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TECHNICAL COMMUNICATION

Detoxification of Cyanide in a Gold Processing Plant Tailings Water Using Calcium and Sodium Hypochlorite

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Abstract In laboratory experiments, cyanide in waste water from the Muteh gold mine in Iran was oxidized by sodium and calcium hypochlorite to cyanate (CNO^-), which is 1,000 times less environmentally hazardous than cyanide. Experiments were conducted using waste water containing 270 mg/L cyanide over a pH range of 6–13 and temperatures between 25 and 50°C. Cyanide was removed completely at a pH of 12.3 at the higher temperatures. The experimental results were simulated in Visual MINTEQ 2003 EPA software using all of the components in the waste water. The model readily predicted most of the chemical reactions in the experiments and explained the mechanism of complexation of cyanide with metals, free cyanide, and cyanide acid formation.

Introduction

Cyanide is present in the effluent waters of several industries. The mining and mineral processing industries, especially gold processing, use a great amount of cyanide (Ingles and Scott 1993), as do a number of chemical synthesis (nylon, fibers, resins, herbicides) and metallurgical (plating and surface finishing) processes (Mosher and Figueroa 1996; Patil and Paknikar 2000). An estimated 20,000 tons of hydrogen cyanide are emitted into the atmosphere worldwide due to extraction of gold from low-grade ores (Korte and Coulston 1998). An estimated 45,300 tons of cyanide are used in the USA in the cyanidation process. The wastes from these processes result in large cyanide-containing ponds near the mining operations (Eisler et al. 1999; Henny et al. 1994; Ma and Pritsos 1997).

Cyanide is highly toxic: short-term exposure can cause rapid breathing, tremors, and other neurological effects, while long-term exposure can cause weight loss, thyroid effects, and nerve damage. Therefore, cyanide must be destroyed or removed from waste water prior to discharge, and strict environmental regulations have been enacted. The techniques that are used to treat cyanide-bearing effluents can be divided into three major groups: natural, chemical, and biological degradation. Chemical options include oxidation, ion exchange, and adsorption by activated carbon or natural zeolite (Adhoum and Monser 2002; Kurama and Catalsarik 2000).

Oxidation transforms free cyanide (CN^-) to cyanate (CNO^-), which has an environmental hazard 1,000 times less than cyanide (Mosher and Figueroa 1996; Wild et al. 1994). Cyanide oxidation by calcium or sodium hypochlorite ($Ca(OCl)_2$ and NaOCl) is an accepted technique for cyanide waste water treatment (Ingles and Scott 1993). The maximum allowable cyanide concentration in drinking water is 0.07 ppm, according to the U.S. Environmental Protection Agency (EPA). Higher concentrations are extremely harmful to aquatic life (Lordi et al. 1980). The cyanide concentration in the waste water from the Muteh Gold Mine facility in Iran exceeds 250 mg/L.

Given appropriate conditions, cyanide can break down to ammonia and CO_2 in the presence of water:

$$NCO^- + 2H_2O \rightarrow CO_2 + NH_3 + OH^- \qquad (1)$$

Cyanide oxidation by $Ca(OCl)_2$ and NaOCl also depends on various parameters such as suspended solids, metal concentration, cyanide complex concentrations, optimum pH, and hypochlorite dosage (Chapman 1992).

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The Muteh gold processing facility, the first gold-processing facility established in Iran, is located in Isfahan province. NaCN is used in this plant for gold leaching. The resultant waste water travels to the tailings dam with little treatment. Thus, cyanide threatens local ground water, the principal source of water for drinking and agricultural purposes. We investigated the optimum conditions for cyanide waste water treatment using $Ca(OCl)_2$ and NaOCl.

Materials and Methods

Waste water is contaminated with cyanide at the gold processing plant in Isfahan province because NaCN is used in this plant for gold leaching. The waste water consists of a colorless solution that is clear, but contains 270 mg/L of cyanide plus sewage and solid waste (mainly black fines of activated carbon) and trace metal contaminants. The liquid portion of the waste water was filtered and sampled for the experimental part of this study. Cyanide concentrations were determined by titration using rhodanine solution, prepared by dissolving para-dimethyl amino benzylidine rhodanine in pure acetone solution (APHA et al. 1992). $Ca(OCl)_2$ and NaOCl were obtained from MERC in powdered form.

Results and Discussion

Cyanide Removal using Calcium Hypochlorite

The oxidation and reduction reactions involving cyanide and hypochlorite result in cyanate formation, as follows (Wild et al. 1994):

$$CN^- + 2OH^- \Leftrightarrow CNO^- + H_2O + 2e^- \tag{2}$$

$$H_2O + OCl^- + 2e^- \Leftrightarrow Cl^- + 2OH^- \tag{3}$$

$$CN^- + OCl^- \Leftrightarrow Cl^- + 2OH^- \tag{4}$$

Thus, two electrons are needed for cyanide oxidation (Wild et al. 1994). The first stage of the cyanide removal experiment was conducted at pH ≈ 12, confirmed with stoichiometric coefficients (APHA 1995). To be sufficient for cyanide neutralization, the amount of $Ca(OCl)_2$ used for reacting with cyanide should be equal to the cyanide solution volume. Therefore, 7 mL of $Ca(OCl)_2$ were added to 7 mL of cyanide waste water. The reaction time was fixed at 30 min, appropriate for cyanide oxidation. Cyanide removal was determined at 12°C for different concentrations of $Ca(OCl)_2$ at pH = 12 (Fig. 1).

The color of the treated cyanide waste water can be used as a guide for recognizing the concentration of residual cyanide in solution. Cyanide solutions with a light green color have residual cyanide concentrations (RCC) of less than about 15 mg/L, while other treated cyanide waste waters have almost no color, like the original waste water.

Considering the results from the first stage, 1.43, 0.85, and 0.71 g/L $Ca(OCl)_2$ solutions were then used to determine the optimum dose of $Ca(OCl)_2$ solution to oxidize cyanide. For pH stabilization, the pH range was set at 7–13, because HCN forms at pH levels between 1 and 7 and evaporates at temperatures above 25.75°C (APHA 1995). The cyanide removal results, for a 1.43 g/L $Ca(OCl)_2$ solution, at pH 7–13 and 12°C, are shown in Fig. 2. There was no detectable RCC at pH = 12.2–12.4; when the pH was increased to 12.5, cyanide removal decreased and the RCC reached 1.32 mg/L. Cyanide removal at pH levels between 7 and 12 was not acceptable. Therefore, the next

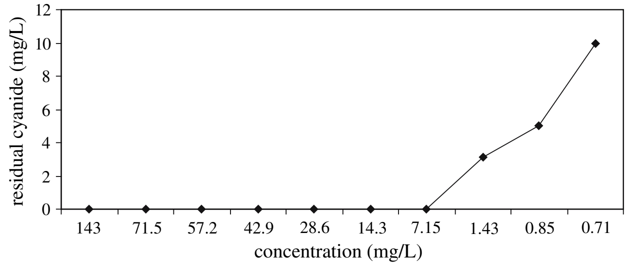

Fig. 1 The effect of calcium hypochlorite concentration on cyanide removal at pH = 12 and 12°C

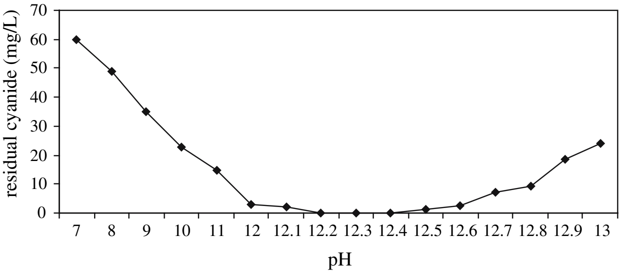

Fig. 2 The effect of calcium hypochlorite concentration on cyanide removal at pH = 7–12 at 12°C

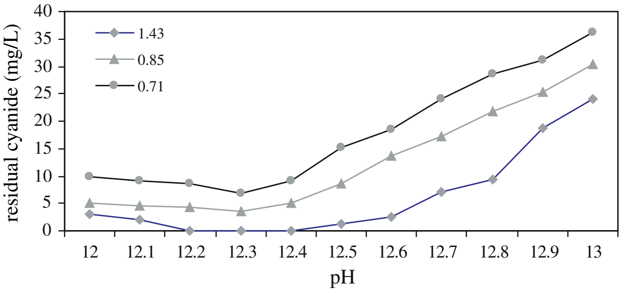

Fig. 3 The effect of pH (12–13) on cyanide removal using 1.43, 0.85, and 0.71 mg/L calcium hypochlorite solutions

experiments were conducted at a pH between 12 and 13, again at 12°C.

The RCC was lowest at a pH of 12.3 (Fig. 3). Hence, this pH was established as the optimum and the next experiments for cyanide removal evaluated the effect of temperature. The RCC for a 0.85 g/L $Ca(OCl)_2$ solution was close to zero at 35°C (Fig. 4). However, cyanide removal at this temperature actually refers to cyanide evaporation as HCN, and is not related to cyanide oxidation and cyanate formation. As soon as the temperature increases, CN^- bonds to H^+ for HCN formation in the aqueous phase, and all of the HCN that is present in the aqueous phase evaporates at 25.75°C. Similarly, a 0.71 g/L $Ca(OCl)_2$ solution had no RCC at 45°C due to HCN formation and evaporation, which cannot be described as cyanide removal.

Cyanide Removal using Sodium Hypochlorite

The redox reaction for CN^- and NaOCl is the same as with CN^- and $Ca(OCl)_2$. Because the oxidant agent, OC_1^-, is present in both solutions, the number of electrons needed for CN^- oxidation remains unchanged at two (Lordi et al. 1980). Thus, according to the stoichiometric balance for the reaction, 7 mL of NaOCl solution should be added to 7 mL of the cyanide waste water sample. The same experiments were conducted as was done for $Ca(OCl)_2$ at pH 12 (Fig. 5); based on those results, 6.91, 5.18, and 3.45 g/L NaOCl solutions were initially tested at pH 7–13, and then over the pH range of 12 to 13, all at 12°C. As in the previous experiments, the minimum RCC occurred at pH 12.3 (Fig. 6). Various experiments were then done using 6.91, 5.18, 3.45, and 1.72 g/L NaOCl solutions at temperatures between 12 and 65°C at the optimal pH of 12.3 (Fig. 7). As in the $Ca(OCl)_2$ experiments, cyanide.

Regarding the economic aspects of cyanide removal from waste water, knowing that the optimum dose of $Ca(OCl)_2$ is 1.43 g/L, the costs of cyanide removal can be calculated. Using the price of 0.039 (EUR)/g of $Ca(OCl)_2$, the cyanide removal costs are $0.039 \times 1.43 = 4.577 \times 10^{-2}$ EUR/L of waste water.

The optimum dose of NaOCl is 8.64 g/L and its price is 23.25 (EUR) per 2.5 L. Thus, the costs of cyanide removal using NaOCl solution can be computed as 66.42×10^{-2} EUR/L of waste water.

Modeling Cyanide Removal using MINTEQA2

Waste water samples from the tailings dam were analyzed by atomic adsorption so that cyanide behavior could be modeled using MINTEQA2 (Gustafson 2005). Cyano-ferro and ferric complexes are the only cyanide complexes with much formation and mobility potential, both in soils and water. The concentration of aqueous cyanide (HCN) is much more important than cyanide concentrations in

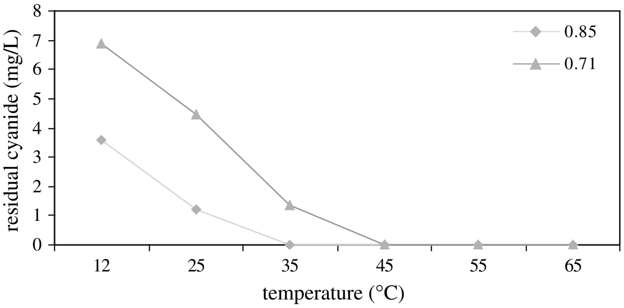

Fig. 4 The effect of temperature (12–65°C) on cyanide removal using 0.71 and 0.85 g/L calcium hypochlorite solution at pH = 12.3

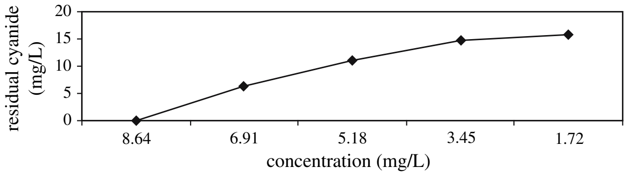

Fig. 5 The effect of sodium hypochlorite concentration on cyanide removal at pH = 12 and 12°C

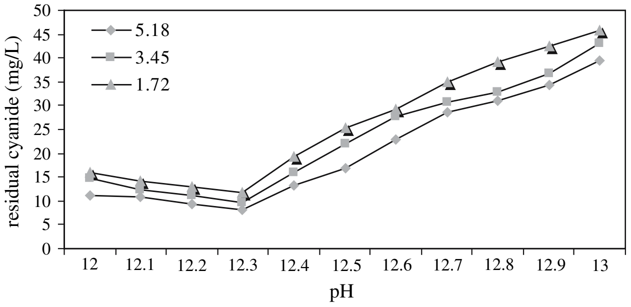

Fig. 6 Cyanide removal at pH = 12–13 and 12°C, using 1.72, 3.45, and 5.18 g/L sodium hypochlorite solutions

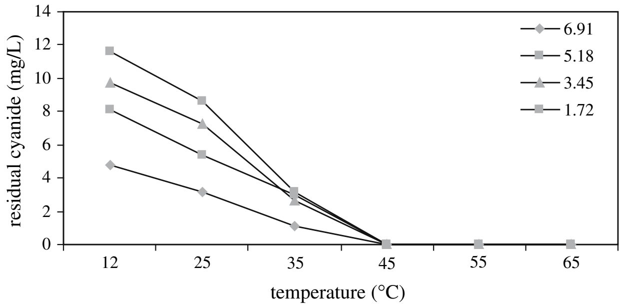

Fig. 7 The effect of temperature (12–65°C) on cyanide removal using 6.91, 5.18, 3.45, and 1.72 g/L sodium hypochlorite solutions at pH = 12.3

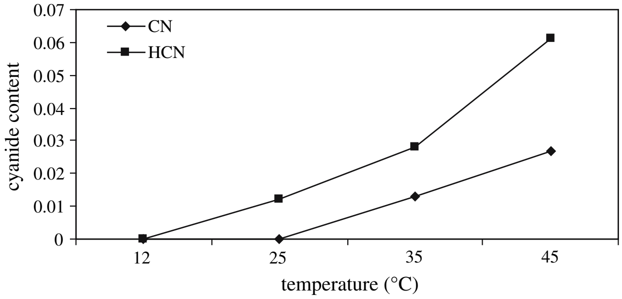

Fig. 8 Predicted changes in cyanide concentration forms at equilibrium pH over a temperature range of 12–45°C

predicting the formation of cyano-complexes. Figure 8 shows the changes in cyanide and HCN concentrations at equilibrium conditions among dissolved and absorbed species at different temperatures. At equilibrium pH and at all temperatures, the cyanide content (%) among the dissolved and absorbed species is less than that of HCN, as both HCN and cyanide concentrations increase at higher temperatures.

Conclusions

In this research, the removal of cyanide from gold industry waste water was studied using $Ca(OCl)_2$ and NaOCl as oxidizing agents. The results indicate that the concentration of the oxidant solution, pH, and temperature are the important factors in the detoxification of waste water contaminated with cyanide. Cyanide removal was optimum at a pH of 12.3, using various concentrations of NaOCl or $Ca(OCl)_2$ solutions at temperatures between 12 and 65°C.

The results also show that, even though temperature is an effective parameter for cyanide removal, this removal is mainly due to HCN evaporation. As the temperature increases, CN^- bonded to H^+ will form HCN, which is completely dissolved in the aqueous phase and evaporates at 25.75°C. Cyanide removal is more efficient and less harmful to the environment at temperatures less than 25°C. In our experiments, the optimal concentration for $Ca(OCl)_2$ and NaOCl solutions were found to be 1.43 and 8.64 g/L, respectively.

Cyanide removal by $Ca(OCl)_2$ was found to be cheaper than with NaOCl. However, $Ca(OCl)_2$ has greater costs for operational factors such as transportation and conditioning tanks. It is also possible to produce NaOCl from NaCl, using the Australian electro-chlorination system (Khouzam 2004)

However, cyanide removal by $Ca(OCl)_2$ and NaOCl forms chloramines, although this is less toxic than cyanide. Additionally, at temperatures above 35°C, pH stabilization was very difficult, and HCN formation and release by evaporation is hazardous.

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