



About the Interaction between water and Pb, Zn, Cu, Cd, Fe, Mn, Ba Mineralized Limestones Rocks

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ABSTRACT: One of the most important environmental concerns at mining sites is acid mine drainage (DAM), which is formed by the exposure sulfide minerals to air and water. The consequent production of sulfuric acid reduces the quality of water bodies and may allow the solubilization of potentially toxic metals such as Pb, Zn, Cu, Cd, Fe, Mn and Al. There is a range of laboratory procedures, classified as static and kinetic. Which have been used to understand the acidification and neutralization potencies of a rock through water/rock interaction process. These procedures seek to describe, quantify and predict the compositional changes of the solid and liquid phases in natural systems. The choice of techniques, methods, procedures and protocols requires the understanding of the problem to be solved or mitigated and is related to the specific geochemical and geological characteristics of the site to be analyzed. The elaboration of experimental procedures involves sampling strategies, selection of methodologies, (Accuracy, precision, sensitivity, speed, cost) and thus equipment and other necessary materials. This work presents the main static and kinetic procedures, highlighting its principles, advantages and limitations for selection and application in carbonate rocks rich in sulphide minerals. PH, Acid-Base Accounting and Net Acid Generation (NAG) are the static methods chosen. While the kinetic procedures chosen for the study of the natural enrichment of toxic metals in sulfate carbonate rocks is leaching columns, the Soxhlet system and reaction reactors. To provide more consistent drainage forecasts and hence better plans for the management of The results of different methods should be analyzed together.

I. INTRODUCTION

Water is a chemically very active solvent, capable of reacting with the percolated medium by dissolving various polar and ionic substances. When considered exclusively natural processes, the main constituents present in the waters result from physical processes (rock fragmentation) and chemical rocks weathering. Chemical weathering involves mineral alteration processes, generating secondary (altering) minerals and releasing soluble ions that are incorporated into the aquatic environment. This phenomenon can be interpreted as the tendency of the water/rock system to reach physical-chemical equilibrium, through hydration / hydrolysis, dissolution, precipitation, oxidation and complexation reactions.

Although most minerals do not exhibit perceptible solubility in pure water, the presence of acidity in the water (generated by the formation of carbonic acid and/or sulfuric acid, due to the absorption of carbon dioxide and exposure of sulfides to air and water. Respectively increases the solubility of many minerals. The chemical reactions of mineral alteration depend on the water/rock contact time, the temperature, the available CO₂ and the presence of inorganic and organic acids. The physical and chemical composition of the waters will reflect the mobility and solubility of the elements involved in the weathering process. This behavior can be altered under strong physical-chemical conditions change (pH and Eh) (HIRATA, 2003).

Mining industries are associated with Amino Drainage (DAM), which is formed when sulfide-containing minerals are oxidized by exposure to air and water. When mediated by bacteria, thiobacillus ferroxidans, for example, the speed of the reactions involved in the generation of AMD can be increased by more than one million times (SENGUPTA, 1993). Water acidification can increase solubilization of minerals and thus mining areas may contain relatively high levels of toxic substances, such as sulfates and cyanides of potentially toxic metals (Pb, Zn, Cu, Cd, Fe, Mn, Ba and Al), which may represent adverse long-term impacts, decreasing their quality (PEREZ-LOPEZ et al., 2007, MURTA et al., 2008, CHOTPANTARAT, 2011). DAM-generating sites remain active for decades and even centuries after their production (MACHADO and

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SCHNEIDER, 2008). In this way, the acidic drainage of rocks, wastes and other components of the mine is one of the most important environmental concerns at the mining sites (MACHADO AND SCHNEIDER, 2008; MURTA et al., 2008; HESKETH et al., 2010).

Several methods have been tested to understand the acidity and neutralization potentials and to predict the chemical composition of the drainage generated by the contact of the water with the rock. The laboratory and field methods for water-rock interaction have as objectives: to describe, quantify and predict changes in the chemical compositions of the solid and liquid phases, in natural systems, in a timely manner and over time. These are subdivided into static and kinetic, in which the water-rock interaction is performed under conditions that simulate the vadose and saturated regions. These simulations allow understanding the kinetic mechanisms of the reactions involved and, in this way, to predict possible genetic contaminations. Several authors have pointed out the difficulties faced in the various methods, including physical, chemical and biological factors. It can be highlighted: (1) the representativeness of the samples considering the size and the geological variety of the rock masses; (2) the large test time; (3) the marked influence of biological processes on the speed of reactions and (4) the difficulty of simulating the actual physicochemical conditions of the site, including oxygen availability (Sobek et al., 1978; MEND 2009).

This paper has as main objective indicate and describe the main laboratory procedures available for the study of chemical weathering, generated by the interaction of mineralized carbonate/rock in sulfides. For the proposed purpose, a comparative study is carried out between the methodologies approached in relation to the equipment used, the proposed modifications and their advantages and disadvantages.

II. STUDY AREA AND CLIMATOLOGICAL ASPECTS

The area chosen for this study is located in the Irecê Sedimentary Basin, located in the central-northern portion of the State of Bahia, Brazil. This region is mineralized in sulfides of copper, lead, zinc and silver (WASHINGTON & MISI, 1992; RIBEIRO et al., 1993). The study was carried out in the state of Bahia, Brazil, in the state of Bahia, in the state of Bahia (Brazil) (BAHIA, 2006), which may indicate possible sources of groundwater contamination.

The aquifer system of Irecê Sedimentary Basin, Domain of Group Una in the State of Bahia, Brazil, does not have enough data and information on the quality of its groundwater, as well as the main vectors of contamination. This reservoir is considered of great importance for the population of this region, since a significant portion is supplied with water withdrawn from the tubular wells.

The search area is located in the semiarid region of northeastern Brazil and presents high spatial and temporal variability of rainfall. According to the classification of KOPPEN the climate of the area is BSWH type, semi-arid, dry sub-humid in winter and very hot and rainy in the summer, with average annual temperatures of 23°C to 26°C. The Irecê Sedimentary Basin presents a marked irregularity in the distribution of rainfall, where variations from 500 to 700 mm/year can be observed in the north, and variations in the order of 600 mm/year to 1200 mm/year in the north. The highest rainfall occurs between November and March. The average evaporation is 2060 mm/year (RAMOS, 2005).

III. DISCUSSIONS

3.1 Identification of minerals

The identification of the minerals present in the rocks can be performed by X-ray diffraction (DR-X) spectroscopy in rock dust, through microscopic analysis and by scanning electron microscopy with dispersive energy X-ray spectrometry (SEM/EDS). These methodologies allow not only to know the mineral assembly but to have information on the degree of weathering through the knowledge of the primary and secondary minerals present in the rock under study.

3.2 Chemical analyzes

The compositional knowledge (main, minor and trace elements) of the leaching and mineralogical fluid of the rock sample, before and after the laboratory procedures of water/rock interaction, allows to evaluate the chemical changes occurring in the rock and the elements leached to the water. The static tests are developed mainly by classical volumetric methods and simple equipment such as pHmeters and conductivity meters. However, the kinetic procedures require specific devices that are made according to the objectives to be achieved. The leaching fluid is also subjected to chemical and physicochemical parameters analysis, such as: temperature, pH, Eh, total dissolved solids (STD), electrical conductivity (EC), O₂ and CO₂, chloride, fluoride, nitrate, sulfate, sulfide, hardness and partial and total alkalinities. The instrumental methods commonly used for chemical and mineralogical analyzes are the induced emission spectrometry with induced argon plasma (ICP-OES), atomic absorption (AAS), mass with plasma source (ICP-MS), fluorescence (XRD) and X-ray diffraction (XRD), in addition to scanning electron microscopy with dispersed X-ray energy spectrometry (SEM / EDS).

3.3 Laboratory Studies

The tendency of a given rock to produce acidity is a function of the balance between acid-consuming minerals (alkaline) and acidity producers (sulphides). If the acid-consuming capacity of a rock exceeds the acid generating capacity it means that the AMD generated by the sulfide minerals has been neutralized by the acid-consuming minerals such as carbonates and silicates. In this way, mine drainage can be acidic, neutral or alkaline.

3.4 Static Geochemical Methods

Although they are not able to define whether the sample will actually produce acid and when this acidity will occur (CHOTPANTARAT, 2011), they are not indicative of the acid potential and self-neutralizing power of a sample (COLLON, 2003; CHOTPANTARAT, 2011). Consider the kinetics of the reactions involved. They run in a short period of time, hours or days.

The most used procedures are paste pH, ABA (standard and with its corrections for silicates and siderite) and NAG tests (single addition of peroxide, sequential and kinetic).

3.4.1 Measurement of pH and electrical conductivity in saturated pulp(EC).

Sobek et al., In 1978, standardized this method, which consisted of saturating a sample (granulometry <1 mm) with water-distilled until a paste was obtained. After the equilibration period, from 12 to 24 hours, the pH and conductivity were measured. This method has undergone some modifications over time. Fixed values were established for volumes and masses (PAGE et al., 1982). The MEND Project (2009) established a new methodology by altering the particle size of the sample and, consequently, the time required to reach the physicochemical balance for pH and conductivity measurement. Unfortunately, there is no standard procedure that applies today. The advantages of this test are related to low cost and speed. However, it has as limitations to consider the kinetics of the reactions and to require the result of other techniques to estimate the potential of acid formation (CHOTPANTARAT, 2011).

3.4.2 Acid-Base Accounting (ABA).

Correspond to the difference between the Acid Potential (PA) and the Neutralization Potential (PN), expressed in kg of CaCO₃/ton of rock. The acid potential is calculated based on the total percentage of sulfur in the sample. The neutralization potential is determined by the presence of carbonates in particular by addition of excess HCl to the sample, spraying at a particle size of less than 60 mesh, and back-titration with NaOH. The amount and concentration of the HCl solution to be added and The concentration of the base is determined empirically by the presence of carbonates in the rock sample (SOBEK et al., 1978, LAPAKKO 1994, LAWRENCE AND WANG 1997, SKOUSEN et al 1997; MEND, 2009).

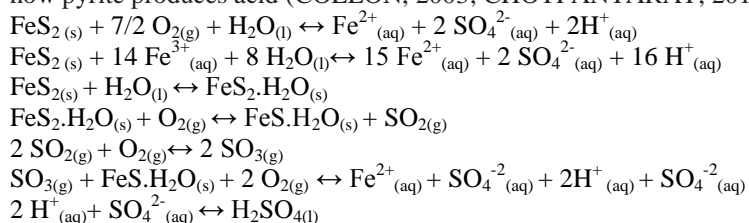
$$ABA = PA - PN$$

Being that:

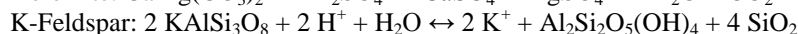
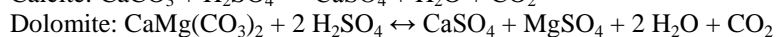
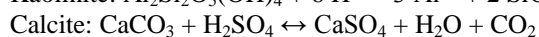
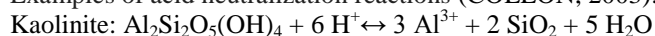
$$PA \text{ (kg CaCO}_3\text{/t)} = (1000/32) \times \% \text{ weight S}$$

$$PN \text{ (kg CaCO}_3\text{/t)} = (\text{HCl consumed, g/g sample}) \times (50/36,5) \times 1000$$

Where the value 32 is the sulfur atomic mass and 36.5 corresponds to the molar mass of the hydrochloric acid. The Neutralization Potential Ratio (RPN) = PN / PA is also used as a criterion for the identification of acidity generation (Table 1). The most common sulphides for the production of H₂SO₄ are the minerals pyrite (FeS), pyrrhotite (Fe_xS_x), calcosite (Cu₂S), covelite (CuS), chalcopyrite (CuFeS₂), galena (PbS), sphalerite (ZnS) and millerite NiS (FARFAN et al., 2004). Examples of chemical reactions that demonstrate how pyrite produces acid (COLLON, 2003; CHOTPANTARAT, 2011):



Examples of acid neutralization reactions (COLLON, 2003):





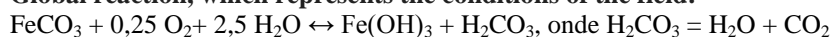
Several ABA procedures are available (SOBEK et al., 1978, LAPAKko, 1994, LAWRENCE and WANG, 1997, SKOUSEN et al., 1997, MEND, 2009). The advantages of these methods are related to the simplicity of the technique, speed of execution, not requiring special equipment, easy interpretation of the results and the possibility of analysis of many samples. However, these procedures differ among them in the methodologies for the determination of acidification and neutralization potentials.

The acidification potential can be calculated by the determination of the sulfur in a Leco high temperature combustion furnace or the sulfide content is established by classical chemical analysis methods. The sulfur determined by the Leco combustion furnace does not allow differentiation of sulfur species (Sulfides, sulfates, organic sulfur) and overestimates the potential for acidification. It is necessary, then, to analyze the sulfur by other techniques such as, for example, volumetric, gravimetric and molecular spectrophotometry methods.

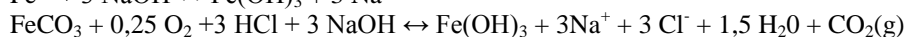
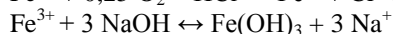
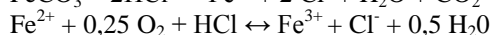
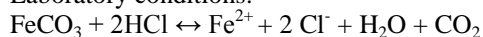
Regarding the neutralization potential, the procedures differ in relation to the acid used and the final pH of the retitulation ranging from 4.5 to 8.5. Very acidic endpoints allow the dissolution of silicates in addition to the carbonates and thus overestimate the neutralization potential. The procedure developed by Lapakko (1994), where the neutralization potential was determined by sulfuric acid decomposition and retro-titration at pH 6 did not present good results. This problem was corrected in 1997 by Lawrence and Wang, who performed the cold decomposition and The retro-titration at pH 8.5 and by the MEND Project which considered the use of hydrochloric acid, the decomposition of the sample with hot HCl and titration endpoint that determines the acid excess at pH equal to 7. Another difference between the methodologies consists the correction or not of the effect of the mineral siderite (FeCO_3). Skousen et al. (1997) modified the Sobek procedure in relation to the neutralization potential (PN) by adding hydrogen peroxide to oxidize Fe (II) and, therefore, corrected the interference of siderite. Initially, being a carbonate, siderite generates neutralization potential. However, other reactions are involved in this chemical balance. The oxidation reaction of Fe^{2+} to Fe^{3+} consumes HCl, however Fe^{3+} reacts with NaOH to form $\text{Fe}(\text{OH})_3$, which precipitates. The global reaction of siderite generates NP null (ie $\text{NP} = 0$). If the effect of this mineral is not corrected, it generates an oversized neutralization potential. This correction is performed with the addition of hydrogen peroxide (H_2O_2) to accelerate the chemical balance of the mineral, prior to the final back-titration with HCl molecular. (SKOUSEN et al., 1997).

Siderite Reactions:

Global reaction, which represents the conditions of the field:



Laboratory conditions:



The general combination of the above reactions is essentially the same as the overall reaction, with the addition of sodium (Na^+) and (Cl^-)

3.4.3 Liquid Acid Generation (NAG- Net Acid Geration)

The NAG test was developed in Australia and aims to account for the net acid generation potential for a given sample (MEND, 2009). In this procedure, the liquid pH of the limestone is measured after addition of a strong oxidant (hydrogen peroxide) under heating. In this case, hydrogen peroxide has the purpose of decomposing the sample and oxidizing the sulfides present to sulfates. If there is carbonate, there will be total or partial neutralization of the acid produced and the excess acid, if any, is titrated with a standard solution of sodium hydroxide up to pH 4.5. What differs from the NAG test of the ABA test is that it is not possible to differentiate separately the acidification and neutralization potentials. (SOBEK, 1978; COLLON, 2003; LIAO et al., 2007; MILLER et al., 1997; MEND, 2009; CHOTPANTARAT, 2011).

The simple addition of hydrogen peroxide may present inaccurate results in some cases and thus additional tests have been described to create a more reliable set of techniques (SHAW, 2005).

The main NAG tests include:

(A) single-addition H_2O_2 NAG test for samples with low sulfide contents - The main limitation of this procedure is that the peroxide can be decomposed prior to the total oxidation of the sulfide present in the sample. The incomplete oxidation of the sulfides may underestimate the total acid generation potential and indicate that the neutralization capacity is greater than that required to maintain neutral or alkaline drainage.

According to AMIRA (2002), only sulfur content of sulfides less than 1% . are completely oxidized with a single addition of H₂ O₂.

(B) Sequential NAG test for samples with high sulfide content-It is used to minimize the effects of peroxide decomposition by successive additions of H₂O₂ in the same sample until the total oxidation of the sulfides (MILLER et al., 1997). The development time of the sequential NAG test may not be adequate for the mineral characterization routine (AMIRA, 2002). This may make the NAG test impractical for projects where the sulfur content of sulfides exceeds 1% or where there is concern about the presence of hydrogen peroxide with organic matter, oxidation products of sulfides or other reactive metals (MEND, 2009).

(C) Kinetic NAG test - Used when knowledge of mineral reactivity is required. The Kinetic NAG test is similar to the NAG of single addition of H₂O₂.

The difference is that the temperature, pH, and electrical conductivity of the solution are monitored as a function of time. The variations of these parameters during the test provide an indication of the kinetics of the reaction (oxidation of the sulfides), acid generation and neutralization of the same.

The pH trend provides an estimate of the mineral reactivity and may help predict the time for the generation of a potentially toxic drainage and the oxidation rates in leach columns (MEND, 2009).

When compared to kinetic procedures, the advantages of these methods are related to the low cost, speed of execution and the possibility of treatment of a large number of samples. However, they require the results of other techniques to estimate the potential for acid formation. They do not consider the reaction kinetics (except the kinetic NAG test) and the hydrogen peroxide can undergo decomposition before oxidizing the total sulfide present in the sample (except the sequential NAG test). The sequential NAG test is the one that provides the best estimate of the AP, but has a longer execution time (CHOTPANTARAT, 2011).

3.5 Kinetic Geochemical Methods

Experimental procedures allow the continuous measurement of weathering and the incorporation of dynamic elements of the physical, chemical and biological systems of interest (HORNBERGER AND BRADY, 1998). The assays tend to mimic the processes found in the demineralized sites, usually at an accelerated rate. Kinetic tests can be used to evaluate different variables in the acid production process, if this occurs. They allow investigate parameters such as temperature, particle size, speed and type of leaching (dry air, humid air, CO₂ free water, CO₂ rich water), inoculation of bacteria among others. These procedures are performed to confirm the results obtained by the static procedures and to estimate the amount and the time in which potentially toxic drainage may occur. The data are evaluated by changes in water quality over time (MEND, 2009; MORAES, 2010).

According to Farfan et al. (2004) and Moraes (2010), the main objectives of kinetic methods are: (1) to provide confirmation of the potential of acid mine drainage; (2) to evaluate the rates of sulfur oxidation and acid production; (3) determine the relationship, if any, between the onset of AMD and the decrease in the neutralization potential; (4) determine the effect of bacteria; (5) to evaluate the degree of leachable metals and to indicate cation/anion concentrations, which can be expected from acid drainage, and (6) select the test to evaluate and manage the waste, plants and control strategies. The main advantages of these tests are the possibility of observing the rocks behavior under conditions close to the reality, and the obtaining of reaction kinetics.

The most used kinetic methods are: extraction by the Soxhlet system, closed reactors, leach columns (open and closed systems) and moist cell.

Table 1 - Criteria for identification of acidity generation for static methods. DAM = Acid Drainage from Mine.

Methods		Criteria	Results	References
Ph		< 4,0	Indicates That There Will Be Formation Of Acid	Sobek <i>Et Al.</i> , 1978
		> 4,0	Indicates That There Will Be Formation Of Acid	
ABA	PN - PA	< - 20	Indicates That There Will Be Formation Of Acid	MEND (2009)
	PN - PA	> + 20	Indicates That There Will Be Formation Of Acid	
	PN - PA	- 20 < X > + 20	Difficult Acid Prediction	
	RPN	< 1:1	Indicates Likely Generation Of DAM	
	RPN	> 4:1	Indicates Likely Generation Of DAM	
	RPN	1:1 < X > 2:1	Indicates That DAM Is Not Expected	

	RPN	2:1 < X > 4:1	Indicates That DAM Will Not Be Generated	
NAG		> 4,5	Non-Acidic Sample	MEND (2009)
		< 4,5	Sample Generating Acid	

3.5.1 Extraction in the Soxhlet system

Composed primarily of a round bottom flask, extraction chamber with a siphon system and a reflux condenser, the Soxhlet System (Figure 1) is generally used for solid/liquid extraction. This system accelerates the possible interactions between the water and the rock, through leaching cycles that are imposed on the sample. The percolated fluid is constantly recycled by successive evaporations and condensations (SOBEK et al., 1978; MORAES, 2010). When the solvent reaches a certain level in the sample compartment, it is siphoned back into the original flask. In this way, the process is cyclic and a new step is initiated when the solvent reaches its boiling temperature. The higher boiling extract remains in the source flask while the pure solvent is evaporated to start a new cycle, which can be repeated until the material is completely depleted. The changes associated with this methodology are related to sample size, number of cycles, time and the possibility of performing partial cycles. In these, it is possible to evaluate the sample as a function of the time that remained immersed in the extraction chamber during the process. Although condensed fluid is at room temperature, the temperature in the extraction chamber will reach a temperature above 60° C, which accelerates the sample's weathering. The Soxhlet System's leaching method requires sophisticated equipment and produces results that are difficult to interpret.

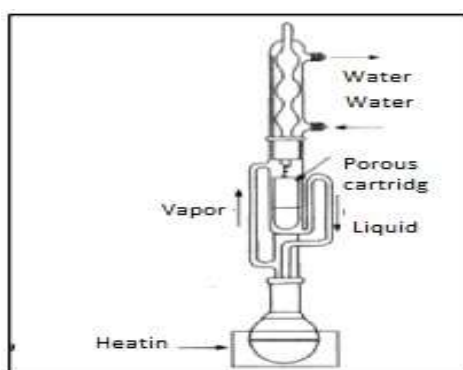


Figure 1 - Leaching of the rock by the Soxhlet System. Method described by Franz Von Soxhlet in 1879..

3.5.2 Testes in closed reactors with periodic agitation

The purpose of these tests is to study the chemical equilibrium established between water and rock under conditions simulating the saturated zone. The principle is simple and is performed in duplicate. In two containers, the rock, in the crushed fraction, is placed in contact with the water, so that it is completely submerged. Both reactors are subjected to manual agitation, daily, for a fixed time. One reactor remains closed and periodically the other is open for analysis of physicochemical parameters (pH, oxy-reduction potential (Eh), electrical conductivity (EC) and total dissolved solids (TDS)). The procedure is repeated until stabilization of the electrical conductivity. That is, when the chemical equilibrium is reached. The stabilization time is dependent on the mineral assemblage and can be reached after several months. When the chemical stability is reached, the reactor water remaining closed is collected and filtered using a cellulose filter of 0,45microns. The physicochemical parameters mentioned above are measured, with determinations of sulfate, sulfide, partial and total alkalinities, fluorides, chloride and nitrates. Another sub-sample is acidified with HNO₃ at pH 2 for the determination of cations. Acidification prevents any precipitation during the storage period.

The procedure requires simple and sophisticated equipment such as pHmeters, conductivity meters, Molecular Spectroscopy (anion analysis) and Optical Emission Plasma Induced Spectrometer (ICP-OES) or Atomic Absorption Spectrometry (EAA) (cation analysis) and mass spectrometry with Source of plasma (ICP-MS) and involves a high cost.

3.5.3.Lixiviation in Colun

According to Machado (2007), the leaching columns are the most versatile kinetic procedures, since several tests can be developed to monitor the evolution of water quality. There is no standardization for the

construction of these columns. Guimarães (2007) in Moraes (2010) gathered some constructive details of leach columns found in the literature. The columns vary in height (20 cm to 2m), diameter (7.56 to 15 cm) and clothing materials (acrylic, PVC and unspecified material). Samples are also leached in different solid/liquid ratios, using or not peristaltic pumps, particle sizes, masses and solid/liquid ratios (particle diameter ranging from 4mm to 4cm, 100g to 12kg) and test time (60 Days to 30 weeks). The particle size of the sample is directly related to the time of the test. Less granulometry allows the chemical equilibrium to be reached more quickly. Collon (2003), carried out rock leaching with granulometry varying from one to zinc, in columns of transparent polycarbonate, with height of 46.5 cm and 19.5 cm in width, for a period of approximately one year. He observed the presence of algae, which locally covered the walls of the columns, and associated this proliferation with high concentrations of nitrate. Algae alter the O₂/CO₂ balance and, in this way, alter the chemical balance between water and rock. The use of transparent materials to make the columns allows visualizing possible problems of the process such as gaps in column filling and development of algae in very long processes. Some disadvantages of column tests are related to the long times required to perform the procedures and the associated high costs.

Into the columns the material leaching rocks can be done in two ways (Figure. 2). When the flow of the descending liquid, i.e., when the injection is made in the top of the column and the solution is by gravity, the sample is in a condition that simulates the vadose zone. When the lixiviation is injected into the bottom pellet of the column, the flow is upward. The sample is completely saturated and the oxygenation availability is controlled by pellet diffusion of the gas in the lixiviation solution. In both assays, the solution is analyzed periodically at the outlet of the device to control Chemical evolution over time. PH, Eh, conductivity, alkalinity, hardness, among others are determined.

The leaching experiments in columns are many simple to program, flexible in function of the objectives and try to reproduce the conditions of the natural environment. However, the major limitation is the choice of scale for the reproduction of the study environment and the main drawback of these tests is their duration. Depending on the material studied, the granulometry of the same and the flow rates chosen for the leaching, the time of the experiments varies greatly, from days to several months.

3.5.4 Column leaching - closed system

In a transparent polycarbonate column, the crushed rock is immersed in water, in a closed system and without water circulation (Figure 03). The electrical conductivity and temperature of the solution are measured daily with three probes, positioned at different heights, connected to the conductivity meters. The partial pressures of O₂ and CO₂ are also measured at the top of the column by means of a gas sensor. All data is collected in a data acquisition system, which records a measurement every five minutes during the 31 days of the experiment. As the system is closed, the oxidation of the sulfide will occur exclusively through the O₂ of CO₂ dissolved in water in constant contact with the rock (COLLON, 2003).

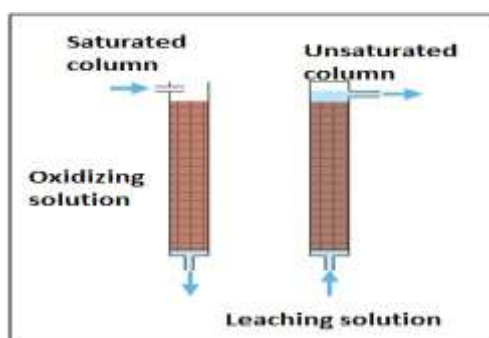


Figure 2 - Simplified scheme of leach columns, in Conditions that simulate vadose and saturated areas Murta (2006).

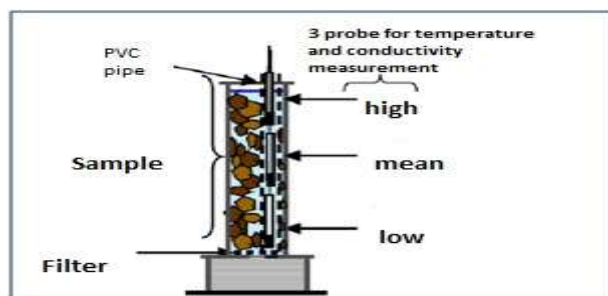


Figure 3 - Column leaching, in a closed system, simulating the saturated zone Collon (2003).

3.5.5 Wet Cell

Several decades ago, for sulphide-rich rocks the wet cell was the kinetic test recommended to predict primary reaction rates under aerobic weather conditions (MEND, 2009). The protocol consists of leaching the sample (1000 g, lower granulometry To 6.30 mm) with dry air for three days, with moist air for another three days and with water (500 mL to 1000 mL) for one day. The seven day cycle should be repeated for at least twenty weeks. The results provide the measurement of the release rates of the elements and acid generation and neutralization, under aerobic geochemical conditions of the tests. The measured rates can be used to estimate the time of mineral exhaustion (MEND, 2009).

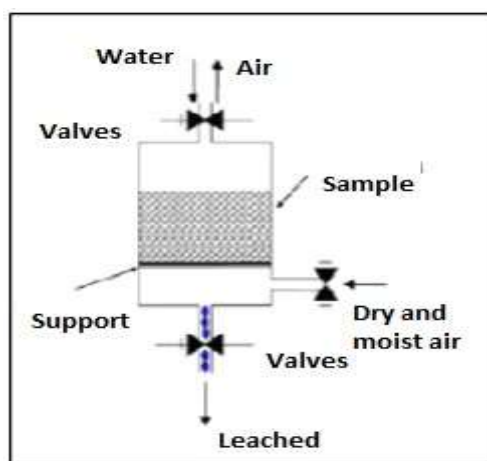


Figure 4 - Simplified Scheme of a Wet Cell (Mills & Robertson, 1997, in Murta (2006)).

In the past, moist cells had a considerable variety of dimensions (PRICE, 1997, SOREGAROLI and LAWRENCE, 1998). However, service laboratories for mining industries have now adopted a degree of standardization, under the reference D5744-96 from ASTM (Standard Test Method for Accelerated Weathering of Solid Materials), to a modified wet cell (ASTM, 1996). This protocol standardizes two dimensions for the cells according to the granulometry of the tailings or rock under study. The advantages of moist cell are related to the possibility of measuring primary reaction rates and the reproducibility of the tests, allowing comparison with results from other sites.

IV. CONCLUSION

Laboratory methods for water-rock interaction are intended to describe, quantify and predict changes in chemical compositions of the solid and liquid phases, in natural systems, in time and over time.

For decades laboratorial tests have been applied to predict the existence and quality of AMD in mining. Several authors (SOBEK et al., 1978; MURTA, 2008, MEND, 2009) have pointed to the difficulties faced in the various methods, including physical, chemical and biological factors. The most important difficulties are related to the representativeness of the samples considering the size and the geological variety of the rock masses; To the great time of the kinetic tests; The marked influence of biological processes on the speed of reactions; To the difficulty of simulating the actual physical-chemical conditions of the site, including the availability of oxygen.

Although many techniques have been developed, none is sufficient to provide accurate data. The estimation of greater reliability of the acid, neutral or alkaline potential of the mine drainage is the result of a set of methodologies. The more accessible static methods provide information that is tested by kinetic methods. Only kinetic methods provide information on kinetics, time of onset of acid drainage and acidity potential. Statistical procedures to be applied on limestone limestone rocks, sulphide mineralized, will be paste pH,

standard and modified ABA tests (correction for silicates and Siderite) and NAG to verify, in a timely manner, the type of drainage generated in the sites under study. These procedures were chosen because they were the most applied in the initial drainage prediction studies because they were easy to perform and did not require sophisticated equipment. In this study, the study was carried out in order to determine the type of drainage generated by the Soxhlet system and the leaching columns, The kinetics of the reactions involved and the maximum concentrations of these elements in the water under the conditions of the water/rock interaction tests. The kinetic procedures will be performed with the same granulometry, so that a comparison of the results can be performed. The ultrapure and / or meteoric water volume to be used in leaching processes will be 700 mL, to simulate the annual rainfall of the study region

Analyzes of the chemical elements will be performed by ICP-MS, due to the expected low concentrations.

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