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ACID MINE WATER TREATMENT USING THE HIGH DENSITY SLUDGE TECHNOLOGY

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Abstract. Acidic mine water drainage (AMD) containing heavy metals from abandoned mine and spoil heaps is a major concern as it may generate significant surface water pollution. Research performed across the main Romanian closed mining perimeters revealed a high variability of chemicophysical characteristics of the AMD flows. Their chemical matrices show various ratios between specific chemical species. The efficiency of the AMD treatment is influenced by these ratios. The priority for the AMD treatment is the pH adjustment and heavy metals removal (most often done by oxidation and precipitation with alkaline reagents). One of the inherent issues, regardless of the treatment method, is represented by the high volumes of amorphous precipitates that are formed. After the gravitational separation – settling, these sludges can represent up to 35% (typically 10–25%) reported to the reaction tank outflow flow-rate. The solids content of the sludge is between 0.5 and 3.0% dry solids. As the generation of acidic mine water will continue for decades or even longer times, the improvement of the treatment methods is a must. Results of sludge densification tests using conventional high density sludge (HDS) method are discussed here, in correlation with the AMD source and the effects on the treated water quality.

Keywords: AMD, HDS, sludge-recycling, density, heavy metals.

AIMS AND BACKGROUND

Acid mine drainage is known as one of environmental problem which results from the mining operations, due to exposing the sulphide minerals to water and oxygen[1,2]. The AMD generation is a biochemical and chemical process, which can be described by three main reactions, as follows[3,4]:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

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[*] For correspondence.

The above reactions are shown for pyrite, but the process is taking place for other sulphide minerals, also[5] (e.g. chalcocite Cu_2S, galena PbS, arsenopyrite FeAsS, chalcopyrite $CuFeS_2$, sphalerite ZnS, millerite NiS, hawleyite CdS, cinnabar HgS).

Mine waters usually have a low pH, down to pH 2.5 (or exceptionally lower), but could be also circum-neutral. As the acid water will pass through different minerals, it will react with calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$, rhodocrosite $MnCO_3$ and also aluminosilicates, with the effect of raising pH and heavy metal precipitation, depending on final pH. Also, the Ca^{2+}, Mg^{2+} and Al^{3+} concentrations will increase.

Acidic mine waters can transport high heavy metals quantities in the receiving natural streams, with an impact on sediments also[6–8]. Most common heavy metals are Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}. Concentration levels of the order of magnitude of hundreds of mg/l are common. Much lower concentrations of As^{3+}, Cd^{2+}, Sb^{2+} and Hg^{2+} can be found, but these are significant due to their toxicity. Sulphate is the most important anion associated with mine water. Mine water discharges can be generated by spoil heaps, pits and underground workings.

Treatment of the AMD discharges is done using the so called active or passive techniques[9]. The passive techniques are more appropriate for those AMDs with moderate pH and with low to moderate heavy metals content. The active methods are usually used for high flow and heavy polluted mine waters.

The conventional alkali neutralisation with lime is the most common treatment process applied for the mine waters and it is based on the low solubility of the heavy metals in alkaline conditions. Neutralisation reagents of choice (but seldom used) are limestone $CaCO_3$, dolomite and sodium hydroxide.

By lime neutralisation, pH is increased to 8.5–10.5 and heavy metals are precipitated as hydroxides (e.g. iron hydroxide) or oxides (e.g. MnO_2). Air sparging is used for the oxidation of Fe^{2+} and Mn^{2+}. Arsenic, molybdenum and selenium, existing as anions in solution will co-precipitate with iron.

Amorphous precipitates are formed in the reaction stage of the process and separated by settling in a clarifier-thickener[10]. A sludge is obtained and can represent up to 35% and typically 10–25% reported to the reaction tank outflow quantity (which is equal, with reasonable accuracy with the mine water inflow). The solids content of the sludge is low, between 0.5 and 3.0% d.s. (dry solids) and this significant process stream has to be managed by pumping to a sludge pond or by mechanical dewatering. The process is therefore named the low density sludge (LDS) process.

A sludge that settles to a much higher density than conventional process can be obtained by high density sludge (HDS) two stage process using recirculated sludge as a seed for further metal precipitation[11–15]. HDS sludge is formed by mixing the recirculated sludge with lime followed by the contact with the mine water (classic HDS) or by reacting the recirculated sludge with mine water followed by a reaction step with lime, dosed to the desired pH set-point (type Geco or Noranda).

Mine water HDS treatment plants produce a ‘densified’ sludge containing 10 to 30% d.s., and so a ten to twenty sludge volume reduction after the settler is obtained, without other dewatering phase. Dewatering using filter press will generate a sludge having about 50% d.s.

The HDS process seems to be the preferred technology abroad, but for the industrial implementation site specific pilot plant level trials are always recommended by the majority of experts in this field.

In Romania, the cease of mining activity resulted in tens of AMD sources with flow-rates from 10 to 500 m^3/h, having to be treated before reaching natural water courses. Mine water treatment is based on conventional lime neutralisation, with good results when it is properly implemented and operated, but it has the common drawback of producing high volumes of sludge that require further dewatering. The HDS process has not any industrial implementation and no laboratory or pilot tests were reported, so research in this domain was necessary.

Both pilot plant research and laboratory tests were carried out to assess the HDS efficiency in relation with the sludge production and also the effluent quality.

Research performed across the main Romanian closed mining perimeters revealed a high variability of chemicophysical characteristics of the AMD flows (pH, conductivity, O/R potential, heavy metals, alkaline and alkaline earth ions, sulphate and chloride). Their chemical matrices show various ratios between specific chemical species (ratios between Fe and other heavy metals and between alkaline earth metals and heavy metals). AMD treatment results are influenced by these ratios, in a similar way, both for the conventional liming process (LDS) and the HDS process.

EXPERIMENTAL

Mine water matrices variability was studied for sources across Romanian main non-ferrous ore mining perimeters, Zlatna-Certej, Turt-Baia Mare and Bucovina. Analytical work was done using appropriate standardised methods including AAS, ICP-MS and ICP-OES for metallic species and ion-chromatography for anions and groups IA and IIA cations.

Laboratory treatment tests for conventional LDS neutralisation were carried out for most of the mine water samples, using lime milk as the alkaline reagent in batch system with mechanical mixing and aeration. The key process parameter is pH, in relation with heavy metal, aluminium, sulphate and TDS final concentrations.

HDS process was tested using two main technological variants, HDS Geco and classic HDS (see Fig.1 for the process flow diagrams).

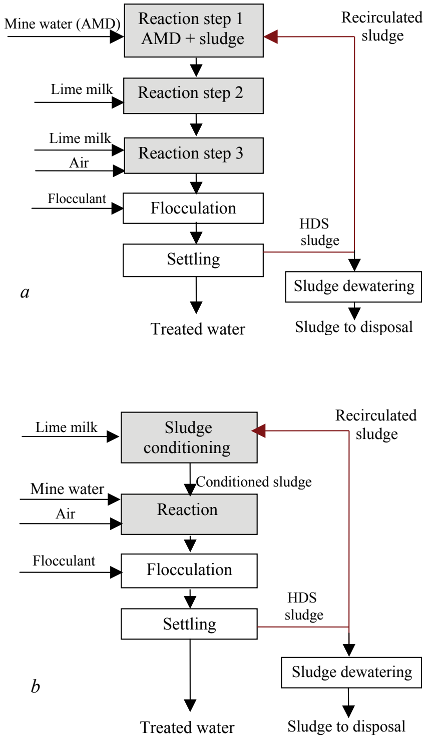


Fig. 1. HDS process, variant derived from GECO (*a*) and classic HDS (*b*)

HDS on-site pilot plant tests were started using an installation designed by ECOIND, commissioned at the Alunis Asecare mine site (max flow 1500 l/h) (Fig. 2). This pilot plant can have three reaction steps, with automatic pH control, followed by flocculation and settling with sludge recycling with a continuous operating regime, 24 h/24 h. Both conventional LDS treatment and HDS type Geco, with the first step of contacting sludge with mine water, were tested (flow 400–1100 l/h).

Conventional treatment tests are mandatory in order to establish the minimum retention time and the optimum pH in the continuous flow process. The efficiency of the reaction phase was assessed by analysing filtered samples of the effluent. Also, the quality of the supernatant after solids-liquid separation in the settler is important and it can be observed by comparing the filtered samples concentration versus non-filtered samples content: heavy metals and aluminium.

For the HDS process, the final working pH was kept equal to the corresponding optimum pH found for the conventional LDS flow sheet. The main parameter of the process is the solids recycle ratio (kg d.s./kg d.s.), representing the mass flow-rate of the solids recirculated as sludge from settler to reaction phase, reported to mass flow-rate of new solids produced (solids production). The solids production was quasi constant during the tests. Sludge solids content (105°C) was determined onsite using a thermo-balance type Precisa XM-60. Settling behaviour was assessed using batch settling diagrams determined for samples taken from reactors and flocculator and also by characterisation of the settler effluent (continuous flow). Supernatant samples were sent to laboratory for chemical characterisation (heavy metals, aluminium, calcium, magnesium and sulphate). Sludge viscosity was measured using a SV-10 vibro-viscometer from A&D Limited. For the particle size distribution analyses by laser diffraction a Malvern Mastersizer 2000 was used.

Fig. 2. ECOIND HDS pilot plant in operation at Alunis-Ilba

The classic HDS process was simulated in the laboratory using a methodology based on successive staged batches. As a first step, sludge to be recycled is produced by treating the mine water with lime using the conventional method. The lime quantity required for the reaction to the desired pH is determined at this stage. After settling, the solids production parameter is determined and the sludge is recovered for the first classic HDS conditioning step. The recycled sludge was treated with 80% of the lime quantity required for the neutralisation, the mixture being mechanically agitated at 350 rpm for 10 min. This was followed by the addition of a AMD quantity in the same reaction vessel, constant for all batches and afterwards by a rapid mixing at 500 rpm for 5 min, without aeration. The last reaction phase of 30 min was done under moderate agitation at 400 rpm and with aeration. Final pH adjustment was done with lime milk. Before settling, the suspension was flocculated with Floerger AN934 polyelectrolyte. A schematic diagram of the batch simulation of the classic HDS and the general laboratory set-up are given (Fig. 3).

The classic HDS was simulated for two different AMD sources, Alunis Asecare and Mestecanis. The two AMD sources differ by the iron to other heavy metals ratios, by Al/Mg ratio and also by sulphate concentration reported to gypsum precipitation equilibrium value $[SO_4^{2-}]_e = 1500$ mg/l (by capacity to precipitate calcium sulphate with lime).

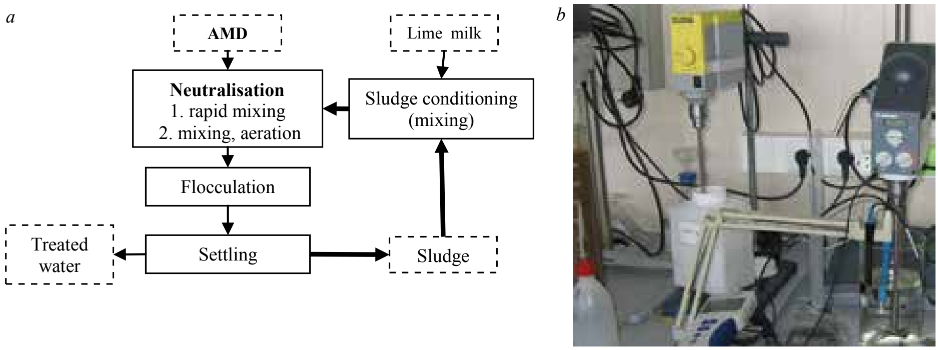


Fig. 3. Batch laboratory simulation of the classic HDS process, schematic diagram (*a*) and a general lab set-up (*b*)

RESULTS AND DISCUSSON

Results for various AMD sources monitoring represent a large set of data, difficult to be condensed here. Depending on source, a large diversity of chemical characteristics of the mine waters (absolute concentrations and also ratios between different heavy metals content and between alkaline earth metals to heavy metals) was observed.

Consequently, various approaches for the mine water treatment are needed. Many mine water sources have high aluminium and manganese content and might present the most difficult conventional treatment.

Composition variability in time for the same AMD source can affect the treatment results for a given technology. Three time variation patterns for short to medium term (one to five years) were observed and are briefly presented here:

– quasi-constant absolute concentrations, but also quasi-constant ratios between relevant species (see an example in Table 1);

– variability of absolute concentrations, but quasi-constant ratios between relevant species. This is exemplified for one heavy polluted source in Table 2.

– significant variability of absolute concentrations, but also of the ratios between relevant species (exemplified in Table 3).

Table 1. Ratios between species concentration (mass) for Mestecanis AMD (value for April 2008 – value for March 2013)

	(mg/l)	Fe	Mn	Zn	Al	Mg	Ca	SO_4^{2-}
		501–555	5.5–9.9	3.1–2.6	95–117	33–25.5	61–74	1711–1868
Fe	501–555	**1.0**	**0.011–0.018**	**0.006–0.005**	**0.19–0.21**	**0.07–0.05**	**0.12–0.13**	**3.42–3.37**
Mn	5.5–9.9	**91.1–56.1**	**1.0**	**0.56–0.26**	**17.3–11.8**	**6–2.58**	**11.09–7.47**	**311–188**
Zn	3.1–2.6	**162–213**	**1.77–3.81**	**1.0**	**30.6–45**	**10.6–9.8**	**19.7–28.46**	**552–718**
Al	95–117	**5.3–4.74**	**0.06–0.08**	**0.03–0.02**	**1.0**	**0.35–0.22**	**0.64–0.63**	**18–16**
Mg	33–25.5	**15.0–21.8**	**0.17–0.39**	**0.09–0.10**	**2.88–4.59**	**1.0**	**1.8–2.9**	**512–73**
Ca	61–74	**8.0–7.5**	**0.09–0.13**	**0.05–0.04**	**1.56–1.58**	**0.54–0.34**	**1.0**	**28–25**
SO_4^{2-}	1711–1868	**0.29–0.30**	**0.003–0.005**	**0.002–0.001**	**0.06**	**0.019–0.014**	**0.036–0.04**	**1.0**

Note: [Cu] = 21.7–20.1 mg/l; [Fe]/[Cu] = 23.1–25.6 mg/mg; concentration ratios in bold.

Table 2. Ratios between species concentration (mass) for Baiaga Tunel AMD (values for September 2007 – value for July 2008)

	(mg/l)	Fe	Mn	Zn	Al	Mg	Ca	SO_4^{2-}
		872–1604	181–400	425–925	168–350	252–556	444–454	8703–21338
Fe	872–1604	**1**	**0.21–0.25**	**0.49–0.58**	**0.19–0.22**	**0.29–0.35**	**0.51–0.28**	**9.98–13.3**
Mn	181–400	**4.8–4.01**	**1**	**2.35–2.31**	**0.93–0.88**	**1.39–1.39**	**2.45–1.14**	**48.1–53.4**
Zn	425–925	**2.05–1.73**	**0.43–0.43**	**1**	**0.4–0.38**	**0.59–0.6**	**1.04–0.49**	**20.48–23.1**
Al	168–350	**5.19–4.58**	**1.08–1.14**	**2.53–2.64**	**1**	**1.5–1.59**	**2.64–1.3**	**51.8–60.9**
Mg	252–556	**3.46–2.88**	**0.72–0.72**	**1.69–1.66**	**0.67–0.63**	**1**	**1.76–0.82**	**34.5–38.4**
Ca	444–454	**1.96–3.53**	**0.41–0.88**	**0.96–2.04**	**0.38–0.77**	**0.57–1.22**	**1**	**19.6–47.0**
SO_4^{2-}	8703–21338	**0.1–0.08**	**0.02–0.02**	**0.05–0.04**	**0.02–0.02**	**0.03–0.03**	**0.05–0.02**	**1**

Concentration ratios in bold.

Table 3. Ratios between species concentration (mass) for Turt Penigher AMD (values for September 2007 – value for August 2008)

	(mg/l)	Fe	Mn	Zn	Al	Mg	Ca	SO_4^{2-}
		19.5–500	8.6–112	28.6–156	8.9–279	16.8–185	173–302	1070–7243
Fe	19.5–500	**1**	**0.44–0.22**	**1.46–0.31**	**0.46–0.56**	**0.86–0.37**	**8.87–0.60**	**54.9–14.5**
Mn	8.6–112	**2.3–4.5**	**1**	**3.34–1.39**	**1.04–2.48**	**1.96–1.65**	**20.21–2.69**	**125–64.5**
Zn	28.6–156	**0.68–3.2**	**0.3–0.721**	**1**	**0.31–1.8**	**0.59–1.2**	**6.06–1.94**	**37.5–46.5**
Al	8.9–279	**2.19–1.79**	**0.96–0.40**	**3.21–0.57**	**1**	**1.9–0.66**	**19.4 –1.08**	**120–26**
Mg	16.8–185	**1.16–2.7**	**0.51–0.61**	**1.7–0.84**	**0.53–1.5**	**1**	**10.3–1.63**	**63.7–39.2**
Ca	173–302	**0.11–1.7**	**0.049–0.37**	**0.17–0.52**	**0.05–0.9**	**0.1–0.61**	**1**	**6.18–23.9**
SO_4^{2-}	1070–7243	**0.018–0.07**	**0.008–0.015**	**0.03–0.02**	**0.008–0.04**	**0.02–0.03**	**0.16–0.04**	**1**

Concentration ratios in bold.

For the conventional treatment of acid mine water, with pH adjustment, oxidation + precipitation using air and lime, some correlations might be mentioned, between ARD chemistry and the optimum process parameters, related to heavy metals and aluminium removal.

Manganese removal below limit of 1 mg/l requires a higher pH than other heavy metals, up to 10.5, if [Fe]/[Mn] ratio is low. If this ratio is high, operating pH can be lowered down to 9.3–9.5 or less, to 8.8–9.0. These values are to be considered together with pH upper limit of 8.50 for discharges to natural receivers. On another hand, one indicator which is not always considered when treating mine waters is aluminium that has to be precipitated to a pH below 8.0. When operating with higher precipitation pH, beyond 8.5, e.g. when targeting manganese removal, the aluminium can be re-solubilised and the limit for this indicator (5 mg/l) is very likely to be exceeded. Conventional AMD technology overcomes this by using a two-step reaction + settling process (e.g. one step at pH = 7 and the second at pH = 9.5–10.5). However, it was observed that a one-step process with higher precipitation pH (9.5 up to 10.0) can be used when required for Mn removal, without having high dissolved aluminium levels in effluent, if magnesium to aluminium ratio is high. This can be explained by hydrotalcite formation and it is quite a frequent situation.

The above correlations were found to be true for the HDS process results also. For the two AMD sources used for HDS tests, Alunis Asecare and Mestecanis, the working concentration, together with chemical matrix, are shown in Tables 4 and 5. The two AMD sources chemical matrices differences can be easily observed from Fig. 4.

Table 4. Chemical matrix for the Alunis Asecare AMD

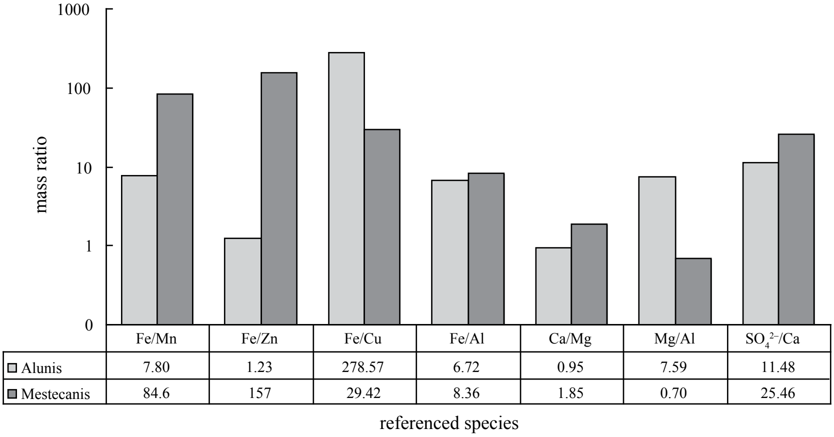
	mg/l	Fe	Mn	Zn	Cu	Al	Mg	Ca	SO_4^{2-}
		195	25	159	1	29	220	210	2410
Fe	195	**1.0**	**0.13**	**0.82**	**0.00**	**0.15**	**1.13**	**1.08**	**12.36**
Mn	25	**7.8**	**1.0**	**6.36**	**0.03**	**1.16**	**8.80**	**8.4**	**96**
Zn	159	**1**	**0.16**	**1.0**	**<0.01**	**0.18**	**1.38**	**1.3**	**15**
Cu	1	**279**	**35.7**	**227**	**1.00**	**41.4**	**314**	**300**	**3443**
Al	29	**6.72**	**0.86**	**5.48**	**0.02**	**1.00**	**7.59**	**7.24**	**83.1**
Mg	220	**0.9**	**0.11**	**0.72**	**<0.01**	**0.13**	**1.0**	**0.95**	**11.0**
Ca	210	**0.93**	**0.12**	**0.76**	**<0.01**	**0.14**	**1.05**	**1.0**	**11.5**
SO_4^{2-}	2410	**0.08**	**0.01**	**0.07**	**<0.01**	**0.01**	**0.09**	**0.09**	**1.0**

Concentration ratios in bold.

Table 5. Chemical matrix for the Mestecanis AMD – working situation

	mg/l	Fe	Mn	Zn	Cu	Al	Mg	Ca	SO_4^{2-}
		423	5	3	14	51	36	66	1670
Fe	423	**1.0**	**0.01**	**0.01**	**0.03**	**0.12**	**0.08**	**0.16**	**3.95**
Mn	5	**85**	**1.00**	**0.54**	**2.88**	**10.1**	**7.10**	**13.1**	**334**
Zn	3	**157**	**1.85**	**1.00**	**5.33**	**18.7**	**13.2**	**24.3**	**619**
Cu	14	**29**	**0.35**	**0.19**	**1.00**	**3.52**	**2.47**	**4.60**	**116**
Al	51	**8.36**	**0.10**	**0.05**	**0.28**	**1.00**	**0.70**	**1.30**	**33.0**
Mg	36	**11.9**	**0.14**	**0.08**	**0.41**	**1.43**	**1.00**	**1.85**	**47.0**
Ca	66	**6.45**	**0.08**	**0.04**	**0.22**	**0.77**	**0.54**	**1.00**	**25.5**
SO_4^{2-}	1670	**0.25**	**0.00**	**0.00**	**0.01**	**0.03**	**0.02**	**0.04**	**1.0**

Concentration ratios in bold.



	Fe/Mn	Fe/Zn	Fe/Cu	Fe/Al	Ca/Mg	Mg/Al	SO_4^{2-}/Ca
□ Alunis	7.80	1.23	278.57	6.72	0.95	7.59	11.48
▨ Mestecanis	84.6	157	29.42	8.36	1.85	0.70	25.46

Fig. 4. Mass ratios for relevant chemical species for Alunis and Mestecanis AMDs (log scale)

For the conventional treatment process, the specificities for the two AMDs are as following:

– for the manganese removal, Alunis AMD has a moderate [Fe]/[Mn] ratio (7.8 mg/mg) and requires a moderate to high pH of 9.50. For this pH value (even up to 10.0) the residual Al concentration will not exceed 0.5 mg/l and it can be noticed that this source has a high Mg/Al ratio (7.6 mg/mg);

– Mestecanis AMD has an exceptional high [Fe]/[Mn] ratio (85 mg/mg) and a pH of 8.8–9.1 is sufficient for the manganese removal by co-precipitation with iron, but with relevant residual aluminium concentration (dissolved). For a higher pH, aluminium level will approach to the limit of 5 mg/l or will exceed it. This source has a low [Mg]/[Al] ratio of only 0.7 mg/mg;

– for both AMD sources, the settling rate is high and the clarification is very good with the aid of flocculants (relative differences of metal concentrations for filtered and un-filtered samples are low).

The onsite pilot tests for Alunis AMD showed that results for LDS and HDS-type Geco are similar for the same process parameters, reaction time and pH (Table 6).

Also, the effluent has similar suspended solids content, quantified as heavy metal content for unfiltered samples (the superficial loading rate *Ih* for the settler can be similar).

Table 6. Relevant onsite pilot tests results for Alunis Asecare – effluent

Type of pilot tests		LDS tests		HDS Geco test		Dis-charge limits
parameter	unit	reaction effluent	settled efluent	reaction effluent	settled effluent	
pH		9.50	9.20	9.50	9.25	6.5–8.5
Reaction time	min	30.00	–	30	–	
Fe	mg/l	0.24	0.40	0.13–0.18	0.19–0.72	5
Mn	mg/l	0.59	0.80	0.47–0.61	0.84–0.97	1
Zn	mg/l	0.19	0.39	0.31–0.36	0.28–0.86	0.5
Al	mg/l	0.28	0.34	0.17–0.20	0.22–0.49	5
Ih	m/h	–	0.60	–	0.60	–

The sludge produced during the HDS Geco tests had a maximum solids content of 13.2% d.s., corresponding to the maximum solids recycling rate of 22.4 kg/kg (Fig. 5). By gradually increasing the AMD inflow rate and as a consequence the new formed solids production rate, thus lowering the solids recycling down to 10 kg/kg, the solids content of the sludge is dropping down to about 11% d.s., which is still well above the maximum value corresponding to the thickened LDS sludge for this AMD, about 1.5% d.s. Without thickening, the LDS sludge solids content can be as low as 0.6% d.s.

Vacuum filtration (–0.9 barG) showed interesting results: by filtration the same volume of sludge, the filtration time for the LDS sludge is 40 times higher compared to HDS Geco sludge. The filtered sludge solids contents and densities were 11.8% d.s. (1.1 kg/dm^3) for LDS and 24.2% d.s. (1.24 kg/dm^3) for HDS, respectively.

The settling rate of the sludge was studied on-site using the batch settling test procedure. On start-up, due to the increase of the solids content of the suspension, the settling rate is significantly lower than for the LDS. After the formation of HDS dense sludge, the settling rate is improving and finally the initial settling rate is comparable to the value for LDS, as it can be seen in Fig. 6 (but remains lower). It should be mentioned that the initial suspension concentration for the HDS was up to 30 g/l versus 1–2 g/l for LDS, but it can be seen that the final the final sludge volumes after 120 min are similar.

The viscosity of the HDS sludge was 22 and 2.4 mPa s for the LDS.

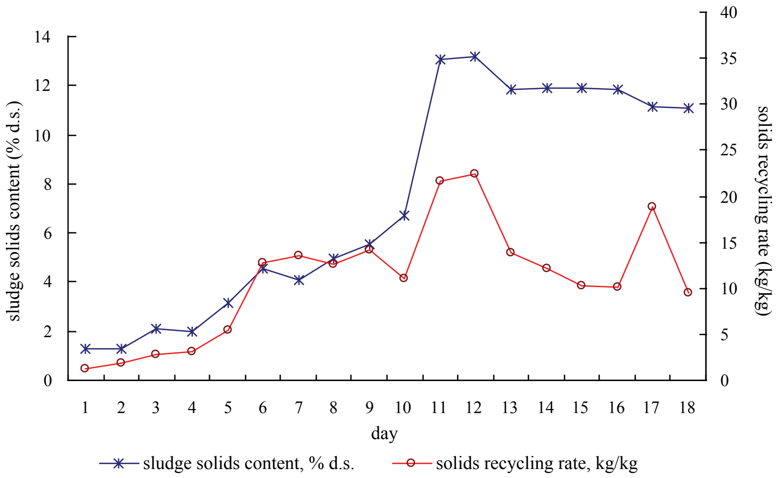


Fig. 5. Sludge solids content and solids recycling rate for HDS pilot plant – Alunis

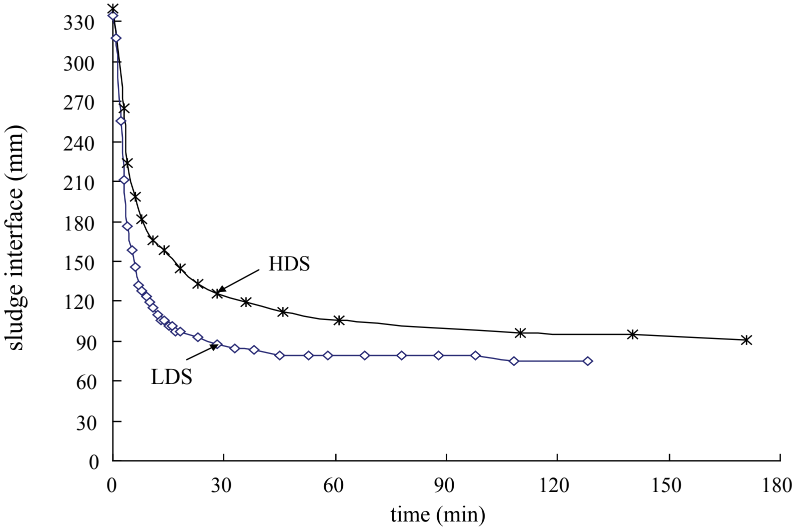


Fig. 6. Batch settling tests results for the LDS sludge and the HDS Geco sludge

Laboratory batch tests for the classic HDS process showed a similar sludge density dependence of solids recycling rate. For the Alunis AMD, it looks that the formation of the HDS sludge is somehow difficult due to the high zinc and aluminium. Figure 7 shows the results of the batch tests for the Alunis and Mestecanis AMDs, the sludge solids content being determined for 1 h and 16 h settling time. Most probably due to the high content iron content, for Mestecanis AMD the start-up of the process is simpler and the overall results are better, especially for a thickening time of 16 h. Taking as a reference the maximum solids recycle rate tested in the HDS Geco pilot configuration, 22 kg/kg, the sludge solids content is lower for the classic HDS tests: about 8% d.s. for Alunis and Mestecanis sources, for a thickening time of 1 h and 10.5% or 11.5% for 16 h thickening time for Alunis or Mestecanis, respectively.

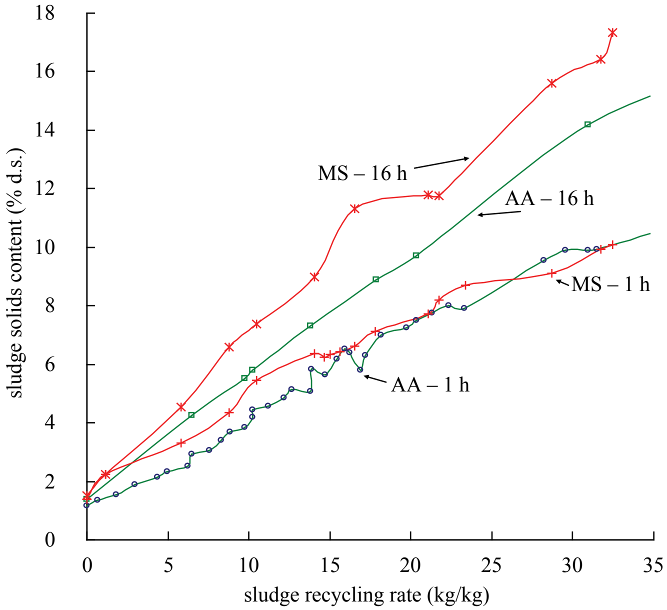


Fig. 7. Batch system simulation of the classic HDS process – Alunis versus Mestecanis AMD Sludge solids content for 1 and 16 h thickening time versus solids recycling rate (AA – Alunis; MS – Mestecanis)

Treated water quality for the classic HDS tests was assessed by comparing filtered samples of supernatant after batch settling with the unfiltered samples. The dissolved phase quality as heavy metal content is a consequence of reaction time and operating pH as explained above, but the overall quality of the effluent, especially for the Alunis AMD is lower in comparison with LDS tests results. Supernatant relevant characterisation data is presented in Tables 7 and 8. The ratios of the quality indicators, HDS reported to the corresponding LDS values are compared side by side in Fig. 8.

Batch settling can be considered ideal or, at least not affected by various disturbing factors common to a continuous flow settling, so the suspended solids presence in the supernatant can be explained by the reaction + sludge recirculation system itself.

According to some studies, the turbidity can be avoided by using a higher flocculant dose, but the dose in the lab was kept below 1 mg/l as active substance.

Table 7. Analytical result for supernatant after settling – classic HDS tests, for Alunis AMD

Solids recycling rate	g/g	20.5		31		52.4	
pH		9.5		9.30		9.5	
Settling time	h	1.0		1.00		1.0	
		filtered	unfiltered	filtered	unfiltered	filtered	unfiltered
Al	mg/l	0.722	1.218	0.40	0.82	0.268	0.616
Cu	mg/l	0.018	0.024	–	–		–
Fe	mg/l	0.149	3.263	0.267	2.46	0.021	1.003
Mn	mg/l	0.034	0.097	0.220	2.08	0.019	0.158
Zn	mg/l	<0.010	0.581	0.880	0.96	<0.01	1.396

Table 8. Analytical result for supernatant after settling – classic HDS tests, Mestecanis AMD

Solids recycling rate	g/g	22.4		32.5	
pH		9.30		9.10	
Settling time	h	1	1	1	1
		filtered	unfiltered	filtered	unfiltered
Al	mg/l	4.050	4.680	0.880	4.230
Cu	mg/l	0.022	0.024	–	–
Fe	mg/l	0.129	3.720	0.075	0.912
Mn	mg/l	0.083	0.134	0.061	0.083
Zn	mg/l	<0.010	0.065	<0.010	<0.010

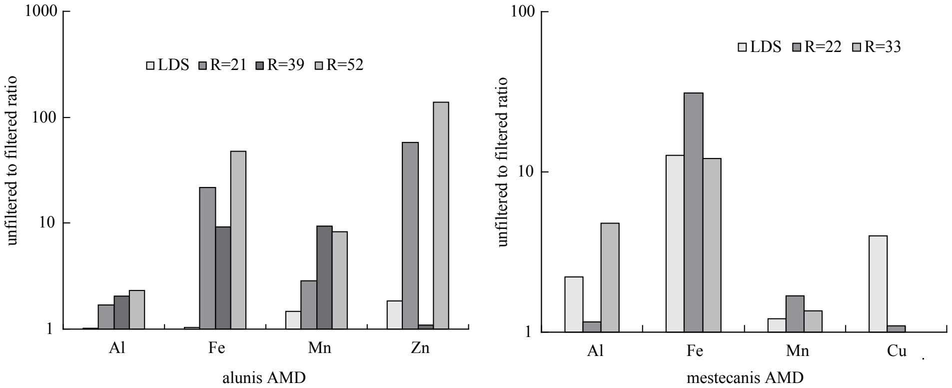


Fig. 8. Classic HDS batch tests: unfiltered to filtered supernatant concentrations after 1 h settling time versus LDS values (*R* – solids recycling ratio, kg/kg)

There are two aspects of the solid-liquid separation: the bulk sludge settling rate of the HDS as measured at the interface and the settling rate of the finest particles produced at the reaction phase.

For the HDS, a particle size distribution shifted to lower values can explain the observed supernatant turbidity. Low size particles will have a lower settling rate which is not compensated by the increase of density. As illustrated shown in Figs 9 and 10, the particle size shifting occurred both for the HDS type Geco tests and classic HDS batch tests. The bimodal distribution indicates both particle growth and abrasion, two counter processes occurring simultaneously[16]. Another hypothesis we can look at is that the hydrophobicity of the HDS particles could be higher than for LDS which can explain the sludge compaction, but it can raise the affinity for air bubbles also and so, a flotation of the small particles can occur.

At the same time, for the systems with sludge recirculation, an optimum sludge purging rate is to be found, as the particles can become coated with the flocculant and reduce the solid-liquid separation efficiency[11].

The decrease of particle size and the increased solids population have a negative effect on bulk settling rate, more pregnant for the batch classic HDS tests than for the HDS Geco. From Fig. 11 it can be observed that the sludge initial settling rate for the classic HDS tests is continuously decreasing as solids recycle rate is increased.

One question which can arise is about the effect of a simple prolonged stirring on sludge properties: is the sludge age sufficient to obtain a compaction such as in the recycling HDS process? This was tested using a LDS sludge produced using Mestecanis AMD which was thickened for 16 h (final solids content 1.73% d.s.). The sludge was stirred at 500 rpm for 6 h, 30 h and 48 h, with intermediate thickening or 16 h in order to determine the volume and solids content. The stirring was realised with the same PBT type agitator used for the classic HDS batch tests. Stirring has the effect of particle attrition as shown in Fig. 12, but the sludge solid content increased from 1.73% d.s. (no stirring) to 2.05% d.s. after 36 h of agitation. After another 48 h agitation time (84 h cumulated), the sludge density did not increase anymore. Thus, the shifting of the particle size distribution to lower values, similar to HDS process, but the sludge densification is not produced by simple stirring.

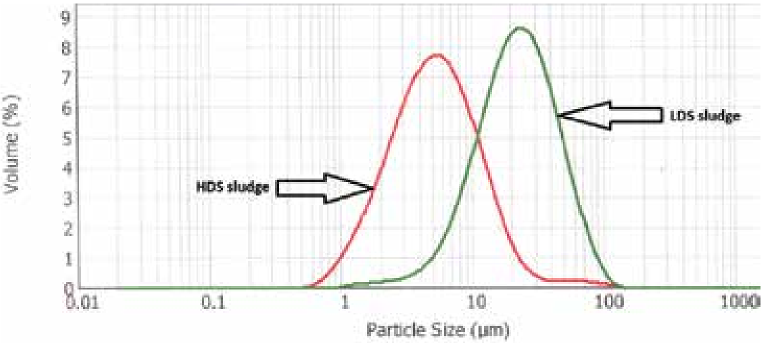


Fig. 9. Particle size distribution for HDS Geco sludge – Alunis AMD

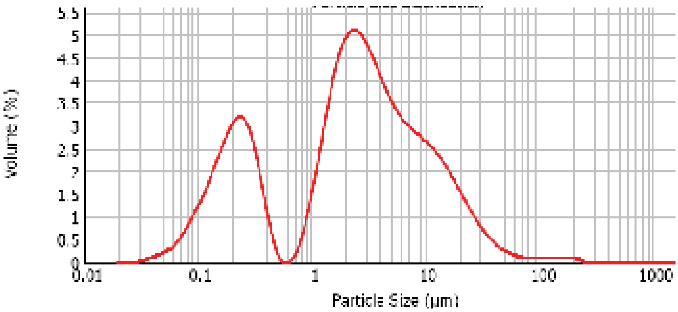


Fig. 10. Particle size distribution for classic HDS sludge – batch type tests for Alunis AMD

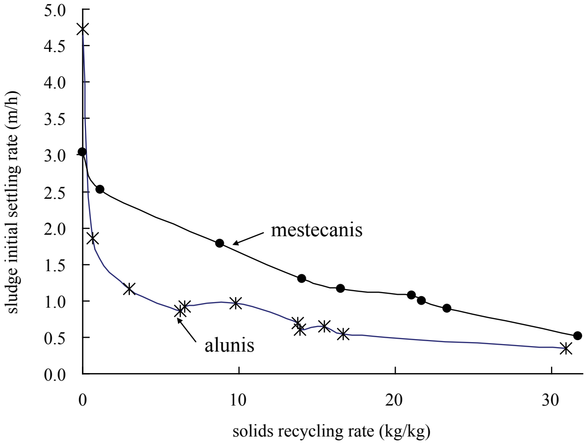


Fig. 11. Sludge initial settling rate versus sludge recycle ratio, classic HDS batch tests

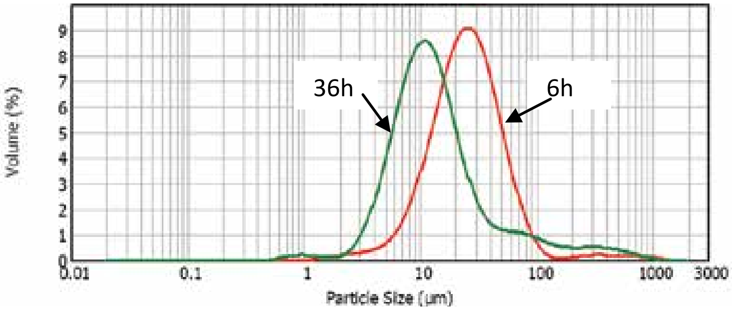


Fig. 12. Prolonged stirring tests using LDS sludge – Particle size reduction for 6 and 36 h stirring time

CONCLUSIONS

The potential of the HDS technology for the mine water treatment was confirmed. The tests performed are the first of this type in Romania.

The HDS staged neutralisation process was tested on site on pilot level using sludge recycling to the first reaction phase. The tests had good results for sludge densification and showed no solid-liquid separation difficulties.

The cyclic batch trials for two different AMD sources have demonstrated that the classic HDS process has a good potential also for the sludge densification, but the sludge bulk settling rate is lower and the effluent after settling contains fine precipitate solids and thus the heavy metal content for unfiltered samples is high comparative to dissolved phase.

The results indicate a need for further, extended research, best on continuous flow onsite pilot level.

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