Reduction of cyanate to cyanide in cyanidation tailings under reducing environments

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Abstract

Residual cyanide in cyanidation tailings can be detoxified by its oxidation to cyanate, as in the Inco and Degussa processes. However, cyanate, the product of detoxification and other oxidation processes, may be reduced to cyanide in reducing environments, e.g., deepwater discharge of cyanidation tailings. This study shows that the reduction of cyanate to cyanide occurs and that the reduction rate increases with decreasing solution redox potential. Solutions with lower pH favor the reduction rate. No significant difference was observed between the results of tests prepared with distilled water and seawater, and the presence of cyanidation solid tailings does not show an effect on the reduction. Because cyanate can be reduced to toxic cyanide, causing environmental concerns, the deepwater discharges of cyanidation tailings must be handled carefully.

Key words: Deepwater discharge, Marine placement, Cyanate reduction, Cyanide, Cyanidation tailings.

Introduction

Deepwater discharge, especially marine discharge, of wastes has been practiced for many decades. Most marine discharges are for disposal of harbor dredged materials, domestic solid wastes and sewage. Chesapeake Bay, New York Bight and Santa Monica Bay are examples of the disposal of dredged materials, domestic solid wastes and sewage, respectively. Marine discharges are permitted, as regulated by the Marine Protection, Research and Sanctuaries Act, if the discharges "will not unreasonably degrade or endanger human health, welfare, or amenities, or the marine environments, ecological systems, or economic potentials" (U.S. EPA, 1977).

Marine discharges, or marine placements, have been practiced for the disposal of mine wastes for several decades. Island Copper Mine (British Columbia, Canada) placed its flotation tailings at depth in Rupert Inlet from 1971 through the mine's closure in 1995. No adverse effects of the placement on fisheries or other ecological systems were claimed during or after the discharge operation (Pol-

ing et al., 2002). Other deepwater discharges of sulfide flotation tailings include the Atlas Mine (Cebu Island, Philippines), the Kitsault Molybdenum Mine (British Columbia, Canada), the Ramu Mine (Papua New Guinea) and the Batu Hijau Mine (Sumbawa, Indonesia).

Deepwater discharges of gold cyanidation tailings have also been practiced. The Minahasa Mine (N. Sulawesi, Indonesia) and the Misima and Lihir Gold Mines (Papua New Guinea) all discharged their tailings into nearby deepwater. In the United States, the Kensington Mine and the A-J Mine, both near Juneau, Alaska, recently proposed to discharge gold cyanidation tailings into nearby waters. The Quartz Hill Mine, on Alaska's panhandle, proposed to dispose of its molybdenum flotation tailings by deepwater placement. The Kensington Mine began mine construction in 2005, but with no gold cyanidation circuits in its final mill design. Both the A-J and Quartz Hill Mines are currently on hold.

During the past three decades, cyanide has been widely used for gold extraction (Oleson, 2003). Gold is extracted

from gold ores by dissolution in cyanide solution followed by recovery of the dissolved gold from solution using carbon adsorption or zinc cementation processes. Historically, the tailings from cyanidation processes have been discharged to tailings ponds without treatment of the residual cyanide. Degradation of cyanide occurs naturally with slow oxidation by air (Halbe et al., 1979; Smith, 1988). However, with more stringent environmental regulations, the treatment of mill effluents, or other waste effluents, containing cyanide is required before discharge into tailings ponds. Alkaline oxidation has been considered as a conventional method for cyanide destruction (Hassan et al., 1991; Wedl and Fulk, 1991; Bucknam, 1997). Photochemical (Kim et al., 1998; Young, 1998) and electrochemical (Dziewinski et al., 1995; Hofseth and Chapman, 1999) methods have been discussed for treating tough-to-break cyanide complexes. Cyanide destruction by biological oxidation (Lien et al., 1990; Mosher and Figueroa, 1996) and acidification (Riveros et al., 1996) has also been evaluated.

In recent years, the Inco SO_2/Air and Degussa processes have been widely used for cyanide destruction due to their cost-effectiveness, and these have been valued as the only reliable processes for slurry treatment. The processes have been used by precious metal recovery plants to treat CIP slurry, Merrill-Crowe barren bleed solutions, repulped filter cakes, tailings pond water discharges and feed to underground backfill plants (Robbins, 1996). They have also been applied to the rinsing and abandonment of heap leach pads and the treatment of high cyanide rinse waters from metal plating shops. Both the Inco and Degussa processes treat cyanidation tailing slurry by oxidizing toxic cyanide to much less toxic or non-toxic cyanate. The destruction of cyanide using Inco and Degussa processes can be expressed by Reactions (1) and (2), respectively

$$CN^- + SO_2 + O_2 + H_2O = CNO^- + H_2SO_4 \qquad (1)$$

$$CN^- + H_2O_2 = CNO^- + H_2O \qquad (2)$$
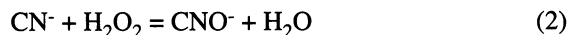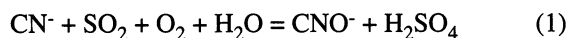
When gold cyanidation tailings are exposed to air, about 80% of the residual cyanide is decomposed by air and sunlight within several months (Smith, 1988). Due to the presence of dissolved oxygen in tailings ponds, the reduction of CNO^- to CN^- does not occur. Instead, CNO^- further decomposes to ammonia and carbonate (Ritcey, 1989), although the decomposition is very slow.

Deepwater discharges of cyanidation tailings are under a different environment. The deepwater environment can be very reducing due to low dissolved oxygen concentration and the presence of organic matter. Under this reducing environment, further destruction of residual cyanide by oxidation may not occur, while the reduction of cyanate to cyanide becomes a concern. The half-cell reaction of cyanate reduction can be expressed as

$$CNO^- + 2H^+ + 2e = CN^- + H_2O \qquad (3)$$
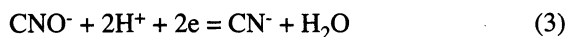
However, there has been little or no work published in the area of cyanate reduction to cyanide under reducing or low redox potential conditions. The objective of this study was to investigate the conversion of cyanate to cyanide, when cyanidation tailings are placed in a reducing environment.

Experimental
Solution preparation. CN^--CNO^- solutions were prepared for the tests, which examined the reduction of cyanate to cyanide, under reducing environments. To prepare the solution using either distilled water or seawater, lime (CaO) was added to about 990 mL of water in a 1,000 mL volumetric flask to adjust

the solution pH to 9.5. Then, 0.094 g of NaCN and 0.025 g of $CuSO_4$ were added to the flask (copper ions serve as a catalyst for the cyanide destruction reaction). A proper amount of 30% hydrogen peroxide solution was added to the 1,000 mL flask, which was then filled to the mark. The solution in the flask was then transferred to a dark glass vessel. The oxidation of the cyanide to cyanate occurs according to Reaction (2).

The solution initially contained 50 mg/L (1.92 x 10^{-3} M) CN^- and 10 mg/L (1.57 x 10^{-4} M) Cu^{2+}. Various amounts of hydrogen peroxide were used to control the extent of the cyanide oxidation and, hence, the initial cyanide and cyanate concentrations. Oxidation was allowed to occur for at least 48 hours.

Gold cyanidation tailings sample. A gold cyanidation tailings sample was obtained from the Fort Knox Mine, Alaska. The sample was taken from the discharge of the cyanide detoxification circuit. The sample was repulped, filtered and dried before testing. The particle size of the solid sample is approximately 65% minus 0.150 mm (100 mesh). Quartz and other silicates are the predominant minerals in this granitic material.

Test procedures. Tests to examine the extent of cyanate reduction to cyanide were conducted using glass reactors. The glass reactors were wrapped with aluminum foil to prevent the exposure of the solution to light. Lime and hydrochloric acid (HCl) were used to control solution pH. Solution redox potentials were controlled by purging the solution with ultra-pure nitrogen gas or hydrogen gas. All tests were conducted at 22°C. Solution samples were taken periodically for cyanide analyses. All tests were controlled in a closed system, except when taking solution samples and monitoring parameters. Solution redox potentials were measured by using a Thermo Orion pH/ORP meter and reported with respect to the standard hydrogen electrode (SHE).

Cyanide analysis. Concentrations of weak acid dissociable (WAD) cyanide were determined with a Perstorp Analytical/ALPCHEM CNSolution Model 3200 Cyanide analyzer, which measures cyanide concentration amperometrically. The accuracy of the cyanide measurement is 0.1 mg/L and the analytical time for WAD cyanide is approximately 2 minutes per sample. An explanation and schematic diagram of this cyanide analyzer were presented previously (Oleson et al., 2005).

Results and discussion
Tests were conducted to examine the extent of cyanate reduction to cyanide. Parameters examined included solution redox potential, solution pH, the presence of gold cyanidation solid tailings and water salinity (distilled water or seawater).

Effect of solution redox potential. Reports on redox potential of deepwater are very limited and the likely factors affecting the redox potential include depth of the water, oxygen penetration, organic matter and under currents. Controlled solution redox potentials of 90, 140, 190 and 240 mV were selected for the tests. Solution pH in each test was adjusted to 9.0. No solids were added in the tests. The results are shown in Fig. 1. The reduction rate of cyanate to cyanide increases with decreasing solution redox potential. A solution with a lower redox potential presents a more reducing environment and, hence, is more favorable for the reduction of cyanate to cyanide. This phenomenon is also depicted in the cyanide system Eh-pH diagram (Fig. 2); at lower solution redox potentials, the system favors HCN or CN^-. The related reactions for the Eh-pH diagram are

$$CNO^- + 2H^+ + 2e = CN^- + H_2O \qquad (4)$$

$$CNO^- + 3H^+ + 2e = HCN + H_2O \qquad (5)$$

$$CN^- + H^+ = HCN \qquad (6)$$
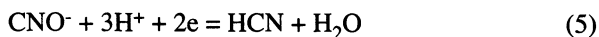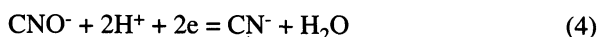
With the free energy of formation of -23.6, 39.6, 26.8 and -56.7 kcal/mol for CNO^-, CN^-, HCN and H_2O, respectively (Weast, 1980), the corresponding equations for the Eh-pH diagram at 25°C can be expressed as

$$E = -0.14 - 0.0295\log([CN^-]/[\ CNO^-]) + 0.059pH \qquad (7)$$

$$E = 0.13 - 0.0295\log([HCN]/[\ CNO^-]) - 0.089pH \qquad (8)$$

$$pH = 9.3 - \log([HCN]/[\ CN^-]) \qquad (9)$$

The Eh-pH diagram was established for $[CN^-] = 3.8 \times 10^{-4}$ M (10 mg/L), $[CNO^-] = 4.8 \times 10^{-4}$ M (20 mg/L) and [HCN] = 4.0×10^{-4} M. The HCN concentration in the system is difficult to estimate. If the actual HCN concentration is lower than the assumed value of 4.0×10^{-4} M, the boundary between CNO^- and HCN in the Eh-pH diagram will shift upward.

As mentioned above, 10 mg/L Cu^{2+}, in the form of $CuSO_4$, was added to the solution during the preparation of CN^--CNO^- solution. Cupric ions form a predominant cyanide complex, $Cu(CN)_3^{2-}$ (Osseo-Asare et al., 1984). The copper concentration in solution remained constant at 10 mg/L during the 48 hours of the CN^--CNO^- solution-preparation period. No precipitation of copper oxide or hydroxide occurs, even at pH 9.0 to 9.5. Approximately 12.2 mg/L (4.71×10^{-4} M) cyanide is bonded in $Cu(CN)_3^{2-}$ for 10 mg/L (1.57×10^{-4} M) Cu^{2+}. Because the initial cyanide concentration was 6.6 mg/L at the start of the tests (Fig. 1), 31.2 mg/L cyanide was oxidized to cyanate during the CN^--CNO^- solution preparation period. The bonded (12.2 mg/L), the initial (6.6 mg/L) and the oxidized cyanide (31.2 mg/L) add to 50 mg/L of added cyanide in the preparation period. During the test, the cyanide concentration increased from 6.6 to 9.5 mg/L at 90 mV in 50 days (Fig. 1), indicating that 9.3% of the cyanate was reduced to cyanide under these conditions. As shown in Fig. 1, the cyanide concentration is still rising after 50 days at 90, 140 and 190 mV, indicating that cyanate still exists and continues to convert to cyanide. The slow but long-lasting increase in cyanide concentration can be an environmental concern when cyanidation tailings are discharged to environments of low redox potentials. It may warrant further investigation of the reduction with longer reaction periods. The result also shows that the reduction is insignificant at 240 mV.

Effect of pH and cyanide concentration. Tests to examine the effect of pH on CNO^- reduction to CN^- were conducted at a solution redox potential of approximately 210 mV. In Fig. 3 the initial CN^- concentration was 6.8 mg/L, while in Fig. 4 the initial CN^- concentration was 1.9 mg/L. Figure 5 shows the effect of pH with a solution prepared with seawater. All three results show that the CNO^- reduction to CN^- is more favorable in solutions with a lower pH. Shown in the Eh-pH diagram (Fig. 2), the equilibrium boundaries between CNO^- and CN^- and between CNO^- and HCN shift toward a higher Eh at a lower pH, indicating that the reduction of CNO^- is more favorable at a lower pH under a fixed potential. Reaction (3) also predicts a more favorable reduction at a lower pH.

The initial cyanate concentrations shown in Figs. 3 and 4 were calculated to be 31.0- and 35.9-mg/L cyanide equivalent, respectively. Because the initial cyanate concentration in Fig.
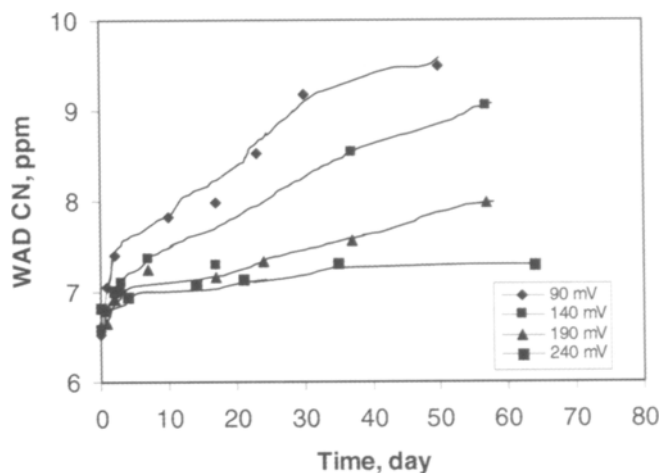

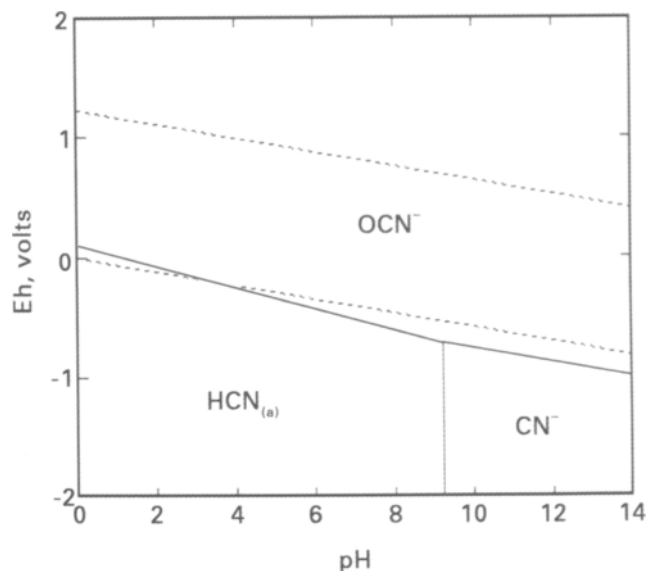**Figure 1** — Effect of solution redox potential on cyanate reduction at a pH of 9.0 in the absence of solids.

Figure 2 — Eh-pH diagram of CN^--CNO^--HCN system.

4 is higher than in Fig. 3, a more significant cyanate reduction is shown in Fig. 4.

Effect of gold cyanidation solid tailings. In tests that examined the effect of gold cyanidation solid tailings on the CNO^- reduction, the mine solid tailings sample was added to the solution at a pulp density of 25% solid (by weight). The results of the tests with the solution prepared using distilled water with a solution redox potential controlled at 210 mV and a pH of 9.1 are presented in Fig. 6. Figure 7 presents the results of a solution prepared using seawater with a solution redox potential controlled at 210 mV and a pH of 7.1. In all tests, the CN^- concentrations increase with time, but the presence of solids does not show a significant effect on CNO^- reduction.

Effect of seawater. To examine the effect of seawater on the reduction of CNO^-, tests were conducted with solutions prepared with both distilled water and seawater. In both tests, solution redox potentials and pH were controlled at 210 mV and 9.1, respectively. No solid tailings were added. The results are
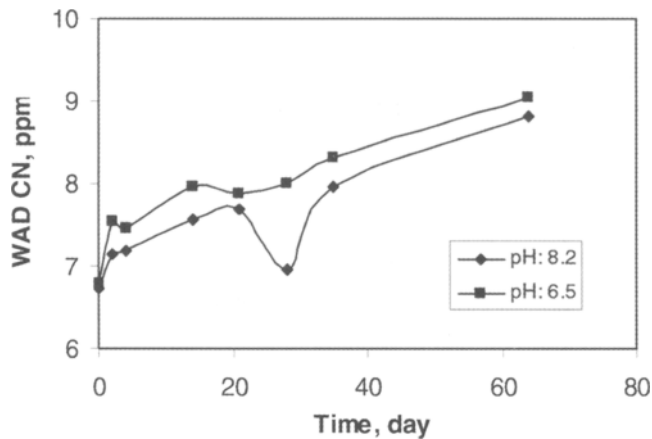
Figure 3 — Effect of solution pH on cyanate reduction for a solution prepared using distilled water, an initial cyanide concentration of 6.8 mg/L and a redox potential of 210 mV in the absence of solids.
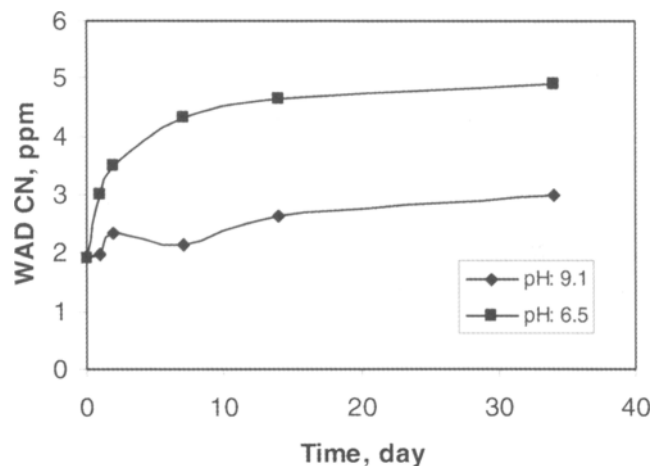

Figure 4 — Effect of solution pH on cyanate reduction for a solution prepared using distilled water, an initial cyanide concentration of 1.9 mg/L and a redox potential of 210 mV in the absence of solids.
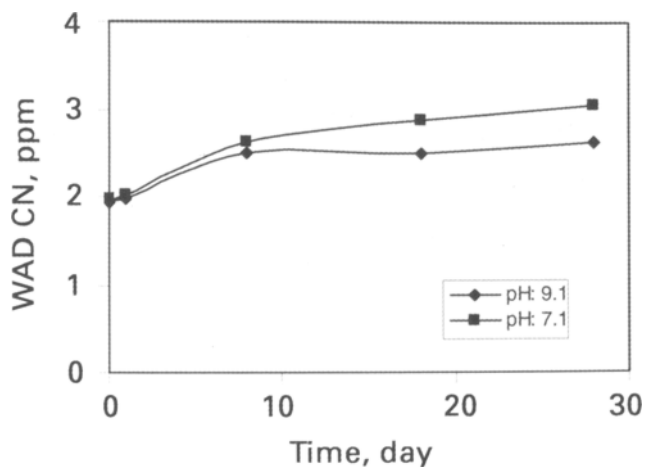

Figure 5 — Effect of solution pH on cyanate reduction for a solution prepared using seawater, an initial cyanide concentration of 1.9 mg/L and a redox potential of 210 mV in the absence of solids.

shown in Fig. 8. In both tests, CN⁻ concentration in the solution increases with time, but no significant difference was observed between the tests with distilled water and seawater.

There has been little or no work published in the area of cyanate reduction to cyanide under reducing environments. However, the formation of an ice-cover on the tailings pond at the Fort Knox Mine, Fairbanks, Alaska, may provide a similar reducing environment for study, and it is worthwhile to examine the seasonal cyanide fluctuations at the Fort Knox Mine's tailings pond. An ice-cover forms on the tailings pond from October to April each year. Before the installation of a tailings wash thickener in 2002, the cyanidation tailings were detoxified to 9-mg/L cyanide from 30-mg/L cyanide using the Inco process in the cyanide destruction circuit. The cyanide concentration decreased to 5 mg/L with an additional reaction time due to the residual detoxification reagents, before reaching the tailings pond. With 5 mg/L Cu^{2+} added to the detoxification circuit, the cyanate concentration was calculated to be 19-mg/L cyanide equivalent at the discharge to the tailings pond. After breakup in April, the cyanide concentration in the tailings pond decreases to below 0.1 mg/L in summer (Hollow et al., 2007), when the cyanide concentration is reduced through oxidation to cyanate by dissolved oxygen, HCN evaporation and runoff water dilution.

The equilibrium between HCN and CN⁻ occurs at pH 9.3 (Fig. 2). Although HCN is miscible with water, HCN in solution can evaporate due to its low boiling point of 25.6°C (Windholz et al., 1983). After the tailings pond freeze-up in October, the cyanide concentration remains below 0.1 mg/L until January, due to the remaining dissolved oxygen in the tailings pond. The cyanide concentration then increases to a peak of 3.0 mg/L in April before breakup (Hollow et al., 2007). The tailings pond holds 5.7 million metric tons of water before freeze-up and 4.8 million metric tons of water and 0.9 metric tons of ice before breakup. A total of 2.6 million metric tons of water in the tailing slurry was discharged to the tailings pond from January to April. A similar amount of water with an average cyanide concentration of 1.5 mg/L was recycled back to the mill from the tailings pond. The calculated peak cyanide concentration in the tailings pond is $((5 - 1.5) \times 2.6 \times 10^6 + 0.1 \times 5.7 \times 10^6)/(4.8 \times 10^6) = 2.0$ mg/L, which is below the actual value of 3.0 mg/L. It is likely that cyanate reduction contributes to the extra amount of cyanide in the tailings pond in the wintertime. High levels of tannin and lignin found in the make up water are believed to contribute to fouling of the activated carbon in the carbon adsorption circuit; they also can lower the redox potential of the tailings pond water, especially between January and April. The redox potential change of the tailings pond water over various seasons at the Fort Knox Mine may warrant a future investigation.

It is worth noting that the cyanidation concentration used in the Fort Knox Mine's cyanidation circuit is very low compared to a typical plant operation due to its mineralogical characteristics. Where a higher cyanide concentration is used, a higher cyanate concentration will result in the detoxification circuit, with potential for reduction to greater amounts of cyanide in reducing environments.

Conclusions

Test results show that CNO⁻ can be reduced to toxic CN⁻ in reducing environments, such as the deepwater discharge of cyanidation tailings. The CNO⁻ reduction rate increases with decreasing solution redox potential. Solutions with lower pH favor CNO⁻ reduction. Effects of solution redox potential and pH on the CNO⁻ reduction are consistent with the Eh-pH dia-

gram of the cyanide system. When considering the deepwater discharge of cyanidation tailings, the CN⁻ concentration and the CNO⁻ concentration in the tailings are both important factors. Also, because many lead, zinc and copper sulfide flotation plants use cyanide as a depressant, the deepwater discharge of such flotation tailings, and the issues of CNO⁻ reduction and CN⁻ concentration, must be handled carefully.

Acknowledgment

References

Bucknam, C.H., 1997, "Cyanide solution detoxification jar tests," Global Exploitation of Heap Leachable Gold Deposits, *Proceeding of TMS Annual Meeting*, pp. 191-204.

Dziewinski, J., Zawodzinski, C., and Smith, W.H., 1995, "Electrochemical treatment of mixed wastes," *Proceeding of the International Conference on Radioactive Waste Management and Environmental Remediation*, Vol. 2, pp. 1225-1228.

Halbe, D., Troutman, L., Neville, R.G., Hart, L., and Ommen, R., 1979, "Destruction of cyanide in Homestake gold mill effluent – a status report," AIME fall meeting presentation.

Hassan, S.Q., Vitello, M.P., Kupferle M.J., and Grosse, D.W., 1991, "Treatment technology evaluation for aqueous metal and cyanide bearing hazardous wastes," *Journal of the Air & Waste Management Association*, Vol. 41, No. 5, pp. 710-715.

Hofseth, C.S., and Chapman, T.W., 1999, "Electrochemical destruction of dilute cyanide by copper-catalyzed oxidation in a flow-through porous electrode," *Journal of Electrochemical Society*, Vol. 146, No. 1, pp. 199-207.

Hollow, J.T., Lin, H.K., Walsh, D.E., and White, D.M., 2007, "The development of an energy balance model to predict the economic impact of installing a tailings wash thickener at the Fort Knox Mine, Fairbanks, Alaska," *Minerals & Metallurgical Processing*, Vol. 24, No. 2, pp. 81-96.

Kim, B.R., Podsiadlik, D.H., Kalis, E.M., Hartlund J.L., and Gaines, W.A., 1998, "Photochemical destruction of cyanide in landfill leachate," *Journal of Environmental Engineering*, Vol. 124, No. 11, pp. 1108-1112.

Lien, R.H., Dinsdale, B.E., Gardner K.R., and Altringer, P.B., 1990, "Chemical and biological cyanide destruction and selenium removal from precious metals tailings pond water," *EPD Congress 90*, TMS, pp. 323-339.

Mosher, J.B., and Figueroa, L., 1996, "Biological oxidation of cyanide: A viable treatment option for the minerals processing industry?" *Minerals Engineering*, Vol. 9, No. 5, pp. 573-581.

Oleson, J.L., 2003, "Investigation and development of a mathematical model for the oxidation of cyanide in the INCO SO_2/O_2 Process," M.S. Thesis, University of Alaska Fairbanks.

Oleson, J.L., Lin, H.K., and Walsh, D.E., 2005, "Modeling of SO_2/air cyanide destruction process," *Minerals & Metallurgical Processing*, Vol. 22, No. 4, pp. 199-204.

Osseo-Asare, K., Xue, T., and Ciminelli, S.T., 1984, "Solution chemistry of cyanide leaching system," *Precious Metals: Mining, Extraction, and Processing*, V. Kudryk, D.A., Corrigan and W. W. Liang, eds., The Metallurgical Society, pp.173-197.

Poling, G.W., Ellis, D.V., Murray, J.W., Parsons, T.R., and Pelletier, C.A., 2002, *Underwater Tailing Placement at Island Copper Mine*, Society for Mining, Metallurgy, and Exploration, Inc., Littleton, Colorado, Chap. 8.

Ritcey, G.M., 1989, *Tailing Management: Problems and Solutions in the Mining Industry*, Elsevier Science Publisher, Amsterdam, The Netherlands, Chap. 12.

Riveros, P.A., Molnar, R., and Basa, F., 1996, "Treatment of a high-cyanide waste solution for cyanide and metal recovery," *CIM Bulletin*, Vol. 89, No. 998, pp. 153-156.

Robbins, G H., 1996, "Historical development of the Inco SO_2/air cyanide destruction process," *CIM Bulletin*, Vol. 89, No. 1003, pp. 63-69.

Smith, A., 1988, "Cyanide degradation and detoxification in a heap leach," in *Introduction to Evaluation, Design and Operation of Precious Metal Heap Leaching Projects*, van Zyl, Hutchison and Kiel, eds., SME, pp. 293-305.

U.S. Environmental Protection Agency, 1977, "Proposed Revisions to Ocean Dumping Criteria," Final Environmental Impact Statement, 201 pp.

Weast, R.C., ed., 1980, *CRC Handbook of Chemistry and Physics*, 61st Edition, CRC Press, Inc., Boca Raton, Florida, p. D-79.

Wedl, D.J., and Fulk, R.J., 1991, "Cyanide destruction in plating sludges by hot alkaline chlorination," *Metal Finishing*, Vol. 89, No. 11, pp. 33-37.

Windholz, M., ed., 1983, *The Merck Index*, 10th Edition, Merck & Co., Inc., Rahway, N.J., p. 696.

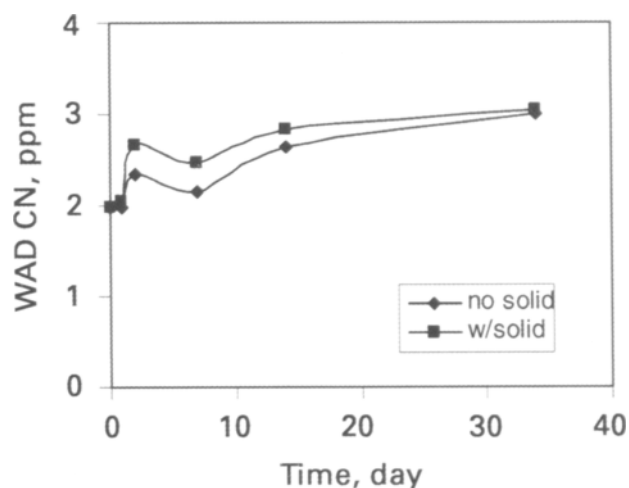Young, C.A., 1998, "Mechanism of the photocatalytic destruction of cyanide species," *EPD Congress*, TMS, pp. 877-886.

Figure 6 — Effect of cyanidation solid tailings on cyanate reduction for a solution prepared using distilled water, a redox potential of 210 mV and a pH of 9.1.
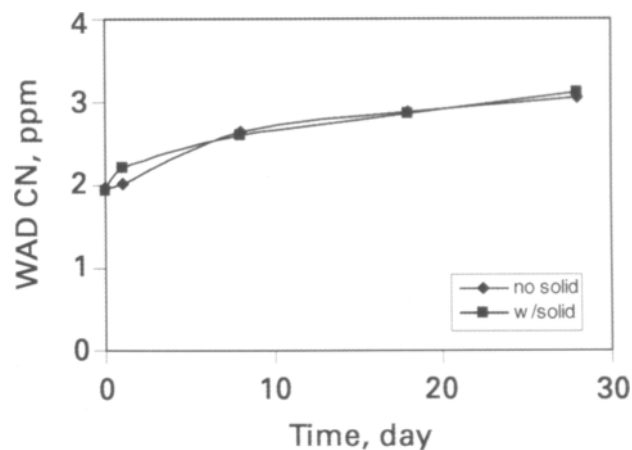

Figure 7 — Effect of cyanidation solid tailings on cyanate reduction for a solution prepared using seawater, a redox potential of 210 mV and a pH of 7.1.
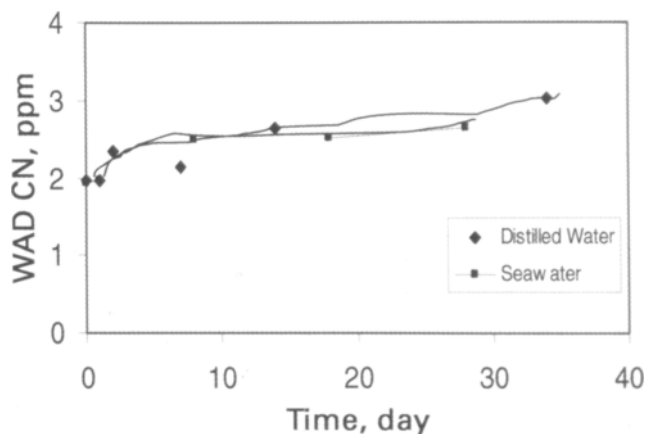

Figure 8 — Comparison of cyanate reduction for solutions prepared using distilled water and seawater at 210 mV redox potential and a pH of 9.1 in the absence of solids.