Chemistry and Treatment of Cyanidation Wastes

SECOND EDITION

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6.12 SULPHUR DIOXIDE AND AIR

6.12.1 Introduction

There are two patented versions of the sulphur dioxide cyanide destruction process. The first patented process and most widely applied is marketed by INCO Ltd. The INCO process is based upon conversion of WAD cyanides to cyanate using a mixture of SO_2 and air in the presence of a soluble copper catalyst at a controlled pH. In the INCO process, the forms of cyanide are removed by different processes. One process involves the conversion of WAD cyanides to cyanate. Iron complexed cyanides are reduced to the ferrous state and precipitated as insoluble copper-iron-cyanide complexes. Residual metals liberated from the WAD cyanide complexes are precipitated as their hydroxides.

The second sulphur dioxide process was developed at Heath Steel Mines Ltd. and the patent assigned to Noranda Incorporated (Ferguson and Walker, 1985). In the Noranda process, pure sulphur dioxide is fed into a solution or slurry to lower the pH into the range of 7.0 to 9.0. A copper sulphate solution is then added at such a rate to yield an effluent containing the desired cyanide concentration.

The INCO process has been used at over 80 mining operations worldwide and is the process addressed in this section. A primary application of the sulfur dioxide and air process is in treatment of tailings slurries, but it is also effective for the treatment of solutions for the oxidation of free and WAD cyanides.

6.12.2 Process Chemistry

Free and weakly complexed metal cyanides (i.e., WAD cyanides) are oxidized to cyanate by sulfur dioxide and air in the presence of a soluble copper catalyst.

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

(6.33) $M(CN)_4^{-2} + 4SO_2 + 4O_2 + 4H_2O \xrightarrow{Cu^{+2}\ Catalyst} 4OCN^- + 8H^+ + 4SO_4^{-2} + M^{+2}$

The reaction is normally carried out at a pH of about 8.0 to 9.0, and due to the formation of acid in the reactions, lime is normally required for pH control. Decreases in process performance can occur if the pH fluctuates outside this optimal range. The optimal pH must be determined experimentally, since maximum cyanide and metals removals occur at different pH values. Temperature has little effect on process performance between 5°C and 60°C.

The theoretical usage of SO_2 in the process is 2.46 grams SO_2 per gram of WAD cyanide oxidized, but in practice the actual usage ranges from about 3.0 to 5.0 grams SO_2 per gram of WAD cyanide oxidized. The SO_2 required in the reaction can be supplied either as liquid sulphur dioxide, sodium sulphite (Na_2SO_3) or as sodium metabisulphite ($Na_2S_2O_5$). Solutions of ammonium bisulphite (NH_4HSO_3) have also been used in the process, but this requires a careful examination regarding the impact ammonia addition will have on the treated effluent. The choice of one reagent versus another is primarily associated with cost and availability.

The approximate lime requirement can be calculated from the above reactions according to the anticipated acid production resulting from SO_2 addition. Oxygen (O_2) is also required in the reaction and this is generally supplied by sparging atmospheric air into the reaction vessels. Required reaction times vary from about 30 minutes to 2 hours.

The soluble copper catalyst is normally added as a solution of copper sulphate pentahydrate ($CuSO_4$-$5H_2O$) to a level of about 10% to 20% of the initial WAD cyanide level. However, in cases where dissolved copper is already present in the tailings solution or slurry, the need for copper sulphate addition may be eliminated.

Iron cyanide removal is initiated by reduction of iron from the ferric to the ferrous state according to the following reaction:

(6.34) $2Fe(CN)_6^{-3} + SO_2 + 2H_2O \rightarrow 2Fe(CN)_6^{-4} + 4H^+ + SO_4^{-2}$

The ferrous cyanide complex is then removed through precipitation with either copper, nickel or zinc according to the following generalized reaction:

(6.35) $2M^{+2} + Fe(CN)_6^{-4} \rightarrow M_2Fe(CN)_6$ (solid)

Trace metals remaining in solution following oxidation of the weakly complexed metal cyanides are precipitated as their hydroxides according to the following generalized reaction:

(6.36) $M^{+2} + 2OH^- \rightarrow M(OH)_2$ (solid)

The oxidation of thiocyanate, which is usually limited to 10% to 20% in the process, and the hydrolysis of cyanate occur according to the following reactions:

(6.37) $SCN^- + 4SO_2 + 4O_2 + 5H_2O \rightarrow OCN^- + 10H^+ + 5SO_4^{-2}$

(6.38) $OCN^- + H^+ + 2H_2O \rightarrow HCO_3^- + NH_4^+$

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 5 mg/L are required. In some cases, solutions treated with this process may be of suitable quality to permit their discharge.

With regard to oxidant supply, sodium sulphite (Na_2SO_3) or sodium meta-bisulphite ($Na_2S_2O_5$) are supplied as powders and must be dissolved in concentrated form prior to use. As a result, a dissolution tank and a chemical storage and feed system are necessary. In the case sulphur dioxide is used, it is usually delivered as a bulk liquid or supplied in one-ton cylinders. Sulphur dioxide gas can also be generated on-site by burning pure sulphur and collecting the combustion products into an acidic solution using a scrubber tower. Exhaust gases can also be directly injected into the slurry or solution without intermediate scrubbing.

In a typical two-stage process configuration, the sulphur dioxide, lime and copper sulphate are introduced into the first stage to complete the oxidation of cyanide. Additional lime or other chemicals (e.g., ferric chloride) are added to the second reactor to maximize metals precipitation. This approach is needed in some instances since the complete oxidation of WAD cyanide requires a lower pH than does the precipitation of metals from the solution or slurry. The flowsheet for a typical two-stage process is shown on Figure 6.21.

The primary process variables include retention time, air feed rate, copper dosage, pH and sulphur dioxide feed rate. The quantity of sulphur dioxide or other reagent used is adjusted based on the WAD cyanide concentration in treated solution, and determined through laboratory and/or pilot plant evaluations. The copper requirement for the process is also determined experimentally. Generally, the copper dosage can be held to <50 mg/L, unless elevated iron concentrations are present which demand additional copper for iron cyanide precipitation. Laboratory evaluations of the process are generally conducted in one or two reaction vessels placed in series. Sulphur dioxide or another source of oxidant is added, either pre-mixed in air or separately as a sulphite solution. The tests are completed at various reagent dosages and pH values to determine the optimal reaction conditions and achievable level of treatment.

6.12.3 Performance

The performance of the INCO process at varying levels of copper addition and pH values is shown on Figure 6.22. As indicated, the process was found to be most effective with a copper concentration above about 10 mg/L and at a pH in the range of about 6.0 to 10.0. Summaries of the cyanide destruction performance and reagent usages achieved for the treatment of several tailings slurries using the INCO process are presented in Table 6.30. A summary of the cyanide destruction performance and reagent usages for the treatment of several barren solutions and decant waters are presented in Table 6.31, and process performances for treatment of three plating solutions are presented in Table 6.32.

Capital costs for the process depend upon whether a slurry or solution is being treated, the level of WAD cyanide, iron cyanide and the concentration of copper in the untreated material. The primary capital items include the reactor(s), agitator(s), an air compressor and piping, a feed system for the sulphur dioxide source (i.e., for either sulphur dioxide, sodium sulphite, or sodium metabisulphite), a copper sulphate storage and feed system, and a slaked lime preparation, storage and feed system.

Operating costs include labour, reagents, electrical power and maintenance. Lower treatment costs are associated with treatment of solutions containing low cyanide levels, while the higher costs are associated with treatment of tailings slurries and higher levels of cyanide. The INCO process is patented technology and does require a license and user fee.

The various advantages and disadvantages of the INCO sulphur dioxide process are presented in Table 6.33.

FIGURE 6.21 Flowsheet for a Two-Stage INCO Cyanide Destruction Process

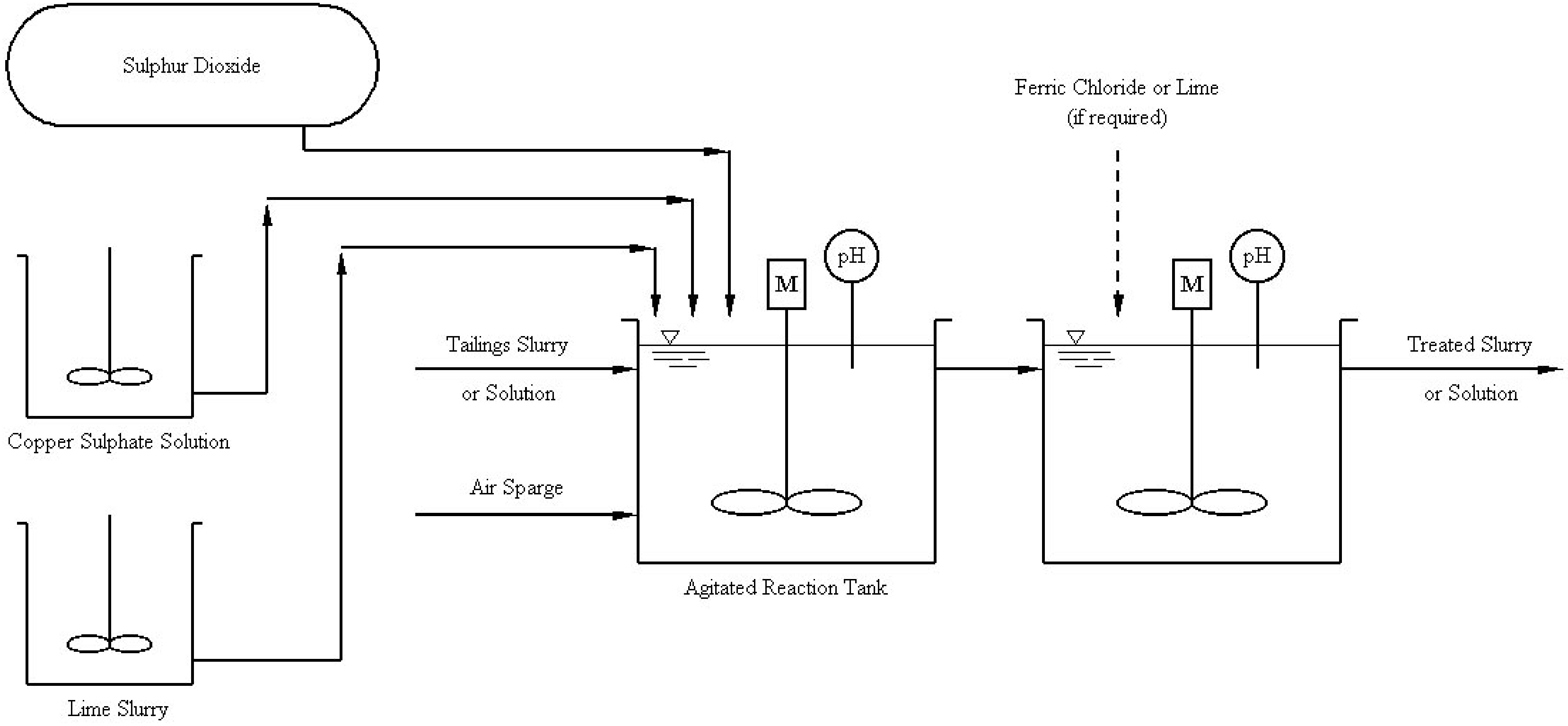
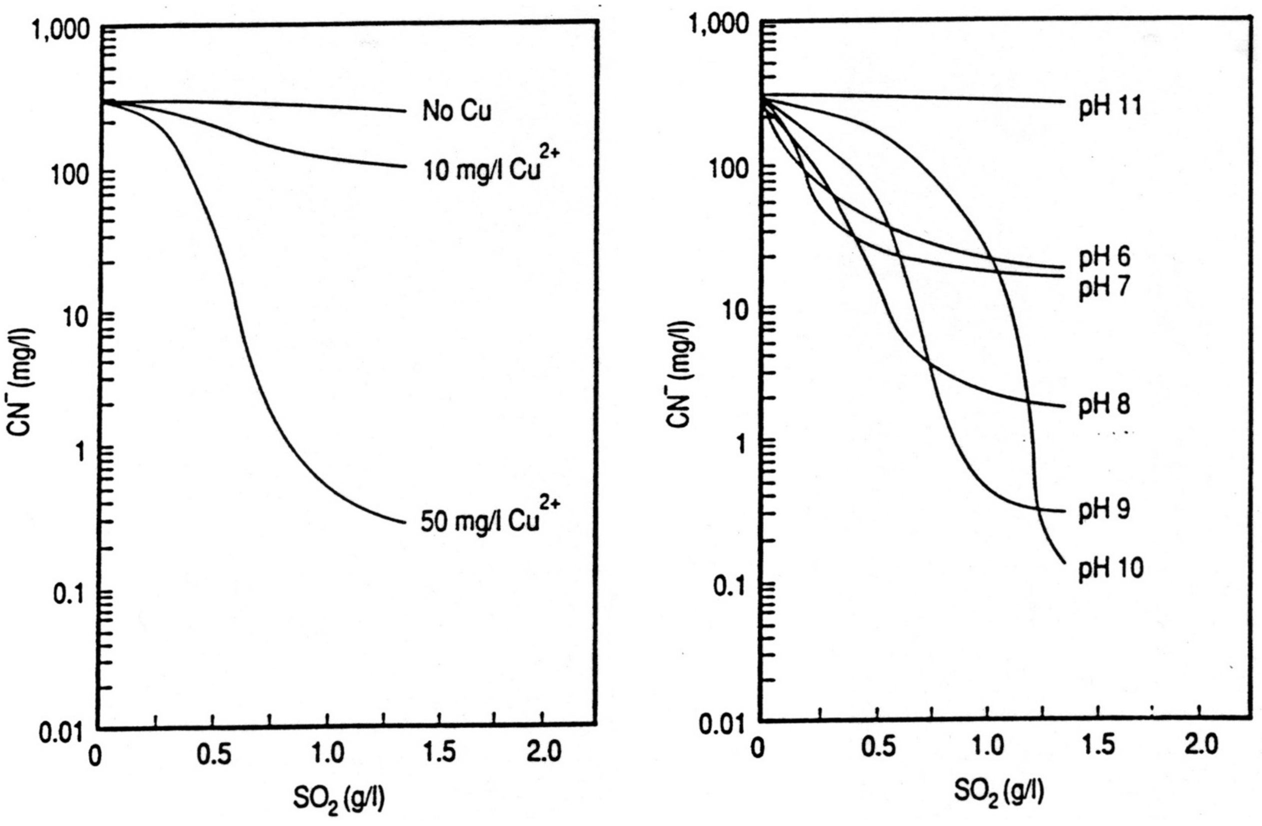


FIGURE 6.22 The Effects of Copper Concentration and pH on the Performance of the INCO Cyanide Destruction Process



Source: Robbins, 1996

TABLE 6.30 Oxidation of Cyanide in Tailings Slurry Using the INCO SO_2/Air Process

	CN_{TOT} Assay (mg/l)		Reagent Usage (g/g CH_{TOT})		
Mine	**Before**	**After**	**SO_2**	**Lime**	**Cu^{+2}**
Colosseum	364	0.4	4.6	0.12	0.04
Ketza River	150	5.0	6.0	0	0.30
Equity	175	2.3	3.4	0	0.03
Casa Berardi	150	1.0	4.5	--	0.10
Westmin Premier	150	<0.2	5.8	--	0.12
Golden Bear	205	0.3	2.8	--	--

Source: Devuyst et al., 1989a, 1989b and 1991

TABLE 6.31 Oxidation of Cyanide in Solutions Using the INCO SO_2/Air Process

	CN_{TOT} Assay (mg/l)		Reagent Usage (g/g CH_{TOT})		
Mine	**Before**	**After**	**SO_2**	**Lime**	**Cu^{+2}**
McBean (barren)	370	0.2	4.0	4.0	0
Lynngold (pond)	106	0.6	7.0	9.0	0.12
Mineral Hill (barren)	350	0.5	6.0	9.0	0
Lac Short (pond)	10	0.5	5.0	--	0
Citadel (barren)	350	5.0	4.0	--	0
St. Andrew (pond)	15	1	5.0	--	0.10

Source: Devuyst et al., 1989a, 1989b and 1991

TABLE 6.32 Oxidation of Cyanide in Electroplating Wastes Using the INCO SO_2/Air Process

	CN_{TOT} Assay (mg/l)		Reagent Usage (g/g CH_{TOT})		
Mine	**Before**	**After**	**SO_2**	**NaOH**	**Cu^{+2}**
Kuntz	150	0.2	6.0	--	--
Precious Plate	30,300	60	2.7	0.6	0
Superfinish	640	1.3	3.4	--	0.02

Source: Devuyst et al., 1989a, 1989b and 1991

TABLE 6.33 Advantages and Disadvantages of the INCO SO_2/Air Process

Advantages	
1	The process has been proven in numerous full-scale applications to yield low effluent cyanide and metals concentrations.
2	The process is effective in treating slurries as well as solutions.
3	The process is suitable for batch or continuous treatment.
4	All forms of cyanide are removed from solution, including the stable iron cyanide complexes.
5	Capital and operating costs are comparable with other chemical treatment processes.
Disadvantages	
1	If treating high levels of cyanide, the costs for reagents and electrical power can be high.
2	Cyanide is not recovered.
3	Undesirable levels of sulphate in the treated solution can result.
4	Additional treatment may be necessary for the removal of iron cyanide, thiocyanate, cyanate, ammonia, nitrate and/or metals for solutions to be discharged to the environment.