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# 10 THE CONTENTS

40	D. GATOT EKO SUSILO, MUNDZIR HASANBASRI MODELING SEAWATER INTRUSION FOR DESIGN OF A SUBSURFACE DAM UNDER DYNAMIC ENVIRONMENT BEHAVIOR	42
41	. M. TIMIROWA, S. MIRZAEV, O. YUSUPBEKOV THE HYDROGEL IS NEW WAY FOR PRESERVATION OF WATER RESOURCES	43
42.	APOSTOLOS G. VLYSSIDES, ANTONIS A. ZORPAS, KARLIS PANAGIOTIS, ARAPOGLOU DIMITRIS THE APPLICATION OF TI/PT ELECTRODES FOR THE TREATMENT OF DOMESTIC WASTEWATER IN DEFERENT PH VALUE	43
43.	. HYUNG-JAE YANG, EUNG-BAI SHIN, DEOK-GIL RHEE, HUN-GEUN CHOL, JAL- WOON LEE SOLUBLE COD REMOVAL USING BIOLOGICAL BS-SBR PROCESS	44
44.	STEPHANIE YOUNG, DANIEL W. SMITH EFFECT OF PULP MILL CHEMICALS ON RIVER FLOCCULATION	45
TR	EATMENT TECHNOLOGIES	47
	OMER AKGIRAY, AHMET M. SAATCI	77
	EVALUATION OF DESIGN METHODS FOR DECLINING RATE FILTRATION	47
46.	OMER AKGIRAY, AHMET M. SAATCI A NEW LOOK AT FILTER BACKWASH HYDRAULICS	48
47.	ORLANDO M. ALFANO, MARÍA J. MARTÍNEZ, RODOLFO J. BRANDI, , ALBERTO E. CASSANO EFFECTS OF THE $\rm H_2O_2$ CONCENTRATION AND UV LAMP SPECTRAL EMISSION ON THE PHOTOOXIDATION OF A WATER POLLUTANT	497
48.	RUI A. BOAVENTURA, MANUEL FONSECA ALMEIDA ALUMINIUM RECOVERY FROM WATER TREATMENT SLUDGES	509
49.	CRAIG BONNEVILLE, DANIEL W. SMITH, AYMAN R. SHAWWA EFFECTS OF PRE-OZONIAN AND SELECTED ADVANCED WATER TREATMENT PROCESSES ON MOUNT SEYMOUR IMPOUNDEMENT WATER	513
50.	RAFAŁ BRAY, KRYSTYNA OLAŃCZUK-NEYMAN THE INFLUENCE OF CHANGES OF GROUNDWATER COMPOSITION ON THE EFFICIENCY OF MANGANESE AND AMMONIA NITROGEN REMOVAL ON MATURE QUARTZ SAND FILTERING BEDS	525
51.	BART VAN DER BRUGGEN, KIM EVERAERT, DIRK WILMS, CARLO VANDECASTEELE THE USE OF NANOFILTRATION FOR THE REMOVAL OF PESTICIDES FROM GROUND WATER: AN EVALUATION	537
52.	ALBERTO E. CASSANO, RODOLFO J. BRANDI, MIGUEL A. CITRONI, ORLANDO M. ALFANO A PROPOSAL FOR STANDARDS OF ABSOLUTE VALUES OF THE TRUE PHOTOCATALYTIC- QUANTUM YIELDS IN SLURRY REACTORS	553
	YOUNG C. CHANG, KAHORI ASANUMA, MASAHIRO HATSU, KAZUHIRO TAKAMIZAWA REMOVAL OF TETRACHLOROETHYLENE IN AN ANAEROBIC FIXED-BED REACTOR IMMOBILIZED WITH CLOSTRIDIUM HIFERMENTANS DPH-1	565
	ZEKIYE ÇINAR, NEVIN SAN THE KINETICS AND MECHANISM OF THE PHOTOCATALYTIC DEGRADATION OF 4-NITROPHENOL IN TIO2 SUSPENSIONS	577
	LUCIANO COCCAGNA LATEST ADVANCEMENTS IN FILTRATION TECHNOLOGY	589
	JAN DAHLQUIS, MAREK KULESZA PRE-TREATMENT WITH DISSOLVED AIR FLOTATION CONSIDERING AN INTEGRATED PROCESS	

<i>57</i> .	EL-DIB MA, BADN ALTERNATIVE PR PRODUCTS
58.	MOHAMED GAMAL OZONE MASS TR MODELING OF OZO
59.	BJORNAR EIKEBRO REMOVAL OF NA LIGHTWEIGHT EXF
60.	MEDHAD H. ELZAF EXPERIMENTAL S DIOXIDE WITH THE
61.	CARLOS R. ESTER- RADIATION FIELD MESHES
62.	KENETH FICEK, P: POTASSIUM PERI PROBLEMS
<i>63</i> .	JERZY GANCZARC WATER COAGULA
64.	ROLF GIMBEL, WO MODELING THE F DEFFERENT TYPE
65.	ROLF GIMBEL, KLA FROM BASIC IN PERMEABLE SYNT
6 <b>6</b> .	MARIAN GRANOP
<i>67</i> .	ONA GYLIENË METAL REMOVAL
68.	GERALD HEINICKS MALTE HERMANS. EXPERIMENTS WI WATERWORKS
69.	RALPH HOBBY, JO LEACHING OF A TREATMENT
70.	MARIE-CHRISTINE CARBOFLUX ®AN CARBON FOR DRI
71.	MARIE-CHRISTINE INNOVATION FOR WATER TREATME
72.	PETER M HUCK, E REMOVAL OF CR LATION

73. JADWIGA KALETA REMOVING OF CEF IV MIĘDZYNARODOWA KONFERENCJA "ZAOPATRZENIE W WODĘ JAKOŚĆ I OCHRONA WÓD" KRAKÓW– POLAND 11-13 września 2000 IV INTERNATIONAL CONFERENCE "WATER SUPPLY AND WATER QUALITY" KRAKÓW – POLAND, SEPTEMBER 11-13,2000

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# ALUMINUM RECOVERY FROM WATER TREATMENT SLUDGES

Aluminum sulfate and polyaluminum chloride are widely used as coagulants in water treatment plants. A chemical sludge containing aluminium hydroxide, adsorbed organic matter and other water insoluble impurities is obtained after the flocculation-clarification process. In Portugal, an estimated amount of 66 000 ton/yr. (wet wt.) water treatment sludge is being disposed of on land or at municipal solid waste (MSW) landfills. Government restrictions to this practice as well as increasing deposition costs and the potential harmful impacts proceeding from the high aluminium content of the sludge have been leading to significant research efforts in order to evaluate different treatment alternatives, namely involving aluminium recovery and subsequent reuse. Despite membrane-based separation and liquid ion exchange processes have been studied for that purpose, the traditional acidic and alkaline extraction methods may be still explored to obtain a product susceptible of use as coagulant for industrial wastewater treatment purposes.

Centrifuged chemical sludge from a water treatment plant using polyaluminium chloride as coagulant was characterised in terms of humidity, volatile matter, Al, Fe, Mn, Cd, Cu, Cr, Pb, Ni and Zn. The dry sludge organic content is about 29% and the major elements determined are aluminium (= 12.6%), iron (= 2%) and manganese (= 0.14%). The aluminium recovery was investigated both by acidic and alkaline leaching processes. Concentrated  $H_2SO_4$  was selected as the acidic leaching medium and the process efficiency was evaluated at different operating conditions. The ratio dry sludge/sulphuric acid solution was varied between 0.5 and 2%, the pH ranged from 1.0 to 4.5, different stirring and settling times were established and the aluminium, iron and manganese dissolution was assessed. A similar study was performed at pH values between 10.0 and 13.6 using 2N/10N NaOH as the extracting solution and operating conditions as those of the acid extraction procedure. Whereas maximum aluminium recovery using  $H_2SO_4$  was about 61% at pH=1.0, the alkaline extraction led to aluminium recoveries of about 71% at pH = 13.6 (2% dry sludge in suspension, 90 min stirring time and 45 min settling time). Decreasing the sludge dosage to 0.5%, aluminium extraction increased to 87.4% at pH=13. As expected, acid extraction led to a higher Fe (18.2%) and Mn (42.1%) dissolution as compared with alkaline extraction at pH=13.6 (Fe=2.1% and Mn=3.2%).

#### 1. Introduction

Surface water treatment for domestic supply generally includes a coagulation/flocculation stage, often using aluminum sulfate as coagulant. Particulate, colloidal and soluble contaminants are entrapped or adsorbed on aluminum hydroxide flocs and further removed from the liquid phase by sedimentation. Since dried sludges have a high aluminum content, recycling this metal has become a

significant environmental issue. Despite membrane-based separation<sup>1</sup> and liquid ion exchange processes<sup>2</sup> have been studied for that purpose, aluminum hydroxide may be dissolved in strong acidic as well as alkaline media due to its amphoteric nature. So, the traditional acidic and alkaline extraction methods are still being explored<sup>3</sup>. According to Panswad and Chamnan<sup>4</sup>, the aluminum recovery by acid extraction (pH between 1.0 and 3.0) can reach 70-90%. Using the alkaline process, the highest removal efficiencies were found at the pH ranges 11.4-11.8 and 11.2-11.6, using NaOH and Ca(OH)<sub>2</sub>, respectively<sup>5</sup>. The aim of this research work is to study the aluminium recovery from the chemical sludge produced at the Lever Water Treatment Plant (Oporto, Portugal) by acidic and alkaline extractions. The effect of some operating parameters such as pH, sludge dosage, stirring and settling time on the extraction efficiency is also investigated. As the sludge contains small amounts of Fe and Mn, the solubilization of these metals is also evaluated.

# 2. Materials and Methods

# 2.1 Water Treatment Chemical Sludge

The humidity of the raw sludge, as received at the laboratory, is 83.9%. Dry sludge was ground and sieved (RMU sieve shaker) and the analyses performed in the < 0.075 mm grain size fraction. The chemical composition (dry wt. basis), in terms of volatile matter and metal content is given in Table 1. Volatile matter was determined by calcinating the dry sludge at  $500\pm50$  °C and metals were measured by AAS (902 GBC spectrophotometer) after sludge acid digesting (2.5 g dry sludge + 12 ml conc. HCl + 4 ml conc. HNO<sub>3</sub>) at 140 °C for 120 min.

Table 1. Main constituents of the Water Treatment Sludge (% dry wt.)

Constituent	% drv wt.
Volatile matter	28.86
AI	12.58
Fe Fe	2.07
Mn	0.14
Cd	< 0.001

Constituent	% dry wt.	
Cr	0.001	
Cu	0.004	
NiNi_	0.003	
Pb	0.028	
Zn	0.025	

# 2.2 Solubilization Tests

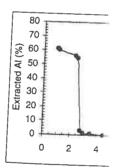
Distilled water (100 ml) was added to 250-mL Erlenmeyer flasks containing weighted amounts of dry sludge. Suspensions were stirred using a multiple position magnetic stirring plate. The effect of pH, sludge dosage, stirring and settling times on Al extraction rate was investigated. The pH was adjusted either using concentrated H<sub>2</sub>SO<sub>4</sub> to solubilize Al as Al<sup>3+</sup> or 2N/10N NaOH to extract

Al as Al(OH), selected as 90, tion to Al extra ferent operatin and Zn, are prelevel, their soll AAS after filter

# 3. Results a

Figure 1 prother acid range 60.9% at pH=11 min. A higher (pH=13.6). The tion efficiency of time (45 min) was achieved at extraction was 58.9%.

Fig. 1. Effect of p



The results of Figure 3. Stirring tively. Extraction effect was observed 0.5% sludge dosal effect of the post-0.5% sludge dosal unaffected by the covery increased variations.

iration<sup>1</sup> and liquid luminum hydroxdia due to its amtion methods are aluminum recov-0-90%. Using the at the pH ranges vely<sup>5</sup>. The aim of e chemical sludge gal) by acidic and uch as pH, sludge y is also investie solubilization of

ory, is 83.9%. Dry nalyses performed on (dry wt. basis), 1. Volatile matter and metals were acid digesting (2.5 for 120 min.

% dry wt.
0.001
0.004
0.003
0.028
0.025

flasks containing ng a multiple pos, stirring and setas adjusted either NaOH to extract Al as Al(OH)<sub>4</sub>. Sludge dosage varied between 0.5 and 2 %. Stirring time was selected as 90, 120 and 150 min and settling time as 15, 30 and 45 min. In addition to Al extraction, the solubilization of Fe and Mn was also assessed for different operating conditions. As other heavy metals, such as Cd, Cr, Cu, Ni, Pb and Zn, are present in the sludge in trace concentrations or below the detection level, their solubilization was not studied. Metals in solution were measured by AAS after filtering the suspensions through Whatman GF/C membranes.

#### 3. Results and Discussion

Figure 1 presents Al extraction results using acid and alkaline solutions. In the acid range (pH between 1.0 and 4.5) the maximum extraction yield was 60.9% at pH=1.0, sludge dosage=2%, stirring time=90 min and settling time=45 min. A higher recovery rate (71.3%) was achieved in alkaline conditions (pH=13.6). The effect of the stirring time (90, 120 and 150 min) on Al extraction efficiency can be observed in Figure 2. Sludge dosage (2%) and settling time (45 min) were kept constant. The highest efficiency (75.7% Al recovery) was achieved at pH=13 and stirring time=120 min. In acid medium (pH=2), Al extraction was less affected by the stirring time, varying between 56.3 and 58.9%.

Fig. 1. Effect of pH on AI recovery

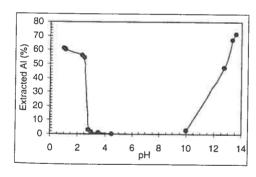
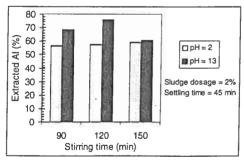


Fig. 2. Effect of stirring time on AI recovery



The results of Al recovery as a function of sludge dosage are presented in Figure 3. Stirring and settling periods were fixed at 120 and 45 min, respectively. Extraction increased as sludge dosage decreased, but a more marked effect was observed at pH=13. The highest Al extraction yields were found at 0.5% sludge dosage, both in acid (58.9%) and alkaline (87.4%) conditions. The effect of the post-reaction settling period on Al solubilization was studied for 0.5% sludge dosage and 120 min stirring time. In acid conditions extraction was unaffected by the settling time and averaged 56%. At pH=13, however, Al recovery increased with the settling time and the maximum extraction yield was 87.4% after 45 min settling.

Fig. 3. Effect of sludge dosage on Al recovery

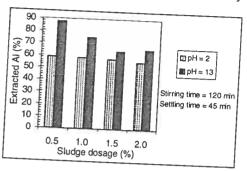
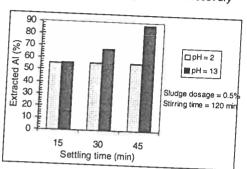


Fig. 4. Effect of settling time on Al recovery



Acid extraction led to higher solubilization rates of iron and manganese. Dissolved Fe reached a maximum of 18.2% at pH=1.0 and Mn extraction averaged 42.1% in the pH range 1.0-3.6. Using the experimental conditions corresponding to the maximum Al recovery yield (pH=13; sludge dosage=0.5%; stirring time=120 min; settling time=45 min), Fe and Mn solubilization rates were 10.7% (11.1 mg/L) and 3.0% (0.20 mg/L), respectively.

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# EFFECTS ADVANO ON MOUL

Three impoundments. Greater Vancouve /ozone/filtration pilo research for the impuniversity of Albert ozonation on the filtration pilotess. Results it subsequent remove absorbing organic reing particles and co

### 1. Introducti

#### 1.1 Project bac

The Mount located in the C West Coast of C mately 30 billic 1.7 million Gre good quality, with the control of t

A dissolved Falls Dam in the Seymour impour ver's drinking war

TABLE VI
Heavy metals in the leachates from ashes and mortars DIN 38414-S-4 tests and *Photobacterium Phosphoreum* toxicity

Parameter	FGI ashes	FGI mortar with 25% of ash	FBI ashes	FBI mortar with 30% of ash	Detection limit
Cd (mg/l) Cr (mg/l) Cu (mg/l) Ni (mg/l) Pb (mg/l) Zn (mg/l) EC <sub>50</sub>	nd 51.7 nd 0.71 nd 0.73 > 45%	nd 0.25 nd nd nd 0.59 > 45%	nd 4.0 nd nd nd 0.51 > 45%	nd 0.15 nd nd nd 0.49 > 45%	0.02 0.03 0.01 0.07 0.4 0.03 45%

nd = not detected; EC<sub>50</sub> = Percentage of leachate that causes the death of 50% of the *Photobacterium* innoculum.

does not significantly modify their adhesion properties relatively to those obtained through the addition of pyrogenous silica as a filler. In general a pre-gel formation is advisable as well as vigorous shaking prior to using the adhesive. The adhesives produced are safe in an environmental point of view and its green colour can be advantageous for use with dark footwear.

The application of ashes as a filler in mortars is admissible from a physical point of view when substituting up to 15% of cement by FBI ashes and up to 5% of cement for FGI ashes. Higher percentages of substitution are not feasible, unless high compressive strength materials are not required.

Including these ashes in mortars works really as a stabilization treatment to this residue, since the chromium leached is significantly less than that expected due to its percentage in the mixture.

An interesting effect of the incorporation of leather ash in mortars, particularly those richer in chromium,

is the strong greenish coloration that a small percentage of this residue produces in the final product. Therefore, ashes from incineration of chromium sulphate tanned leather scrap may be used as pigment in mortars and cement, too.

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