

# PROPOSAL FOR AN INNOVATIVE APPROACH TO PREVENT ACID DRAINAGE FROM URANIUM MILL TAILINGS BASED ON THE APPLICATION OF NA-FERRATE (IRON VI)<sup>1</sup>

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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. 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 can take place and result in the contamination of underground and surface waters through the leaching of heavy metals and radionuclides. 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. Despite numerous beneficial properties in environmental applications, ferrate (VI) has remained commercially unavailable. Producing the 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. Preliminary results presented in this paper show that the oxidation of pyrite by ferrate has 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.

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## Introduction

The operation of U mining and milling plants may give rise to huge 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 surficial waters through the leaching of heavy metals and radionuclides (Fernandes et al., 1996). The acid generation process may continue long after the cessation of mining operations. Clean up costs can run into the millions of dollars per site.

Fernandes et al (1996) proposed that the mechanisms summarized in Fig. 1 may take place in the tailings pond environment: 1) wastes are introduced in the tailings dam along with an alkaline solution (pH ~ 10); 2) the solution moves downward to the base of the dam; 3) O<sup>2</sup> diffuses through the tailings being the residual pyrite oxidized in this region. Pyrite oxidation generates acid solutions that will remove metals and radionuclides from the solid phase; 4) when the acid solution reaches the zone of the tailings in which the waters are alkaline (interface) the precipitation of the transported soluble species will take place. This region may be considered the neutralising zone.

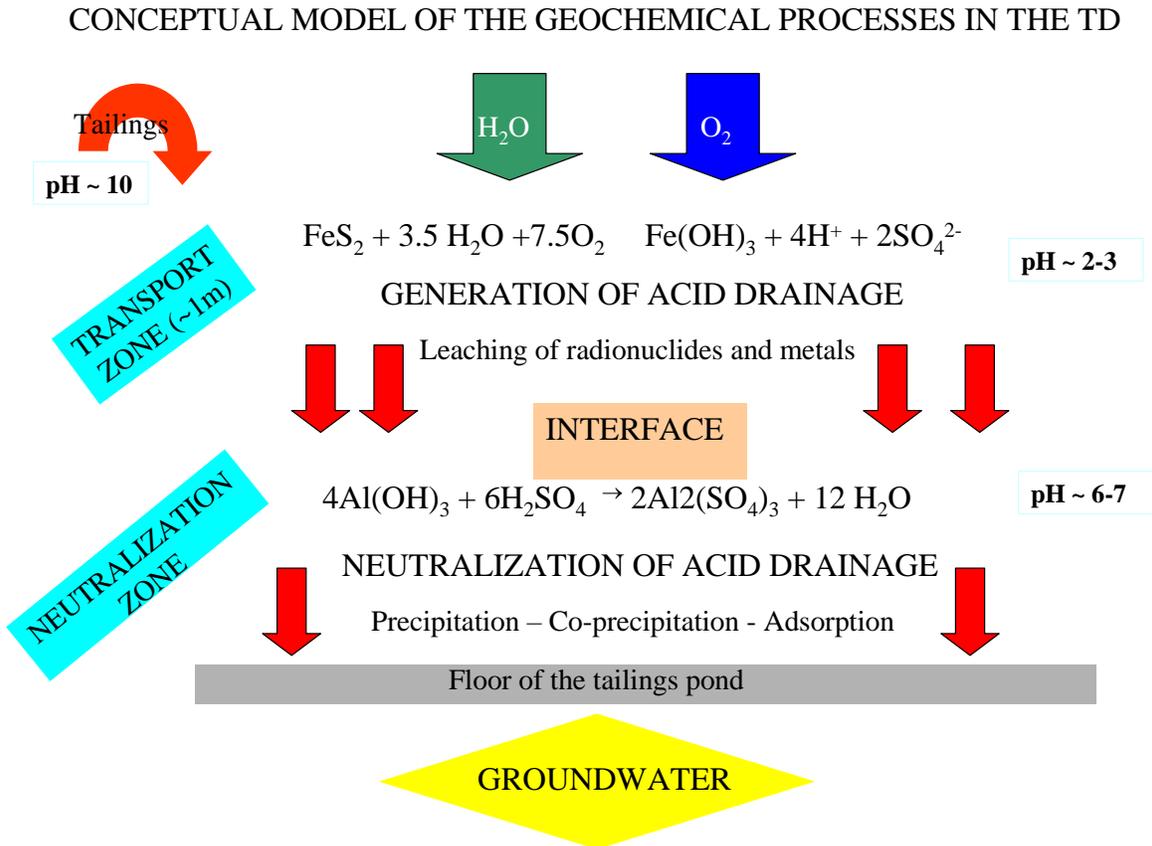


Figure 1: Basic geochemical processes occurring in the tailings environment

Elberling et al (1994) reported that high oxidation rates are observed in the initial time after tailings deposition. During this initial period of high rates, an apparent shift occurs from kinetic to diffusional control over a period of time that depends on the composition and properties of the tailings. Based on simulation results the authors suggest that the overall rate of oxidation after a few years will be controlled dominantly by the diffusion of O<sub>2</sub> rather than by biological or non-biological kinetics in the tailings.

The thickness of the oxidation layer can be estimated by means of mathematical calculations if the Intrinsic Oxidation Rate (IOR) (Ritchie, 1995) is known. A net acid production in sulfidic tailings of 6.8 mol H<sup>+</sup>.m<sup>-3</sup> has been reported (Snodgrass et al. 1982). This rate can be converted to IOR if pyrite oxidation reaction is taken into account as reported in equation 1.



A value equal to 1.20 x 10<sup>-8</sup> kg(O<sub>2</sub>).m<sup>-3</sup>.s<sup>-1</sup> would be achieved. Elberling et al. (1994) reported a O<sub>2</sub> diffusion coefficient equal to 1 x 10<sup>-7</sup> m<sup>2</sup>.s<sup>-1</sup> for well drained tailings. Under these assumptions, the thickness of the oxidising layer can be calculated by means of equation 2 as proposed by Ritchie (1995):

$$X = \sqrt{\frac{2DC_0}{\text{IOR}}} \quad (2)$$

Where, D = diffusion coefficient (m<sup>2</sup>.s<sup>-1</sup>); C<sub>0</sub> = air O<sub>2</sub> concentration (mg.m<sup>-3</sup>); IOR = Intrinsic Oxidation Rate (kg(O<sub>2</sub>).m<sup>-3</sup>.s<sup>-1</sup>)

A value of 2.0 m would be achieved for X. This value is very close to the oxidising layer thickness suggested by Fernandes et al (1996) for the tailings of the Poços de Caldas mining site. This layer represents the acid generating portion of the tailings. The time T for all the pyrite present in the tailings be consumed would be achieved by means of equation 3 (Ritchie 1994):

$$T = N\varepsilon\rho_{\text{rs}}/\text{IOR} \quad (3)$$

Where, N = number of oxidizing layers; ε = mass of O<sub>2</sub> consumed per unit of S oxidized mass; ρ<sub>rs</sub> = S density in the form of pyrite (kg.m<sup>-3</sup>).

As in the case of the Poços de Caldas, N would be equal to 10 (10 layers of 2.0 m), and it would take about 200 years for all the pyrite present in the tailings be consumed if O<sub>2</sub> could diffuse throughout the tailings accumulated in the tailing pond.

### Remedial Actions

So far, most of the strategies dealing with acid generation from mine wastes have focused on the inhibition of the catalytic oxidation of Fe<sup>+2</sup> since, in the absence of such catalysis, the oxygenation rate of Fe<sup>+2</sup> is too low to be of any consequence in the formation of acidity. Another possibility frequently considered is the exclusion of oxygen through sealing of the system, which is economically infeasible in most cases. A further method proposed by Belzile et al. (1997) is the use of passivating agents in order to create reversible interactions protecting and altering the surface of pyritic solids. They claim that the use of passivation (especially with pre-oxidation) proved to be effective

The remediation scheme, considered to be able to reduce the acid drainage generation of the Poços de Caldas tailings dam to marginal environmental levels, was discussed by Leoni et al (2004). The application of a dry cover was selected as an operationally feasible strategy. The total

area to be covered would be  $1.86 \times 10^5 \text{ m}^2$  and accordingly to MEND (1995) costs associated with the selected remediation strategy would vary in the range of US\$ 5 - 10 million.

### **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 (Sharma, 2002). 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, flocculent, and coagulant based on its higher reactivity and selectivity than traditional oxidant alternatives (Sharma, 2002).

Murshed et al. (2003) used solid K ferrate (VI) to oxidize sulfide mine tailings but highlighted the necessity for ferrate manufacture to become economically feasible. In fact, 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. Manufacturing a stabilized ferrate (VI) product requires numerous process steps and leads to excessive synthesis costs that are too expensive for bulk industrial use. However, a novel synthesis method for the production of liquid ferrate (VI) based on hypochlorite oxidation of  $\text{Fe}^{+3}$  ion in strongly alkaline solutions has been discovered recently (USPTO 6,790,428; September 14, 2004). This process dramatically reduces the manufacturing cost of ferrate (VI). The patented ferrate (VI) synthesis processes use inexpensive chemicals to produce a ferrate (VI) product, thus providing an economical alternative approach to treating pyritic tailings.

The advantage of this approach, i.e., oxidation of the sulfide-rich tailings 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.

The objective of the present project is to investigate the potential of a methodology to prevent the generation of acid drainage by applying ferrate(VI) to acid generating tailings prior to their disposal in impoundments or piles. Oxidizing the pyritic tailings 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. The application of ferrate would take place in a slurry pipeline during the post-treatment of tailings prior their disposal into heaps or dams.

### **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  $\text{FeS}_2$ . As a result, the mechanism of pure pyrite oxidation by  $\text{Fe}^{+6}$  is important to be evaluated 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)<sub>2</sub> and FeCl<sub>3</sub>. 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 (Jerz and Rimstidt (2004).

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 μm Fisherbrand nylon filter to remove suspended solids with 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<sup>-1</sup> cm<sup>-1</sup>.

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 BaCl<sub>2</sub> 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<sup>2</sup> = 0.9889 was obtained for the sulfate calibration curve.

Finally, it must be remembered that Fe (VI) is not stable. For example, Na<sub>2</sub>FeO<sub>4</sub> in 50% NaOH decomposes quite slowly at room temperature and may be kept with little decomposition for a month at 0°C (Murmah and Robinson 1974). If no oxidizable substances are present in the solution, the FeO<sub>4</sub><sup>-2</sup> reacts with water over a period of an hour or less depending on the temperature and pH, and liberates molecular O<sub>2</sub>.

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

## **Results and Discussion**

### **Ferrate stability**

Figure 2 shows the variation of Fe (VI) relative 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 relative absorbance and time, respectively. The value of r<sup>2</sup> 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<sup>+3</sup>.

Figure 3 shows the plots of ln [Fe<sup>+6</sup>] versus time for each of the runs. After 30 minutes the absorbance of Fe<sup>+6</sup> could no be measured

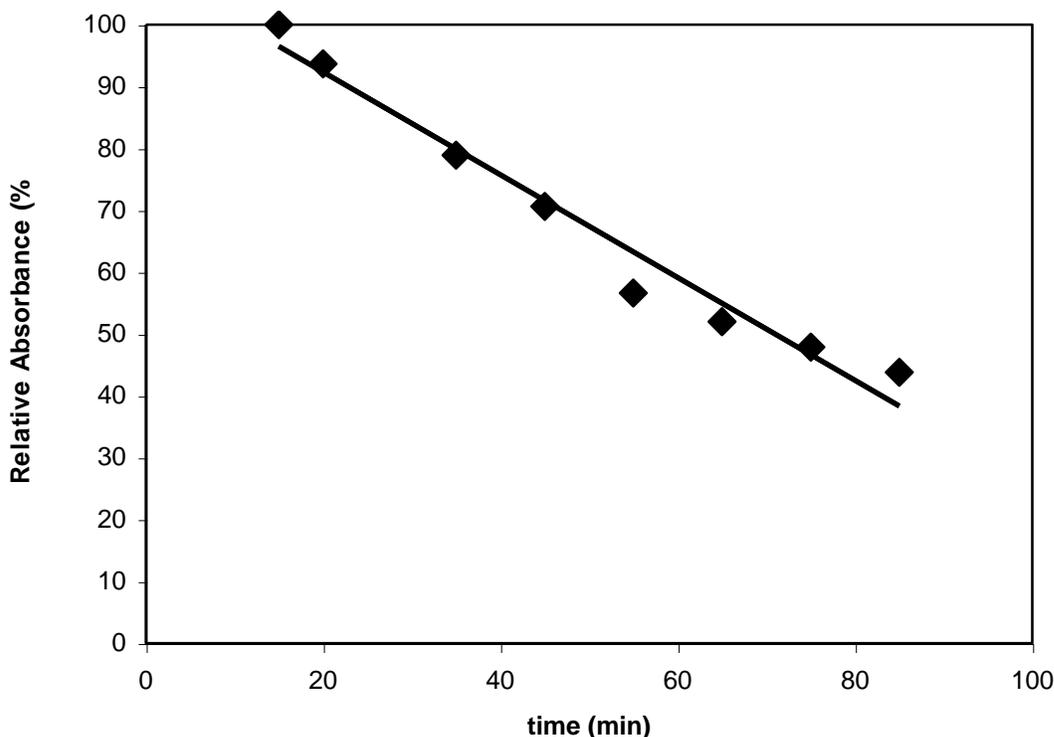


Figure 2: Variation of Fe (VI) absorbance with time

The slopes of the of  $\ln[\text{Fe}^{+6}]$  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  $\text{Fe}^{+3}$  (pH 2 and  $m \text{Fe}^{+3} = 10^{-3}$ ) (Wiersma. and Rimstidt1984) showing that the  $\text{Fe}^{+6}$  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  $m \text{Fe}^{+6} = 10^{-2}$ )

#### Amount of Pyrite Consumed in the Reaction

The oxidation of pyrite can be evaluated by the production of  $\text{SO}_4^{-2}$ . Sulfate concentration was measured in the test solution in one of the experiments. Care was taken to account for the initial  $\text{SO}_4^{-2}$  concentration of the solution when pyrite was added to water. It was found that 72.81 mg ( $7.6 \times 10^{-4}$  moles) of  $\text{SO}_4^{-2}$  were produced during the experiment. It corresponds to 0.024 g of S. If it is taken into account that in this particular experiment the original concentration of S 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  $1.0 \times 10^{-3}$  moles of  $\text{Fe}^{+6}$  were consumed in the process of pyrite oxidation. It can be roughly estimated that 0.027 moles of  $\text{Fe}^{+6}$  would be necessary to destroy 100% of the pyrite in the system (0.0105 moles of  $\text{FeS}_2$ ). This gives us a relation of 3 moles of  $\text{Fe}^{+6}$  for approximately 1 mol of pyrite. A relation of 1:5 has been previously proposed (Murshed, et al.2003). Just for comparison, the ratio of  $\text{Fe}^{+3}$  to  $\text{FeS}_2$  is 14 to 1 in the oxidation reaction of pyrite by  $\text{Fe}^{+3}$  (Wiersma. and Rimstidt, 1984).

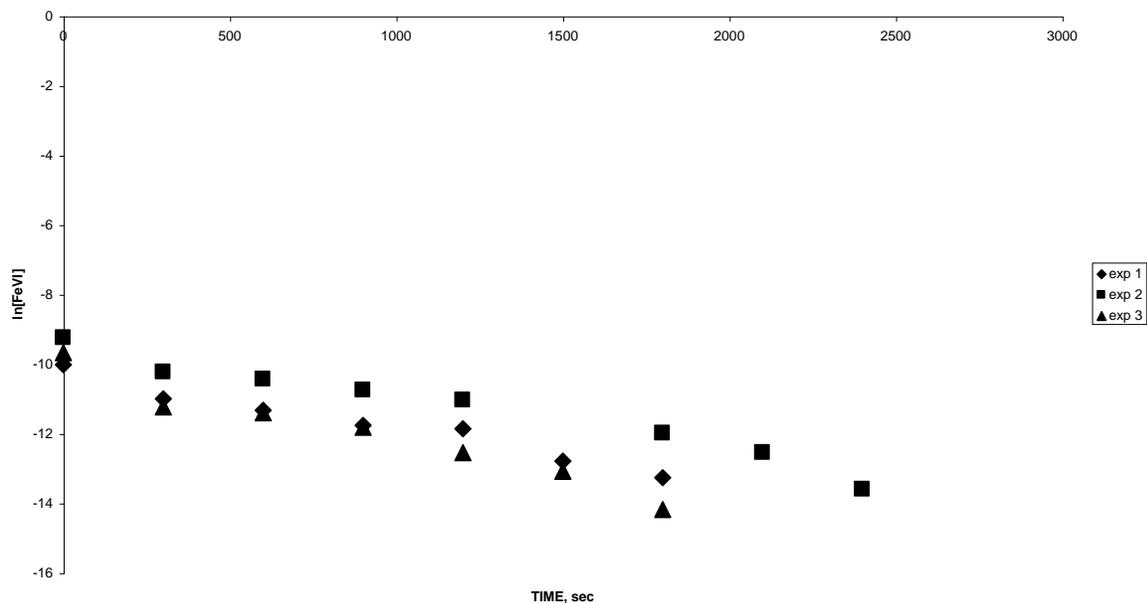


Figure 3: Plot of  $\ln [\text{Fe}^{+6}]$  versus time (in seconds) for the three runs (25°C, pH 13.0). The first data point corresponds to concentration of the solution before the addition of pyrite at time = 0)

#### Application to the Poços de Caldas Mining Site

Fernandes et al (1996) reported 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  $1.89 \times 10^6$  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 Fig. 1, the concentrations of radionuclides and heavy metals in seepage waters made it necessary the treatment of the liquid effluents leaving 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) ( $1.61 \times 10^5 \text{ m}^3$  of ferrate solution) would have been necessary to oxidize the total amount of pyrite contained in the Poços de Caldas tailings prior to their deposition in the tailings dam, i.e., if the whole amount of tailings were to be treated.

However, it was demonstrated above that it would not have been necessary to treat the total amount of the deposited tailings. Only the layer with a thickness of 1 to 2 m does contribute to the acid generation.

Taking this picture into account as well as the costs associated with the application of other remediation strategies the oxidation of pyritic tailings with Fe(VI) shows a great potential to be used in the abatement of acid generation in sulfide rich tailings especially if well planned remediation schemes are put in place.

## **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), 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<sub>2</sub> to 3 moles of Fe(VI). The production of ferrate by the technology used in this work represents an enormous contribution to this objective.

## **Future Work**

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<sub>2</sub> 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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