

Destruction of cyanide and thiocyanate by ferrate [Iron(VI)]

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ABSTRACT

A cyanide-laden effluent of the gold mining industry must be treated before it can be released to the aquatic environment. Current treatment methods such as natural degradation, sulfur based, hydrogen peroxide, ozonation, and alkaline chlorination are not adequate for meeting newer treatment standards. A new chemical oxidant that utilizes iron in the +6 oxidation state, ferrate [Fe(VI)] was studied to oxidize cyanides in gold mill wastewater. Reactions of cyanide and thiocyanate with Fe(VI) were analyzed to determine kinetic parameters, stoichiometry, and products. The complete removal of cyanide and thiocyanate can be achieved in seconds to minutes with the formation of less harmful products. Destruction of cyanide resulted in cyanate while sulfate and cyanate were the products of thiocyanate oxidation. Ferrate is therefore a suitable candidate as a new environmental friendly oxidant for gold mining wastewater. © 2003 SDU. All rights reserved.

Keywords: Cyanide; Thiocyanate; Gold mill wastewater; Ferrate; Iron(VI)

1. INTRODUCTION

Gold mining contributes significantly to the economy of the United States. The United States was, as of 2001, the second largest producer of gold in the world, accounting for approximately 13% of the yearly production. Cyanidation has been the main process for the extraction of gold from its ore for over a century (Pristos and Ma, 1997; Delanaey and Fletcher, 1999; Carrillo-Pedroza and Soria-Aguilar, 2001). After the completion of gold processing, chemically contaminated effluents containing cyanide (free or metal-complexed species) are generated. Because of the toxicity of cyanide to living species, it must be removed from effluents before discarding to the environment.

Metal-complexed cyanides are classified as weak-acid dissociables (WADs) and strong-acid dissociables (SAD). WADs complexes have weaker metal-cyanide bond such as with cadmium, copper, nickel, and zinc and are less toxic than free cyanide. Thiocyanate (SCN⁻) is also a WAD and its toxicity is a concern at elevated concentrations (Boucabeille *et al.*, 1994). The toxic effects of thiocyanate include inhibition of halide transport to the thyroid gland, stomach, cornea, and gill as well as the inhibition of a variety of enzymes (Boening and Chew, 1999). A concentration greater than 150mg/l in mammalian blood is critically dangerous (Boening and Chew, 1999). Examples of SADs include cyanide complexes of cobalt, gold, and iron, which are relatively non-toxic (Young, 2001).

In the mining industry, concentrations of cyanide in effluents are decreased by exposing the solution to sunlight in large ponds, a process called "natural degradation". While natural degradation is slowly taking place, the effluent may continue to pose a threat to humans and animals. Although natural degradation does not require capital investments or chemical costs, it may never reduce cyanide levels to within the limits specified by the environmental agencies. A chemical oxidation process is necessary to achieve complete destruction of cyanide. The methods to destroy cyanide in effluents are based on the INCO process, alkaline chlorination, the Degussa process with hydrogen peroxide, and ozonation (Rowley and Otto, 1980; Gurol and Bremen, 1985; Kurek, 1995; Pak and Chang, 1997; Carrillo-Pedroza and Soria-Aguilar, 2001). The destruction of thiocyanate has also been studied using both biological and chemical methods (Wilson and Harris, 1960; Luthy and Jones, 1980; Jensen and Tuan, 1993; Boucabeille *et al.*, 1994;

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Hung and Pavlostathis, 1997; Akcil and Mudder, 2003). The activated sludge method can remove 90-99% influent SCN⁻ and aerobic biodegradation can completely convert SCN⁻ to ammonia, bicarbonate, and sulfate. Chemical methods use sulfur dioxide, chlorine, hypochlorite, hydrogen peroxide, and ozone to oxidize SCN⁻ (Young, 2001).

The most common method in the laboratory for removal of cyanide and thiocyanate in wastewater is direct alkaline chlorination or the addition of hypochlorite. This method, although adequate, has disadvantages such as chloride contamination and involvement of reactants that are hazardous and unsafe to handle (Lanza and Bertazzoli, 2002). Ozonation is limited by mass transfer process and thereby leads to the requirement of excess amount of ozone. Additionally, ozone must be manufactured where it is used which adds a high capital cost to this treatment process (Kurek, 1995).

The commonly used techniques at mining operations are Degussa and INCO processes (Young, 2001, Akcil, 2002). The Degussa process uses hydrogen peroxide, which has little or no effect on thiocyanate (Young, 2001). The mixture of sulfur dioxide and air in the INCO process is non-reactive with SADs. This process is most effective at pH 9.0 and lime is added for pH control that generates sludge of metal hydroxides and gypsum (Young, 2001). Alternate methods addressing environmental considerations and cost effectiveness are needed to treat cyanide and thiocyanate in wastewater. We herein propose a novel oxidant, ferrate [Iron(VI)] for destruction of cyanide and thiocyanate in gold mill wastewaters.

2. FERRATE (IRON(VI))

Iron commonly exists in the +2 and +3 oxidation states; however, in a strong oxidizing environment, higher oxidation states of iron such as +4, +5 and +6 can also be obtained (Jeannot *et al.*, 2002; Scholder *et al.*, 1956). In recent years, +6 oxidation state of iron, ferrate [Fe(VI)], has received much attention. Salts of Fe(VI) have been used in organic synthesis, "super-iron" batteries, and wastewater treatment processes (Delaude and Laszlo, 1996; Sharma, 2002a; Licht *et al.*, 2002).

In general, Fe(VI) can be conveniently produced by three types of synthesis: a dry method, heating of various potassium- and iron containing minerals (Scholder, 1962); electrolyzing a potash solution with an iron anode (Bouzek *et al.*, 2000); and a wet method, oxidizing a basic solution of Fe(III) salt by hypochlorite (eq 1) (Schreyer *et al.*, 1953).



Fe(VI) ion has the molecular formula, FeO₄²⁻, and is isostructural with permanganate [Mn(VII)]. Under acidic environment, the redox potential of Fe(VI) ion is the highest of any other oxidants used in wastewater treatment processes (Table 1). Fe(VI) is a strong oxidizing agent and decomposes into Fe(III) ions or ferric hydroxide in solution (Goff and Murmann, 1971).



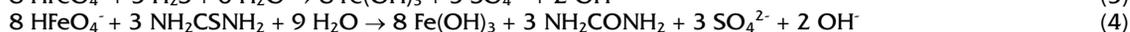
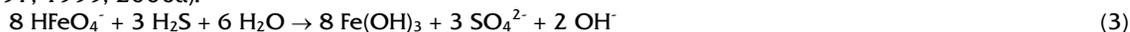
Table 1
 Redox potential for the oxidants/disinfectants used in water and wastewater treatment

Disinfectant/Oxidant	Reaction	E°, V
Chlorine	Cl ₂ (g) + 2e ⁻ ⇌ 2 Cl ⁻	1.358
Hypochlorite	HClO + H ⁺ + 2 e ⁻ ⇌ Cl ⁻ + H ₂ O	1.482
	ClO ⁻ + H ₂ O + 2 e ⁻ ⇌ Cl ⁻ + 2 OH ⁻	0.841
Chlorine Dioxide	ClO ₂ (aq) + e ⁻ ⇌ ClO ₂ ⁻	0.954
Perchlorate	ClO ₄ ⁻ + 8 H ⁺ + 8 e ⁻ ⇌ Cl ⁻ + 4 H ₂ O	1.389
	ClO ₄ ⁻ + H ₂ O + 2 e ⁻ ⇌ ClO ₃ ⁻ + 2 OH ⁻	1.390
Ozone	O ₃ + 2 H ⁺ + 2 e ⁻ ⇌ O ₂ + H ₂ O	2.076
	O ₃ + H ₂ O + 2 e ⁻ ⇌ O ₂ + 2 OH ⁻	1.240
Hydrogen peroxide	H ₂ O ₂ + 2 H ⁺ + 2 e ⁻ ⇌ 2 H ₂ O	1.776
	H ₂ O ₂ + 2 e ⁻ ⇌ 2 OH ⁻	0.880
Dissolved Oxygen	O ₂ + 4 H ⁺ + 4 e ⁻ ⇌ 2 H ₂ O	1.229
	O ₂ + 2 H ₂ O + 4 e ⁻ ⇌ 4 OH ⁻	0.400
Permanganate	MnO ₄ ⁻ + 4 H ⁺ + 3 e ⁻ ⇌ MnO ₂ + 2 H ₂ O	1.679
	MnO ₄ ⁻ + 2 H ₂ O + 3 e ⁻ ⇌ MnO ₂ + 4 OH ⁻	0.588
	MnO ₄ ⁻ + 8 H ⁺ + 5 e ⁻ ⇌ Mn ²⁺ + 4 H ₂ O	1.507
Ferrate(VI)	FeO ₄ ²⁻ + 8H ⁺ + 3e ⁻ ⇌ Fe ³⁺ + 4H ₂ O	2.20
	FeO ₄ ²⁻ + 4H ₂ O + 3 e ⁻ ⇌ Fe(OH) ₃ + 5OH ⁻	0.70

The reduction of Fe(VI) results in a non-toxic by-product iron(III) (eq 2), which suggests that Fe(VI) is an environmentally friendly oxidant. Moreover, ferric oxide, produced from Fe(VI), acts as a coagulant and adsorbant for removal of metals, non-metals, and radionuclides (Waite and Gray, 1984; Jiang and Lloyd, 2002). Fe(VI) has also been investigated as an alternative to chlorine for the disinfection of water and wastewater (Jiang and Lloyd, 2002; Gilbert *et al.*, 1976). Fe(VI) was very effective to kill *Escherichia coli* (*E. coli*) and known pathogens (Waite, 1979). The ability of Fe(VI) to inactivate viruses has also been demonstrated (Schink and Waite 1980; Kazama, 1994, 1995).

Fe(VI) can oxidize a large number of inorganic and organic pollutants in aquatic environment (Carr *et al.* 1985; Lee and Chen, 1991; Lee and Gai, 1993; Johnson and Sharma, 1999; Read *et al.*, 2000, 2001; Sylvester *et al.*, 2001). Recently, we have studied oxidation of nitrogen- and sulfur-containing pollutants by Fe(VI) (Sharma *et al.*, 1997, 1998a, b, 1999, 2002a, b).

For example, oxidation of sulfur-containing pollutants such as hydrogen sulfide (H₂S), thiourea (NH₂CSNH₂), and thioacetamide (CH₃CSNH₂) by Fe(VI) can be accomplished in seconds to minutes and oxidation reactions are stoichiometric with formation of non-hazardous products (Eqs. 3-5) (Sharma *et al.*, 1997, 1999, 2000a).



These results demonstrate the potential use of Fe(VI) as a treatment chemical for removing pollutants from industrial effluents. Results for the oxidation of cyanide and thiocyanate by Fe(VI) are summarized in the ensuing section.

3. OXIDATION OF CYANIDE AND THIOCYANATE

Kinetic measurements have been determined for the oxidation of cyanide and thiocyanate by Fe(VI) (Sharma *et al.* 1997, 2002b). The rate expression for the reactions can be expressed as

$$-d[\text{Fe(VI)}]/dt = k[\text{Fe(VI)}][\text{P}] \quad (6)$$

where [Fe(VI)] and [P] are the concentrations of Fe(VI) and cyanide (or thiocyanate), respectively, and k is the overall reaction rate constant. The reaction rate constants were determined as a function of pH and found to increase with decreasing pH (Figure 1). The dependence is mostly related to the Fe(VI) concentration. Fe(VI) is a powerful oxidant throughout a pH range, however, its reduction potential is much higher in acidic conditions (Table 1). Fe(VI) has therefore higher oxidizing power at low (or acidic) pH. Moreover, Fe(VI) is a stronger oxidant upon protonation so the reaction rates were expected to increase with decreasing pH, which explains the results in Figure 1.

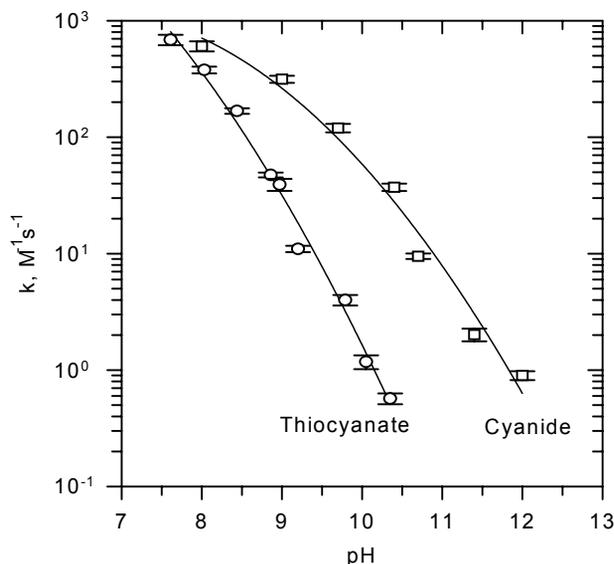
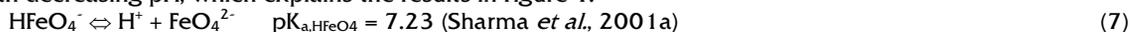


Figure 1. Oxidation of cyanide and thiocyanate by iron(VI)

The reactions of Fe(VI) with cyanide and thiocyanate were studied as a function of temperature (5 - 45°C) in alkaline medium. The results are plotted as log k versus 1/T (K⁻¹) and are shown in Figure 2. The activation energies obtained from linear plots were 38.9 ± 1.0kJ/mol and 32.7 ± 2.1kJ/mol for cyanide and thiocyanate, respectively.

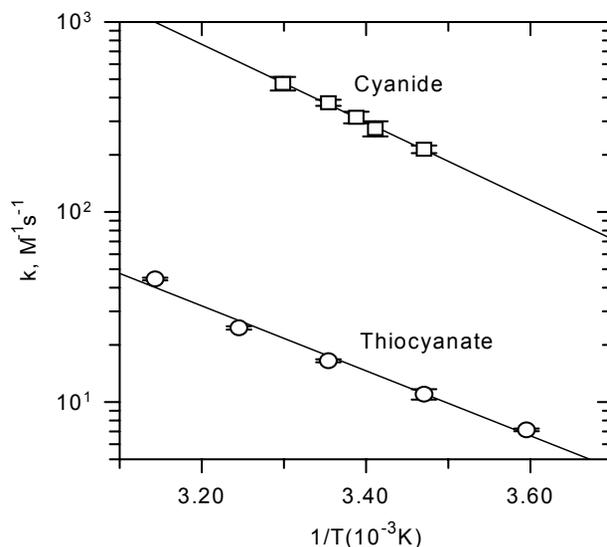


Figure 2. Temperature dependence of Fe(VI) oxidation of cyanide and thiocyanate (Cyanide (pH = 9.0); Thiocyanate (pH = 9.2))

The experiments on stoichiometry and reaction products for the oxidation of cyanide and thiocyanate by Fe(VI) were conducted at pH 9.0. These experiments were carried out by mixing equal volumes (5ml) of deoxygenated Fe(VI) and cyanide (or thiocyanate) solutions together. The results are shown in Figures 3 and 4.

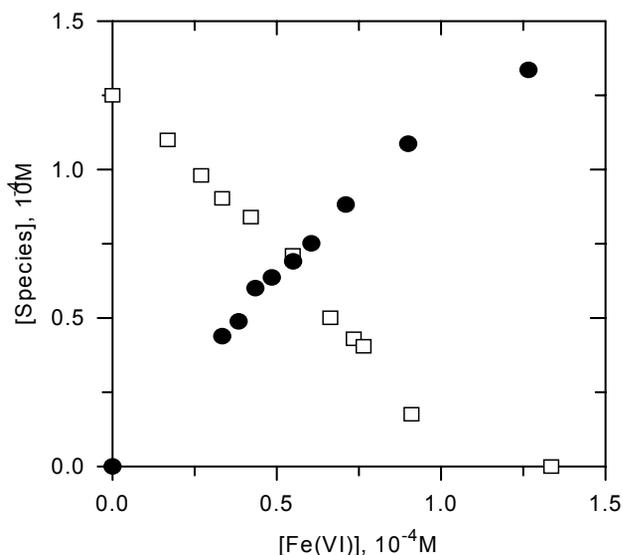


Figure 3. A plot of cyanide consumption and cyanate formation versus [Fe(VI)] at pH 9.0 (Initial [cyanide] = 1.25 × 10⁻⁴M; ● - Cyanide; □ - CNO⁻)

The ratio of Fe(VI) consumed to cyanide was found to be 0.85 ± 0.03. A similar ratio was found in our earlier work on Fe(VI) oxidation of cyanide under oxygenated solutions. Cyanate and nitrite were the products of the reaction (Sharma *et al.*, 1997). In a later study (Sharma *et al.*, 2002b), cyanate was the only product of the reaction and the ratio of Fe(VI) to cyanate formation was 0.83 ± 0.03 (Figure 3). A further

oxidation of cyanate under oxygenated conditions would have resulted in nitrite in a previous study. The observed stoichiometry of the reaction of Fe(VI) with cyanide is in reasonable agreement with the stoichiometry of reaction(8):

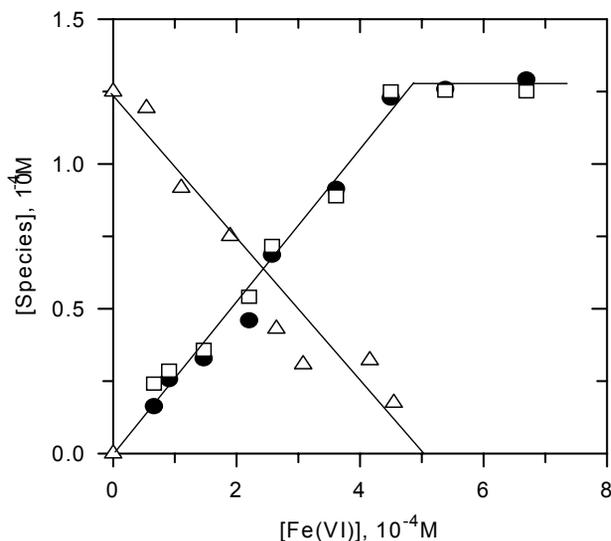


Figure 4. A plot of SCN^- consumption and products formed versus $[\text{Fe(VI)}]$ at pH 9.0 (Initial $[\text{SCN}^-]$: 1.25×10^{-4} M; Δ - SCN^- ; \bullet - SO_4^{2-} ; \square - CNO^-)

The concentrations of consumed SCN^- and generated sulfate (SO_4^{2-}) and cyanate (CNO^-), as two products of the reaction of SCN^- with Fe(VI) at pH 9.0 are shown in Figure 4. The decrease in the amount of SCN^- concentration was nearly equal to the amount of sulfate and cyanate formed. The slopes of the resulting lines were: -0.24 ± 0.02 , 0.26 ± 0.02 , and 0.27 ± 0.02 for SCN^- , SO_4^{2-} , and CNO^- , respectively. This indicates a stoichiometric conversion of SCN^- to SO_4^{2-} and CNO^- ions at all Fe(VI) concentrations with a stoichiometry of 4: 1 (Fe(VI) : SCN^-). Fe(III) was the final product of Fe(VI) reduction and the gas produced in the reaction was identified as oxygen. The observed stoichiometry of the reaction is in reasonable agreement with the stoichiometry of reaction 9:



Although cyanate is much less toxic than cyanide, it is chemically unstable and may have an adverse effect on the natural environment. It is therefore important to convert the cyanate into other stable inert end products. Ferrate reacts sluggishly with cyanate to give simple byproducts CO_2 (HCO_3^-) and NO_2^- (NO_3^-) (Sharma *et al.*, 1997). The photocatalytic oxidation of cyanate on TiO_2 surfaces in presence of ferrate may be a viable method for faster decontamination of cyanate into nitrate (Sharma *et al.*, 2001b, 2002c). A highly reactive Fe(V) species, produced in photocatalytic processes, is $10^3 - 10^5$ times more reactive with compounds than is ferrate (Sharma *et al.*, 2001b, 2002c, 2003). Fe(V) thus has the ability to oxidize cyanate, which cannot be easily oxidized by ferrate.

4. TREATMENT OF GOLD MILL WASTEWATER

Removal of free and total cyanide from gold mill wastewater was sought by adding solid potassium ferrate to the synthetic samples. Synthetic samples were prepared by adding salts of KSCN , KCN , and $\text{K}_3\text{Cu(CN)}_4$ to deionized water at pH 9.1. The composition of gold mill wastewater was used as described by Rowley and Otto (1980) for a Canadian gold mine. Cyanide concentrations were determined before and after addition of ferrate to 0.25L of wastewater. Free cyanide concentrations in samples were determined by an ion selective electrode method and total cyanide was quantitatively determined by an established method (Standard Methods, 1992).

Figure 5 shows the effectiveness of ferrate in treating gold mill wastewater. The addition of 0.010g of ferrate resulted in 77.0% and 59.4% removal of free cyanide and total cyanide, respectively. However, after addition of 0.128g of ferrate, complete removal of free cyanide was obtained and total cyanide removal was more than 98%. The results clearly demonstrate that ferrate is an effective oxidant in removing cyanide from gold mill wastewaters.

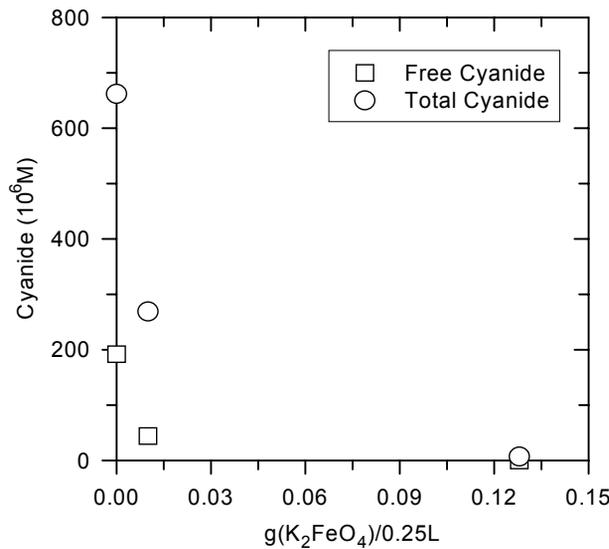


Figure 5. Removal of free and total cyanide from Gold Mill wastewater by Fe(VI)

5. CONCLUSIONS

The reactions of ferrate with cyanide and thiocyanate were found to be first order for each reactant. The reaction rates obtained at different pH can be utilized to determine half-lives of the reaction. If concentration of Fe(VI) is five-fold higher than cyanide concentration, 100 μ M, the half-life for reaction of Fe(VI) with cyanide would be 9.3s at pH 9.0 and 15 $^{\circ}$ C. Under similar conditions, the half-life for oxidation of thiocyanate by Fe(VI) would be approximately 180s (3 minutes). The reaction rates are pH dependent as are the half-lives of the reactions. Destruction of cyanide and thiocyanate by Fe(VI) resulted in relatively non-toxic by-products. The effective removal of cyanides from gold mill wastewater can be achieved by ferrate.

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