PILOT SCALE STUDY ON ACID MINE WATER TREATMENT USING HIGH DENSITY SLUDGE TECHNOLOGY

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This paper is focusing on the first Romanian application of High Density Sludge (HDS) technology on a pilot scale for acid mine water treatment. The pilot HDS treatment plant (Geco variant) had a modular structure, very flexible in operation, able to operate in Low Density Sludge (LDS) and HDS systems, with three reactors, one flocculation tank and one settling tank. The main advantages of HDS technology were the lower amount of $Ca(OH)_2$ *(10% lower), lower volume of the sludge and the higher content of dry substance (15%) in the sludge.*

Keywords: mine waters, High Density Sludge, Low Density Sludge

1. Introduction

Acid mine water is one of the most significant pollution sources of surface waters in the area of mining activity or close mines due to its high acidity level and heavy metals content.

Mine water is generated by rainwater infiltration into underground, dumps, proximity groundwater or by technological water used for drilling. The water is always present in the ore extraction. Therefore, there is a need to pump the water outside through specific evacuation systems and treat it in order to be discharged into natural receivers.

After mine closure, the water level increases progressively to the level before excavation. Thus, mining closure and its flooding generate optimal conditions for rapid degradation of residual sulphides to sulphates, because of dissolved oxygen presence. Fe(III) and bacteria catalyse the reactions.

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The metals removal as metallic hydroxides is a well-established method, simple and cheaper than others. Common techniques use basic precipitation reagents as calcium hydroxide, sodium hydroxide and magnesium hydroxide, lime being the most used one [1].

Low Density Sludge (LDS) conventional treatment process was not significantly improved during the time. On the other hand, High Density Sludge (HDS) technology represents a significant improvement. In this process, metals are removed as stable and easily settled precipitates, generating sludge with high value of dried substance. Calcium sulphate (gypsum) precipitate and iron coprecipitate (metallic hydroxide) are formed on the surface of recirculated sludge.

Precipitates stability is influenced in a positive way by a high ratio between iron and other metals from the influent (mine water). In LDS treatment, neutralization reagent dosage is done directly in mine water. HDS process variants are two: mixing of recirculated sludge with lime before the contact with mine water (classic method), and directly mixing of recirculated sludge with mine water before adding lime.

At international level, HDS tends to become the preferred option for mine water treatment [2]. This is an innovative process because it minimizes the sludge volume that must be dewatered and disposed.

Particles with lower water affinity are generated through recirculation process of the sludge compared to metallic hydroxides used in classic method (LDS), which involves large amount of interstitial water.

HDS is adequate only for wastewater with soluble metal content, not for metallic precipitates content. One of HDS process disadvantage is generation of sludge with high viscosity level, which leads to significant deposits on the pipes and reaction tanks' walls. This is one of the reasons for which hybrid systems – Geco (name of the Canadian mine) – Staged Neutralization Process are preferred.

Usually HDS process operates in 8.5-9.5 pH range, because the majority of metals precipitate within this domain. The oxidation of ferrous ion Fe(II) to ferric ion Fe(III) is rapid at such pH values, atmospheric oxygen being the best oxidation agent. The efficient oxidation is an important element of the process, because the sludge with trivalent iron is more stable compared to bivalent iron content sludge.

Similar GECO variant (or UNIPURE) is considered to be a HDS multistage process. In this case, the treatment process has two steps, first phase at 4-7 pH domain, and the second phase of final pH correction with lime [3].

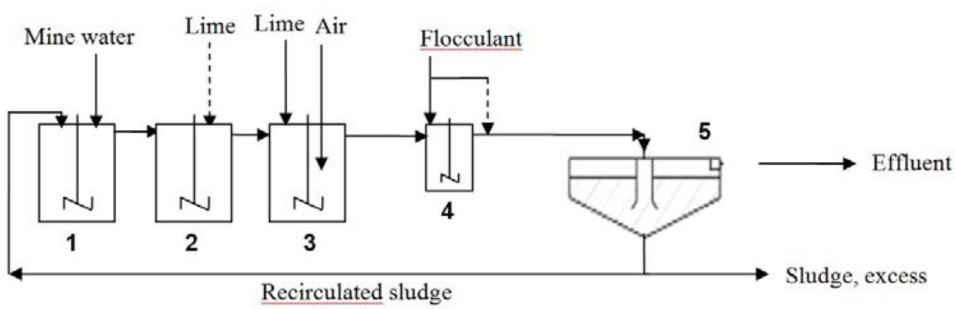
This process (HDS) can reach 10-30% dry substance content. The technology has a positive influence on process stability (pH control), effluent quality and can improve sulphate separation as gypsum [4].

At international level the usual procedure is to perform pilot tests prior to industrial design/implementation. This study represents the first Romanian approach of HDS process for a particular case of mine water from a close mine located in the North of the country.

1. Experimental

2.1 On-site HDS pilot test

The experiments were performed using a HDS pilot installation, GECO model, (located in the perimeter of acid mine water treatment plant – Ilba-Alunis, Asecare mineshaft). Fig. 1 shows the operating scheme. Metal removal tests were performed in order to compare LDS and HDS technologies using the same modular and flexible pilot installation.



1-mixing/reaction tank for mine water and recirculated sludge (R1); 2- tank of lime adding/reaction (R2); 3-reaction/oxidation/lime adding tank (R3); 4-flocculator F; 5- vertical settler (S)

Fig. 1 HDS pilot installation treatment flow

Technological phases and sub-phases are as following:

- independent mine water supply, with adjustable flow (pilot installation has the same mine water source with mine water treatment plant – evacuation point of mineshaft);
- multistage reaction – maximum three reaction phases for oxidation and heavy metals precipitation from which two with automatic pH control and lime dosage (independent pH control for both metal precipitation phases);
- flocculation (polyelectrolyte dosage) and settling of reaction products-precipitates;
- sludge recirculation from the settler to first reaction phase (adjustable rate flow);
- systems for the preparation of lime, polyelectrolyte and reagents for pH correction – if it was the case.

HDS installation comprises the following modules:
- module for mine water supply (horizontal centrifugal pump, flow-meter, pipe lines and fittings);
- reaction tanks module (three reaction tanks and one flocculation tank with propeller stirrers – controllable speed, two pumps for lime dosage and one pump for polyelectrolyte, two pH controllers, air blower, supporting structure of tanks and pumps, operator platform);
- module of settler and sludge pump (vertical settler – 45^0 angle cone, peristaltic pump with controllable speed and integrated frequency converter);
- module of vessels for reagent preparation (two tanks with propeller stirrer for 5-10% milk lime and one for 0.05-0.1% polyelectrolyte preparation);
- electric panel;
- ground sewer system.

2.2 Characterization of the influent

The influent of HDS installation was the one used by wastewater treatment plant – Ilba – Alunis – Asecare mineshaft. Table 1 shows mine water characterization data (year 2012) and the admissible values for discharge into natural receivers. Physical-chemical characteristics of mine water were constants during the tests.

Physical-chemical characterization data of mine water (installation influent) underlines the following aspects:

- *Alunis-Asecare* mine water is a pollution source with significant acidity characteristic (pH≤3);
- from the heavy metals category, iron is the dominant specie especially in the form Fe(II). This ionic iron specie leads to the necessity of aeration in order to be oxidized to Fe(III). The oxidation works with satisfactory rate at pH≥7. Thus, bivalent iron precipitation to pH>9 (recommended 9-11 pH range) leads to unstable ferrous hydroxide precipitate/sludge with acid;
- zinc concentration was ~ 150 mg/L. pH precipitation of zinc is relative high ~9 and needs more severe conditions for precipitation in order to be separated as hydroxide, by settling;
- manganese concentration was ~35 mg/L and it was difficult to reduce residual content in the effluent below admitted limit (Romanian regulation NTPA001); manganese hydroxide is not stable below pH 10.2, oxidation of Mn(II) and its precipitation as MnO_2 are very slow processes below pH 9, after iron precipitation. Usually, manganese precipitates within 9.5-10.2 pH domain with aeration;
- lead, copper, and arsenic (total arsenic) levels are exceeding the admissible values – five times for lead and eight times for copper and arsenic.

Table 1

Chemical-physical characteristics of mine water- Asecare mineshaft (installation influent)

Indicator	M.U.	Asecare mineshaft, year 2012	Admissible values NTPA001 / 2005
pH	-	**2.97**	6.5-8.5
Electric conductivity	mS/cm	2.4	-
CODMn	mg O_2/L	17.0	-
TDS	mg/L	**4260**	2000
SO_4^{2-}	mg/L	**2905**	600
Cl^-	mg/L	30	500
NO_3^-	mg/L	4.8	-
Ca^{2+}	mg/L	273	300
Mg^{2+}	mg/L	**225**	100
Na^+	mg/L	106	-
Al	mg/L	**65/64 (h/f)**	5.0
Cu	mg/L	**0.77/0.765 (h/f)**	0.1
Fe	mg/L	**210/144 (h/f)**	5.0
Mn	mg/L	**34/31 (h/f)**	1.0
Ni	mg/L	0.223/0.22 (h/f)	0.5
Pb	mg/L	**0.97**	0.2
Zn	mg/L	1**52/150 (h/f)**	0.5
As	µg/L	**8.66**	0.1
h/f – homogeneous / filtered			

2.3 Main operational parameters/ indicators

Main operational parameters/ indicators of both operation systems were:

- **LDS classic treatment process** (Fig. 2)**:**
  - influent flow rate: 300-800 L/h;
  - pH of the first treatment phase: 4.5;
  - pH of the second treatment phase: 8-9.5;
  - hydraulic retention time (HRT): 30 min for each tank.

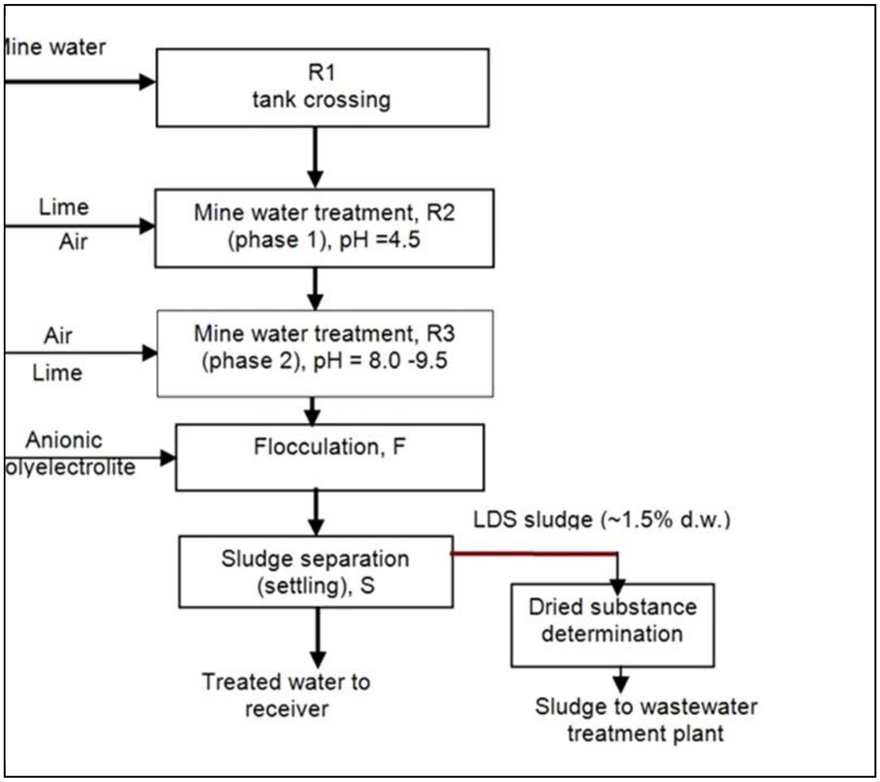


Fig. 2 LDS mine water treatment flows

- **HDS/Geco treatment process – parameters after 11 days/16 days of continuous operation** (Fig. 3)**:**
  - influent flow rate: 480/620 L/h;
  - pH of R1 tank (mixing of mine water and recirculated sludge): 7.46/6.86
  - pH of the first treatment phase (R2): 8.75;
  - pH of the second treatment phase (R3): 9.47/9.51;
  - HRT: 56/34 min (for each tank);
  - Dry weight of the sludge from the settler: 13.1/11.9%;
  - Solids generating: 2.5/2.5 kg dry weight/m^3 (2.5/2.5 kg d.w. /m^3);
  - Flow rate of new solids: 850/1375 g/h;
  - Flow rate of recirculated solids: 18340/16632 g/h;
  - Recirculation ratio: 21.6/12.1 kg/kg;
  - Solids concentration in tanks: 4/2.6%;

– Solids amount to settler: 19190/18007 g/h.

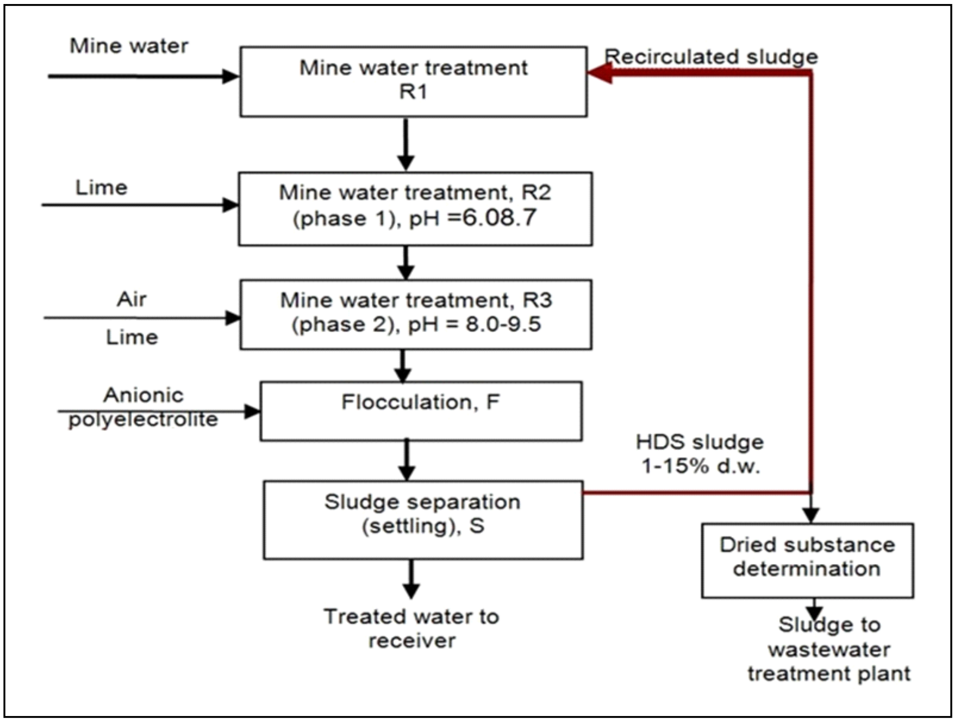


Fig. 3 HDS mine water treatment flows

2.4 Leaching tests of settler's sludge

Leaching tests (sludge:water ratio = 10:1, contact time 24h) were performed for settler's sludge in order to establish disposal conditions, both for LDS and HDS systems.

3. Results and discussions

Obtained results are presented below for both treatment systems.

3.1 Classic LDS system

Residual metals concentrations in soluble form for each treatment phase (tanks R2, R3, flocculator F and settler S) of the process (no sludge recirculation) were established. These data are presented in table 2 at three pH operating conditions – 8; 9 and 9.5.

Table 2

Residual heavy metals concentrations along the treatment flow of LDS technology

Indicators	Residual metals concentrations (mg/L) for three different precipitation pH: pH 8/ pH 9/ pH 9.5 (values in the final reactor R3)				Admissible values NTPA001 / 2005
	R2	R3	F	S	
Fe	22.1/22.1/22.1	0.202/0.24/0.052	0.17/0.36/0.15	0.43/0.26/0.15	5.0
Mn	27.9/27.9/27.9	**7.96**/1.92/0.44	6.9/1.97/0.26	**8.41/3.69**/0.29	1.0
Zn	192.8/192.8/192.8	0.39/0.36/<0.01	0.51/0.14/<0.01	**1.83**/0.06/<0.01	0.5
Al	47.5/47.5/47.5	0.05/0.12/0.07	0.024/0.21/0.06	0.007/0.025/0.055	5.0
Cu	0.32/0.32/0.32	0.011/0.01/0.009	0.011/0.009/0.01	0.009/0.009/0.01	0.1
Pb	0.042/0.042/0.042	0.006/0.006/0.006	0.006/0.006/0.006	0.006/0.006/0.006	0.2
As	0.05/0.05/0.05	0.021/0.02/0.026	0.028/0.021/0.016	0.019/0.011/0.024	0.1

Metal residual concentrations in soluble form (settling effluent - S) were situated below admissible values for discharge into natural receiver excepting manganese (98.41 mg/l at pH 8 and 9) and zinc (1.83 mg/L at pH 8).

3.2 HDS/Geco system

Iron, manganese, zinc and aluminium concentrations (soluble form) along the treatment flow were monitored and the main characteristics of the sludge were determined (including comparative settling curves HDS/LDS). Table 3 show metals concentrations in the HDS phases for two selected days –the 11th and the16th. Residual metal concentrations in soluble form, including manganese, were situated below admissible values for discharge in natural receivers both in R3 and settling tank S (final effluent).

Table 3

Residual metals concentrations along HDS treatment flow – final precipitation pH 9.5 (in R3)

Indicators	Residual metal concentrations (mg/L) -day 11 and day 16-					Admissible values NTPA001 / 2005
	R1	R2	R3	F	S	
Fe	0.56/0.79	0.24/0.37	0.29/0.13	0.10/0.14	0.85/0.19	5.0
Mn	25.5/34.4	3.57/4.12	0.33/0.47	1.04/0.53	0.78/0.87	1.0
Zn	4.56/5.8	0.31/0.5	0.30/0.31	0.24/0.19	1.14/0.21	0.5
Al	-/-	0.23/0.31	0.22/0.17	0.19/0.22	0.63/0.22	5.0

Table 4 shows metal concentrations in solid phase (sludge) along the treatment flow.

Table 4

Metals concentrations in the sludge along HDS treatment flow – day 11 and day 16

Tank reactor	Metal content, g/kg d.w.									
	Mg	Al	Ca	Mn	Fe	Ni	Cu	Zn	As	Pb
R1-day11	62.2	40.9	60.1	19.0	125	0.14	0.085	117	<0.01	0.077
R2-day11	65.1	41.6	65.9	19.6	122	0.131	0.262	116	<0.01	0.059
R3-day11	66.3	39.8	72.1	19.3	118	0.136	0.065	111	<0.01	0.072
F-day11	71.2	42.8	77.3	19.3	119	0.128	<0.04	111	<0.01	0.078
S-day11	64.9	39.1	108	72	18.4	112	0.146	0.099	105	0.065
R1-day16	64.7	46.2	66.5	19.9	135	0.166	0.068	127	<0.01	0.082
R2-day16	64.3	43.9	68.2	20.6	131	0.134	0.086	123	<0.01	0.081
R3-day16	64.0	42.5	71.1	20.0	125	0.145	0.044	117	<0.01	0.072
F-day16	61.2	40.4	66.9	19.4	120	0.138	0.208	112	<0.01	0.063

The leaching capacities of the chemical sludge (pH, metals content, organic load - table 5) are corresponding to no dangerous waste category.

Table 5

Leachate characteristics for LDS and HDS sludge

Indicator	M.U.	Leaching ratio: water/dry sludge - L/S =10 l/kg Contact time: 24h		Limits for no dangerous waste, mg/kg d.w.
		LDS sludge	HDS sludge	
pH	-	7.60	7.40	>6
As	mg/kg d.w.	0.009	0.015	2
Cu	mg/kg d.w.	0.048	0.057	50
Ni	mg/kg d.w.	0.084	0.096	10
Pb	mg/kg d.w.	0.021	0.017	10
Fe	mg/kg d.w.	0.032	0.09	-
Mn	mg/kg d.w.	0.103	0.862	-
Al	mg/kg d.w.	0.06	0.095	-
DOC	mg/kg d.w.	1.09	1.67	800
TDS	mg/kg d.w.	11960	4540	60000

It can be noticed that the metal content is higher in HDS sludge leachate probably due to three reasons:

- lower alkalinity of HDS;
- the capacity of HDS process to concentrate a higher amount of metals;
- the metals adsorption on sludge surface, which means a better chance to be transferred into solution.

There is a large difference between TDS values (lower in case of HDS) probably due to the gypsum formation.

Comparative analyse of settling curves (2h) for LDS and HDS sludge underlines the following aspects:

- at the beginning, the sludge characteristics are degrading because of recirculation (the charge of solids in the settler increases);
- settling characteristics are improving once the HDS sludge is formed;
- conventional sludge settling (LDS) is running with higher speed (Fig. 4).

However, HDS has the tendency to reach a comparable settling speed in time. It must be considered that LDS sludge settling starts from an initial concentration (homogeneous phase) of 1-2 g d.w./L to 15 g d.w./L (1.5%) while the HDS sludge starts with 20-30 g d.w./L reaching in time100-120 g d.w./L (11-12%).

Final volumes of the sludge are similar, about 27-30% vs. initial suspension.

In this context, it must be noted that sludge viscosity (after 10 days thickening) within the settler was 10 times higher in case of HDS process (22 mPa.s), compared to LDS sludge (2.4 mPa.s) and particle size were smaller in case of HDS sludge (Fig. 4, precipitation pH in VR3 was 9.5).

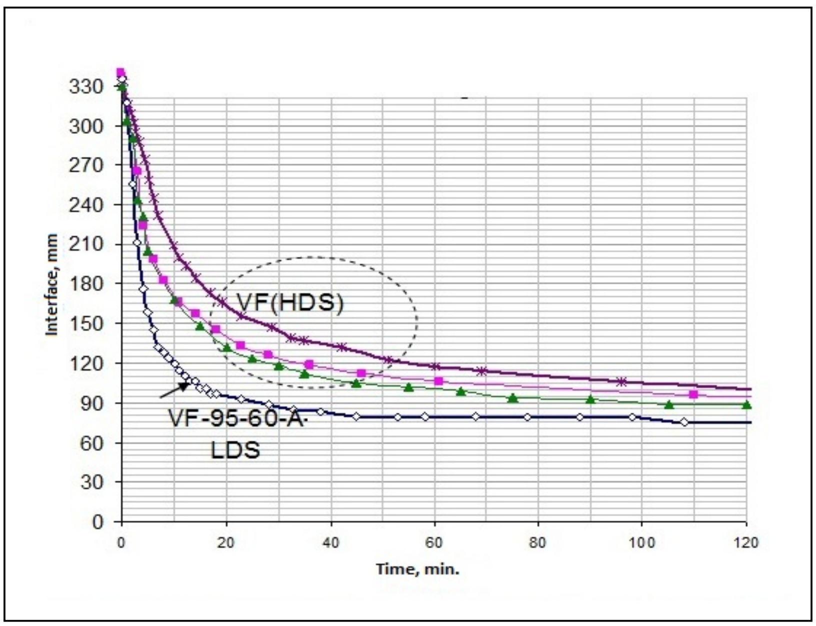


Fig. 4 Comparative settling curves HDS vs. LDS (pH 9.5, HRT 60 min., aeration) – flocculator

Experimental results on pilot level leaded to the following observations regarding the implementation of HDS process:

- two reaction steps/tanks are needed;

- strong mixing systems in all reaction phases and aeration in the second phase are necessary;
- sludge recirculation must be permanent. Stopping recirculation rapidly leads to the loss of HDS properties;
- process starting and restarting are relatively difficult – a recirculation rate of 20 kg/kg must be assured;
- pilot tests for each mine water source are needed, the results cannot be extrapolated.

4. Conclusions

Pilot tests experiments performed in order to treat a mine water source (from the North of Romania – Ilba, Alunis), using High Density Sludge (HDS) showed that HDS experimental pilot test confirmed the technology potential. HDS/Geco variant, with sludge recirculation in the first reaction phase (first tank, no lime) was applied. Milk lime was added in the second and third tanks. The obtained settled sludge had maximum 15% dry weight content. The decrease of settled sludge amount was ten times higher compared to LDS operating system. HDS process doesn't allow pH decrease compared to LDS. Lime consumption was 10% lower *vs*. conventional treatment process (LDS).

Taking into account the local conditions, HDS process could be feasible to be implemented in the existing acid mine wastewater treatment plant.

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