Efficient Methodologies in the Treatment of Acid Water from Mines with Recovery of Byproducts

Osvaldo Aduvire^{1,2}, Mayra Montesinos^{2,3}, Nereyda Loza^{1,2}

¹SRK Consulting, Peru ²Pontifical Catholic University of Peru (PUCP), Peru ³Hudbay S.A.C., Peru

Abstract

In general, the treatment of acid mine water is done via a one-stage process, at a determined pH level (Direct Treatment). In this article, a staged treatment methodology is presented (Staged Treatment), that makes the recovery of byproducts with economic value possible, as well as benefiting the environment by reducing contamination. This is achieved because we diminish the amount of non-usable slurry. For this reason, we will present the obtained results in Direct Treatment compared to those the Staged Treatment had, plus which byproducts were collected at different pH levels in the Staged Treatment. Finally, we will show a flow sheet explaining the Staged Treatment.

Mining activity generates a large volume of mining residues and exposed surfaces with the presence of sulphides that in contact with the atmosphere and water in rainy seasons initiate complex processes of physical, chemical and biological transformations, which give rise to the generation of acidic mine drains that require a treatment before unloading them to a receiving body.

Lately, the population is demanding the development of sustainable mining projects with greater environmental control, lower water consumption, which include methodologies that consider solid or liquid mining waste as second generation resources with possibilities of use and recovery to obtain by-products with economic value.

To incorporate these expectations into mining projects, have the potential to use mining waste and reduce discharges to the environment, we have developed acid water treatment systems that allow to recover by-products sequentially to certain pH ranges and obtain sludge with specific metal load values that we have called Stage-divided Treatment ou Staged Process.

In the sizing of acid water treatment systems, it is essential to have a good geochemical characterization of the effluent, ranging from field monitoring, using portable equipment to perform in situ measurements of flow, pH, eh, dissolved oxygen, conductivity, temperature, flow, turbidity, acidity, alkalinity, to water sampling for chemical analysis in total and dissolved concentrations.

To choose the sequence in the treatment system, experimental neutralization and precipition tests are carried out on equipment such as imhoff jug and cone tests where various reagents are tested for treatment and at various pH values, with which we obtain the dosing of reagents and the sequencing of the treatment. Based on the results obtained in the hydrogeochemical characterization of the effluents and the results of the tests, the processes and stages to be considered are chosen in the design of the processing facility.

These methodologies will reduce the costs of treating minewater, extend the life of waste deposits and reduce the discharge of solid and liquid waste into the environment, in addition to the recovering and collecting of by-products with possibilities of economic use.

Keywords: Treatment, Acid Water, Staged, Recovering, By-products

Methodology

Prior to experimental tests, field measurement were carried out with portable equipment for pH, Eh, disolved oxigen, elctrical conductivity and flow.

Sample-taking was performed pursuant to standardized procedures in 250 and 500 ml HDPE flasks, which were first washed with 10% nitric acid and rinsed water from the sampling point. In the laboratory, metals were analized in total and dissolved concentrations, they were filtered al 0.45 microns, preserved with HNO₃ to pH<2 and chilled to 4C° for transportation purposes.

Experimental neutralization and sedimentation tests were carried out seeking to obtain doses of reagents to be used in treatment processes by means of curves in which hydrolysis zones were identified.

Experimentation and Results

In the experimental tests, the flow rates to be treated and the concentrations present in the effluents are also taken into account, the latter determining whether only treatment will be carried out or treatment will be carried out along with metal recovery. If only treatment is chosen, the process will be in a single stage (Direct Process), but, if we opt for the recovery of byproducts with economic value, the treatment will be staged with separation of solid phases (Staged Process). The equipment used in the laboratory includes pH meter, beaker, magnetic stirrer, precision balance, redox potential meter, jar test, imhoff cones, etc.

Direct experimental tests and trials included the monitoring of specific parameters for indirect tracking neutralization reactions and the construction of experimental reagent consumption curves required to reduce mine drainage acidity. The reagent used was lime and the various neutralization curves constructed evidenced hydrolysis and/or buffer zones, where solid phases are for the case under study.

A. Direct and Stages process comparison. Case 1.

Table 1 shows the quality of a mine drainage whose pH<3 with Fe, Mn, Zn and other contents. To treat this water, a series of experimental trials have been carried out aimed at obtaining final concentrations that comply with the LMP of the current legislation for the mining-metallurgical sector. The estimation of the lime consumption for the treatments is presented below by means of a direct and staged test.

The first alternative is to perform neutralization tests by direct process, where the pH of 2.3 is increased until reaching pH 10, in Table 2 we can see the concentrations at the

 Table 1 Characteristics of mine drainage before treatment.

	Fe	Al	Mn	Mg	Pb	Zn			
рН	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L			
	Total Concentrations								
2.3	259	18.1	353	98	2.8	50			

Table 2 Characteristics of acid drainage afterdirect neutralization.

 Table 3 Characteristics of acid drainage after each stage of neutralization.

Tot.

0.06 0.03 3.56 0.153 <0.01 0.035

Parameter U	Unit	Final Concentrations				Concent.		Concent.	
	Unit	Totals	Dissolved	Parameter	Unit	Sta	ge 1	Sta	ge 2
pН	u.e		10			Tot.	Dis.	Tot.	Тс
Fe	mg/L	1.5	0.9	рН		4.5	-5.0	5.5	-10
AI	mg/L	1.02	0.8	Fe	mg/L	0.29	0.1	0.08	0.
Mg	mg/L	6.5	4.3	AI	mg/L	1.07	1.08	0.06	0.0
Mn	mg/L	180	166	Mg	mg/L	59	51.5	3.9	3.
Pb	mg/L	0.09	0.02	Mn	mg/L	305	266	0.963	0.1
Zn	mg/L	1.1	0.72	Pb	mg/L	1.03	0.98	<0.01	<0
				Zn	mg/L	49.3	17.8	0.13	0.0



Diagram 1 Design of a staged acid water treatment plant.

end of the neutralization process, where Mn contents are still evident. This would indicate that to continue withdrawing Mn of water, the process should be continued and flocculants or other reagents added to make the Mn pass to the solid phase. The consumption of lime in the alternative of Case 1 (Direct Test) to obtain the results of Table 2 reached 620 mg/L.

The second alternative of treatment of mine water and taking into account the concentrations present in the sample (Table 1) has been to design a treatment in two (2) stages, in the first stage pH 5.5 was reached and the slurry was mainly removed from Fe and in less quantity of Al, in the second stage the treatment reached the pH 10 where a sediment was obtained with an important content of Zn and Mn with possibilities of recovery of the first one.

Unlike direct treatment where only one

slurry is obtained, in the staged treatment two more slurries are obtained, therefore, once the first stage is finished, the slurry is removed, then the process is continued with the addition of neutralizing reagent until reaching the final pH where the second neutralization stage ends, after which the formed solids will also be required.

The results obtained in the staged test are clear, in terms of the effectiveness of removing metallic load from water. Table 3 shows the concentrations of metals in the water after the 2 stages of treatment, achieving effective removal of Zn and Mn, a result not achieved with the direct test.

The mass balance performed as part of the monitoring of the reactions involved in the process, as shown in Fig. 1, also highlights the removal of metals of interest at each stage of the test.



Figure 1 Variation of the mass content of Fe, Zn and Mn among other minors in the staged-type test.

Sampling Point	рН	STS	As	Cr	Cu	Fe	Pb	Zn	Al	Mn
Parameters		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Nv 2C (Total Conc.)	3.5	382	0.94	0.108	10.67	210.3	7.06	936.8	72.14	14
Nv 2B (Dissolved										
Conc.)	3.5	382	0.01	0.067	10.38	51.24	1.96	891.6	64.61	14
LMP	6-9	50	0.1	-	0.5	2	0.2	1.5	-	-

Table 4 Mine effluent for experimental tests.

The lime consumption in the alternative of the case 1 (Staged Test) to obtain the results of table 4, is as follows: 260 mg/L in the first stage and 240 mg/L in the second stage, reaching a total lime consumption of 500 mg/L. Diagram 1 shows the sequence corresponding to the acid water treatment system by means of stage neutralization.

As a result of the comparison of the direct and staged treatments, in the latter, better results are achieved in the removal of metallic load, in addition to consuming 120 mg/L less of lime.

B. Direct and Staged processes comparison. Case 2.

For this comparison we have chosen a mine effluent called Nv 2 that has a pH of 3.5, the electrical conductivity exceeds 4170 μ S/cm and some values of the majority elements measured in total and dissolved concentrations (mg / l) exceed the LMP of reference according to current Peruvian legislation (DS N° 010-2010-MINAM) for the discharge of liquid effluents from mining-metallurgical facilities.

The results obtained in the tests to determine the consumption of neutralization reagent give the following results: in the case of direct testing or direct neutralization, a lime consumption of 1080 mg/L was estimated to reach a pH of 8.5 (Fig. 2), while for the staged test the consumption of lime to reach a pH = 8.5 was 820 mg/L (Fig. 3).

Comparing the lime consumption obtained in the process of direct neutralization and staged neutralization, it can be deduced that for effluents with a significant metallic load, the staged neutralization consumes 260 mg/L less of reagent, which represents an appreciable saving in the lime consumption, when it comes to important volumes of mine water to be treated. For instance, if we consider implementing a staged neutralization plant of 500 l/s and that the lime cost is 0.5 US\$/kg, a saving of 4'043,520 kg of lime is obtained per year, equivalent to a saving of 2'021,760 US\$/year.

This will result in a process of lower cost of mine water treatment, but in addition there are added improvements such as obtaining byproducts with possibilities of economic



Figure 2 Lime consumption in the direct test.



Figure 3 Lime consumption in the staged test.

рН	Fe	AI	Mn	Mg	Pb	Zn		
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		
	Total Concentrations							
2.9	180	90	95	70	5	1200		

Table 5 Characteristics of a mine drainage before neutralization.

use, lower requirement in the handling of slurry, among other secondary advantages.

C. Neutralization and recovery tests in three stages.

Table 5 shows the majority of metallic load and the pH of a mine drain, which has been carried out neutralization tests in three stages to obtain three byproducts with high contents of Fe, Al, and Zn.

The zone of buffering and hydrolysis can be observed in the curves of lime consumption both in terms of pH and redox potential. Figure 4 shows the evolution of the redox during the neutralization process, where the values of Eh descend to values of 50 mV that correspond to natural waters without affection.

Picture 1 shows the slurry obtained in a three stage neutralization test: in the first stage the pH 4 was reached and orange ocher colored sludge (M-1) that would correspond to Fe hydroxides was removed, in the Second stage the neutralization process was continued until reaching pH 5.5, where white-colored slurries (M-2) corresponding mainly to the hydroxides of Al, and finally in the third stage of treatment the pH reached higher values to 8.5 where a dark brown to black slurry (M-3) was recovered and it would correspond to the solid phases of Zn as a major compound and in a smaller proportion to the rest of elements such as Mn, Mg, Pb present in the mine water that passed to the solid phase at pH above neutral.

If the slurry of Fe and Al of the treatment process, at pH higher than the range of mobilization of these 4 and 5.5 elements respectively, these formed solid phases are redissolved and go again to water, so it would require adding as many of alkaline material (lime) to form again solid phases (pH 8) and to remove them from the water, which increases the lime consumption in the process, as well as requiring in some cases flocculants, coagulants and scavengers additions, therefore, the cost of the acidic mine water treatment is higher.

The slurries obtained in the treatment of mine water by means of a 3-stage system could have the following applications: the slurry with Fe content (M-1) could be used as a ceramic pigment, the slurry with aluminum (M-2) would be used in the blasting work to improve the explosives, and the slurry at the high Zn (M-3) content would be used to obtain a zinc concentrate.

When the concentrations of metals (Al, Cu and Zn) present in the mine water have



Figure 4 Evolution of Eh in the treatment.



Picture 1 Solid phases obtained in a sequential staged test by removing solid phases.

significant values (higher than 300 or 500 mg/L), it is feasible to study the recovery of these elements as byproducts, the experimental tests must be staged in order to obtain at each stage a slurry with a high metallic content, which could be sent to the concentrator plant or a similar process for its recovery, and in some cases to be reused as the slurry with high aluminum content that can be sent to mine for the improvement of Anfo as an explosive and to obtain Anfo aluminized.

D. Unit operations that constitute a staged treatment system.

The main Unitary Operations involved in a staged treatment system are: Dissolution (of process reagents), Agitation and Decantation (Fig. 5) in each stage and they are complemented by secondary operations that allow controlling the process.

Implementing staged acidic water treatment system allows obtaining slurry with well-defined characteristics and the same peculiarities, with chances of recovering metals from slurry process. The water from the treatment process can be discharged to a local natural watercourse (receiving body), after controlling its quality in order to cause minimum environmental impact, while the slurries that do not have a recovery interest will be stored in adequate containers for it or generally sent to the tailings deposit or another deposit prepared for this purpose. After the experimental stage, a pilot must be carried out to allow measuring adequately the treatment system for each type of mine water.

Conclusions

The sizing of the acid water treatment system based on the content of acidity and staged, on one side, it allows to take better advantage of the resources by spending less lime in the neutralization process, and on the other side, it allows to recover metals from the slurries of the process. This makes acidic water treatments more efficient, less expensive and with greater environmental control.

Obtaining byproducts with economic value can have a direct economic advantage by consuming less quantity of lime, but it also



Figure 5 Unitary operations that constitute a staged treatment system.

entails other added benefits such as: reducing the volume of slurries to be transferred to the storage deposits, thus increasing life of these deposits and operating costs are reduced, among others.

References

- Aduvire, O. and Aduvire, H. (2005) Aguas ácidas de mina: caracterización, mineralogía y microbiología. Ingeopres 141, pp. 52-62.
- Aduvire, O. 2006. Drenaje Acido de Mina: Generación y Tratamiento. Madrid: Instituto Geológico y Minero de España. Edición IGME. Código: SID-63187. Publicación Electrónica 136p.
- Bigham, J.M., Schwertmann, U., Carlson, L. y Murad, E. (1990). A poorly crystalized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in AMD. Geochimica Cosmochimica Acta, 54, 2743-2754.
- Bigham, J.M. y Nordstrom, D.K. 2000. Iron and aluminum hydroxysulfates from acid sulfate waters.En:Alpers,C.N.,Jambor,J.L.yNordstrom, D.K. (eds), Sulfate minerals: crystallography, geochemistry and environmental significance. Reviews in Mineralogy & Geochemistry, MSA, Virginia. USA. (40), 350-403.
- Buamah, R. 2009. Adsorptive Removal of Manganese, Arsenic and Iron from

Groundwater. UNESCO-IHE, Institute for Water Education, Delft, The Netherlands.

- Jönsson, J., Jönsson, J. and Lövgren, L. (2006) Precipitation of secondary Fe(III) minerals from acid mine drainage. Applied Geochemistry 21, pp. 437-445.
- Nordstrom, K. 1985. The rate of ferrous iron oxidation in a stream receiving acid mine effluent. Hydrologic Sciences, 1, 113-119.
- Nordstrom, K. 2000. Aqueous redox chemistry and the behavior of iron acid mine waters. En: Wilking, R., Ludwig, R, y Ford, R. Proceeding of the Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration. Cincinnate, OH, USA. 43-47.
- Rose, A., Means, B. y Shah, P. 2003. Methods for passive removal of manganese from acid mine drainage. Annual West Virginia Surface Mine Drainage Task Force Symposium. Morgantown, WV, USA. 12pp.
- Sánchez, J., López, E., Santofimia, E., Aduvire, O., Reyes, J. Barettino. D. 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel river, Spain): geochemistry, mineralogy and environmental implications. Applied Geochemistry, 20, pp. 1320-1356.
- Stumm, W. and Morgan, J.J. 1996. Aquatic Chemistry, chemical equilibria and rates in 3rd; Wiley; New York.