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# Removal of Cyanide and Metals From Mineral Processing Waste Waters

By Joseph E. Schiller



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8836

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**UNITED STATES DEPARTMENT OF THE INTERIOR**  
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**BUREAU OF MINES**  
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
h	hour	mmol/L	millimole per liter
<u>M</u>	molar (mole per liter)	mol	mole
mg/L	milligram per liter	ppm	part per million

# REMOVAL OF CYANIDE AND METALS FROM MINERAL PROCESSING WASTE WATERS

By Joseph E. Schiller<sup>1</sup>

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## ABSTRACT

The Bureau of Mines is investigating methods to treat waste water that contains cyanide. This report describes a new method that removes heavy metals and all forms of cyanide. In the first step, hydrogen peroxide and sodium thiosulfate are added at pH 7 to 9 in a 1:2 molar ratio to convert free and weakly complexed cyanide to nontoxic thiocyanate. Then steryldimethylbenzylammonium chloride is added to precipitate ferrocyanide, and finally, ferric sulfate is added as a sweep floc and sequestrant for heavy metals. After the suspended solids settle, the water is polished by filtering. The water initially contained 1 to 5 mg/L Fe, 1 to 5 mg/L Cu, and 10 to 30 mg/L total cyanide; the level of each of these constituents was reduced to less than 0.02 mg/L.

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## INTRODUCTION

The Bureau of Mines is conducting research to improve methods for treating mining and mineral processing waste waters. Water is needed in virtually every mineral operation, and new technology is needed to purify the aqueous wastes so that the resultant clean water can be recycled or discharged safely. Process waters may contain a variety of contaminants, including suspended particles, undesirable dissolved metals or nonmetal ions, and chemicals used in mining and beneficiation processes. One current need is for better methods to handle mineral processing wastes that contain cyanide.

Cyanide is used widely in leaching precious metal ores, and it is sometimes employed in flotation of sulfide minerals. For over 50 years, cyanide leaching has been the method of choice for dissolving finely disseminated gold and silver from their ores. In typical commercial operations, a 0.1- to 0.3-pct caustic cyanide solution is percolated through crushed or ground ore to dissolve the precious metals. The gold and silver are won from the "pregnant" leach solution, usually by cementation with zinc dust. This leaves a waste solution that contains some of the original free cyanide along with complexed cyanides, base metals (such as copper and iron), and thiocyanate. These ions were formed by reaction of cyanide with various gangue minerals in the ore. The dilute solutions, diverse forms of cyanide and metals, and high toxicity make effective treatment of precious metal leaching wastes a definite necessity and a significant challenge.

None of the present cyanide treatment methods are very effective with precious metal leach solution. Therefore, the Bureau is conducting studies to devise a method for handling the constituents commonly found in mining wastes. Due to the present high price for gold and silver, many new cyanide leaching operations are being started. A large fraction of these

are small and located in remote areas. Therefore, a treatment process is needed that is reliable, is capable of being automated, and does not use difficult-to-handle chemicals.

This report describes a new approach for removing heavy metals and strongly complexed cyanides from water and converting free and weakly complexed cyanide to nontoxic thiocyanate and cyanate. The method utilizes three steps that accomplish the following: (1) conversion of free and weakly complexed cyanides to nontoxic forms, (2) precipitation of strongly complexed cyanides and metals, and (3) sedimentation and filtration to remove solids. In the first step, hydrogen peroxide reacts with the thiosulfate ion to form an intermediate (1)<sup>2</sup> that, in turn, reacts with most of the free and weakly complexed cyanide to form thiocyanate.

The method described in this report was evaluated in laboratory-scale experiments. It was developed mainly for treating waste waters from precious metal ore leaching, but it could be used for other wastes containing similar metals and forms of cyanide. Depending on site-specific agreements, Federal and State regulations generally require that the total cyanide content of water discharged to the environment be less than 0.02 mg/L (2). Since mining and mineral processing operations seldom release water into municipal treatment systems, treatment methods used by these operations must enable their discharged water to meet these requirements.

Technical or economic problems make existing treatment methods undesirable to the mining industry. Either the cost is considered excessive, or the cyanide content is not reduced to sufficiently low levels. Common industrial processes to

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<sup>2</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

treat cyanide wastes include oxidation, ion exchange, complexation, volatilization with or without cyanide recovery, and other lesser used methods (3-4). Although mining companies have evaluated these methods on a small scale, none have gained universal acceptance. Most commonly, mines in North America treat cyanide wastes by oxidation or by discharging waste water after dilution and detention in a tailings pond. The most widely used oxidation system is alkaline chlorination, where reactions are quite rapid and most metals are removed. However, ferrocyanide is not destroyed in this method, and chlorine consumption can be very high, since thiocyanate and other sulfur species react with chlorine.

Alternatively, ozone and hydrogen peroxide have been investigated as oxidants. Both are usually more costly than chlorine, and they do not destroy ferrocyanides. Anion exchangers are effective for multiple-charged complex cyanides, but they are not sufficient for free cyanide and also tend to become fouled in actual use. Complexation of free cyanide with iron is often employed in the

chemical industry prior to secondary treatment. This method is unsuitable as the sole treatment, because the cyanide remains soluble and appears in the total cyanide analysis. By acidifying a waste to liberate gaseous hydrogen cyanide, most of the free cyanide in a waste can be removed. This form of cyanide can be recovered by absorption in a base or vented if quantities are small.

Two very new methods specifically designed for mining wastes use sulfur dioxide or sulfite salts (5-6). In the International Nickel Co. (INCO)<sup>3</sup> process, 2 to 5 pct SO<sub>2</sub> in air is bubbled through a waste containing at least 50 mg/L dissolved Cu. Cyanide levels are reduced from several hundred milligrams per liter to 1 mg/L in 10 to 30 min. This method would best be applied to very concentrated wastes. In the second method, sodium sulfite and Fe<sup>2+</sup> are reacted with the waste water at pH 5. Ferrocyanide is converted to insoluble prussian blue, Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>, and the free and weakly complexed cyanide is converted to products (unidentified) that do not appear in the cyanide analysis procedure.

#### EXPERIMENTAL WORK

The overall treatment process developed during this research consists of three steps: (1) destruction of free and weakly complexed cyanide with liberation of metal ions, (2) precipitation of ferrocyanide and metal ions, and (3) settling and filtration to remove solids. The first step in cyanide conversion is reaction with peroxide and thiosulfate. The optimum pH is about 8, and 3 to 4 mol

thiosulfate and 2 to 3 mol peroxide are used for each mole of free and weakly complexed CN<sup>-</sup> present. Water that contains 10 mg/L or less of free cyanide requires for treatment 30 mg/L hydrogen peroxide and 150 mg/L sodium thiosulfate.

<sup>3</sup>Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

TABLE 1. - Analysis of cyanide-containing solutions before treatment, milligrams per liter

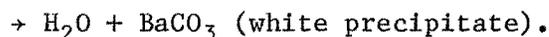
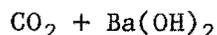
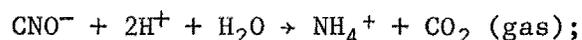
Sample origin	Cyanide		Cu	Fe	SCN <sup>-</sup>
	Free	Total			
Prepared KCN.....	9.4	9.4	0.0	0.0	0.0
Prepared KCN, CuSO <sub>4</sub> , and K <sub>4</sub> Fe(CN) <sub>6</sub> .....	21.4	24.2	5.3	1.5	.0
Precious metal leaching wastes.....	5.6	11.4	1.6	1.0	120
Molybdenum flotation waste.....	.40	.45	.10	1.5	1-2

After a reaction time of 2 to 4 h, 5 mol oleyl- or steryldimethylbenzylammonium chloride is added for each mole of ferrocyanide to be removed, and then 100 mg/L ferric sulfate is added while the pH is maintained between 8 and 9. Finally, 1 mg/L anionic polyacrylamide flocculant (Separin AP-30, Dow Chemical Co.) is added to reduce settling time and increase floc size; then the mixture is filtered.

Four different waters were treated according to this procedure. The first was simply a dilute solution of potassium cyanide. The second was a prepared solution containing potassium cyanide, cupric sulfate, and potassium ferrocyanide. The remaining two were waste waters from precious metal leaching and molybdenite flotation, respectively. Typical analyses are given in table 1.

Cyanide analyses were done using the standard distillation procedure with  $MgCl_2$  as a catalyst (7). Thiocyanate was

determined colorimetrically as the ferric complex, and metals were measured using atomic absorption spectroscopy. The reaction products of free cyanide and the combination of peroxide and thiosulfate were identified by reacting a 20 mg/L  $CN^-$  solution with  $1 \times 10^{-3} M$   $H_2O_2$  and  $S_2O_3^{2-}$ . After the solution had stood for 4 h, the cyanide was determined with a specific ion electrode (Ag/S<sup>=</sup>), and an aliquot was withdrawn for colorimetric thiocyanate analysis using  $Fe^{3+}$ . The remainder of the reaction mixture was acidified to convert any cyanate formed to ammonium carbonate. The presence of cyanate was confirmed by collecting the liberated  $CO_2$  in barium hydroxide solution. Chemical equations for cyanate identification follows:



## RESULTS AND DISCUSSION

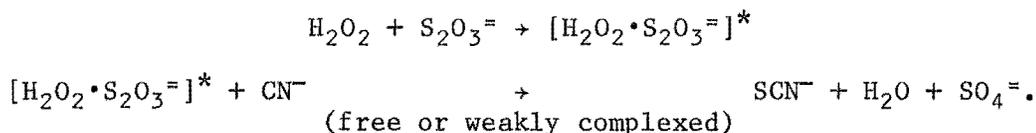
### CYANIDE AND METALS REMOVAL

After treatment of each solution listed in table 1, free and total cyanide concentrations were below 0.02 mg/L, which is the analytical limit of detection for cyanide. Copper and iron levels were less than 0.02 mg/L and 0.05 mg/L, respectively, which is their limit of determination using available methods.

### THEORY OF OPERATION

Each step in the treatment process is intended to handle a certain form of

cyanide. In the first step, where hydrogen peroxide and sodium thiosulfate are added, free and weakly complexed cyanide is converted primarily to thiocyanate and to lesser amounts of cyanate. Peroxide and thiosulfate react together to give a mixture of tetrathionate and sulfate (1), but when cyanide is present, an intermediate in the peroxide thiosulfate reaction converts cyanide to thiocyanate according to the reactions



Direct oxidation of cyanide by peroxide gives cyanate. After reaction of free and weakly complexed cyanide, generally the only cyanide species remaining is ferrocyanide. This is precipitated with octyl- or steryldimethylbenzylammonium chloride. Since ferrocyanide carries a -4 charge, the large organic singly charged cation would give a ferrocyanide salt of molecular weight about 2,000. The nonpolar character of the organic groups and their high molecular weights are sufficient to render the quaternary ammonium ferrocyanide insoluble. In preliminary experiments, an amorphous white precipitate formed when the quaternary ammonium compound was added to solutions of ferrocyanide.

The rate of conversion of free and weakly complexed cyanide to thiocyanate is determined by the rate of the peroxide-thiosulfate reaction. Adding excess peroxide and thiosulfate will shorten the time needed for the first process step, but higher costs and secondary problems with residual peroxide or thiosulfate may not justify the reduced reaction time. Lower temperatures may extend the time needed for thiocyanate formation. In common with most other chemical reactions, decreasing the temperature by 10° C approximately halves the rate of the peroxide-thiosulfate reactions. Thus, very cold water (0° to 5° C) may need 12 to 16 h reaction time, but water warmer than 25° C would need less than 4 h.

#### EFFECT OF pH ON FREE-CYANIDE REACTION RATE

The pH during reaction of peroxide and thiosulfate with cyanide must be controlled at about 8 to 9 to obtain the fastest reaction rate possible. The effect of pH on the rate of disappearance of free cyanide during the peroxide-thiosulfate reaction was determined by reacting a solution initially comprising  $3.8 \times 10^{-4}$  M cyanide,  $6 \times 10^{-3}$  M hydrogen peroxide, and  $10^{-2}$  M sodium thiosulfate. Separate reactions were performed at

various pH values in the range of 7 to 10. At various times during each reaction, aliquots were withdrawn and analyzed for cyanide. Table 2 shows the initial reaction rate for disappearance of cyanide as a function of pH. Although the reaction proceeds throughout the range of 7 to 10, the optimum pH is near 8.

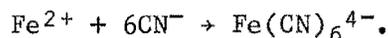
TABLE 2. - Pseudo first-order rate constant for the disappearance of free cyanide (initially at 10 mg/L) in a solution initially containing  $6 \times 10^{-3}$  M hydrogen peroxide and  $10^{-2}$  M sodium thiosulfate

pH	<u>Pseudo first-order rate constant,<sup>1</sup> <math>10^{-2} \text{ min}^{-1}</math></u>
7.....	5.5
8.....	8.7
8.5.....	6.4
9.....	5.7
10.....	1.5

<sup>1</sup>The rate of cyanide reaction depends on the concentrations of hydrogen peroxide, thiosulfate, and cyanide. However, by using a large fixed excess of hydrogen peroxide and thiosulfate, their concentrations can be lumped into a pseudo rate constant, and the concentration of cyanide is essentially the only variable in the rate expression.

#### REACTION OF $\text{Fe}^{2+}$ WITH CYANIDE

$\text{Fe}^{2+}$  reacts with cyanide to form ferrocyanide according to the reaction:



However, this reaction alone cannot reduce free cyanide levels below about 2 ppm. Table 3 shows the effect of pH on the reaction, and table 4 indicates the lower limit of free cyanide obtainable with  $\text{Fe}^{2+}$ . To obtain these data, 0.01M ferrous sulfate solution was added to a potassium cyanide solution while the pH was maintained at the values indicated in tables 3 and 4. Trends in both tables

TABLE 3. - Effect of pH on residual free cyanide when 0.5 mmol/L Fe<sup>2+</sup> is added to a 10-mg/L cyanide solution

pH	Free cyanide remaining, mg/L
7.75.....	5.6
8.00.....	3.5
8.25.....	3.6
8.50.....	2.8
8.75.....	3.3
9.00.....	4.4

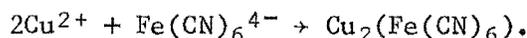
TABLE 4. - Residual cyanide after addition of Fe<sup>2+</sup> to a solution of free cyanide at pH 8.5

Fe <sup>2+</sup> added, mmol/L	Free CN <sup>-</sup> , mg/L
0.....	10.0
0.164.....	4.4
0.328.....	3.8
0.488.....	3.0
0.656.....	2.9
0.816.....	2.8

result from the competition between hydroxide and cyanide for Fe<sup>2+</sup>. The optimum pH for the Fe<sup>2+</sup>-cyanide reaction is near 8.5. This pH represents a balance between the solubility of Fe(OH)<sub>2</sub> and the HCN-CN<sup>-</sup> equilibrium. At pH values below 8.5, where Fe<sup>2+</sup> is more soluble, a greater proportion of cyanide exists as HCN, so its lone pair of electrons is not free to complex with metals. Above pH 8.5, the amount of CN<sup>-</sup> is greater, but the Fe<sup>2+</sup> encounters more hydroxide and precipitates before it has a chance to complex. The same reasoning applies when greater amounts of Fe<sup>2+</sup> are added at a fixed pH. As shown in table 4, addition of more Fe<sup>2+</sup>, even at the optimum pH of 8.5, does not substantially reduce the free cyanide level below 2 to 3 mg/L. The excess Fe<sup>2+</sup> that is added simply forms Fe(OH)<sub>2</sub>, since the CN<sup>-</sup> level has been lowered to the point where it can no longer effectively compete with OH<sup>-</sup>.

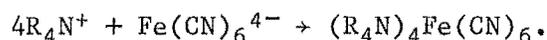
#### MECHANISM OF METALS AND FERROCYANIDE REMOVAL

When waters were treated that contained dissolved copper and ferrocyanide, a pink precipitate formed during the peroxide-thiosulfate reaction. This precipitate appeared to be Cu<sub>2</sub>(Fe(CN)<sub>6</sub>), produced by the reaction



It would form after the free cyanide and weakly complexed cyanide were destroyed. At that point in the reaction, uncomplexed Cu<sup>2+</sup> had been liberated. The pink precipitate dissolved in excess cyanide at above pH 9 but was stable in acid. A similar solid was observed after mixing Cu<sup>2+</sup> and Fe(CN)<sub>6</sub><sup>-4</sup> solutions. This precipitate indicates an important mechanism by which copper, iron, and strongly complexed cyanide are removed. It may be the major pathway in solutions where the Cu:Fe is near 2:1.

Ferric sulfate and a quaternary ammonium salt are generally required to lower copper and ferrocyanide to below 0.1 mg/L. Quaternary ammonium salts, such as oleyl- or steryldimethylbenzylammonium chloride, make insoluble compounds with the tetravalent ferrocyanide by the reaction

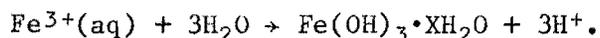


When solutions of these salts are added to ferrocyanide solutions, a white, cloudy mixture results. Ferric sulfate functions as a coagulant for the quaternary ammonium ferrocyanide salt and as a sequesterant for copper and other heavy metal ions. Addition of an anionic polyacrylamide gives a solid that settles and can be filtered more readily.

#### USE OF Fe<sup>3+</sup> SALTS FOR Cu<sup>2+</sup> REMOVAL

When ferric salts are added to water, the pH is lowered, and hydrated Fe(OH)<sub>3</sub>

is precipitated according to the reaction



Ferric salts are often employed as coagulants and flocculants for suspended solids, but the hydrous  $\text{Fe}(\text{OH})_3$  can also aid in removing dissolved metals. In the process described in this paper, copper removal is improved by adding ferric sulfate; table 5 shows data for iron addition during copper precipitation from a  $\text{CuSO}_4$  solution. From data in table 5, it appears that 10 to 20 mg/L  $\text{Fe}^{3+}$ , when precipitated, can collect up to about 0.5 mg/L  $\text{Cu}^{2+}$ .

TABLE 5. - Copper remaining in a solution treated with  $\text{Fe}_2(\text{SO}_4)_3$  in the pH range of 5 to 8, milligrams per liter

pH	$\text{Fe}^{3+}$ added		
	5 mg/L	10 mg/L	20 mg/L
5.....	5.4	4.6	3.1
6.....	1.2	.83	1.2
7.....	.85	<.10	.17
8.....	.44	<.10	<.10

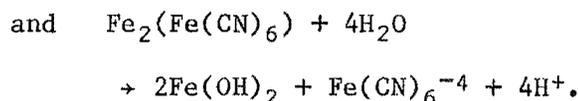
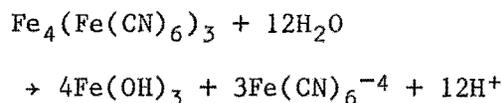
<sup>1</sup>Original  $\text{Cu}^{2+}$  concentration was 6.4 mg/L.

#### ACTIVATED CARBON AND PRUSSIAN BLUE

During earlier phases of this research, activated carbon was investigated for removal of copper. Although carbon is employed for gold and silver cyanide adsorption at pH 9 to 11, copper was adsorbed on carbon most efficiently at pH

4.5. The capacity of the carbon for copper was quite low, since 100 mg/L C would adsorb only 1 to 2 mg/L at pH 4.5. Work on this possibility was suspended, since most process waste waters are naturally buffered above pH 7 and large amounts of chemicals would be required to lower the pH (for carbon adsorption) and to raise it up again.

Removing ferrocyanide as prussian blue was also investigated early in the research, but chemical requirements for pH adjustment were large. For ferrous or ferric ferrocyanide to be a stable precipitate, the pH had to be kept below about 5. If the pH were higher, then ferrous or ferric ion formed the hydroxide, and ferrocyanide was put into solution according to the reactions



The reactions could readily be observed. When base was added to a deep blue acidic suspension of prussian blue, no change was observed until the pH reached about 5. The color of the suspension then changed slowly to green, then brown, as more base was added to bring the pH up to about 6. After the mixture at pH 6 was filtered, analyses of the filtrate showed that ferrocyanide had dissolved.

#### CONCLUSIONS

In this laboratory study, the treatment method described was effective in reducing the cyanide concentration of prepared solutions and industrial processing waste waters to less than 0.02 mg/L. The procedure uses chemicals that are relatively nontoxic and easy to handle. In addition, since the peroxide-thiosulfate system does not react appreciably with thio-cyanate, chemical usage is minimized.

The method includes three treatment steps: (1) reacting the waste cyanide

solution with hydrogen peroxide and thio-sulfate, (2) precipitating and flocculating with quaternary ammonium salt, ferric sulfate, and a polymer flocculant, and (3) filtering the solution. Laboratory results indicate that a major pathway for removal of ferrocyanide from solutions that contain copper is precipitation of  $\text{Cu}_2(\text{Fe}(\text{CN})_6)$  and that quaternary ammonium compounds are effective precipitants for ferrocyanide ions.

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