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Best Available Techniques in the Characterization and Treatment of Acid Mine Effluents

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ABSTRACT

Considering that an adequate characterization of the drainage produced by mining operations enables a correct selection of their treatment system. The use of the best available techniques (BAT) is essential to develop methodologies for the characterization and treatment of acid mine water, such as total acidity, which includes mineral acidity as well as protonic acidity, accompanied by neutralization and precipitation tests that promote the formation of physical and chemical processes that modify the Eh and pH conditions of discharges, favoring the formation of insoluble species and the removal of metallic load dissolved in the water.

In these acid water characterization tests, the most important are the determination of hydrolysis zones and the formation of initial solid phases of iron and aluminum that precipitate as hydroxides, oxyhydroxides or hydroxysulfates at pH values between 2.7 and 6, which induce the adsorption and coprecipitation of metals even those dissolved such as zinc, cadmium, manganese and others. If tests continue at pH values between 6 and 11, the remaining hydrolysis zones of the other constituents dissolved in the water will continue to be identified. This aspect is linked to the pH-Eh ranges in which the metal load present in effluents can be removed.

This hydrogeochemical characterization methodology, based on the estimation of total acidity and the identification of the hydrolysis zones, makes it possible to dimension more efficient mine water treatment systems, known as direct and staged systems, which lead to lower consumption of reagents and better environmental control. In the case of staged neutralization processes, the sludge or solids generated in each stage are removed sequentially, in order to avoid the redissolution of solid phases, enhance the efficiency of the treatment system and reduce costs and reagent consumption.

This paper reviews the techniques for geochemical characterization of effluents that have contributed to develop more efficient treatment systems and that make it possible for discharges to receiving bodies to comply with current legal requirements stipulated by the Peruvian mining and environmental legislation.

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INTRODUCTION

The development of sustainable mining projects implies the implementation of cleaner processes by applying the best available techniques (BAT), with greater environmental control and effluent discharges that do not alter the surrounding aquatic and terrestrial ecosystems.

This requires the implementation of treatment systems whose dimensioning is adjusted to the hydrogeochemical characterization of effluents produced by the mining operation.

In mining operations, the problem of acidic waters is solved through treatment in neutralization/precipitation plants to which a series of additional mechanisms are added, such as ultrafiltration, ion exchange, reverse osmosis, among others, which is an expensive solution that generates large volumes of sludge that must be stored in tanks designed for that purpose.

METHODOLOGY FOR EFFLUENT CHARACTERIZATION

The geochemical characterization of effluents is performed through direct measuring of physicochemical parameters and by determining the total and dissolved metal content. This is followed by a series of neutralization and precipitation tests to determine the hydrolysis or buffer zones induced by the concentrations found in the mine effluents.

Portable equipment is used for field data collection to carry out in situ measurements of pH, Eh, dissolved oxygen, conductivity, temperature, flow rate, turbidity, acidity, alkalinity, Fe^{2+}, Fe^{3+}, and total Fe, using equipment such as: pH meter, conductivity meter, oximeter, portable filtration equipment (Millipore), multiparameter probe, in addition to collecting water samples for the experimental stage. For total and dissolved concentration analysis, unfiltered and filtered water samples are collected at 0.45 microns, preserved with HNO_3 up to $pH<2$ and cooled to 4 Cº for transport to registered laboratories, following sampling standards.

CHARACTERIZATION OF MINING EFFLUENTS

Acidic effluent formation occurs from the chemical oxidation of sulfides, accelerated in many cases by bacterial action. The main elements involved are: reactive sulfides, oxygen and water (steam or liquid), and as a catalyst element, bacteria.

In general, acid mine drainage (AMD) has a pH between 2 and 6, contains cations and anions in solution, predominantly SO_4, Fe, Mn, Al, Cu, Pb, Zn, as well as Cd, Ca, Na, K, Mg and others. In general, acid mine water can degrade aquatic habitats and change water quality due to its toxicity, corrosion and other effects produced by the dissolution of its constituents.

Therefore, the characterization of mine effluents in terms of acidity includes protonic acidity by free hidrogen ions (H+) and mineral acidity mainly due to the concentrations present (Fe, Al, Mn, others). These metals are considered generating acids because through oxidation and hydrolysis they can generate H^+, according to the following reactions:

$Fe^{3+} + 2\,H_2O \rightarrow FeOOH + 3\,H^+$ Eq. 1
$Al^{3+} + 3\,H_2O \rightarrow Al\,(OH)_3 + 3\,H^+$ Eq 2
$Mn^{2+} + \frac{1}{4}O_2 + 3/2H_2O \rightarrow MnOOH + 2H^+$ Eq. 3

Fe^{3+} hydrolysis occurs mainly at pH 2.7 - 4.8 and precipitates as ferric hydroxide, generating 3 moles of acidity (Eq.1). At pH below the oxidation rate of pyrite, it is controlled by the Fe^{3+} concentration, as it interacts with the reactive surfaces of sulfides more effectively than oxygen.

Eq.2 represents the hydrolysis of Al^{3+}, which when passing to a solid phase provides acidity to the system, similar to ferric ion, which through oxidation and hydrolysis processes can precipitate in the form of oxides, hydroxides, oxyhydroxides or hydroxysulfates.

These valence III metals (Al^{3+} or Fe^{3+}) are poorly soluble under neutral pH conditions, however the mobility of these metals precipitates in solid phases, both oxidizing (oxides and hydroxides) and reducing (carbonates and sulfates). Therefore, solubility plays an important role in the mobilization of elements present in water, inducing their mobility in the form of cation, anion or dissolved complex.

Therefore, in order to adjust the treatment system's efficiency, it is advisable to determine the hydrolysis zones, such as those shown in Figure 1.

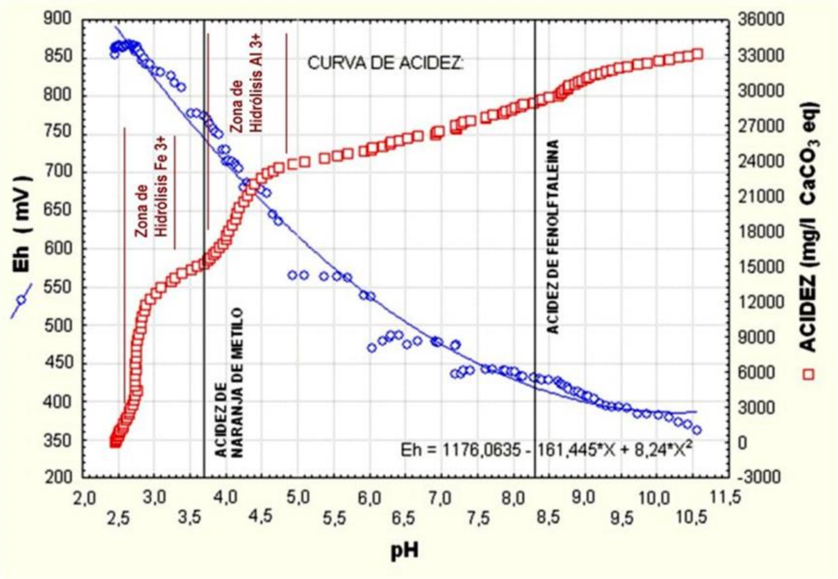

Figure 1. Hydrolysis zones in an acidity curve as a function of a mine effluent's pH.

Generally, in acidic media, Fe^{3+} forms solid phases which, if not removed from the treatment process at a pH greater than 5, are redissolved and pass back into the liquid phase. Similarly, the mobilization and redissolution of solid phases of aluminum (aluminum hydroxides) formed in the neutralization process generally occurs in pH ranges of 3.7 and 5.8, and if they are not removed from the treatment process at pH greater than 6, they are redissolved and pass again into the liquid phase. In both cases, this increases treatment costs and sludge volume, in addition to reducing treatment effectiveness.

TREATMENT SYSTEM DIMENSIONING

With the results obtained in the experimental curves of neutralization and precipitation tests where hydrolysis zones have been identified and the consumption of reagents, flocculants and others estimated, the sequences or stages of the treatment system are chosen. For the design, several tests are usually performed, considering independent samples and representative mixtures in the same proportions found in the mine drainage; therefore, numerous acidity or dosage curves are obtained where hydrolysis or buffer zones are detected, mainly of Fe, Al, Mn and other elements with significant presence, thus identifying the curve sections where solid phases (hydroxides, hydroxysulfates and others) would be formed, a basic condition where metal load removal can be achieved through solid-liquid separation.

The performance of neutralization and precipitation tests must meet quality standards to ensure the originality and representativeness of the mine water samples collected on site. Once the laboratory stage is over, field pilots are carried out.

Finally, the treatment system is dimensioned taking into account the results of tests and piloting with which it is possible to comply with the Maximum Allowable Limits (MAL) contemplated in the current legislation, MAL being understood as the concentration or content of physical, chemical and biological elements, substances or parameters that characterize an effluent, which when exceeded causes or may cause damage to health, human well-being and the environment.

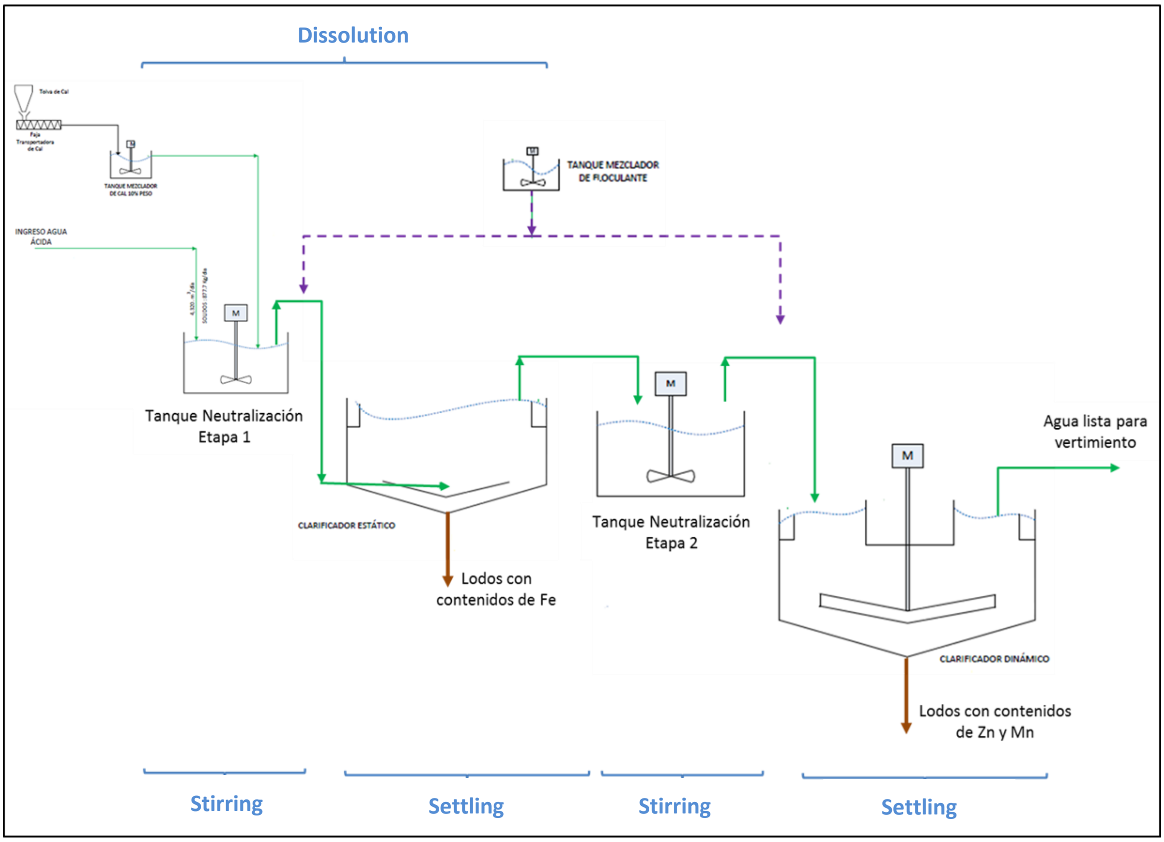

Figure 2. Design of a staged acid water treatment plant.

In the case of Peru, the MAL for treated effluents from new or operating mining and metallurgical facilities is contemplated in S.D. No. 010-2010-MINAM and their compliance is legally required by the relevant competent authorities. To this end, control points are set up before discharging into the receiving body where total and dissolved concentrations of regulated parameters, discharge volume and monitoring frequency are measured.