Innovative Approach to Prevent Acid Drainage from Uranium Mill Tailings Based on the Application of Na-Ferrate (VI)

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ABSTRACT

The operation of uranium mining and milling plants gives rise to huge amounts of wastes from both mining and milling operations. When pyrite is present in these materials, the generation of acid drainage can take place and result in the contamination of underground and surface waters through the leaching of heavy metals and radionuclides. To solve this problem, many studies have been conducted to find costeffective solutions to manage acid mine drainage; however, no adequate strategy to deal with sulfide-rich wastes is currently available. Ferrate (VI) is a powerful oxidizing agent in aqueous media. Under acidic conditions, the redox potential of the Ferrate (VI) ion is the highest of any other oxidant used in wastewater treatment processes. The standard half-cell reduction potential of ferrate (VI) has been determined as +2.20 V to +0.72 V in acidic and basic solutions, respectively. Ferrate (VI) exhibits a multitude of advantageous properties, including higher reactivity and selectivity than traditional oxidant alternatives, as well as disinfectant, flocculating, and coagulant properties. Despite numerous beneficial properties in environmental applications, ferrate (VI) has remained commercially unavailable. Starting in 1953, different methods for producing a high purity, powdered ferrate (VI) product were developed. However, producing this dry, stabilized ferrate (VI) product required numerous process steps which led to excessive synthesis costs (over \$20/lb) thereby preventing bulk industrial use. Recently a novel synthesis method for the production of a liquid ferrate (VI) based on hypochlorite oxidation of ferric ion in strongly alkaline solutions has been discovered (USPTO 6,790,428; September 14, 2004). This on-site synthesis process dramatically reduces manufacturing cost for the production of ferrate (VI) by utilizing common

commodity feedstocks. This breakthrough means that for the first time ferrate (VI) can be an economical alternative to treating acid mining drainage generating materials. The objective of the present study was to investigate a methodology of preventing the generation of acid drainage by applying ferrate (VI) to acid generating materials prior to the disposal in impoundments or piles. Oxidizing the pyritic material in mining waste could diminish the potential for acid generation and its related environmental risks and long-term costs at disposal sites. The effectiveness of toxic metals removal from acid mine drainage by applying ferrate (VI) is also examined. Preliminary results presented in this paper show that the oxidation of pyrite by ferrate is a first-order rate reaction in Fe(VI) with a half-life of about six hours. The stability of Fe(VI) in water solutions will not influence the reaction rate in a significant manner. New low-cost production methods for making liquid ferrate on-site makes this technology a very attractive option to mitigate one of the most pressing environmental problems in the mining industry.

INTRODUCTION

The operation of mining and milling plants gives rise to substantial amounts of wastes from both mining and milling operations. Terrestrial deposition is the predominant method of disposal for waste-rock and tailings. When pyrite is present in these materials, the generation of acid drainage may take place and result in the contamination of underground and surface waters through the leaching of heavy metals and radionuclides (1). Presently, billions of tons of sulfide rich acid generating material are being generated globally. It affects, for example, over 23,000 km of streams in the United States (2). The acid generation process may continue long after the cessation of mining operations. Many present-day problem sites are mines that have been abandoned for over 100 years. Clean up costs can run into the millions of dollars per site.

Milling wastes disposed of in the environment may often contain elevated concentrations of residual sulfur, mainly in the form of pyrite, varying in the range of 3 to 14% (3). High concentrations of sulfates, Fe, Mn, As, Al, Sr, Zn, Ni, Be, Se, Cr, V, and other hazardous, and in some cases radioactive, elements are measured in the acid leachates generated. Long-term, cost-effective treatment techniques for mine drainage have been avidly pursued, particularly in regions such as the western US where between 20,000 and 50,000 mines are generating acidity . Many studies have been conducted to address cost-effective solutions to manage acid mine drainage; however, no adequate strategy to deal with sulfidic wastes is currently available.

Figure 1 summarizes the geochemical processes taking place in the tailings environment. As long as these conditions are maintained no significant acid generation will take place. This situation can be achieved if the tailings are submerged. In fact this is one of the possible management strategies generally put in place in some mining sites. On the other hand, wastes subjected to humid-drying cycles produce acid waters. This is the situation in the upper part of the tailings system showed in Figure 1. The extent of this upper region will be proportional to the diffusion capacity of atmospheric oxygen into the tailings as well as to the concentration of sulfidic minerals in the tailings. Heavy metals and radionulides leached by the acid solutions will be transported downward in the direction of the alkaline environment. Acid-base reactions will take place and, as long as acid-consuming agents exist, the acidic solution will be neutralized. However, part of the acid drainage may be transported to surface waters and therefore, these

drainages need to be collected and treated. However, collect-and-treat strategies may not be regarded as permanent solutions because acid generation may last for hundreds of years.

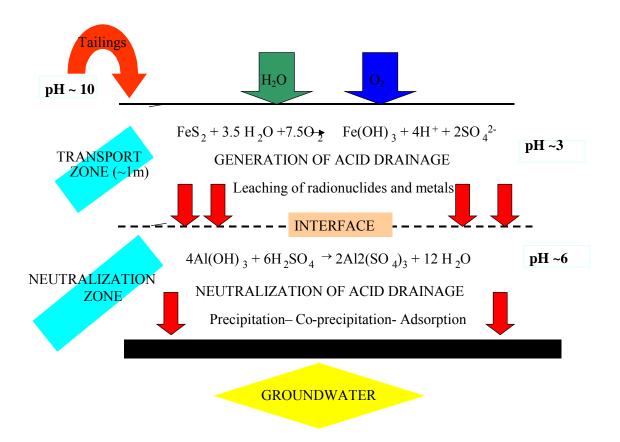


Fig. 1. Conceptual model of the geochemical processes in the tailings

Instead of the application of active management strategies, permanent (walk-away) solutions are pursued. Management strategies may be summarized as follow:

LOAD REDUCTION

- · Isolation by flooding or covering
- · Relocation/removal
- · Diversion of up-gradient surface water and groundwater

METAL RECOVERY (speed up the overall oxidation)

- · Ion exchange
- · Solvent extraction

ACID DRAINAGE TREATMENT

- · Neutralization
- Passive Treatment

To date, most of the strategies dealing with acid generation from mine wastes have focused on the inhibition of the catalytic oxidation of Fe^{2+} since in the absence of such catalysis, the oxygenation rate of Fe^{2+} is too low to be of any consequence. Another possibility frequently considered is the exclusion of oxygen through sealing of the system, which is economically infeasible in most cases. The use of passivating agents in order to create reversible interactions protecting and altering the surface of pyritic solids has been proposed (4). The authors claim that the use of passivation (especially with pre-oxidation) proved to be effective.

The use of potassium ferrate(VI) ion (FeO₄²⁻) to oxidize sulfide mine tailings has been investigated (5). In fact, in the reaction system adopted Fe⁶⁺ replaces Fe³⁺ as the oxidant, since they used the ferrate(VI) directly with the tailings in beakers. The authors did not discuss or propose the reaction mechanism, and the reaction rate constant, but they showed that the ferrate(VI) reduction is nearly complete in 10 minutes, i.e., rates on the order of 10^{-6} mol.m⁻³.s⁻¹ were obtained.

The challenge in the remediation of mining areas where acid generation tailings are disposed, demands the application of a strategy the can be effective in the long run, i.e., that will not demand active controls.

The objective of the present project is to investigate a methodology to prevent the generation of acid drainage by applying ferrate(VI) to acid generating materials prior to their disposal in impoundments or piles. Oxidizing the pyritic material in mining waste and diminishing the potential for acid generation will reduce the long-term issues related to the disposal of this material and will reduce environmental risks at the disposal sites.

Use of Ferrate (VI) as an Oxidant

Ferrate(VI) is a powerful oxidizing agent in aqueous media. Under acidic conditions, the redox potential of Ferrate(VI) ion is the highest of any other oxidant used in wastewater treatment processes (6). The standard half-cell reduction potential of ferrate(VI) has been determined as +2.20 V to + 0.72 V in acidic and basic solution, respectively. Ferrate(VI) exhibits a multitude of advantageous properties; as a disinfectant, antifoulant, flocculant, and coagulant based on its higher reactivity and selectivity than traditional oxidant alternatives (6). Despite the advantageous properties of ferrate(VI) in environmental applications, it has been unavailable commercially. Although different methods for the production of ferrate(VI) have been developed in the past decades, generating products of high purity, the powdered product is extremely expensive to obtain. Producing a stabilized ferrate (VI) product requires numerous process steps and leads to excessive synthesis costs that are too expensive for bulk industrial use. However, recently a novel synthesis method for the production of liquid ferrate(VI) based on hypochlorite oxidation of ferric ion in strongly alkaline solutions has been discovered (USPTO 6,790,428; September 14, 2004). This process dramatically reduces manufacturing cost for the

production of ferrate (VI). The patented ferrate (VI) synthesis processes use inexpensive chemicals to produce a ferrate (VI) product on-site, thus providing an economical alternative for treating acid drainage generating material.

The advantage of these studies (the oxidation of acid-generating materials by ferrate(VI)) in comparison with other remediation schemes is that it can be seen as a permanent solution, i.e., when the pyrite material is oxidized to appropriate levels, no long-term acid generation and leaching of metals from these materials will take place. This approach offers great advantages in relation to other treatment techniques that involve long-term maintenance because they do not serve as a definitive solution. In addition, ferrate(VI) oxidation of acid drainage may provide a low-cost, simple approach to remediating existing contaminated mining sites.

Mechanisms of Pyrite Oxidation

The oxidation of pyrite (FeS₂) and the release of acidity into waters draining from sulfidic tailings can be represented by the following reaction sequence (7):

Initiation reaction:

Propagation cycle:

Fe²⁺ + O₂(aq)
$$\rightarrow$$
 Fe³⁺ (Eq. 2)
Fe³⁺ + FeS₂(s) \rightarrow Fe²⁺ + SO₄²⁻ (Eq. 3)

 Fe^{2+} is released in the initiator reaction either by simple dissociation of the iron pyrite or by oxidation of the pyrite by oxygen. After the sequence has been initiated, a cycle is established in which Fe^{2+} is oxidized by oxygen to Fe^{3+} which is subsequently reduced by pyrite thereby generating additional Fe^{2+} and acidity. The reaction cycle develops until all the pyrite available is consumed.

The relative reactivities of pulverized samples (100–200 mesh) of 3 marcasite and 7 pyrite specimens from various sources at 25°C and pH 2.0 in ferric chloride solutions with initial ferric iron concentrations of 10^{-3} molal were determined in laboratory (8). The rate of the reaction:

$$\text{FeS}^{2+} 14\text{Fe}^{3+} + 8 \text{ H}_2\text{O} \Longrightarrow 15 \text{ Fe}^{2+} + 2\text{SO}_4^{2-} + 16 \text{ H}^+$$
 (Eq. 4)

was determined by calculating the rate of reduction of aqueous ferric ion from measured oxidation-reduction potentials. They demonstrate that the reaction is first-order and follows the empirical rate law:

$$-d(Fe^{3+})/dt = k(A/M)(Fe^{3+})$$
 (Eq. 5)

where (Fe^{3+}) is the molal concentration of uncomplexed ferric iron, k is the rate constant and A/M is the surface area of reacting solid to mass of solution ratio. The measured rate constants, k, range from 1.0×10^{-4} to 2.7×10^{-4} sec⁻¹ ± 5%, with lower-temperature/early diagenetic pyrite having the smallest rate constants, marcasite intermediate, and pyrite of higher-temperature hydrothermal and metamorphic origin having the greatest rate constants.

The oxidation of pyrite by Fe^{3+} .with varying pH was also investigated (9). An overall rate law was proposed:

Rate =
$$k[Fe^{3+}]^{0.5}[H^+]^{-0.5}$$
 (Eq. 6)

Generally speaking it can be proposed that abiotic pyrite oxidation takes years when oxygen is the only oxidant present. The rates are much faster when ferric iron alone and ferric iron plus oxygen are present, with the relative rates of these two reactions depending on the Fe^{2+}/Fe^{3+} ratio (10). Thus if this conversion can be accelerated, the overall pyrite oxidation will be increased as well. It is also reported that microbial mediation by Acidithiobacillus ferrooxidans, (formerly Thiobacillus - Kelly and Wood (2000) in Gleiser and Herbert, (2002) (11) accelerates the reaction by a factor greater than 10^6 . Because they require oxygen, Thiobacteria are most important to sulfur oxidation above the groundwater table, as in mine tailings and mine-spoils materials.

METHODOLOGY

Acid-generating mining spoils (like tailings and waste-rock residues) are rather a complex mixture of rock-occurring minerals and different chemicals that are added to the milling process. In addition to this, in tailings samples, ferrate may be reduced in oxidation reactions irrelevant to the oxidation of FeS₂. As a result, the mechanism of pure pyrite oxidation by Fe^{6+} is important to evaluate in a first step. In a second step, a detailed understanding of the Fe (VI) reaction with tailings will be achieved. Therefore, the goal of this research was to delineate the kinetic oxidation of pyrite by Fe (VI). The following reaction protocol was used.

Na-Ferrate solution was prepared by the mixing of NaOH, $Ca(OCl)_2$ and FeCl₃. Twenty milliliters of de-ionized water were added to a beaker followed by 1.0g of pure pyrite to create slurry. The diameter of pyrite grains was 50 mesh. Consequently, the specific surface area of these grains was too low to be determined reliably by BET surface area analysis (12).

Run solutions were prepared by combining the appropriate volume of the ferrate solution with 20 mL of distilled water. The 1 gram of charge material (pyrite) was added to each of the run solutions. The solution pH was checked before and after each run by using a Metrohm Ion Analysis pH meter Model 719 S Titrino. The slurry was continuously stirred by a teflon-coated magnetic bar in such away to create a vortex. Standard run length was about 30 minutes. Solutions were assayed at 5 minutes intervals during a run by extracting 0.1 mg aliquots. Prior to the Fe(VI) absorbance readings in a Ocean Optics ISS-UV-VIS spectrophotometer coupled with a OOICHEM Version 1.02.00 software the samples were filtered through a 0.45 μ m Fisherbrand nylon filter to remove suspended solids wit the aid of 13 mm Syringes (one syringe and one filter used for each analysis). The reduction of Fe (VI) was monitored by means of successive measures of its absorbance at 510 nm wavelength at different time intervals The Fe (VI) concentrations were determined by using a molar coefficient of 1150 M⁻¹ cm⁻¹. The apparent rate of consumption of Fe(VI) r' was calculated as:

$$\mathbf{r}' = (\mathbf{C}_{tfFe(VI)} - \mathbf{C}_{t0 Fe(VI)}) / \mathbf{M} \cdot \Delta t$$
(Eq. 7)

where $C_{tf(FeVI)}$ and $C_{t0Fe(VI)}$ correspond to the number of moles of Fe(VI) at the time of the end and beginning of the reaction respectively; M is the mass of the solution and Δt is time interval between t_f and t_0 .

The reaction rate for a standard system with 1 m^2 of surface area would be

$$r = r'/A$$

Sulfate determinations were made in one of the four experiments using an adaptation of the HACH Method 8051 in which a SulfaVer® powder pillow salt containing BaCl₂ was added to the samples prior to the absorbance readings in the spectral band of 450 nm. A calibration curve was constructed prior to the determination of sulfate concentration in the test solution. A regression coefficient, $r^2 = 0.9889$ was obtained for the sulfate calibration curve.

(Eq. 8)

Finally, it must be remembered that Fe (VI) is not stable. For example, Na₂FeO₄ in 50% NaOH decomposes quite slowly at room temperature and may be kept with little decomposition for a month at 0° C (13). If no oxidizable substances are present in the solution, the FeO₄²⁻ reacts with water over a period of an hour or less depending on the temperature and pH, and liberates molecular oxygen.

In order to examine the stability of the ferrate solution, Fe (VI) was monitored. The same amount of ferrate solution was then added to a beaker containing only distilled water and the absorbance of Fe (VI) was monitored over time.

RESULTS AND DISCUSSION

Ferrate stability

Fig. 2 shows the variation of Fe (VI) corrected absorbance with time in the reference solution (distilled water + ferrate). The observed points in the graphic fit the linear equation y = -0.2813 x + 36.90 where y and x are the corrected absorbance and time, respectively. The value of r^2 for this curve is 0.9684. The intercept represents the relative absorbance value at t = 0, i.e., 100%. After one hour, 50% of the initial content of Fe(VI) in solution was converted to Fe (III).

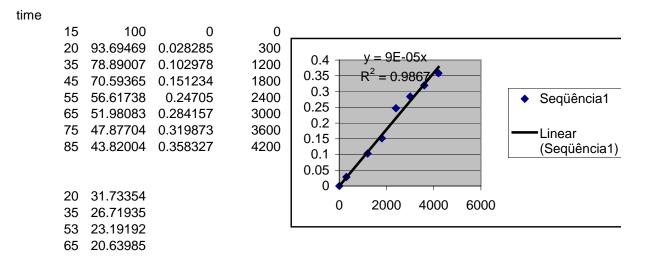


Fig. 2. Variation of Fe (VI) absorbance with time

In order to compare reaction rates of ferrate with ferric, it was assumed that first order kinetics apply. Fig. 3 shows the plots of $\ln [Fe^{6+}]$ versus time for each of the runs. After 30 minutes the absorbance of Fe⁶⁺ could not be measured. Although the data are not highly correlated, a rough comparison could be made.

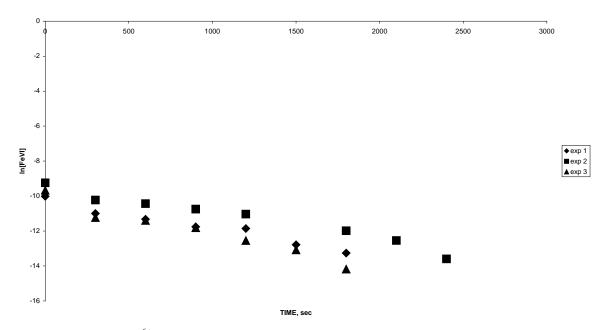


Fig. 3. Plot of $\ln [Fe^{6+}]$ versus time (in seconds) for the three runs (25°C, pH 13.0). The first data point corresponds to concentration of the solution before the addition of pyrite at time = 0)

The slopes of the of $\ln[Fe^{6^+}]$ versus time plot for the three experiments were virtually the same and give a k' value of 1.0. This value for instance is practically five orders of magnitude higher than those reported for the oxidation of pyrite by Fe^{3^+} (pH 2 and $mFe^{3^+} = 10^{-3}$) (8) showing that the Fe^{6^+} reduction of pyrite is far more efficient in the conditions of this work in comparison to the prevailing ones in their investigation (pH 13 and $mFe^{6^+} = 10^{-2}$).

In order to examine the half-life of Fe(VI) in the reaction system and compare with the results from its reduction in the water/ferrate system for the sake of simplicity, the data was treated as if the reaction was homogeneous. For this particular situation the rate expression for the reaction can be expressed as according to (14):

$$-d[Fe(VI)]/dt = k[Fe(VI)]^{x}[FeS_{2}]^{y}$$
(Eq. 9)

where [Fe(VI)] and $[FeS_2]$ are the concentrations of Fe(VI) and pyrite, respectively; x and y are the orders of the reactions with respect to Fe(VI) and FeS_2 respectively, and k' would be a fictional reaction rate constant. By assuming the concentration of FeS_2 greater than that of Fe(VI) the equation can be rewritten as:

 $d[Fe(VI)]/dt = k_{obs}[Fe(VI)]^{x}$ (Eq. 10)

For this pseudo- first-order-reaction and after separating and integrating Equation 11 is obtained:

$$d[Fe(VI)]/[Fe(VI)] = kdt$$
 (Eq. 11)
or
-ln[Fe(VI)]/[Fe(VI)]_0 = k_{obs}t (Eq. 12)

A plot of the average values of ln ($C_{Fe(VI)}/C_{Fe(VI)0}$ vs t is shown in Figure 4. A determination coefficient of 0.9440 was found. The slope, corresponding to k_{obs} in Equation 4 can be taken as 0.0018 +/- 0.0004 s⁻¹. As a result, the half-life of the reaction, i.e., the time necessary for the consumption of 50% of the initial Fe (VI) concentration is 6.38 minutes for the pH at which the reaction was evaluated. These data suggest that the reduction of Fe(VI) by water will not interfere in the oxidation of pyrite significantly.

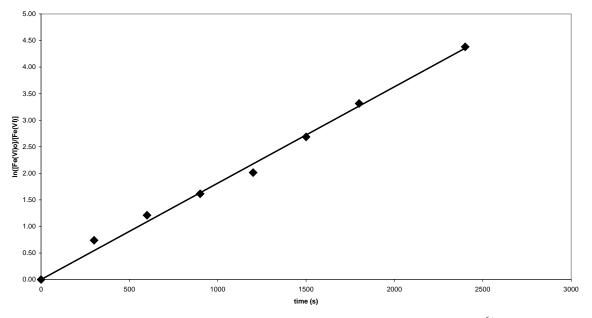


Fig. 4. Plot of $\ln (C_0/C)$ versus time for the reduction of Fe⁶⁺

Rate Equations

The data were further analyzed to determine the actual order of the reaction. The effect of Fe(VI) concentration on the reaction rate can be expressed as

$$dm_{Fe}^{6+}/dt = r' = k(m_{Fe}^{6+})n$$
 (Eq. 13)

where \mathbf{k} is the apparent reaction rate constant and \mathbf{n} is the reaction order for Fe(VI). Taking the logarithm of both sides of equation (13) yields

$$\log r' = n \log (m_{Fe}^{6+}) + \log k$$
 (Eq. 14)

so that a plot of log r' versus log mFe⁶⁺ should be a straight line with a slope of **n**. The rate data from all experiments are given in table I

Exp Number $T = 25^{\circ}C$	РН	$\log m_{\rm Fe}^{6+}$	log r
		$(mol.kg^{-1})$	$(mol.s^{-1})$
1	13	-1.51	-6.38
2	13	-1.81	-6.49
3	13	-1.48	-6.33

Table I.	Rate Data	from All	Experiments
10010 11	1		

The plot of log r' x log mFe⁶⁺ fits the equation y = 0.45x - 5.67 with a determination coefficient, $r^2 = 0.9442$. As a result the apparent rate equation for these conditions can be expressed as:

$$r' (mol.s^{-1}) = 2.1 \times 10^{-6} [Fe^{6+}]^{0.45}$$
 (Eq. 15)

Amount of Pyrite Consumed in the Reaction – Application at the Mill tailings of the Poços de Caldas Uranium Mining site.

The oxidation of pyrite can be evaluated by the production of sulfate. Sulfate concentration was measured in the test solution in one of the experiments. Care was taken to account for the initial sulfate concentration of the solution when pyrite was added to water. It was found that 72.81 mg (7.6 x 10^{-4} moles) of SO₄ were produced during the experiment. It corresponds to 0.024 g of sulfur. If it is taken into account that in this particular experiment the original concentration of sulfur was 0.67 g (present in pyrite) it can be inferred that 3.6% of pyrite was destroyed in about 30 minutes. On the other hand 1.0 x 10^{-3} moles of Fe⁶⁺ were consumed in the process of pyrite oxidation. It can be roughly estimated that 0.027 moles of Fe⁶⁺ would be necessary to destroy 100% of the pyrite in the system (0.0105 moles of FeS₂). This gives us a relation of 3 moles of Fe⁶⁺ for approximately 1 mol of pyrite. A relation of 1:5 has been previously proposed (5). Just for comparison, the ratio of Fe³⁺ to FeS₂ is 14 to 1 in the oxidation reaction of pyrite by Fe³⁺ (8).

It is reported (1) that the amount of tailings deposited in the tailings dam of the Poços de Caldas uranium mining site during 15 years of operation was about 1.89×10^6 tons of tailings. These authors also report that the average concentration of pyrite in these tailings is about 0.2%. As a result of the geochemical processes pictured in figure 1, the concentrations of radionuclides and heavy metals in seepage waters made it necessary the treatment of the liquid effluents leaving the tailings dam.

One of the potential remediation strategies to be applied to this site would be covering the material in order to reduce the diffusion of oxygen into the tailings and consequently the oxidation of pyrite. In fact, the application of dry covers over acid generating tailings constitutes a strategy largely utilized in different mining sites. It also has the benefit of reducing the emissions of radon from the tailings to the atmosphere. It also provides shielding against the gamma radiation. The drawback of this strategy has to do with the fact that long-term maintenance of the cover is needed, as the material will be eroded with time. If the presence of potential intruders in the tailings area can be controlled by some sort of institutional control

measures, the release of contaminants from the tailings, as a consequence of the cover failure, will be a much more difficult task to be accomplished. As a result, if the tailings are no longer acid generating, that will represent a very important contribution in the overall management strategy of the tailings dam.

According to the preliminary results reported in this work, it can be estimated that about 4,840 metric tons of Fe(VI) (1.61 x 10^5 m³ of ferrate solution) would have been necessary to oxidize the total amount of pyrite contained in the tailings prior to their deposition in the tailings dam

Present costs of production of Na-Ferrate are about US\$ 4.40/kg. This figure is 10 times lower than the reported costs of production of K-Ferrate (US\$ 44/kg) but still prohibitive for the treatment of pyritic tailings. For example the treatment costs of the oxidation of pyrite in the tailings of the Poços de Caldas mining site would have cost hundreds of millions of dollars, which is obviously not competitive with the economics of the available technologies. However, the decision making regarding the feasibility of this technology has to be compared with the costs observed with the utilization of other technologies keeping in mind that the oxidation of pyrite will be a permanent solution in opposition to other technologies like collect (effluents) and treat ones.

CONCLUSIONS

The preliminary results presented in this paper represent the first step in the description of the mechanism and rate law equation of the oxidation of pyrite by Fe (VI), which is a very important issue in the planning of sulfide rich tailings treatment. It could be demonstrated that the half-life of the reaction of pyrite oxidation by Fe(VI) is about 6 minutes, which is significantly less than the time needed to reduce 50% of the Fe (VI) by water. This issue is very important because it allows for different adjustments in the ratio of solid to liquid phases in the treatment slurry.

The stoichiometry of the oxidation reaction seems to be 1 mol of FeS_2 to 3 moles of Fe(VI). If on the one hand the velocity of this reaction makes its use very attractive on the other hand its economical feasibility will depend very much on the ability of producing ferrate solution at very low costs. The production of ferrate by the technology used in this work represents an enormous contribution to this objective.

FUTURE WORKS

Future steps of this research involve the determination of the real reaction rate and examine the dependency of the reaction rate with pH and temperature. After the understanding of the overall mechanism of FeS_2 oxidation by Fe (VI) tailings samples will be assayed and the economic feasibility of the oxidation of pyritic tailings by ferrate will be assessed.

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