribe will rise among the local politicians.

Statement	**TRUE (%)**	**FALSE (%)**	**DK/ NA (%)**
Most of the benefits belong to the mining company	72	18.6	1.2
The project will affect people's traditional way of living	36.7	51.7	1.7
Local politicians and business men will earn money through corruption	51.7	29.1	19.2
After the mines opens, the quality of the public services will improve	60.5	23.2	16.3
The company has the obligation to invest in medical and educational services	63.7	21.8	14.4
Foreign employess will be preferred to the best jobs and salaries	41.6	42.8	15.5
The mining project will pollute the area and will affect agriculture	57.7	29.3	13.1
The mining company will pay higher salaries than other companies	69.9	14.2	14.9
The company will offer jobs for those who have less chances to be employed	69.5	15.8	14.7
The working conditions will be better than elsewhere in Romania	39.2	26.4	34.5

Figure 8.4. Respondents' reactions to multiple statements concerning the Rovina mining project. "When it comes to the Rovina mining exploitation, do you find the following statements true or false?"

Besides the benefits and the fears, there are some expectations as well. A large percentage of the respondents (63.7%) believe that the mining company must invest in the public services of the community.

The interviewed population of Rovina feels that those who would gain the most from the mining activity in the area are those from the mining company (45.9%), followed by the community itself (9.8%), by the stakeholders (5.8%), the politicians (2.8%), the business people, and the local council/ local institutions. The ones who would lose the most from respondents' points of view are therefore the inhabitants of the community (28.5%), and the state (3.5%).

8.2.5 Socio-demographic data

The total income of the respondents hardly overpasses the minimum threshold. Most of the respondents earn between 0-999 RON/month. Regarding the total income of the family, as the data show, there are some who live with less than 1000 RON/month. 28% of the respondents declared that all the members of their families gain a total amount of 1000-1999 RON/month, while 28.7% reach the range 2000-3999 RON/month (Fig 8.5).

It appears that generally, the inhabitants make no savings, but spend almost all of their gains. Most of their revenue comes from pensions from the state (42.3%) and from salaries from the private sector (28.5%).

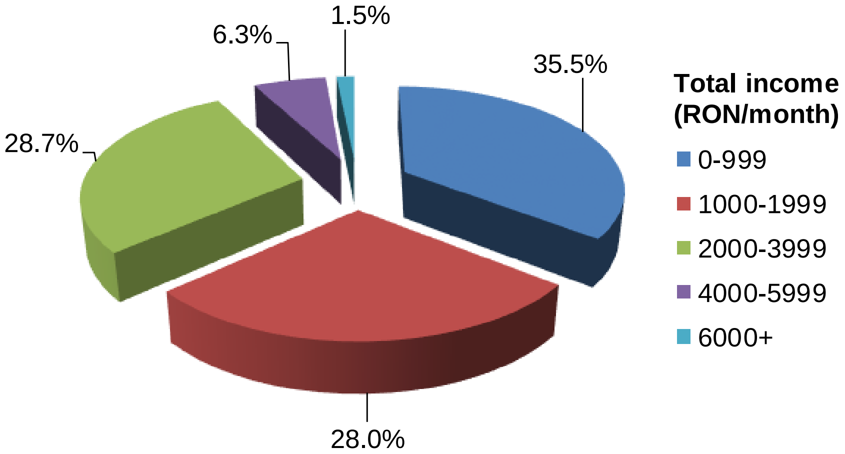

Figure 8.5. Total monthly income of a household in the Rovina study area.

According to respondents' statements, it appears that most of them own lands around their households (82%). Almost half of them (48.9%) declare to have at least 2 hectares, 20.9% have between 0.50 and 1.99 hectares, and 30.8% say they own less than 0.50 hectares.

Out of those who declared to own some land, 11.8% said they also have some parcels close to the proposed mining area, and 71.3% of them confess to actually benefit from the crop obtained from their lands. Very few of them sell their products at the market (2.3%) and instead use the harvest for their own consumption. Besides working their lands, some of the respondents said they also grow animals (63%) and 9.1% of them sell animal products at the market.

In case the mining operation begins, most of the owners do not know yet what they will decide regarding their lands (67%). Only 4.3% already know for sure that they will sell it.

The qualitative study reveals the perception that the mining initiative in Rovina area is a positive one for the community, not only in financial or economic terms, but also in what concerns the relationship/stability/balance within families and people's sense of personal appreciation. All these point to the perceived benefits on all dimensions of life, not only the economic ones.

8.2.6 Testimonies

In the qualitative/quantitative study, the people were asked "*What if the mine opens…*" Their responses are listed below

- "It would be very good because there are many persons who need a job. And here, most of the population already knows how it is to work in a mine"
- "It would be the greatest gift from God for the community"
- "I see it as a chance for community"

In general the answers showed that the positive aspects of the mine in local community are the following:

- People will have a job.
- The constructions/buildings from the commune will be revived.
- People from outside the commune will come here for work.
- The roads/infrastructure will be improved.
- There will be stability and harmony within families because there will be less financial concerns.
- People will start feeling useful.
- The community will have a better living standard and people will need no social financial support.
- People will have no stress regarding the lack of money.
- People will have hope.
- Investments will start in the area.
- The young people will return.
- New businesses will be opened which offer monetary flow.
- The local community will benefit from the taxes paid by the company and will be able to use the money for improvements in the commune.
- People will receive money for selling or lending their lands.

The negative aspects of the exploitation are overpassed by the positive ones and refer mainly to the environmental problems which some people think may arise:

- The environment will be affected and the vegetables will not grow.
- The state will gain too little from the exploitation.
- The area will remain poor in resources.
- The area will be polluted.
- Much dust in the air.
- Too much noise.
- They might find radioactive ore within the mountain, which will affect the population after the deposit is uncovered.

The relationship with the mining company in local community is expected to be very good and productive:

- The community has a lot of things to gain from the presence of the mining company in the area: the company offers support for the ones in need, restores old buildings, contributes to building parks, educational and recreational spaces for children.
- The company organizes periodic meetings with the community and asks for their advice for any activity that they want to proceed with.

8.3 Roadmap for research of social impacts in Finland

8.3.1 Development of Finnish mining industry

Mining industry in Finland was fading during the 1990’s. At the start of the new millennium the industry started a rapid rise to fulfil the need of raw materials for the growing markets in China. Also the EEA (European Economic Area) agreement made by Finland in 1994, which gave international exploration and mining companies the same rights as Finnish companies, was important for the industry’s positive development (Kivinen et al. 2015). When the economic depression in Europe started in 2008, the mining industry operating in Finland was increasing in productivity, as measured in tonnage, and new operating mines were opened. (Figure 8.6).

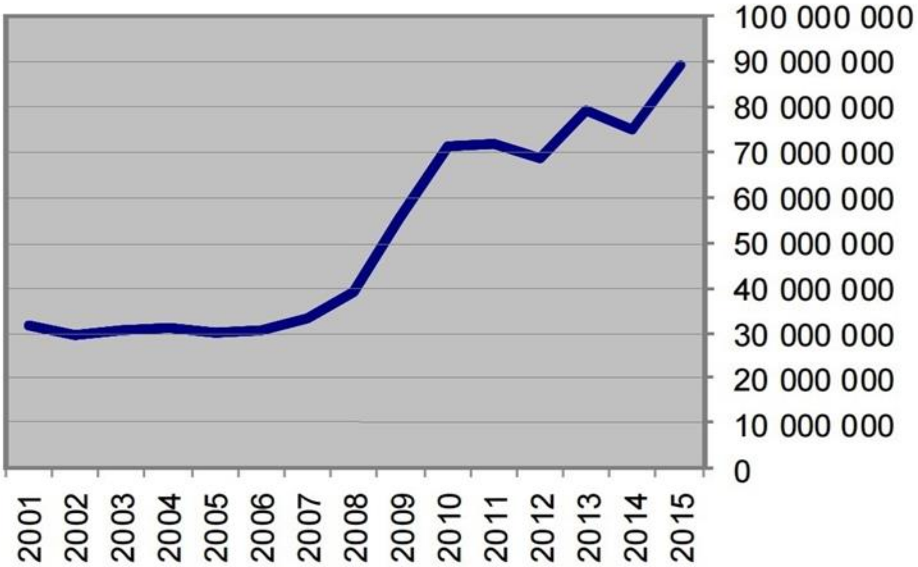

Figure 8.6. Total tonnage of mining in Finland between years 2001-2015 (modified after Liikamaa 2016).

Companies were investing in exploration projects (Figure 8.6) which increased the visibility of the mining industry to a greater number of people. The increased visibility and the poor communication of some exploration companies (Eerola & Solismaa 2015) led to increasing concern by some local people near the exploration target areas. Also non-governmental organizations (NGOs) and individual citizens outside of the actual exploration project sites were concerned with the increased activity and its possible impacts on nature and the life of local society.

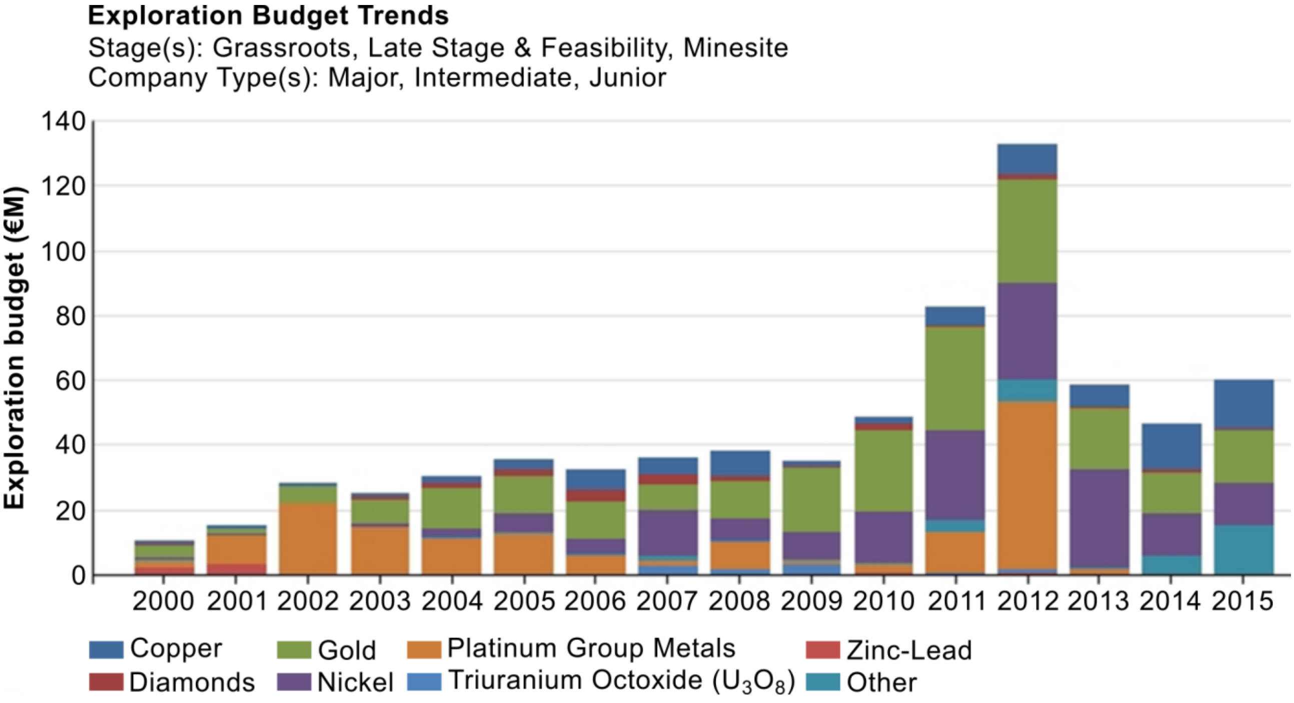

Figure 8.7. Exploration budget trends of Finland (SNL 2016)

8.3.2 Academic awakening

Uranium exploration projects in Eastern Finland from 2006-2009 and the subsequent disputes ignited academic interests in corporate social responsibility (CSR), social license to operate (SLO) and stakeholder activities (Eerola 2007). After the "Uranium disputes", an environmental accident at one metal mine in 2012 started a new public discussion that needed answers. Those single events marked the beginning of rapid growth in research on social impacts of mining in Finland. The resulting projects are presented in Tables 8.2 – 8.4.

8.3.3 Classification of the research projects

Since 2010 there have been many different types of projects dealing with the responsibility of mining and industry's social license to operate. The different projects can be listed and categorized as research projects (Table 8.2), promotional and development projects (Table 8.3), and other projects (Table 8.4).

Table 8.2. Finnish research projects since 2010 with an important socio-economic component (Modified after Eerola 2014). GTK = Geological Survey of Finland, VTT = Technical Research Centre of Finland Ltd, SYKE = Finnish Environmental Institute, Metla = Finnish Forest Research Institute.

Project	**Responsible organization(s)**	**Duration**
Finnish mining companies in global change: Capacities of local reception?	University of Eastern Finland	2010 – 2012
Sparsely inhabited country-side as mining industry's operational environment	University of Eastern Finland	2010 – 2012
Commensurability of economic benefits and environmental impacts of mining and comparison to other industries	Pellervo Economic Research	2013
DILACOMI	University of Lapland, University of Oulu, Metla	2011 – 2013
Increasing the impact of globalized tourist industry in tourism and regional development in Kuusamo	Naturopolis Ltd., University of Oulu	2012 – 2014
Argumenta: Responsible mining	University of Eastern Finland	2013 – 2014
SoLiMi	University of Eastern Finland	2013 – 2014
Sustainable Acceptable Mining – SAM	VTT, GTK, SYKE, University of Helsinki	2013 – 2015
KAMYK	Metla	2013 – 2014
SUMILCERE	University of Lapland	2013 – 2014
SUSMIN	GTK	2013 – 2016
Social licence to operate: a real tool or rhetoric	University of Eastern Finland	2014 – 2018
Multivariable ecotoxicological, environmental and health risks evidence evaluation of people's experiences towards metal emissions from mining to natural waters	University of Eastern Finland	2014 – 2018
Understanding the cultural impacts and issues of Lapland mining: A long term perspective on sustainable mining policies in the north	University of Oulu	2014 – 2018
GovAda	University of Lapland	2014 – 2018

Table 8.3. Promotional/development projects (Modified after Eerola 2014). GTK = Geological Survey of Finland, Sitra = The Finnish Innovation Fund, FinnMin = The Finnish Mining Association.

Project	**Responsible organization(s)**	**Duration**
Mining Academy	GTK	2012 – 2014
Making Finland a leader in the sustainable extractive industry – action plan	Ministry of work and employment, Ministry of environment	2012 – 2030
Network of sustainable mining industry	Sitra/FinnMin	2013 –
KaViKe	GTK	2013 – 2014

Table 8.4. Other projects (Modified after Eerola 2014).

Project	**Responsible organization(s)**	**Duration**
Guest professorship of journalism	University of Tampere	2010 – 2012
Professorship of justice of natural resources	University of Lapland	2013 – 2015
Professorship of mine politics	University of Eastern Finland	2014 – 2018
Professorship of environmental politics	University of Eastern Finland	2011 –

8.3.4 Findings of the research projects.

Different research projects have drawn relatively uniform conclusions. The importance of honest, respectful, open and widespread communication between a mine and the local community is usually emphasized (*e.g.* Kokko et al. 2013, Jartti et al. 2014, Suopajärvi et al. 2016) It is also recommended that social impacts are to be studied more extensively in the future, and that zoning, feasibility studies and environmental impact assessments including social assessment, should all be conducted in unison (Kokko et al. 2013). A large portion of the results have been published as guidebooks aimed to inform general public, decision makers, mining- and junior companies in *e.g.* social impact, CSR and SLO related questions (see for example Kokko et al. 2013 and Kestävän kaivostoiminnan verkosto 2016).

Jartti et al. (2014) and Suopajärvi et al. (2016) both conducted surveys on public opinion towards the mining industry. Attitudes towards mining and ore exploration were generally found to be positive. Jartti et al. (2014) studied also feelings related to different types of mining- and exploration projects. Extraction of natural stone was considered to be almost harmless and attitude towards metal mining was also positive, yet feelings towards uranium mining were slightly negative. However, the general acceptance towards mining sector wasn’t unconditional and mining was considered to be agreeable only if certain conditions are met. One of the most common preconditions was that a mine should benefit local communities and that local workforce should be preferred when hiring staff for the mine. However, Kokko et al. (2013) noted that in reality this wish is rarely fulfilled as most of the mine staff migrates from elsewhere and employment situation in the municipality might stay close to pre-mine levels. One reason for this is that the local unemployed workforce is often insufficiently qualified to work in a mine. Kokko et al. (2013) also noted that in some cases positive impacts from future mining projects had been exaggerated. When the high expectations on new jobs and tax income weren’t fulfilled, people from the local communities sometimes felt betrayed. Also, in the survey by Jartti et al. (2014) respondents generally felt that local communities didn’t have enough control on mine related subjects and felt illinformed about the local mining projects, yet in the same study acceptance towards mining was observed to increase with knowledge about operational Finnish metal mines further highlighting the importance of open communication and education.

Jartti et al. (2014) also studied trust towards different operators in the mining sector. Respondents generally trusted state research institutions, but stance towards state officials and politicians in charge of mining related subjects was more sceptical. Environmental- and nature conservation organisations were seen trustworthy when dealing with mining related subjects. Finnish mining companies were generally considered to be trustworthy, while foreign mining companies were seen as slightly distrustful. Population of Finnish Lapland was clearly more trustful towards all mining operation when compared to answerers from other parts of Finland – possibly showing the long existing relationships between mines and the local residence.

8.3.5 Executive organizations and project relations to other themes

There are a number of different organizations that are involved in research and development projects related to mining in Finland. The Finnish Innovation Fund (SITRA) released a database of mine related projects from 2010 to 2014 (SITRA 2014). The majority of the projects are dealing with manufacturing processes and management of waste and secondary materials (Fig 8.8).

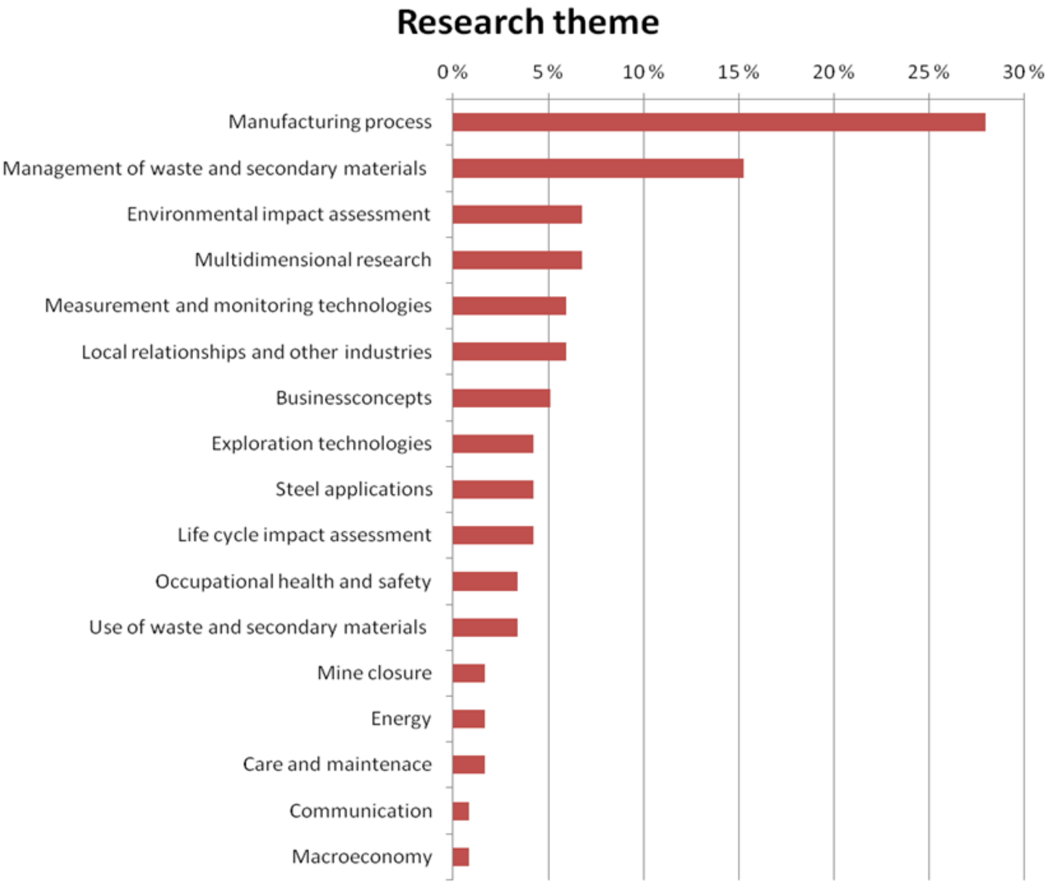

Figure 8.8. Different themes of research (modified after Sitra 2014).

The most common keywords of the project descriptions (Fig 8.9) are in line with the most common research themes. Most of the research themes are more technologically than social scientifically oriented. In keywords, the social license to operate is the 8th most common keyword, with approximately 8% coverage of all projects. The total number of all projects in the database is 118 and 10 of them had the keyword SLO.

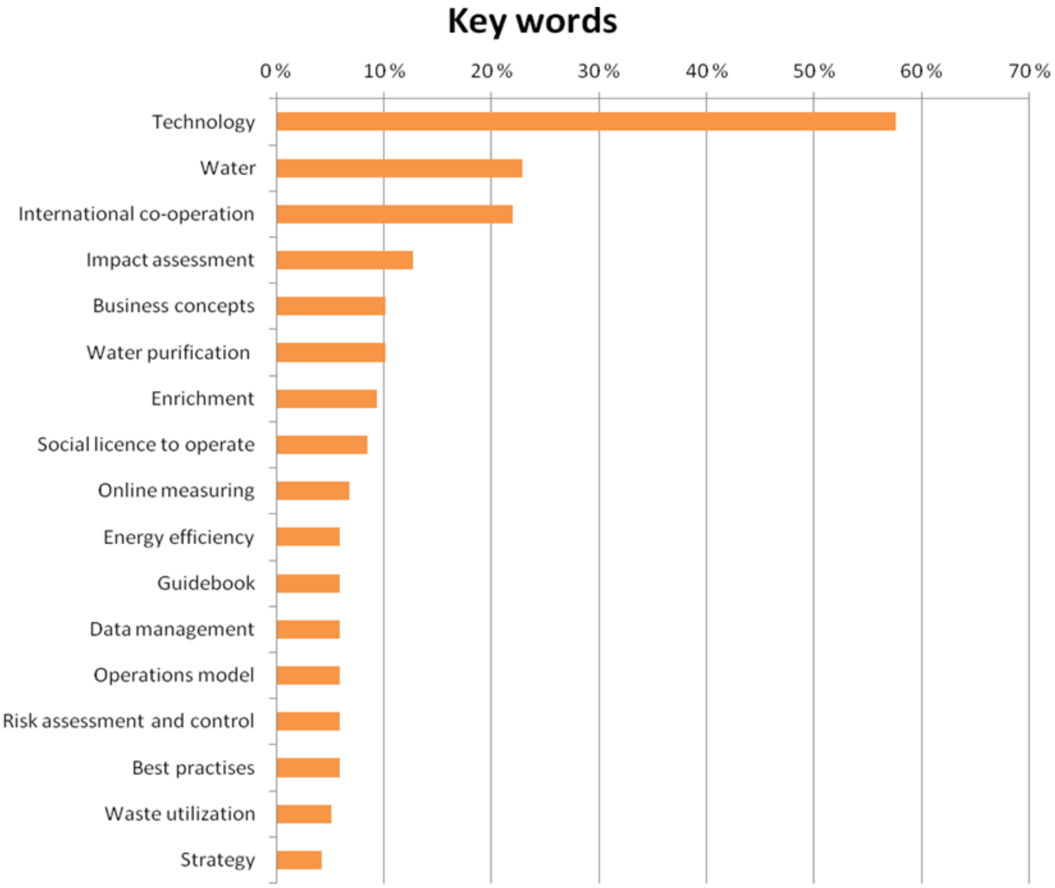

Figure 8.9. The most common keywords in project descriptions (modified after Sitra 2014).

The organizations running these 118 projects are presented in Figure 8.10. It can be seen that the Geological Survey of Finland and the University of Oulu have taken part in over 50% of all mine related projects in Finland. Comparing Figure 8.10 and Tables 8.2 – 8.4 one can observe that most of the projects focusing on research on the social impacts of mining are not led by the organizations that conduct the technologically oriented projects. For example the University of Eastern Finland has the most socially related projects in Tables 8.2 – 8.4.

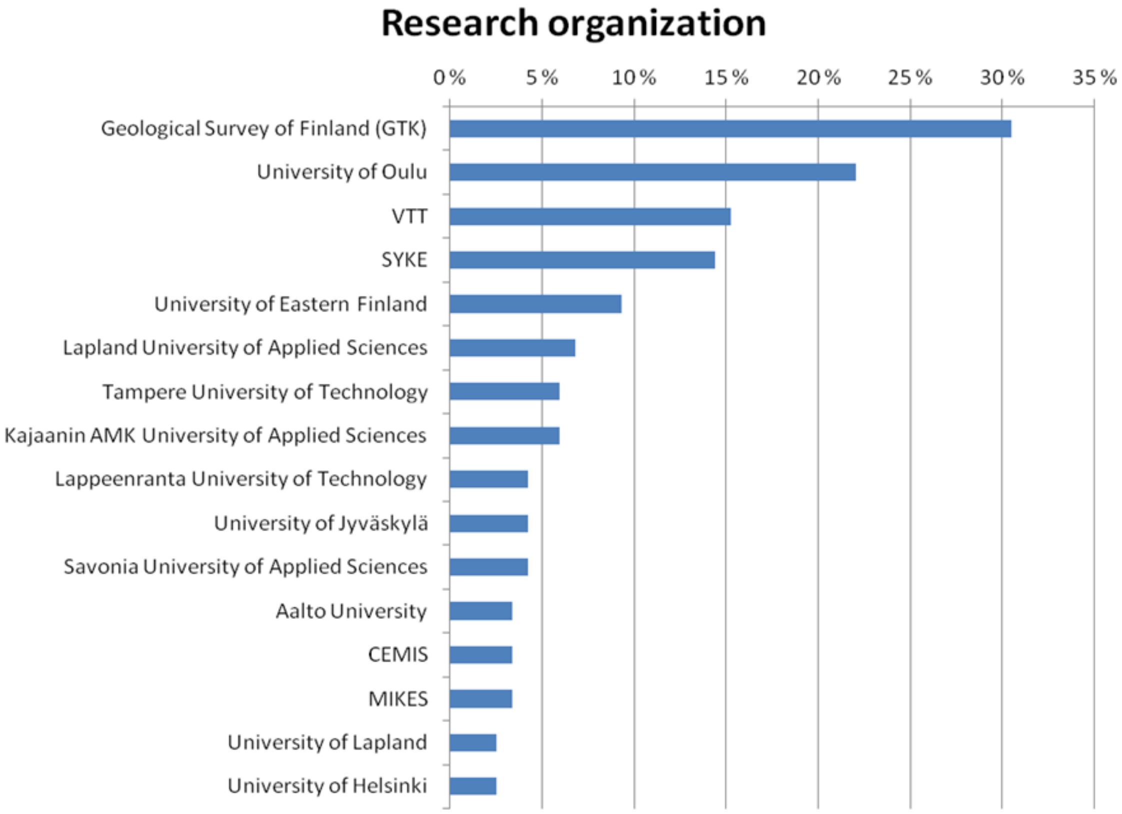

Figure 8.10. The participation percentages of different research organizations (modified after Sitra 2014).

In Figure 8.11 the relations of different SLO and CSR projects to state, universities and research institutes are represented. Placement of research projects are nearer to research institutes and universities, while promotional projects are closer to state (Eerola 2014).

Figure 8.11. Social licence to operate (SLO) and Corporate social responsibility (CSR) projects and their relations to state, universities and research institutes (modified after Eerola 2014).

8.4 Conclusions

A detailed sociological investigation was performed in Rovina area in order to better understand the population's perception on the complex issues related to mining. A quantitative study was conducted using 400 questionnaires completed face-to-face at respondents' homes with random sampling, and a qualitative study using 13 semi-structured interviews with authority representatives, community leaders, mining representatives and local inhabitants within the area. A series of relevant social indicators were analysed: employment, income, education, community cohesion and trust in order to draw the social profile of the community. The population sample was balanced, with 48% females and 52% males. The average age was 57 years, showing that the population in the area is quite aged. Most of the population is retired, about 17% used to work in the mining sector. The respondents' perception is that the area has good economic opportunities due to the natural resources and people, in spite of the current situation of economic depression and lack of works.

More than 60% of the respondents are not pleased to a certain extent with their way of living. The lack of working places is one of the main problems of the community. A rather high percentage of the respondents declared to trust the representatives of the mining company. Regarding the working places, the respondents appreciate stability more than good salary. More than 80% of the respondents that know about the mining company believe that its presence in the area would bring benefits to the community, such as: working places, financial welfare, personal stability/security, economic development, community development, improvement of the living conditions, etc.

The relation between the local community and the mining company is generally perceived as good and productive. Mining is hoped to bring some benefits in financial terms, improve social relations between people, increase balance between family members, increase people's financial stability and personal appreciation, etc. The dialogue that the company has initiated with the local community give the inhabitants the feeling that their opinions matter, and they are taken into account within the technical design of the mine, and within the future program of industrial development of the area.

Numerous studies have been conducted in Finland on the social impact of mining during the recent years. The evolution and development of the socio-economic approach of the Finnish mining industry has shown that single events can have a major influence on the prominent topics of research. Environmental problems have raised interest in the socio-economic and environmental influences of mining. One of the challenges in Finnish academic research on the social impacts of mining is that mining itself has a bigger impact on the surrounding nature and society than exploration, though proper communication during the early stages (*e.g.* the exploration phase) is essential to gaining the SLO that is necessary throughout the whole lifespan of the project (Eerola 2014).

It has also been noticed that SLO and CSR development is most efficient when action is planned through co-operation between the local people, NGO's, administration, and corporations. The participation of mining industry representatives or researchers with sufficient knowledge in natural sciences is important in social scientific research of mining to avoid misunderstandings and problems during the interpretation of results. A lot of the SLO and CSR research related to mining has been done in developing countries and it is not always possible to adapt these results directly to Finnish conditions (Eerola 2014).

In the mining industry there is critical need for collaboration and dialogue between technical experts and community members, NGOs, employees or public servants, in order to respect alternative values and to ensure stakeholders' support by incorporating their values on the mining system design, operation and closure (Muradian et al. 2003). As regards the variables and factors that affect and intermediate SLO, the most important ones are: the perception of environmental risks, the preferred decision-making mechanisms, trust in experts, trust in government institutions, fairness in the distribution of burdens and benefits and the attitude of the national (major) stakeholders able to shape public opinion. Usually, the project's assessment and approval lacks if there are: disagreement between experts, between the local population and the mining company, between mining company and other relevant stakeholders, distrust in institutions or lack of participatory procedure.

Public pressure and increased awareness is generally pushing the development of the mining industry to a more environmentally and socially conscious direction. The expectations towards the mining industry and public administration are a lot greater than hundred years or even couple of decades ago. The size and the number of the mining operations do not always have a direct connection to social acceptance and environmental problems. Every mine is different and every society is different, but through development and implementation of SLO and CSR on a site-specific basis, sustainable development is possible.

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9 SUMMARY

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When developing methodologies for sustainable gold production, vast multidisciplinary challenges need to be overcome. Environmental issues in mining concern nearly all the aspects of natural and engineering sciences as well as human and legal sciences. The SUSMIN -project took this challenge with a consortium of multidisciplinary and multinational team of scientists. Even though all the challenges could not be addressed in a single project, the team concentrated on major issues recognised locally and globally.

Both environmental and social management can be improved in all the stages of the life of mine. Risks for conflicts and financial losses can be minimised by addressing issues early and finding the best solutions to them through continuous development.

In the exploration stage direct environmental risks are usually low, but social acceptance need to be achieved already in this stage. Despite of low direct environmental risk, the exploration stage can have a huge impact on the environmental risk of the possible mine. If higher grade ores can be found and developed the need for quarrying and water and chemical use can be lower. Also waste rock quality can be studied already during the exploration and the best available techniques for the management can be used to reduce environmental risk.

When the mine is started the mineral processing plays a major part in the mine’s profitability. High recovery rates are necessary, but the beneficiation process can also be developed to produce less harmful waste materials, use less chemicals or substitute environmentally harmful chemicals to less harmful. Also water circulation can be increased to minimise the discharge of waste water.

Water is the major medium to transport possibly harmful substances outside the mining area. Water related issues also concern the general public the most and proper water management is an absolute necessity to maintaining the social license to operate and low environmental impact. Water treatment processes for mining effluent are constantly under development, but the need for lower effluent discharges is imminent, thus moving the water treatment part of the mining process from the current “last step before discharging the effluent to the nature” approach into an integral part of mine operation. The chemical and physical condition of the water inside and outside of the mining area need to be known, as well as the surface water and groundwater flow paths and the reactions during the transport. Sophisticated methodologies to study and model mining water are currently in use but the need for new methodologies and their acceptance from authorities is high.

All mines produce waste, which is stored. Such waste are *e.g.* waste rock, tailings and chemical residues. These are usually dammed in waste or tailings management facilities. Dam breaches have caused some of most serious mining accidents in the world and the mine safety is one of the most important issues in waste management. The methods that increase the stability of harmful elements, *e.g.* arsenic in gold mining, reduce their environmental impacts, and thus, make more inexpensive structures for waste areas possible.

Overall, gold mining can be made more sustainable if several multidisciplinary challenges can be solved. On the other hand, for example the recycling of the extracted material need to be organized properly, so that the demand of new extraction can be kept lower and a true sustainability can be achieved.

E R A · M I N

NETWORK ON THE INDUSTRIAL HANDLING
OF RAW MATERIALS FOR EUROPEAN INDUSTRIES

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