

Application of polysulfide for pretreatment of spent cyanide liquors

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Concentrated spent cyanide liquors are by-products of several different industrial processes. Although they are usually produced in relatively small quantities, their storage, transport, treatment, and disposal present considerable hazards and serious technological difficulties. Examples of spent liquors are spent cyanide solutions from electro-plating and metal finishing shops, and barren bleed solutions from gold and silver extraction operations.

Concentrated cyanide solutions often accumulate in electro-plating and metal polishing shops. These accumulations of 4.5 to 9.0 m³, which may be collected over a period of years, are generally in concentrations of 1-3% cyanide, although higher concentrations may occur.

Disposal of these concentrated cyanide containing wastewaters poses considerable problems to the waste generator. Waste haulers are often reluctant to transport these wastes because of the difficulties and expense of final disposal. Transportation of these highly toxic wastewaters involves considerable risks as leakage or rupture of the container would result in a potentially lethal situation. These disposal problems are of particular concern to operators of electroplating and metal finishing shops that are usually located in highly populated urban areas. Often, the concentrated cyanide-containing wastewaters remain stored in tanks and create a hazardous situation for workers. Sometimes these wastewaters are discharged in a clandestine fashion into the municipal sewer systems, creating problems downstream.

Considerable efforts have been devoted to the treatment of cyanide-containing wastewaters and several treatment technologies have been developed. A well-known and commonly used treatment method for cyanide-containing wastewaters, particularly in the electroplating industry, is the alkaline chlorination oxidation process, which is practically applicable for wastewaters containing up to 500 mg/l CN⁻. Other treatment processes include: peroxide oxidation, iron precipitation, ozonation with ultraviolet irradiation, carbon adsorption with catalytic oxidation, formaldehyde treatment, electrolytic oxidation, and catalytic SO₂ treatment.

Some of the common technologies applicable for the treatment of cyanide-containing wastewaters are not applicable to concentrated spent cyanide liquors. Some treatment methods are associated with high capital and operating costs, or operational complexities that render them unsuitable for small industrial plants.

The purpose of this study was to develop a simple method of treating highly concentrated cyanide liquors that contain metal cyanide complexes, so that the treated wastewater is acceptable for discharge to a municipal sanitary sewer system.

PREVIOUS WORK

An objective of this research was to study the reaction of cyanide with polysulfide-sulfur to form thiocyanate, a much

less toxic and more environmentally acceptable compound. This reaction was used as early as 1896 to remove hydrogen cyanide from coke oven gas. For cyanide solutions, the reaction was originally investigated by Wernlund and Zunick³. Luthy *et al.*^{4,5} and Luthy and Bruce⁶ studied such transformations in coke plant and coal gasification plant effluents. International Environmental Consultants^{7,8} investigated the use of the cyanide-polysulfide reaction for treatment of cyanide-containing wastewaters from the gold milling industry. However, no published data were available on the cyanide-polysulfide reaction in concentrated cyanide-containing wastewaters before the preliminary study by Takoaka and Ganczarczyk⁹. These experiments were conducted to investigate the cyanide-polysulfide reaction in a 2% solution (20,000 mg/l CN⁻) solution of sodium cyanide. The reaction proceeded very rapidly, both at room temperature and at 3°C. It was 95% complete within one hour, and cyanide concentrations were non-detectable within two weeks at a cyanide-to-poly-sulfide ratio of 1:2 by weight. It was also discovered that the initial rate kinetics of the reaction differed significantly from previously reported results at lower cyanide concentrations. These experiments also revealed that the reaction is moderately exothermic. Experiments at room temperature (23°C to 24°C) showed an initial temperature increase to 34°C to 34.5°C. No additional experiments were conducted to determine heat of reaction.

Calcium polysulfide converts waste cyanides to thiocyanates and precipitates metals to levels generally within sewer use ordinances.

Further unpublished experiments by the authors were performed on cyanide-containing wastewaters from a gold leaching process. A cyanide-to-polysulfide ratio of 1:1.5 by weight effectively reduced cyanide concentrations from 1.4% (14,000 mg/l CN⁻) to non-detectable levels within 3 days. Metal-cyanide complexes dissociated and the metals were removed from solution. The completeness of metal precipitation increased with higher polysulfide-to-cyanide ratios.

MATERIALS AND METHODS

Two different wastewater streams from an electroplating operation were studied. One wastewater was dragout from the first rinse tank in a copper and cadmium plating process. The wastewater was a clear solution with a pH greater than 12.0. The second wastewater was a stripper solution for removal of metal plate (Cu/Ni plate stripping liquor); it was orange-red and contained a settleable yellow precipitate. The pH of the stripper solution was greater than 12.0. A partial analysis of the two wastewaters is given in Table 1.

Table 1 – Analysis of wastewaters

	Dragout	Stripper
CN ⁻ (mg/l)	11,400.0	56,200.0
Cd (mg/l)	228.0	10.5
Cr (mg/l)	1.9	0.6
Cu (mg/l)	120.0	29,015.0
Fe (mg/l)	222.0	110.0
Ni (mg/l)	21.4	5,125.0
Zn (mg/l)	5.2	7.1

The source of polysulfide-sulfur was a commercially available pesticide/fungicide called Lime Sulfur. This product, obtained by dissolving elemental sulfur in a hot suspension of lime in water, is a solution of calcium polysulfide. Lime Sulfur is used to spray fruit trees, rose bushes, and other ornamental plants. The studied sample of Lime Sulfur contained 238.5 g/l polysulfide-sulfur.

The experiments were performed in glass bottles sealed with rubber stoppers (except when samples were withdrawn). The reaction vessels were kept in a dark cold room at 3°C. At daily intervals, samples of the reactor contents were collected for subsequent analysis for total cyanide (CN⁻), thiocyanate (SCN⁻), and soluble metals (cadmium, chromium, copper, iron, nickel, and zinc). Each series of experiments was conducted for a minimum of 6 days.

The standard procedures for sample preservation were adapted from those used by Luthy *et al.*,⁵ Luthy and Bruce,⁶ and International Environmental Consultants.⁸ To obtain a sample for determination of CN⁻ or SCN⁻, 20 ml of the reactor contents were withdrawn in a volumetric pipette, transferred to a 250-ml volumetric flask, and diluted to the mark with distilled water. A few milliliters of a suspension of lead sub-acetate in water were added to the diluted sample to precipitate sulfides. The addition of the lead sub-acetate was stopped when the supernatant became cloudy-white, which indicated the presence of lead hydroxide. Normal sodium hydroxide solution was added to the samples in measured quantities during the sulfide precipitation process to maintain a pH range of 10 to 11. The lead sulfide precipitate was

immediately separated from the sample by filtration under vacuum through a glass fiber filter. The filtrate was collected and its pH increased to greater than 11 with sodium hydroxide solution. The treated samples were stored in the dark at 3°C.

The method for CN⁻ determination was adapted from the method by Knechtel and Conn as cited by Conn.¹⁰ This method is similar to the acid reflux/distillation method in “Standard Methods”¹¹ with an argentometric titration finish. The method adopted for SCN⁻ determination was based on mercuric titrimetry after Vogel,¹² using 0.1 N mercuric sulfate. An excess of iron alum (ferric ammonium sulfate) was added to the sample under acidic conditions to produce the characteristic deep red color of ferric thiocyanate. After mercuric titration, the mercuric ion replaces the ferric ion and the red color gradually disappears, leaving the solution colorless. Polysulfides were determined with a procedure developed by Schulek as cited by Karchmer.¹³ This method was based on the reaction of alkali cyanides with the soluble polysulfides under anaerobic conditions to form one SCN⁻ ion for every atom of polysulfide-sulfur. The cyanide-polysulfide reaction was carried out in a boric acid medium. Hydrogen sulfide and excess hydrogen cyanide were driven off by boiling the acidified solution; the SCN⁻ and the thiosulfate remained unaffected in solution. The determination of SCN⁻ and thiosulfate was performed by indirect indometric titration with a starch indicator.

The analysis for soluble metals was performed using an atomic absorption spectrophotometer. A measured volume of sample filtered by 0.45-μ membrane filter was boiled with 20 ml of concentrated nitric acid to decompose the residual cyanide that could interfere with the metals analysis. After cooling, the sample was diluted to 250 ml with distilled water and subjected to atomic absorption spectrophotometry.

EXPERIMENTAL PROGRAM AND RESULTS

The first series of experiments involved treating 500 ml of the copper/cadmium plating dragout wastewater with 37.1 ml of the Lime Sulfur so that the cyanide-to-polysulfide ratio was 1:1.5 (w/w). At daily intervals a sample was withdrawn from the reactor and analyzed for cyanide, thiocyanate, and soluble metals.

Table 2 – Liquid phase pollutant concentrations (mg/l) in treatment of dragout wastewater from copper/cadmium plating, Series 1. (Initial cyanide-to-polysulfide ratio 1:1.5 by weight.)

Pollutants	Duration of the experiments						
	Initial	1 day	2 days	3 days	4 days	5 days	6 days
CN ⁻	11,400.0	58.0	ND*	ND	ND	–	–
SCN ⁻	0	7,430.0	5,300.0	5,580.0	4,070.0	3,020.0	4,230.0
Fe	222.0	7.9	4.8	2.4	0.8	0.8	0.6
Zn	5.2	4.3	1.1	0.5	0.7	1.1	0.5
Cu	120.0	8.7	7.6	0.9	1.5	1.4	0.7
Cd	228.0	4.1	0.8	0.6	4.8	5.0	3.5
Cr	1.9	–	0.5	0.1	0.4	0.2	0.3
Ni	21.4	5.1	1.9	0.8	0.6	0.7	0.7

*ND = non-detectable

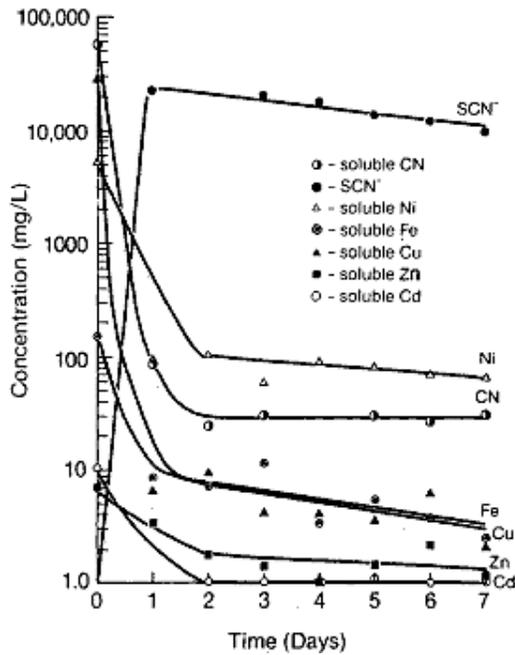


Figure 1–Conversion of cyanide and precipitation of metals in treatment of the dragout wastewater from copper/ cadmium plating. Series 1.

This experiment was continued for 6 days. The analytical data is presented in Table 2 and Figure 1.

The second series of experiments combined 300 ml copper/nickel plate stripper wastewater with 104 ml Lime Sulfur in a reactor vessel so that the cyanide-to-polysulfide ratio was 1:1.15 (w/w). Daily sampling and analysis for CN⁻, SCN⁻, and soluble metals was performed for 7 days (Table 3 and Figure 2).

The third series of experiments was also performed on the stripper wastewater for 7 consecutive days. 300 ml of this wastewater was mixed with 141 ml of Lime Sulfur so that the cyanide-to-polysulfide ratio was 1:2 (Table 4 and Figure 3).

No attempt was made to determine the extent of CN⁻ complexation of metal ions. However, preliminary tests of

metal precipitation by addition of Lime dosages equivalent to the alkalinity of the applied dosages of polysulfide reagent indicated substantial complexation. It seems that the experiments precipitated metals as sulfides that were at least partially in colloidal form, which caused a persistent black coloration in the samples.

DISCUSSION

A rapid degradation of CN⁻ occurred in all three series of experiments. In Series 1, CN⁻ was reduced to non-detectable levels within 2 days at an initial cyanide-to-poly-sulfide sulfur ratio of 1:1.5. The residual CN⁻ was reduced by 99.9% within 2 days in Series 2, which was performed at the same ratio but at a much higher initial CN⁻ concentration. In Series 3, which was a repetition of Series 2 except with a higher dosage of polysulfide-sulfur, the effective removal of CN⁻ occurred within 3 days.

These experiments basically confirmed that cyanide-to-polysulfide ratios that were only slightly greater than stoichiometric requirements (stoichiometric ratio is 1:1.23) were sufficient to carry the reaction to completion. Nevertheless, it seems that at extremely high CN⁻ concentrations more polysulfide is necessary to drive the reaction to completion.

The rate of CN⁻ removal was remarkable in view of the known stability of many of the metal-cyanide complexes present in the wastes. In fact, at the cyanide-to-polysulfide ratios studied, CN⁻ was reduced more successfully and more rapidly than during preliminary experiments conducted on 2% solution of sodium cyanide.⁹ Therefore, it is postulated that the metals in the wastewater act as a catalyst in the cyanide-polysulfide reaction. However, this hypothesis has yet to be confirmed experimentally.

In all the experiments the decrease in CN⁻ was accompanied by an increase in SCN⁻ although the increases in SCN⁻ were not consistent with the decreases in CN⁻. Significant losses of levels of SCN⁻ gradually dissipated with time in each series. Some individual tests indicated as much as 94% loss of SCN⁻; losses were more pronounced at the higher ratios of polysulfide-sulfur to cyanide.

Table 3 – Liquid phase pollutant concentrations (mg/l) in treatment of the stripper wastewater from copper/nickel plating, Series 2. (Initial cyanide-to-polysulfide ratio 1:1.5 by weight.)

Pollutants	Duration of the experiments							
	Initial	1 day	2 days	3 days	4 days	5 days	6 days	7 days
CN ⁻	56,200.0	87.5	25.0	31.3	50.0	31.3	28.1	31.3
SCN ⁻	0	20,330.0	16,260.0	20,910.0	19,460.0	14,060.0	12,490.0	10,750.0
Fe	110.0	8.9	7.4	11.5	3.4	5.5	3.8	2.6
Zn	7.1	3.2	1.6	1.3	0.9	1.5	2.2	1.1
Cu	29,020.0	6.5	9.3	4.1	4.0	3.6	6.2	2.2
Cd	10.5	3.0	0.5	0.8	0.5	1.0	1.1	0.9
Cr	0.6	ND*	ND	ND	ND	ND	ND	ND
Ni	5,130.0	94.1	105.0	59.8	92.0	83.5	69.4	66.9

*ND = non-detectable

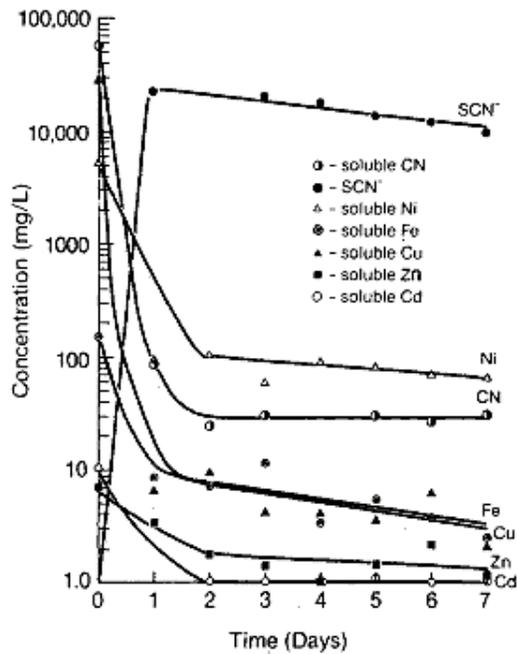


Figure 2—Conversion of cyanide and precipitation of metals in treatment of the dragout wastewater from copper/ nickel plating. Series 2.

Initially, it was postulated that SCN^- was lost through hydrolytic oxidation to carbonates, sulfates, and ammonia by the excess polysulfide. Ganczarczyk^{14,15} discussed this phenomenon in a study on biological treatment of coke plant wastewaters. However, just as in these experiments, the amount of SCN^- lost tended to fluctuate, and it was later hypothesized that SCN^- formation of non-soluble polythiocyanates might be responsible. The possibility of insoluble polythiocyanic acid formation was also suggested by Cousins and Mindler.¹⁶ None of these hypotheses was investigated further in this research.

In each of the three series of experiments, the exothermic nature of the cyanide-polysulfide reaction was noted. The temperature usually increased by 10°C to 12°C when the reaction was initiated. The heat of reaction was not quantified

in greater detail because the generated heat values were not substantial.

Although metal removals in these experiments were generally at the level required by municipal sewer use by-laws, some fluctuations in the results warrant a more in-depth study on the subject. It is thought that the addition of the polysulfide solution to the wastewater causes the dissociation of the metal-cyanide complexes, and the precipitation of ionized metals as sulfides. However, this does not explain sufficiently the “resolubilization” of cadmium that occurred in Series 1, nor the persistence of residual nickel that occurred in Series 3. Therefore, an initial precipitation of some metal-cyanide complexes, followed by a resolubilization at a later time, cannot be excluded as a possibility. It is also possible that post-treatment coagulation of the liquors would improve metal removal.

CONCLUSIONS

This study was conducted to examine the effectiveness of the cyanide-polysulfide reaction in treating concentrated cyanide liquors that contained soluble metal compounds presumably in the form of metal-cyanide complexes. The primary objective was to produce an effluent acceptable for discharge to municipal sanitary sewer systems. Although many questions of scientific interest were left to be resolved, the following conclusions were made.

- The reaction effectively converted CN^- to SCN^- within 2 to 3 days at 3°C, broke down metal-cyanide complexes, and precipitated metals generally to the levels required by municipal sewer use bylaws.
- The polysulfide dosages necessary to achieve these goals was only about 20% higher than stoichiometric requirements, but at very high CN^- concentrations somewhat higher dosages might be needed.
- It seems that the cyanide-polysulfide reaction was catalyzed by the presence of metal-cyanide complexes in wastewater and was only moderately exothermic.
- SCN^- produced by CN^- conversion was partially lost during the process.

Table 4 – Liquid phase pollutant concentrations (mg/l) in treatment of the stripper wastewater from copper/cadmium plating, Series 3. (Initial cyanide-to-polysulfide ratio 1:2 by weight.)

Pollutants	Duration of the experiments							
	Initial	1 day	2 days	3 days	4 days	5 days	6 days	7 days
CN^-	56,200.0	30.0	ND*	ND	ND	ND	ND	ND
SCN^-	0	9,000.0	15,220.0	7,260.0	2,030.0	870.0	4,940.0	3,490.0
Fe	117.8	5.7	5.8	3.0	3.2	3.1	2.7	3.7
Zn	7.5	2.2	1.2	1.6	1.5	1.2	1.0	1.3
Cu	29,920.0	9.3	1.5	2.0	3.3	2.1	2.2	2.0
Cd	10.4	2.4	0.9	1.0	1.0	0.7	0.6	0.7
Cr	0.5	ND	ND	ND	ND	ND	ND	ND
Ni	5,020.0	25.2	28.4	20.0	17.9	7.6	22.1	20.3

*ND = non-detectable

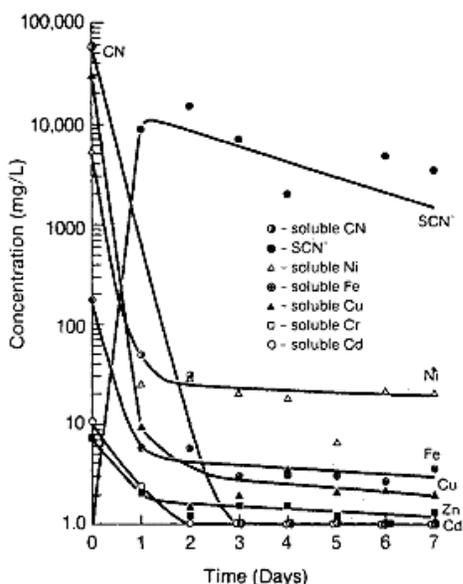


Figure 3—Conversion of cyanide and precipitation of metals in treatment of the dragout wastewater from copper/ nickel plating. Series 3.

It is believed that the cyanide-polysulfide reaction provides a safe, effective, and practical means of detoxifying highly concentrated waste cyanide solutions. The simplicity of the process and the ready availability of the polysulfide reagent make this technology appropriate for use in some small electroplating shops or developing countries.

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