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Fe-Al RECOVERY FROM MINE WATER TREATMENT RESIDUALS AND PRODUCT TESTING FOR WASTEWATER TREATMENT - PHOSPHATE AND TURBIDITY REMOVAL

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Abstract
Mine water treatment scope is to produce an effluent which satisfies the discharge limits according to permits. However, the production of metal-rich sludge is a consequence of the mine water treatment and its disposal as a waste raises the cost of the whole operation, so ways to convert the sludge into marketable products are desirable. For example, mine water treatment sludge can be used for adsorbents or pigments production or some of the sludge components can be extracted and utilized as coagulants. Coagulants were obtained from mine water after partial precipitation of metal species or after conventional treatment, by leaching the sludge with acid. The effectiveness of coagulants considering phosphate, chemical oxygen demand and turbidity is presented in this paper, alongside with some of the drawbacks as observed.

Keywords: *mine water, coagulation, recycling*

Introduction
Mine water treatment generates important quantities of chemical sludge irrespective of the treatment process applied, active or passive (Hedin 2003). In particular, mine water generated from non-ferrous minerals sites, contains various heavy metal species and the precipitation product will contain Fe, Al, Zn, Mn, Cu, As, Cd, Cr, Ni. The metal-rich sludge disposal as a waste raises the operating costs, and efforts to recover some value from the residues are done. One option is the chemical extraction of the major elements from the sludge in order to obtain coagulants suitable for wastewater treatment (Menezes et al 2010, Janneck et al 2018).
Alongside with the recovery of the iron and aluminium process difficulties and efficiency of the coagulant solution obtained, the concentration of trace heavy metal is very important for conformity with existing coagulant standards and for market acceptability.

The aim of this work was to produce ferric-alumino sulphate solution starting from mine water sourced from a non-ferrous ore mining site and to assess the results for heavily polluted wastewater treatment, but also to address the susceptibility of releasing heavy metal in the treated water. A separate discussion is done, related to the quality of the coagulant solution itself compared to the parameters limited by standards for Fe/Al for coagulants. Because mine water from the non-ferrous mineral production sites is often treated by liming (Dinu et al 2018), we choose to use calcium hydroxide for metal precipitation and to evaluate the results obtained for sludge production to pH ≤ 5, aiming a product with higher Fe+Al content and higher purity, but also for pH =8.5, expecting a lower purity for this case. Because it was considered highly desirable to observe the effects of processing a sludge produced as in the normal operation of a mine water treatment facility, we present here the tests for the pH value at precipitation step of 8.5.

Experimental

Mine water from *Nicodim Tunel*, having 1939 mg Fe/L (80% Fe^{3+}) and 346 mg Al/L (see also Table 1 for other parameters) was processed by precipitation heavy metal species and aluminium with calcium hydroxide at pH = 8.5. The water was separated by settling and the sludge was concentrated to 18.2% dry solids (*d.s.)* by centrifugation (1500 x *g,* 10 min). Coagulant solution was obtained by dissolving the precipitate, at room temperature, with sulphuric acid (96%), using a 37% acid excess, reported to iron and aluminium only. The reaction mixture resulting after 2h mixing time is a paste, a viscous phase and it was diluted with distilled water (total volume 2.5 L final volume for 1 kg of centrifuged sludge) and the coagulant was extracted by orbital mixing for 16 h, followed by centrifugation (1500 x *g,* 10 min). The final coagulant product is a clear solution and was analyzed for Fe, Al and other metal and metalloid species by inductively coupled plasma optical emission spectrometry (ICP-OES), method SR EN ISO 11885:09, using an AVIO 500 Perkin Elmer Spectrometer.

Table 1 Mine water characterization, Nicodim

Parameter	Units	Values	Parameter	Units	Values
SO_4^{2-}	mg/L	8498	**Cr**	mg/L	0.21
Ca^{2+}	mg/L	588	**Cu**	mg/L	7.70
Mg^{2+}	mg/L	378	**Fe**	mg/L	1939
TDS	mg/L	13210	**Mn**	mg/L	252
Al	mg/L	346	**Ni**	mg/L	5.22
As	mg/L	3.44	**Pb**	mg/L	0.20
Cd	mg/L	3.03	**Zn**	mg/L	497
Co	mg/L	1.70			

Municipal WWTP Focsani sludge leachate (COD-Cr = 396 mg O_2/L, with 196 mg PO_4^{3-} /L) was subjected to treatment tests by coagulation using the product obtained as described above, following the process flow diagram as shown in 0. Coagulation treatment phase was optionally followed by flocculation with a cationic polymer (7 mg/L). The pH adjustment was not needed for the coagulant amounts used in these tests, but for the highest dose a distinct test with pH correction was done, mostly to observe the effect on phosphate removal. Analysis for water obtained after settling focused on chemical oxygen demand, turbidity (samples after gravity separation, with no filtration), and also heavy metal species were also determined by ICP-OES, for unfiltered samples also, preserved with nitric acid. Orto-phosphate was determined in filtered samples by ion-chromatography (IC Dionex 3000).

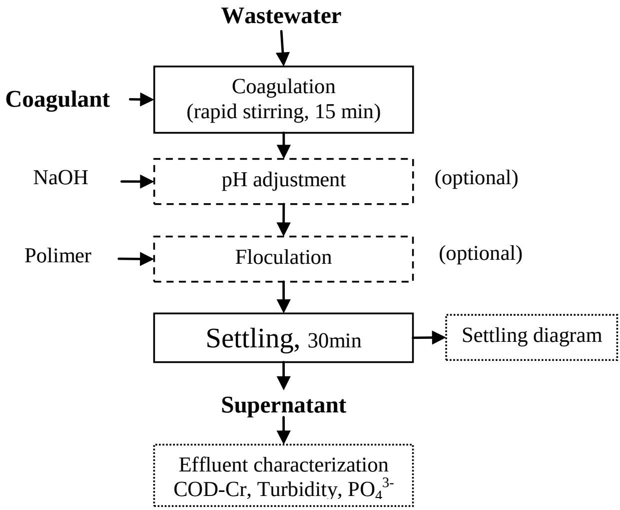

Figure 1. Waste water treatment test using coagulants, flow-sheet

Results and Discussion

Iron content of the coagulant solution increased with sulphuric acid amount, but the aluminium solubilisation is lower for the higher H_2SO_4 doses. In addition, the iron content does not increase significantly for the products obtained using higher acid amount, beyond the minimum value, so, taking into consideration the need of pH adjustment for the further wastewater treatment, only the coagulant product with minimum acidity was considered of interest (0). This coagulant contains also other heavy metals such as manganese and zinc, as the pH for the sludge production is high enough to allow precipitation from mine water (0).

Treatment of the municipal leachate by coagulation followed by flocculation had good results starting from 1.4 mEg/L (3.4 mL/L) with respect to global organic load and turbidity (settling supernatant, no filtration), with slightly improvement for coagulant doses up to 5.4 mEg/L Fe^{3+} and Al^{3+}.

Table 1. Coagulant solution grades obtained by processing mine water sludge

Parameter	**Units**	*H_2SO_4 96%*		
		0,53 g/g d.s.	*1,06 g/g d.s.*	*2,11 g/g d.s.*
Fe	mg/L	**5580**	6015	6635
Al	mg/L	**926**	688	749
Acidity	m Eg/L	**670**	1350	2710

Table 2. Heavy metals and metalloids - coagulant

Parameter	Units	Concentration	Parameter	Units	Concentration
As	mg/L	10,8	**Pb**	mg/L	0,61
Cd	mg/L	10,4	**Ni**	mg/L	19,7
Co	mg/L	5,05	**Mn**	mg/L	586
Cr	mg/L	1,23	**Zn**	mg/L	1955
Cu	mg/L	30,4			

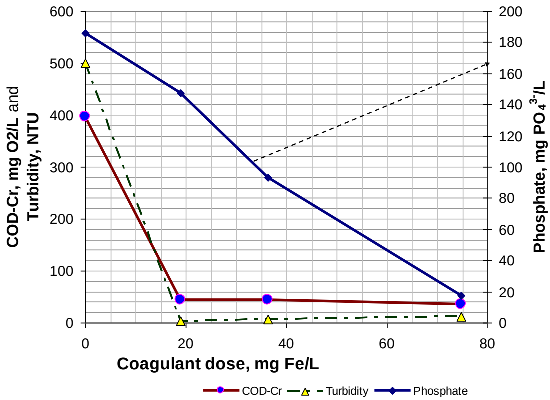

Figure 2. Waste water treatment tests using coagulants

Chemical oxygen demand dropped from 396 mg O_2/L down to 44 mg O_2/L (89% efficiency), while turbidity decreased from more than 500 NTU to 21 NTU. For the maximum coagulant dose the values are 35.2 mg O_2/L (91% efficiency for COD-Cr) and 11.4 NTU, respectively. Phosphate is removed by precipitation with ferric iron and aluminium and adsorption on solids, efficiency being continuously increased by the coagulant dose, as applied. Concentration of PO_4^{3-} in solution drops from 186 mg/L down to 17.6 mg/L, adsorption explaining a difference from maximum expected removal by precipitation and the effective phosphate elimination from solution.

A comparative test was done using only organic polymer: by simple flocculation, some of the suspended solids are removed, water after settling having a turbidity of 62.5 NTU and COD-Cr = 88 mg O_2/L (77% efficiency). As expected, there was no effect on phosphate.

Wastewater treatment by coagulation, followed by flocculation has a better efficiency than coagulation alone and the use of aluminum and iron salts is usually associated with flocculation adjuvant is well-established in the field of water and wastewater primary treatment (Buciscanu et al 2008, Tociu et al 2017). For our case study, comparative tests were done using 13.4 mL/L coagulant (5.4 mEg Fe^{3+} and Al^{3+}). Without flocculation a turbidity of 31.3 NTU is achieved after settling *versus* 11.4 NTU after coagulation and flocculation. Also the organic load (determined as

COD-Cr for homogenous phase after settling) is better with flocculation (35.2 mg O_2/L and 52.8 mg O_2/L, respectively).

The pH adjustment after coagulation, often necessary for this operation, it was not needed for this particular wastewater and coagulant amounts. However, for the maximum coagulant dose, 5.4 mEg Fe^{3+} and Al^{3+}, a test with pH adjustment was done, raising the pH from 6.6 to 7.7, using sodium hydroxide. Slightly better values for COD-Cr (26.4 mg O_2/L), turbidity (10.7 NTU) and phosphate (12.2 mgPO_4^{3-}/L) were recorded.

Another step to check the applicability of the coagulants obtained from mine water, was to assess the residual heavy metal concentration in the treated water. Of special interest was the effluent after the tests performed the highest coagulant product dose used in this experiment. Without the secondary treatment step, flocculation, the iron and also manganese and zinc had relevant high concentrations, explained both by precipitates remaining in suspension and also by species remaining in solution (especially manganese). With flocculation all values are better, due to better separation of the metal hydroxides from water (0). For the test ran with pH adjustment, final values for zinc and manganese were further improved. It can be discussed that the residence time in an industrial settler will be of 60-180 min, higher than for this experiment (30 minutes) and some improvements might be expected.

Table 3. Heavy metals and metalloids - concentration in water after treatment

Parameter	**Units**	***Coagulant only***	***Coagulation & flocculation***	***Coagulation with pH adjustment & flocculation***
As	mg/L	0.0078	<0.005	<0.005
Cd	mg/L	0.013	0.002	<0.0015
Co	mg/L	0.031	0.012	0.004
Cr	mg/L	<0.0013	<0.0013	<0.0013
Cu	mg/L	0.027	0.024	0.022
Fe	mg/L	5.50	0.45	0.29
Mn	mg/L	3.39	1.20	0.58
Ni	mg/L	0.13	0.063	0.013
Pb	mg/L	0.005	0.004	0.005
Zn	mg/L	1.86	0.13	0.035

Comment: Samples were analysed after settling, without filtration.

Water treated using the coagulant product obtained from mine water is acceptable to be discharged to surface water bodies, but a discussion is to be made regarding the quality of the coagulant as a product. Compared with commercial products, obtained from high purity raw materials (*e.g.* iron ore), available to meet standards for ferric and/or aluminium based coagulants to be used for treatment of water intended for human consumption, the coagulant obtained from the mine water has high ratios of heavy metal or metalloids to iron and aluminium. Taking into account the values showed in 0, even if the coagulant obtained from mine water is to be recommended only for wastewater applications, the perception on the market is expected to be unfavourable.

Table 3. Heavy metals and metalloids ratios to Fe and Al for the product

Ratio to Al and Fe	**Units**	**Mine water coagulant**	***EN 878 (**)***	**EN 887 (**)**	**EN 890 (***)**
As/Al	mg/kg Al	11663	*<100*		
Cd/Al	mg/kg Al	11231	*<100*		
Cr/Al	mg/kg Al	1328	*<1000*		
Ni/Al	mg/kg Al	21274	*<1000*		
Pb/Al	mg/kg Al	659	*<800*		
As/Fe	mg/kg Fe	1935			<20 mg/kg Fe
Cd/Fe	mg/kg Fe	1864			≤ 25 mg/kg Fe
Cr/Fe	mg/kg Fe	220			<350mg/kg Fe
Ni/Fe	mg/kg Fe	3530			≤350mg/kg Fe
Pb/Fe	mg/kg Fe	109			<100mg/kg Fe
As/(Al+Fe)	mg/kg {Al+Fe}	1660	-	<14	<20mg/kg Fe
Cd/(Al+Fe)	mg/kg {Al+Fe}	1599	-	<6	≤ 25mg/kg Fe
Cr/(Al+Fe)	mg/kg {Al+Fe}	189	-	<50	<350mg/kg Fe
Ni/(Al+Fe)	mg/kg {Al+Fe}	3028	-	<150	≤350mg/kg Fe
Pb/(Al+Fe)	mg/kg {Al+Fe}	94	-	<15	<100mg/kg Fe

* EN878, Aluminium sulphate, Type 3

(**) Aluminium Iron (III) Sulfate (Acorn Water, Technical specification sheet, ACE800, Spec.2106, retrieved 10.07.2019, http://www.acornwater.ie/content/files/ products/ 7_2_2106ACE800liquorSPEC.pdf

(***) Grade I Type 2 Iron(III) sulphate solution, Chemifloc Ltd., Product specification, Ferric Sulphate 140, rev.4, 2016, retrieved 10.07.2019, https://chemifloc.com/media/1286/ferric-sulphate-125-specification-rev-3.pdf

Conclusion

Coagulant Fe(III)-Al solutions were prepared using sludge from mine water treatment originating from a non-ferrous ore mining site, with the goal to valorise the precipitates from normal operation of the water treatment plant (pH = 8.5, neutralization with lime). Iron and aluminium content of the product is lower than for the marketed products due to moderate processing conditions. The coagulant had good performance on tested wastewater with respect to phosphate precipitation and suspended solids and organic load removal. As a consequence of the mine water origin and characteristics and conditions used for the source sludge production, the coagulant product has a significant content of unwanted metal species such as Mn, Zn, but also As, Cd, Ni, Pb. Heavy metal transfer water after treatment is low, acceptable, but the perception of the coagulant product on the market is expected to be unfavourable even for wastewater treatment, because the purity criteria are not met.

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