OVERVIEW OF CYANIDE TREATMENT METHODS

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ABSTRACT

An integral and key component of many water management systems at mining sites is the approach adopted to manage cyanide-containing solutions and slurries. Excluding the bulk storage of cyanide reagents such as sodium cyanide, most cyanide present at mining sites will be present in water solutions. Therefore, to a great extent the management of water and the management of cyanide can be considered as one and the same and should be simultaneously considered when developing water management and cyanide management plans.

All mining sites that utilize cyanide for metals recovery should have a comprehensive and well-maintained cyanide management plan. A good cyanide management plan will include descriptions of how cyanide-containing solutions and slurries are to be handled, stored, contained and monitored, and in many cases the plan will also include a description of treatment plants used to remove cyanide from solutions or slurries. This article is included in this special edition of *Mining Environmental Management* to describe cyanide treatment processes that have been successfully proven on a full-scale at a number of mining sites worldwide.

BACKGROUND

In the mining industry, cyanide is primarily used for extracting silver and gold from ores, but cyanide is also used in low concentrations as a flotation reagent for the recovery of base metals such as copper, lead and zinc. At these operations, cyanide treatment systems may be required to address potential toxicity issues in regard to wildlife, waterfowl and/or aquatic life. This may include the removal of cyanide from one or more of the following:

- Slurry tailings from milling operations
- Bleed solution from Merrill-Crowe operations
- Excess solution from heap or vat leaching operations
- Supernatant solution from tailings impoundments
- Seepage collected from ponds or tailings impoundments

The term ‘cyanide’ refers to one of three classifications of cyanide, and it is critical to define the class of cyanide that is to be removed in a treatment plant. The three classes of cyanide are: (1) total cyanide; (2) weak acid dissociable (WAD) cyanide; and (3) free cyanide as shown in Figure 1.

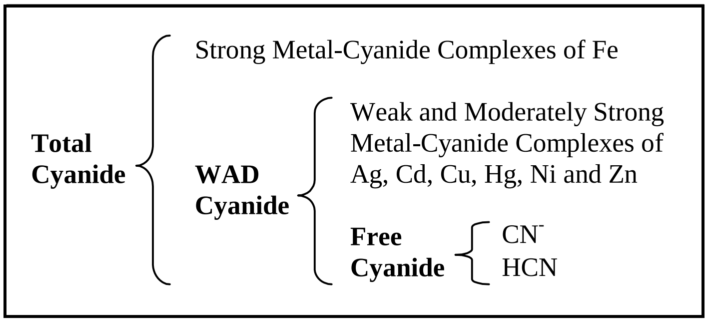

Figure 1
Classifications of Cyanides

The appropriate selection for most situations is WAD cyanide since this includes the toxicologically important forms of cyanide, including free cyanide and moderately and weakly complexed metal-cyanides. Total cyanide includes free cyanide, WAD cyanide plus the relatively non-toxic iron-cyanide complexes.

Cyanide treatment processes are classified as either a destruction-based process or a recovery-based process. In a destruction process, either chemical or biological reactions are utilized to convert cyanide into another less toxic compound. Recovery processes are a recycling approach in which cyanide is removed from the solution or slurry and then re-used in a metallurgical circuit.

Selection of an appropriate cyanide treatment process involves the consideration of many factors, but generally the number of candidate processes for a particular application can be narrowed following an inspection of the untreated solution/slurry chemistry and the desired level of treatment. In the following sections, several destruction and recovery processes are discussed along with their typical areas of application. With all of these processes, laboratory and/or pilot testing is required to confirm the level of treatment achievable and to evaluate the associated reagent consumptions.

CYANIDE DESTRUCTION

Most cyanide destruction processes operate on the principle of converting cyanide into a less toxic compound through an oxidation reaction. There are several destruction processes that are well proven to produce treated solutions or slurries with low levels of cyanide as well as metals.

INCO Sulfur Dioxide/Air

The sulfur dioxide (SO_2) and air process was developed by INCO Limited in the 1980's and is currently in operation at over thirty sites worldwide. The process utilizes SO_2 and air in the presence of a soluble copper catalyst to oxidize cyanide to the less toxic compound cyanate (OCN^-).

$$SO_2 + O_2 + H_2O + CN^- \xrightarrow{Cu^{+2}\ Catalyst} OCN^- + SO_4^{-2} + 2H^+$$

The primary application of the sulfur dioxide and air process is with slurry tailings, but it is also effective for the treatment of solutions for the oxidation of free and WAD cyanides. Iron cyanides are removed in the process through precipitation of insoluble copper-iron-cyanide complexes.

The theoretical usage of SO_2 in the process is 2.46 grams SO_2 per gram of CN^- oxidized, but in practice the actual usage ranges from about 3.5 to 4.5 grams SO_2 per gram of CN^- oxidized. The SO_2 required in the reaction can be supplied either as liquid sulfur dioxide or as sodium metabisulfite ($Na_2S_2O_5$).

Oxygen (O_2) is also required in the reaction and this is generally supplied by sparging atmospheric air into the reaction vessels. The reaction is typically carried out at a pH of about 8.0 to 9.0 in one ore more agitated tanks, and lime is added to neutralize the acid (H^+) formed in the reaction to maintain the pH in this range. Lime usage is generally on the order of about 3.0 to 5.0 grams per gram of CN^- oxidized. As indicated, copper (Cu^{+2}) is required as a catalyst, which is usually added as a solution of copper sulfate ($CuSO_4$-$5H_20$) to provide a copper concentration in the range of about 10 to 50 mg/L. Upon completion of the indicated reaction, metals previously complexed with cyanide, such as copper, nickel and zinc, are precipitated as metal-hydroxide compounds.

This process is capable of achieving low levels of both cyanide and metals. Generally, the best application of this process is with slurries containing low to moderately high initial levels of cyanide when treated cyanide levels of less than about 1 to 5 mg/L are required. In some cases, solutions treated with this process may be of suitable quality to permit their discharge.

Hydrogen Peroxide

The hydrogen peroxide treatment process chemistry is similar to that described for the INCO process, but hydrogen peroxide is utilized rather than sulfur dioxide and air. With this process, soluble copper is also required as a catalyst and the end product of the reaction is cyanate.

$$H_2O_2 + CN^- \xrightarrow{Cu^{+2}\ Catalyst} OCN^- + H_2O$$

The primary application of the hydrogen peroxide process is with solutions rather than slurries due to the high consumption of hydrogen peroxide in slurry applications. The process is typically applied to treat relatively low levels of cyanide to achieve cyanide levels that may be suitable for discharge. The hydrogen peroxide process is effective for the treatment of solutions for the oxidation of free and WAD cyanides, and iron cyanides are removed through precipitation of insoluble copper-iron-cyanide complexes. As indicated in the above reaction, hydrogen peroxide reacts to form cyanate and water, a process which limits the build-up of dissolved solids in the solution being treated.

The theoretical usage of H_2O_2 in the process is 1.31 grams H_2O_2 per gram of CN^- oxidized, but in practice the actual usage ranges from about 2.0 to 8.0 grams H_2O_2 per gram of CN^- oxidized. The H_2O_2 used in the process is typically provided as a liquid in 50% strength.

The reaction is typically carried out at a pH of about 9.0 to 9.5 for optimal removal of cyanide and metals such as copper, nickel and zinc. However, if iron cyanide must also be removed to low levels, then the pH is lowered somewhat to increase the precipitation of copper-iron-cyanides at the expense of lowering the removal efficiencies of copper, nickel and zinc. As indicated, copper (Cu^{+2}) is required as a soluble catalyst, which is usually added as a solution of copper sulfate ($CuSO_4$-$5H_20$) to provide a copper concentration in the range of about 10% to 20% of the initial WAD cyanide concentration. Upon completion of the indicated reaction, metals previously complexed with cyanide, such as copper, nickel and zinc, are precipitated as metal-hydroxide compounds.

This process is capable of achieving low levels of both cyanide and metals. Generally, the best application of this process is with solutions containing relatively low initial levels of cyanide when treated cyanide levels of less than about 1 mg/L are required. Oftentimes, solutions treated with this process may be of suitable quality to permit their discharge.

Caro's Acid

Peroxymonosulfuric acid (H_2SO_5), also known as Caro's acid, is a reagent used in a recently developed cyanide treatment process that has found application at a few sites.

$$H_2SO_5 + CN^- \rightarrow OCN^- + SO_4^{-2} + 2H^+$$

Caro's acid used in the process must be produced on-site using sulfuric acid and hydrogen peroxide since Caro's acid decomposes rather quickly (Norcross, 1996). Caro's acid is used in slurry treatment applications where the addition of a copper catalyst is not desirable, which is typically only in situations where the sulfur dioxide and air process is not suited. In solution applications, other destruction processes, such as the hydrogen peroxide process, are preferred to the Caro's acid process.

The theoretical usage of H_2SO_5 in the process is 4.39 grams H_2SO_5 per gram of cyanide oxidized, but in practice 5.0 to 15.0 grams H_2SO_5 per gram of cyanide oxidized is required. Acid produced in the reaction (H^+) is typically neutralized with lime.

Alkaline Chlorination

Alkaline chlorination at one time was the most widely applied of the cyanide treatment processes, but it has gradually been replaced by other processes and is now only used occasionally. Alkaline chlorination is effective at treating cyanide to low levels, but the process can be relatively expensive to operate due to high reagent usages. The cyanide destruction reaction is two-step, the first step in which cyanide is converted to cyanogen chloride (CNCl) and the second step in which cyanogen chloride hydrolyzes to yield cyanate.

$$Cl_2 + CN^- \rightarrow CNCl + Cl^-$$

$$CNCl + H_2O \rightarrow OCN^- + Cl^- + 2H^+$$

In the presence of a slight excess of chlorine, cyanate is further hydrolyzed to yield ammonia in a catalytic type of reaction.

$$OCN^- + 3H_2O \xrightarrow{Cl_2\ Catalyst} NH_4^+ + HCO_3^- + OH^-$$

If sufficient excess chlorine is available, the reaction continues through 'breakpoint chlorination' in which ammonia is fully oxidized to nitrogen gas (N_2).

$$3Cl_2 + 2NH_4^+ \rightarrow N_2 + 6Cl^- + 8H^+$$

In addition to reacting with cyanide, cyanate and ammonia, the alkaline chlorination process will oxidize thiocyanate, which in some cases can lead to excessively high consumptions of chlorine.

$$4Cl_2 + SCN^- + 5H_2O \rightarrow SO_4^{-2} + OCN^- + 8Cl^- + 10H^+$$

The primary application of the alkaline chlorination process is with solutions rather than slurries due to the high consumption of chlorine in slurry applications. The process is typically applied to treat low solutions flows initially containing low to high levels of cyanide to achieve cyanide levels that may be suitable for discharge. The process is effective for the treatment of solutions for the oxidation of free and WAD cyanides, but a lesser amount of iron cyanides are removed depending on the levels of other base metals in the solution being treated. As can be seen in the above reactions, a significant increase in the treated water dissolved solids concentration may result, particularly with chloride.

The theoretical usage of Cl_2 to oxidize cyanide to cyanate is 2.73 grams Cl_2 per gram of CN^- oxidized, but in practice the actual usage ranges from about 3.0 to 8.0 grams Cl_2 per gram of CN^- oxidized. The Cl_2 used in the process can be provided as a liquid Cl_2 or as a 12.5% solution of sodium hypochlorite (NaOCl). Chlorine consumptions for the oxidation of ammonia and thiocyanate can be calculated from the above reactions, which may significantly add to chlorine required in the process. In addition, the above reactions generate varying amounts of acid (H^+) which is typically neutralized by adding lime or sodium hydroxide to the reaction vessels.

The reaction is carried out at a pH of greater than 10.0 to ensure cyanogen chloride is completely hydrolyzed to cyanate. An advantage of the process is that copper is not required as a catalyst as with the sulfur dioxide/air and hydrogen peroxide processes. Upon completion of the cyanide oxidation reaction, metals previously complexed with cyanide, such as copper, nickel and zinc, are precipitated as metal-hydroxide compounds.

This process is capable of achieving low levels of both cyanide and metals. Generally, the best application of this process is with low flows of solutions containing high to low initial levels of cyanide when treated cyanide levels of less than about 1 mg/L are required. Oftentimes, solutions treated with this process may be of suitable quality to permit their discharge.

Iron-Cyanide Precipitation

Free, WAD and total cyanides will all react with ferrous iron to yield a variety of soluble and insoluble compounds, primarily hexacyanoferrate (III) ($Fe(CN)_6^{-3}$), Prussian blue ($Fe_4[Fe(CN)_6]_3$) and other insoluble metal-iron-cyanide ($M_XFe_Y(CN)_6$) compounds such as those with copper or zinc (Adams, 1992).

$$Fe^{+2} + 6CN^- + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe(CN)_6^{-3} + \tfrac{1}{2}H_2O$$

$$4Fe^{+2} + 3Fe(CN)_6^{-3} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe_4[Fe(CN)_6]_3 + \tfrac{1}{2}H_2O$$

The iron-cyanide precipitation process is limited in its suitability to situations where the precipitation reactions can be controlled and the precipitated solids can be separated and properly disposed. In the past, this process was widely used to convert free and WAD cyanides to less toxic iron-cyanide compounds, but its present utility is primarily as a polishing process to reduce total cyanide concentrations to less than about 1 to 5 mg/L.

The process is optimally carried out at a pH of about 5.0 to 6.0 and iron is added as ferrous sulfate ($FeSO_4$-$7H_2O$). Ferrous sulfate usage ranges from about 0.5 to 5.0 moles Fe per mole of CN^- depending on the desired level of treatment (Adams, 1992 and Dzombak et al., 1996).

Activated Carbon Polishing

Activated carbon has a relatively high affinity for many metal-cyanide compounds, including the soluble cyanide compounds of copper, iron, nickel and zinc. Activated carbon is suitable for use as a polishing treatment process to remove cyanide to relatively low levels. This is a simple and effective process, convenient for installation at sites where activated carbon is used in metallurgical processes for precious metals recovery.

Biological Treatment

Biological treatment processes have recently become more widespread in the mining industry due to the success of the plant installed at Homestake Lead, USA in the 1980’s (Mudder et al., 1998a). In this plant, an aerobic attached growth biological treatment is used to remove cyanide, thiocyanate, cyanate, ammonia and metals from tailings impoundment decant solution prior to discharge into a trout fishery. The plant has been operating successfully for over fifteen years, producing high-quality effluent.

A biological treatment plant was installed by Homestake Nickel Plate, Canada in the mid-1990's to treat tailings impoundment seepage (Given, 2001). This plant is a suspended sludge system with both aerobic and anaerobic treatment sections to remove cyanide, thiocyanate, cyanate, ammonia, nitrate and metals.

Another passive biological treatment process was developed for the Homestake Santa Fe, USA mine to treat draindown from the decommissioned heap leach operation (Mudder et al., 1998b). This process, known as the Biopass process, is suitable for solution flows of less than about 10 m^3/hour for the removal of cyanide, thiocyanate, cyanate, ammonia, nitrate and metals.

The applicability of biological processes for the treatment of cyanide solutions in the mining industry is somewhat limited, but in certain situations they are the optimal selection. Their applicability is primarily in with continuous solution flows with temperatures above about 10^oC.

CYANIDE RECOVERY

A number of cyanide recovery processes have been investigated over the previous one hundred years, but only two have found widespread application.

Stripping and Recovery

The stripping and recovery approach to recovering cyanide, also known as the acidification-volatilization-reneutralization (AVR) and Cyanisorb processes, remove cyanide from solution as hydrogen cyanide gas. At a pH of less than about 8.0, free cyanide and some WAD cyanide compounds are converted to hydrogen cyanide gas, which can then be air-stripped from solution. Once removed from solution as hydrogen cyanide gas, the hydrogen cyanide is easily absorbed into an alkaline solution of sodium hydroxide.

The three main reactions involved with the cyanide recovery process are as follows.

$$2CN^- + H_2SO_4 \rightarrow 2HCN_{(aq)} + 2SO_4^{-2}$$
(acidification)

$$HCN_{(aq)} \rightarrow HCN_{(g)}$$
(stripping)

$$HCN_{(g)} + NaOH \rightarrow NaCN + H_2O$$
(absorption)

This basic process has been used at about ten sites worldwide to affect WAD cyanide recoveries ranging from about 70% to over 95% with both slurries and solutions (Moura, 2001; Goldstone & Mudder, 1998; Botz et al., 1995 and Omofoma and Hampton, 1992). Its application is primarily with solutions or slurries with moderate to high concentrations of cyanide under both high and low-flow conditions. The presence of dissolved copper in untreated solution can cause difficulties with conventional cyanide recovery processes, and in some cases pre-treatment of the solution with sodium sulfide (Na_2S) may be required to precipitate copper sulfide (Cu_2S) prior to cyanide recovery.

Water Recycle

Cyanide can effectively be recovered and re-used by recycling cyanide-containing solutions within a metallurgical circuit. This is commonly conducted using tailings thickeners or tailings filters to separate solution from tailings solids, with the solution being recycled in the grinding and/or leaching circuits. This approach to recovering cyanide should be evaluated for all operations utilizing cyanide, and its performance can be determined by a simple mass balance calculation.

NATURAL CYANIDE ATTENUATION

It is well known that cyanide solutions placed in ponds or tailings impoundments undergo natural attenuation reactions which result in the lowering of the cyanide concentration. These attenuation reactions are dominated by natural volatilization of hydrogen cyanide, but other reactions such as oxidation, hydrolysis, photolysis and precipitation also occur. Natural cyanide attenuation occurs with all cyanide solutions exposed to the atmosphere, whether intended or not. At several sites, ponds or tailings impoundments are intentionally designed to maximize the rate of cyanide attenuation, and in some cases resultant solutions are suitable for discharge.

Two approaches have been developed to predict the rate of cyanide attenuation in ponds and tailings impoundments. The first method is empirical in nature and uses experimentally derived rate coefficients to estimate the rate of attenuation using a first order decay equation (Simovic et al., 1985). This approach is relatively simple to apply, but its applicability at a given site must be verified by conducting field testwork and the results may not be accurate under changing weather, pond/impoundment geometry or chemistry conditions.

The second approach to modeling natural cyanide attenuation was developed by Botz and Mudder (2000). This approach utilizes detailed solution chemical equilibria and kinetic calculations to predict the rate of cyanide losses from ponds and impoundments through a variety of reactions. This approach can be time-intensive to apply at a given site, but the results are accurate under a wide variety of weather, pond/impoundment geometry and chemistry conditions.

An example of the use of natural attenuation would be with a cyanide recovery facility where solution or slurry with a cyanide concentration of about 20 mg/L is placed into a lined pond or impoundment. The lined pond or impoundment could then be designed to maximize natural attenuation such that the resultant cyanide concentration would be less than about 1 mg/L.

SUMMARY

As indicated in the previous discussion, there are over ten cyanide treatment processes that have been successfully used worldwide for cyanide removal at mining operations. The key to successful implementation of these processes is by considering the following:

- Site water and cyanide balances under both average and extreme climatic conditions
- The range of cyanide treatment processes available and their ability to be used individually or in combination to achieve treatment objectives
- Proper testing, design, construction, maintenance and monitoring of both water management and cyanide management facilities

By carefully considering these aspects of water and cyanide management before, during and after mine operation, operators can reduce the potential for environmental impacts associated with the use of cyanide.

Another aspect of cyanide treatment to be considered is the potential environmental impact of the cyanide related compounds cyanate, thiocyanate, ammonia and nitrate. These compounds may be present in mining solutions to varying extents and may require treatment if water is to be discharged. Each of these cyanide related compounds is affected differently in the treatment processes discussed and this should be considered when evaluating cyanide treatment alternatives for a given site.

Table 1 provides a simplified summary of the general applications of various treatment technologies for the removal of cyanide and its related compounds cyanate, thiocyanate, ammonia and nitrate. This table represents a very simplified summary, but can be used as a conceptual screening tool when evaluation cyanide treatment processes.

Table 1
Preliminary Selection Guide for Cyanide Treatment Processes

Treatment Process	**Iron Cyanide Removal**	**WAD Cyanide Removal**	**Slurry Application**	**Solution Application**
SO_2/Air	✓	✓	✓	✓
Hydrogen Peroxide	✓	✓		✓
Caro’s Acid		✓	✓	✓
Alkaline Chlorination		✓		✓
Iron Precipitation	✓	✓	✓	✓
Activated Carbon	✓	✓		✓
Biological	✓	✓		✓
Cyanide Recovery		✓	✓	✓
Natural Attenuation	✓	✓	✓	✓

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