

Acid mine drainage treatment process optimization for manganese content reduction by sequential neutralization

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SUMMARY

Many times the quality of a treated effluent from a mining operation does not comply with the required legislation as in the case of Peru, where Maximum Permissible Limits for mining operations are not met due to the content of metals such as manganese, which usually requires specific conditions for removal. Therefore, some re-evaluation tests were made to the treatment system, mainly in the neutralization stage of the effluent, in order to identify the problem and propose possible solutions.

The study considers a first stage or experimental phase in which a set of laboratory tests were carried out. The first differentiating criterion is the type of neutralization applied (direct or sequential neutralization); the second criterion is to minimize the number of reagents in the process while maintaining the effectiveness of the implemented treatment system. In addition to the tests, there are continuous measurements carried out before, during and after the experimental tests, of parameters such as pH, electrical conductivity and the oxide reduction potential, which allowed for the identification of cut-off times in the proposed treatment.

As a result of the study, the manganese surplus was removed from the treated effluent; we were able to identify the sequence that allowed compliance with Peruvian Maximum Permissible Limits; finally, we agreed on the need to implement a modification to the existing treatment system, in compliance with the legislation, and with the lowest operational possible cost.

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INTRODUCTION

Acid mine drainage, depending on the mineralogical nature of the area in which they are generated, will carry different metal loads, which will be associated with conditions such as the reaction rate of materials that will be excavated, acid/base capacity of minerals and barren, material size and solubility, water neutralization capacity, oxygen transport, interstitial water mobility, permeability, climate and temperature, evaporation and infiltration, catalytic action of bacteria, adsorption of metals, etc. Therefore, it is important to carry out a proper characterization of the effluents that are generated in mining processes, since this directly influences the type of treatment to be used for acid drainage remediation, and it can also condition the different stages of the treatment process.

The chosen treatment must comply with environmental regulations approved in recent years in Peru; that is, it must guarantee compliance with the Maximum Permissible Limits and environmental quality standards, so that the discharges do not alter the quality of aquatic ecosystems existing in receiving bodies.

OBJECTIVES

To optimize acid drainage treatment systems so that the treated water complies with the MPL and WQS for surface water, mainly regarding the content of manganese since this is the most difficult element to clean in mine drainage.

METHODOLOGY

Prior to experimental tests, field measurements were carried out with portable equipment for pH, Eh, dissolved oxygen, electrical conductivity, temperature 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 with water from the sampling point. In the laboratory, metals were analyzed in total and dissolved concentrations; they were filtered at 0.45 microns, preserved with HNO₃ to pH<2 and chilled to 4 C° 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. For this purpose, the following reagents and equipment were used (See Photo 1).

- Samples of mine acid drainage
- Neutralization reagents: lime
- Reagents for flocculation-sedimentation
- Beaker
- Magnetic stirrer
- Balance
- pH-meter and Potential Redox meter



Photo 1. Equipment for experimental tests.

MINE ACID DRAINAGE CHARACTERIZATION

Acid drainage formation

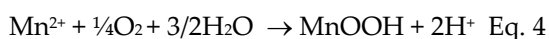
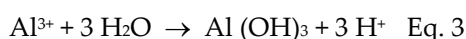
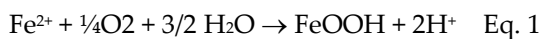
Acid drainage is generated from the chemical oxidation of sulphides, and is accelerated in many cases by bacterial action. The main elements involved are reactive sulphides, oxygen and water (vapor or liquid), and bacteria as a catalyst element.

The reaction rate is a very important variable: if the process is slow, the effect on the medium may be negligible; however, if acid drainage generation is produced at a faster rate, then there is a problem since the environment will be contaminated.

Although the reaction rate depends on several factors such as the temperature, amount of sulphides, grain size distribution, presence of water, air and bacteria, certain mineralogical species are more reactive than others. For example, marcasite, which has the same chemical formula as pyrite, is very unstable and may generate acidic drainage at a fast rate. The sulphides of other metals (lead, zinc or copper) are generally less reactive than iron sulphides, in part due to greater stability of their crystalline structure and also because they form less soluble minerals that cover the surface of the sulphides, preventing their oxidation from progressing.

The amount and size of mineral grains have an effect on the reaction rate. Fine textures with poorly crystallized varieties oxidize faster than coarse crystalline grains. For example, a form of pyrite developed under low temperature conditions can produce much faster acidity than a large mass of sulphides developed at high temperature due to a lower surface/volume ratio.

In general, acid mine drainage (AMD) has a pH between 2 to 6; it contains cations and anions in solution, predominating SO_4 , Fe, Mn, Al, Cu, Pb, Zn in addition to Cd, Ca, Na, K, Mg and others. The hydrogeochemical characterization of mine drainage includes protonic acidity due to free hydrogen ions (H^+) plus mineral acidity due to dissolution of Fe, Al, Mn and others. These metals are considered acid generators since they can generate H^+ by means of oxidation and hydrolysis, according to the following equations:



Eq. 1 can be guided and catalyzed by several species of oxidizing bacteria of Fe and S (Thiobacillus ferrooxidans, Leptospirillum ferrooxidans and others), which convert Fe^{2+} to Fe^{3+} . This reaction occurs at low pH and consumes one mole of acidity. Bacteria of the Acidithiobacillus genus (previously known as Thiobacillus) require dissolved CO_2 , O_2 , a reduced form of Fe or S, N and P

for their metabolism; to that end, they produce enzymes that catalyze oxidation reactions and use the released energy to transform inorganic carbon in cellular matter.

The characterization of acid mine drainage as a function of acidity helps to choose the most suitable and efficient treatment system, because in addition to proton acidity, there is mineral acidity, an aspect that is not usually considered in classic characterization methods. A mine drainage is usually considered as acid when it has a pH of less than 4.5 and high metal load contents, while the Mn^{2+} ion can pass directly to manganese hydroxide or oxyhydroxide in an aqueous solution, thus increasing the pH above 7 (Eq. 4).

To adjust the efficiency of the treatment system, water acidity curves should be determined, which are prepared by the addition of OH^- ions from a base or alkali (NaOH solution, 0.02N). Reagent consumption curves can also be constructed by means of neutralization tests in order to determine the hydrolysis zones of the elements with majority presence.

Another aspect to be taken into account when choosing the treatment system is the mobilization range of existing mineral species and/or compounds that will be formed in neutralization processes (hydroxides, carbonates, sulfides), as seen in Figures 1 and 2. Identification of these hydrolysis zones avoids re-dissolution of solid phases and unnecessary consumption of neutralization reagent or material.

The behavior of the iron and Mn forms is strongly influenced by redox and acidity/alkalinity conditions in water. Figures 1 and 2 show the stability regions of Fe and Mn forms as a function of Eh/pH. The precipitated Fe region is larger than that of the soluble form, whereas the soluble Mn region is larger than that of the precipitated forms (as opposed to Fe).

In acidic media, the Fe^{3+} hydrolysis is produced primarily at a pH 2.7-4.5 and precipitates as ferric hydroxide, generating 3 moles of acidity (Eq. 2 and Fig. 1). If they are not removed from the treatment process at pH greater than 5, they are re-dissolved and return to the liquid phase. Likewise, the mobilization and re-dissolution of solid phases of aluminum (aluminum hydroxides) formed in the neutralization processes generally occurs at pH ranges of 3,7 and 5,8. If they are not removed from the treatment process at pH greater than 6, they are re-dissolved and return to the liquid phase. In both cases, this increases treatment costs and sludge volumes, and reduces the effectiveness of the treatment.

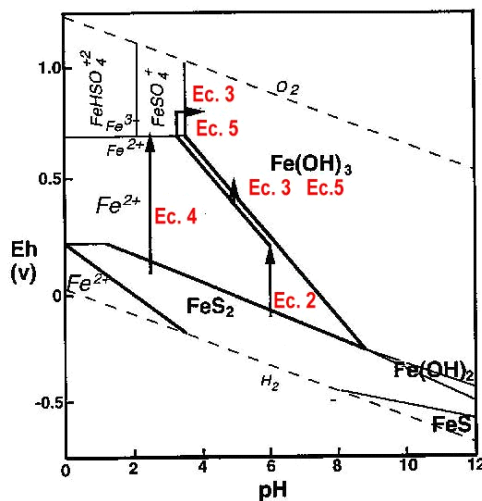


Figure 1. Eh-pH diagram showing theoretical domains for the Fe-O-H-S system. The boundaries of stability areas between solid phases and dissolved phases for Fe (modified from Nordstrom, 1985 and Rose & Cravotta, 1999).

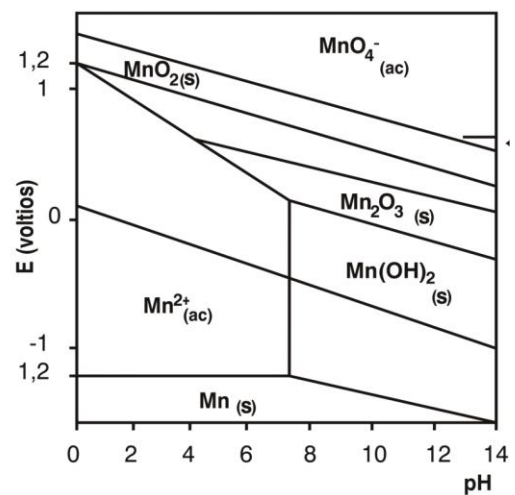


Figure 2. Formation ranges of solid phases of Mn mobilization as a function of pH-Eh (modified from Stumm & Morgan, 1996).

In the case of Mn, its solid phases are formed at pH greater than 8 (Fig. 2). When Fe and Mn are present in the mine drainage to be treated, typically at pH less than 5, the Fe is generally in solid phase and the Mn is dissolved; the opposite occurs at pH greater than 8, where the Mn goes to solid phase and the Fe is re-dissolved and returns to liquid phase. In practice, an overall treatment of these elements generates an overdose, which increases treatment costs and sludge volumes, and reduces the effectiveness of the treatment.

Maximum Permissible Limits (MPL) and Water Quality Standards (WQS)

They are measures of concentration or the degree of elements, substances or physical, chemical and biological parameters, which characterize an effluent or emission (MPL) and a receiving body whose water quality reference is made with the (WQS) which, when exceeded, generate a risk of damage to health, human welfare and the environment. Compliance is legally enforceable by the respective competent authority. Table 1 shows the respective values for each MPL and WQS reference device of water.

Parameter	Unit	D. S. 010-2010-MINAM		D. S. 004-2017-MINAM	
		Any moment	Annual Average	Category 3a	Category 3b
pH	e.u.	6-9	6-9	6.5-8.5	6.5-8.4
STS	mg/l	50	25	-	-
Manganese	mg/l	-	-	0.2	0.2
Lead	mg/l	0,2	0,16	0.05	0.05
Copper	mg/l	0,5	0,4	0.2	0.5
Zinc	mg/l	1,5	1,2	2.0	24.0
Iron (1)	mg/l	2,0	1,6	5.0	-
Chromium H.	mg/l	0,1	0,08	0.2	0.5
Arsenic	mg/l	0,1	0,08	0.1	0.2

Table 1. Maximum Permissible Levels for Effluents from Mining Metallurgical Units and Water Quality Standards for Category III.

DIAGNOSIS AND DISCUSSION OF RESULTS

Next we will present a mine drainage treatment case that did not meet the MPL and WQS in the receiving body mainly due to Manganese (Mn) concentrations. To carry out this study, an initial characterization of the acid mine drainage was carried out, the results of which allowed us to program a series of experimental neutralization tests aimed at optimizing the process that was being applied; direct and stepwise tests were performed with separation of solids formed in the neutralization process. In these tests, the reagent consumption necessary to reach effluent neutralization was estimated in order to experimentally determine the basic parameters for the preliminary design of the devices that will make up the treatment system, the sequence of operation and residence times in each stage.

Experimental Tests

Direct experimental tests and trials included the monitoring of specific parameters for indirect tracking of 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 formed as hydroxides for the case under study.

The recorded data showed the experimental mobilization ranges of elements that provide acidity to mine drainage as well as lime consumption. Table 2 shows the initial characteristics of the drainage to be treated, such as $\text{pH} < 3$ and its most significant concentrations (Fe, Al, Mn, Zn).

pH	Fe	Al	Mn	Pb	Zn
	mg/l	mg/l	mg/l	mg/l	mg/l
Total Concentrations					
2,1	285	22	350	3.1	70

Table 2. Initial characteristics of the drainage to be treated

Direct Neutralization Tests

These tests were carried out with continuous addition of lime, knowing that initial concentrations of Fe, Al, Zn, Pb and Mn were around 350 mg/l. The process showed a pH increase from 2.1 to 9.5 on average. During the test, sludge formation was observed at specific pH ranges (formation of insoluble solids corresponding to Fe, Al, Mn, Zn and Pb hydroxides according to the metal content of the sample). As pH increased the color of the sludge varied. This test simulates the generalized process in acid treatment plants installed in various mining operations. Fig. 3 shows a representative scheme.

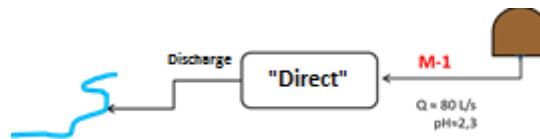


Figure 3. Typical scheme of a processing system using direct neutralization.

At the end of the neutralization process, and once sludge was separated, the treated water showed the characteristics recorded in Table 3, where it is evident that Mn contents are still at levels that require reduction, which in many cases need the addition of more treatment devices based on ultrafiltration, ion exchange or others to the treatment system.

Parameter	Unit	Final Concentrations	
		Total	Dissolved
pH	e.u	9.5	
Fe	mg/l	1.8	1.2
Al	mg/l	1.02	0.8
Mn	mg/l	140	136.5
Pb	mg/l	0.15	0.09
Zn	mg/l	1.8	1.6

Table 3. Acid drainage characteristics after direct neutralization.

Staged neutralization tests

The main objective of neutralization tests where lime was added in stages, with Mn contents greater than 200 mg/l, was to remove metals contained in samples according to the pH range in which they theoretically form insoluble solids. Also, to obtain not only a better quality of the effluent (optimized treatment system) but also sludge, in each stage, with significant metal content from which specific metals could be recovered or, in some cases, allocated to a new application.

The set of tests involved two-staged and three-staged neutralization tests, as well as the separation of sludge obtained in each stage. The best results regarding reagent consumption and quality improvement of effluents were obtained in two-staged neutralization tests. In these tests, the first stage involved a pH increase up to 5.5, where mainly Fe and Al solid stages were formed. In the second stage, the neutralization process continued until a pH of 10 was obtained, with production of black sludge, which may correspond to solid phases of Zn, Mn, and Pb, among others, depending on their initial content in mine drainage. The test simulated a stepwise neutralization treatment. Figure 4 shows a representative scheme.

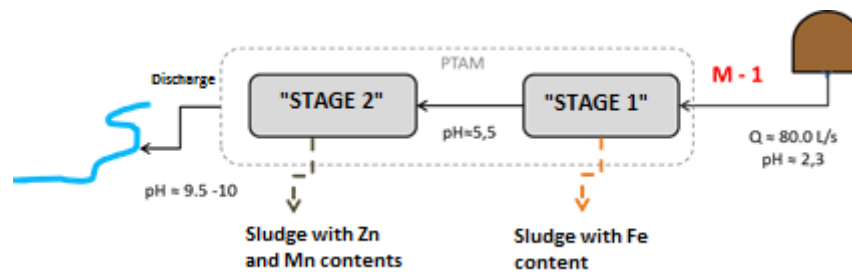


Figure 4. Typical scheme of the treatment system applying staged neutralization.

This sequential procedure would allow avoidance of re-dissolution of sludge formed in pH<5 ranges and minimize possible interference in the removal of metals that form solid phases at higher pH ranges, as well as lower reagent costs.

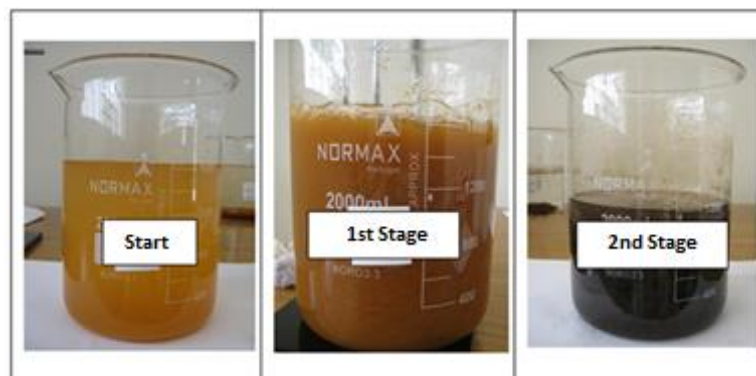


Photo 2. Sludge color as pH increases.

The results obtained in the staged neutralization treatment are quite clear in terms of the effectiveness of metal load separation from mine drainage. Table 4 shows metal concentrations in the sample after each treatment stage, with effective removal of Zn and Mn.

Parameter	Unit	Concentration Stage 1		Concentration Stage 2	
		Tot.	Dis.	Tot.	Dis.
pH	e.u.	4.5-5.5		5.5-10	
Fe	mg/l	0.29	0.1	0.18	0.10
Al	mg/l	1.07	1.08	0.11	0.05
Mn	mg/l	320	298	0.22	0.14
Pb	mg/l	1.03	0.98	<0.01	<0.01
Zn	mg/l	63.8	50.3	0.95	0.15

Table 4. Acid drainage characteristics after each neutralization stage.

The curves were built based on recorded data. Figures 5 and 6 show lime consumption and redox evolution curves during the neutralization process. In this particular case, Figure 5 shows solid phase or buffering formation zones due to Fe, Zn and Mn hydrolysis mainly. These zones correspond to the pH ranges in which solid phases of these elements are formed. As pH is increased, the Eh values decrease below 80 mV, which corresponds to unaffected natural waters.

Due to the shape of curves and the results obtained in laboratory tests, it is confirmed for this case, that the treatment of this effluent should be carried out in two (2) stages: the first stage would be implemented until a pH of 5 and 5.5 is reached. At this point, mainly Fe solid phases would be removed. Then the process would continue with the addition of lime until a pH of 10 is reached. In this second stage the formed sludge, mainly hydroxides or oxyhydroxides of Mn and Zn and other elements in smaller amount, such as Pb, should be removed.

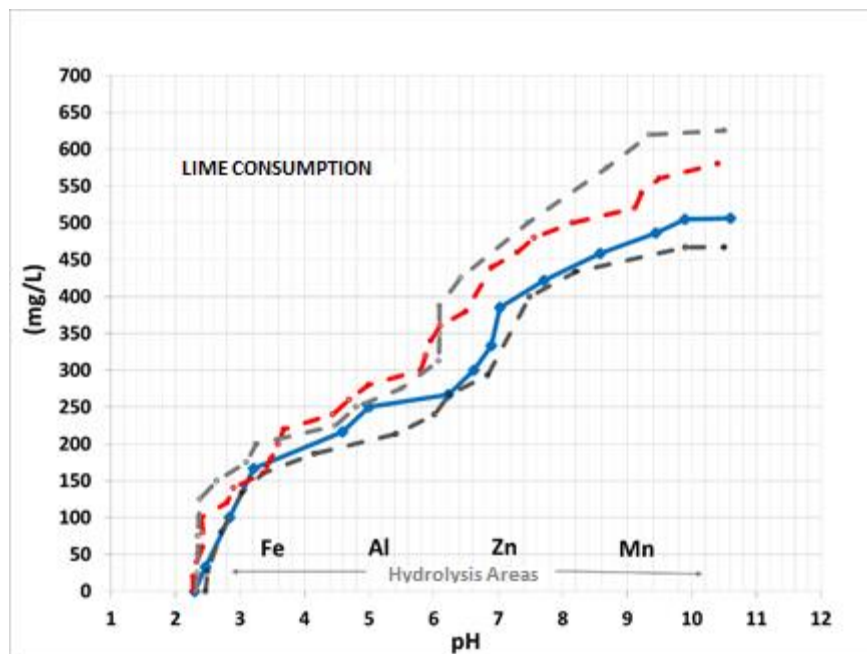


Figure 5. Neutralization curve and formation zones of Fe, Zn and Mn solid phases

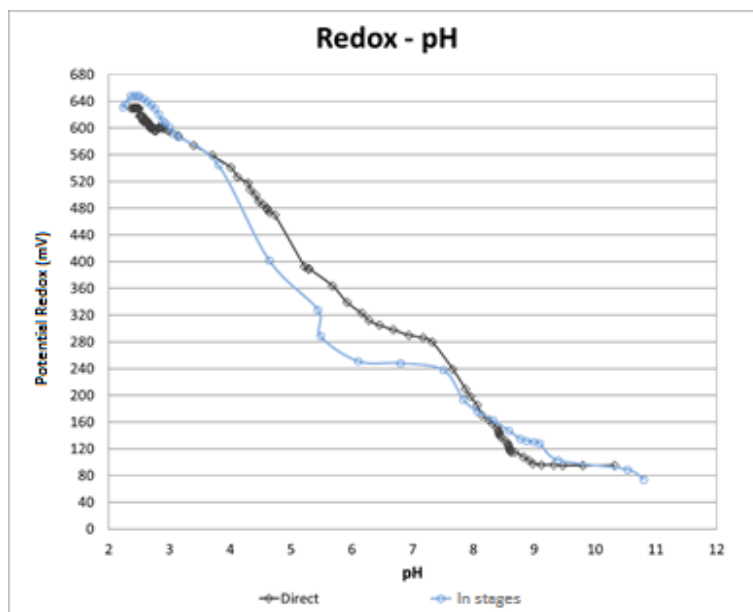
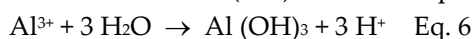
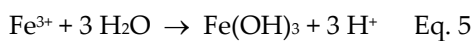


Figure 6. Potential Redox evolution in treatment

Figure 5 shows the buffer zones on the lime consumption curve (equivalent acidity), indicated by the pH and changes in the slope of the curve, from where a necessary lime dosage is estimated to be used in the neutralization process to remove Fe and Al contents from water in the form of solid phases.

The hydrolysis zones in acid range corresponding to Iron (pH 2.5-3.7) and Aluminum (pH 4.5-5.5) represent the removal of metal load from water, which in turn generates acidity. As a result, the system is temporarily buffered, evidenced in the following reactions:



From pH 6.5 to pH 8 and pH 10, the system also experiences buffering, in this case induced by the Zn and Mn content in this effluent with the latter having a less steep slope associated with lower reaction rates corresponding to the formation of Mn oxyhydroxides.

Photo 2 shows the solid phases obtained in the test: in the first stage, the solids have an ochre coloration (in some cases especially orange), where major phases are iron hydroxides. In the second stage, the solids obtained at the end of the test at pH 9.5 to 10.0 has a black or very dark brown coloration, which corresponds mainly to Zn and Mn solid phases.

The staged tests show processing times greater than direct tests, mainly due to the waiting time for the solid-liquid phase separation necessary for the removal of solids formed in the first and second stages.

The material balance performed as part of the follow-up of the reactions involved in the process, as shown in Fig.7, also evidences removal of metals of interest in each stage of the test.

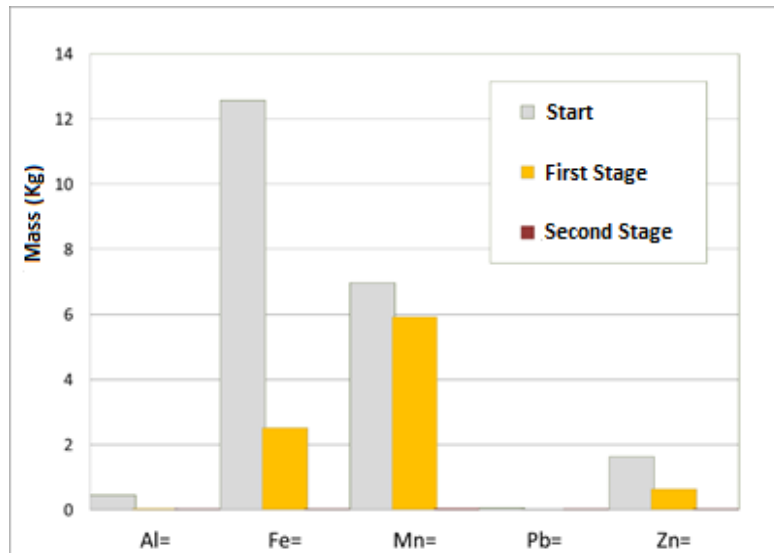


Figure 7. Mass content variation of Fe, Zn and Mn, among other minor elements, in the staged test.

Comparison of lime consumption.

In the staged treatment, passing Fe and Al contents to a solid phase requires a pH of 5.5, and 280 mg/L of lime. Passing all Zn contained in water to a solid phase requires lime addition until a pH of 9.5 to 10 is reached, where lime consumption reaches 520 mg/l (Fig. 8). If sludge from the first stage is not removed, then it can be re-dissolved and return to the water of the system; therefore, more lime should be added to precipitate the sludge by supersaturation, thus, increasing the cost of acid drainage treatment.

By comparing a 2-staged treatment to a direct single-stage treatment regarding lime consumption, there are lime savings between 15 and 20%. This situation implies a reduction in the cost of treatment and a more efficient process when reducing the Mn content to levels required by current legislation.

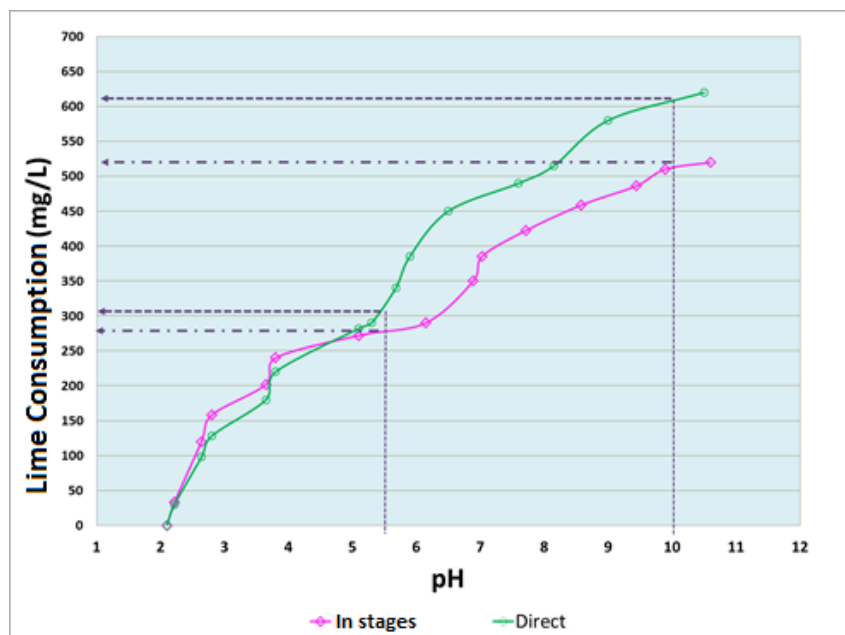


Figure 8. Lime consumption in tests.

In general, staged lime neutralization processes allow us to comply with discharge limits for heavy metals. The following steps are worth mentioning:

- pH control and agitation/retention, in order not to incur in lime passivation, obtaining lime dissolution and metal precipitation.
- Solid-liquid separation, to allow metal oxide/hydroxide sedimentation. It can be obtained by means of flocculation, coagulation or solid-phase sequestration processes.
- Discharge of a clean effluent in compliance with quality and relevant standards.

Unit Operations in a staged treatment system

The main Unit Operations involved in a staged treatment system are: Dissolution (of process reagents), Agitation and Decantation (Fig. 9) in each stage. They are complemented by secondary operations that allow controlling the process.

By applying a staged acid drainage treatment system, the obtained sludge has well-defined characteristics and the same peculiarities, with possibilities of recovering metals from process sludge.

Water from the treatment process can be discharged into a natural watercourse (receiving body), after being subjected to quality control in order to minimize the environmental impact. The sludge without recovery interest will be stored in suitable tanks or sent to the tailings pond or other deposit prepared for this purpose.

After the experimental stage, a pilot test should be carried out in order to adequately dimension the treatment system for each type of mine discharge.

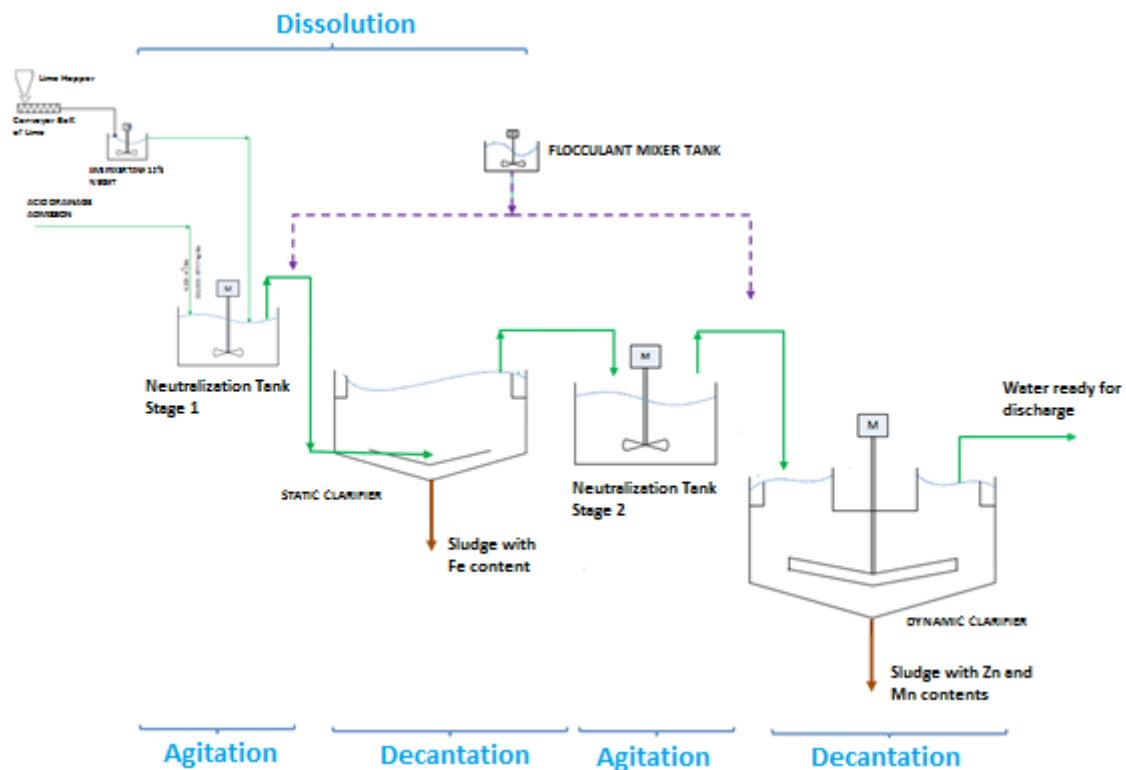


Figure 9. Unit operations in a staged treatment system.

CONCLUSIONS

Characterization of acid mine drainage in function of acidity helps to choose the most suitable and efficient treatment system, either through active or passive systems, since not only proton acidity but also mineral acidity is included, aspect that is not usually considered in classic characterization methods.

When mine drainage contains mainly Fe and Mn, staged neutralization can be applied in order to optimize mine water treatment processes; being fundamental for the conditioning of the treatment system: a phase of initial tests in laboratory followed by field tests that will allow to tune-up the operation parameters.

The application of a mine drainage treatment system based on acidity content and staged neutralization would provide benefits such as an optimal use of resources with less spending of lime in the neutralization process, the possibility of recovering metals of economic interest from process sludge, improvement of efficiency of the treatment system and greater environmental control.

NOMENCLATURE

MPL	Maximum Possible Limit
WQS	Water Quality Standard
T °	Water temperature (C°)
PH	Coefficient that indicates the acidity or basicity degree of an aqueous solution
TDS	Dissolved Total Solids
OD	Dissolved Oxygen

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