EVALUATION OF THE SO_2/AIR OXIDATION PROCESS FOR TREATMENT OF CYANIDE-CONTAINING WASTEWATER

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1. INTRODUCTION

Cyanide, in its various free and complex forms, has been shown to be toxic to receiving water biota when discharged to the aquatic environment (1). Furthermore, cyanide discharges to municipal sanitary sewer systems can impair the biological processes in water pollution control plants. Complex cyanides are not amenable to biodegradation (2) and pass through conventional biological treatment systems to the receiving waters. Many Canadian municipalities restrict the concentration of cyanide in industrial discharges to the sanitary system.

Gold mining and metal finishing operations are major sources of cyanide-containing wastewaters (3). Most Canadian gold mining facilities utilize the cyanidation process in which gold is precipitated from a gold-cyanide complex by zinc addition. A waste stream, termed barren bleed, is discharged from the mill circuit to control the accumulation of heavy metals, such as copper, in the leach stream (4,5). In metal plating operations, discharges of cyanide result from the rinsing of finished products from cyanide-type plating operations, most commonly copper cyanide, zinc cyanide and cadmium cyanide (6). In both gold mining and metal finishing operations, treatment is often required to reduce the concentrations of cyanides and heavy metals to acceptable levels.

Cyanide is most commonly removed from wastewaters through oxidation in the presence of strong oxidants such as chlorine (7,8) or ozone (8,9). Although ozone has recently generated considerable interest for cyanide oxidation, chlorine, applied under alkaline conditions, is the most common treatment procedure for cyanide wastes in both gold mining and metal finishing applications.

INCO Research have recently developed a process, based on the oxidation of cyanide with sulphur dioxide and air in the presence of a copper catalyst, for the destruction of cyanide in industrial wastewaters (10,11,12). The process appears to offer significant environmental, operational and economical advantages over conventional treatment technologies such as alkaline chlorination.

In order to confirm the applicability of the process for the treatment of cyanide-containing wastewaters, CANVIRO Consultants Limited were retained by Environment Canada to conduct laboratory-scale treatability studies aimed at assessing the technical and economical feasibility of the INCO process. This report presents the results of these investigations.

2. PROGRAM OBJECTIVES

The overall objective of the investigative program was to assess the effectiveness of the sulphur dioxide (SO_2)/air oxidation process as developed by INCO, for the treatment of wastewaters containing cyanide. Specifically, the objectives of the program were as follows:

- To evaluate the effectiveness of the SO_2/air oxidation process for removing cyanide, arsenic and heavy metals from aqueous solutions containing iron cyanide and other metal cyanide complexes.
- To assess the technical feasibility of treating wastewaters from operating gold mills in Canada by the SO_2/air oxidation process.
- To assess the technical feasibility of treating rinsewaters from selected metal finishing operations by the SO_2/air oxidation process.
- To develop a conceptual process design for a wastewater treatment facility for a model gold mill using the SO_2/air oxidation process.
- To estimate operating and capital costs for a treatment facility at a model gold mill using the SO_2/air oxidation process.
- To develop a conceptual process design for a wastewater treatment facility for a model copper plating plant using the SO_2/air oxidation process.
- To estimate operating and capital costs for a treatment facility at a model copper plating plant using the SO_2/air oxidation process.

3. TECHNICAL BACKGROUND

In the metal finishing industry, cyanide plating baths are commonly used to maintain metallic ions, particularly cadmium, zinc and copper, in solution. Drag-out from these plating baths contaminates rinsewater baths with free cyanide and metal cyanide complexes. The rinsewater baths must be continuously diluted to prevent an adverse effect on the finished surface quality due to an accumulation of contaminants. Cyanide concentrations in plating line rinsewater samples have been shown to range from approximately 2 $mg.L^{-1}$ (13) to more than 700 $mg.L^{-1}$ (14), dependent on the type of product, the amount of drag-out from the plating baths and the degree of recirculation of rinsewater in the specific plating operation. Cyanide concentrations are typically in the range of 100 to 200 $mg.L^{-1}$ from a well-controlled electroplating line (15).

Wastewaters from gold mills utilizing the cyanidation process for gold recovery are also major sources of cyanide, due to the discharge of a fraction of the leaching solution to control the accumulation of heavy metals in the mill circuit. Wastewaters from the gold mill operations are considerably more complex than those from metal finishing processes. The barren bleed solutions typically contain, in addition to free cyanide, thiocyanate, cyanate, heavy metals including copper, zinc, nickel and iron, and a variety of other metal cyanide complexes. Arsenic may also be present at high concentrations, depending on the nature of the ore processed. The actual composition of gold mill effluents varies considerably depending on the source of the ore and the nature of the milling processes.

A variety of processes have been proposed for treatment of cyanide-containing wastewaters, particularly those generated from the metal finishing industry. Recovery of cyanide by ion exchange (16), by membrane processes such as reverse osmosis (17), or by evaporation (18), have been shown to be technically feasible in specific applications. Ion-exchange systems have also been evaluated for treatment of gold mill effluents (19,20).

Despite the inherent advantages of such recovery processes, chemical oxidation of cyanide wastes is the common practice. The process most frequently employed is cyanide destruction by chlorination (15,21,22). Ozone oxidation has also been shown to be an economically practical and technically feasible alternative for both metal finishing (8) and gold milling (9,20) effluents. Other processes including electrolytic decomposition

(23), destruction in the presence of hydrogen peroxide and formaldehyde by the Kastone process (24), and adsorption and catalytic oxidation on activated carbon (12) are in varying stages of development and have not yet found widespread application.

INCO laboratories have recently developed a cyanide destruction process which is applicable for treatment of metal finishing rinsewaters and gold mill effluents (10,11,12). Cyanide is oxidized to cyanate by means of a gaseous mixture of sulphur dioxide in air in the presence of a copper catalyst. The process appears to be capable of removing iron cyanide complexes from solution. Iron cyanide complexes are generally unaffected by chlorination and ozonation processes (3,25). In addition, reagent requirements are reduced as the process does not oxidize thiocyanate as is the case during chlorination and ozonation.

In the following subsections of the report, the alkaline chlorination process, the ozonation process and the copper-catalyzed SO_2/air oxidation process are discussed in terms of the simplified chemistry of cyanide destruction and their relative advantages and disadvantages for treatment of metal finishing rinsewaters and gold mill effluents.

3.1 Cyanide Destruction By Alkaline Chlorination

Cyanide oxidation to cyanate by chlorination under alkaline conditions is generally accepted to proceed as a two-stage reaction (3,7,26). Cyanogen chloride is formed initially according to the reaction:

$$CN^- + Cl_2 \longrightarrow CNCl + Cl^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This reaction is rapid and not pH-dependent (3). Cyanogen chloride is highly toxic (3), but readily hydrolyzes under alkaline conditions to cyanate as follows:

$$CNCl + 2\ OH^- \longrightarrow CNO^- + Cl + 2\ H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The theoretical chlorine requirement for conversion of simple cyanides to cyanate is 2.73 g Cl_2 per g CN^- oxidized.

Cyanate generated from the oxidation of cyanide can be further oxidized according to the reaction:

$$2\ CNO^- + 3\ Cl_2 + 6\ OH^- \longrightarrow 2HCO_3^- + N_2 + 2H_2O + 6\ Cl^- \ldots\ldots (3)$$

The complete oxidation of cyanide to nitrogen and bicarbonate theoretically requires a total of 6.82 g Cl_2 per g CN^- removed.

During treatment of gold mill effluents containing thiocyanate, the chlorine requirements are increased significantly by the preferential oxidation of thiocyanate to cyanate according to the reaction:

$SCN^- + 4\ Cl_2 + 10\ OH^- \longrightarrow CNO^- + SO_4^{-2} + 8\ Cl^- + 5\ H_2O$......(4)

The additional chlorine demand associated with thiocyanate oxidation is 4.88 g Cl_2 per g SCN^- oxidized (26).

In general metal cyanide complexes of copper and zinc can be readily destroyed by chlorination and the metals removed as hydroxide precipitates. Nickelocyanides are more resistant to chlorination. In wastewaters containing iron as ferrocyanide, the ferrocyanide is oxidized to ferricyanide during alkaline chlorination; however, the ferricyanide complex is not destroyed by chlorine (3).

3.2 Cyanide Destruction By Ozonation

The reaction of ozone with free cyanide can be represented by the simplified reaction (27):

$CN^- + O_3 \longrightarrow CNO^- + O_2$ ....(5)

The oxidation reaction is extremely rapid. Cyanate is also oxidized by ozone to nitrogen according to the reaction (27):

$CNO^- + 3O_3 + H_2O \longrightarrow 2HCO_3^- + N_2 + 3O_2$....................(6)

However, the kinetics of this reaction are relatively slow compared to the initial oxidation of cyanide to cyanate.

As is the case in alkaline chlorination of gold mill effluents, the presence of thiocyanate significantly increases the reagent requirements of the ozonation process. Thiocyanate oxidizes rapidly to cyanate according to the reaction (9):

$SCN^- + 4O_3 + 2\ OH^- \longrightarrow CNO^- + SO_4^{-2} + 4\ O_2 + H_2O$..........(7)

The theoretical ozone demand for thiocyanate oxidation is 3.3 g O_3 per g CNS, compared to an ozone requirement of 1.85 g O_3 per g CN for oxidation of cyanide to cyanate.

Copper cyanide complexes are readily oxidized by ozone (28). Nickel and zinc cyanide complexes can also be destroyed by ozonation, although the reaction is slower than the oxidation of simple cyanides and copper cyanide complexes. Cadmium cyanide is more resistant to oxidation than nickel or zinc cyanide. Iron cyanide complexes are not destroyed by ozone except at elevated temperatures or in the presence of UV radiation (9), although ferrocyanide is oxidized to ferricyanide.

3.3 Cyanide Destruction By the SO_2/Air Oxidation Process

The SO_2/air oxidation process has been described in three recent publications by INCO (10,11,12). Although the chemistry and reaction kinetics have not been intensively investigated, mechanisms have been postulated for the cyanide destruction reactions.

The oxidation of cyanide occurs according to a simplified reaction as follows:

$$CN^- + SO_2 + O_2 + H_2O \longrightarrow CNO^- + H_2SO_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Based on the stoichiometry of this reaction, the SO_2 requirement is 2.47 g SO_2 per g CN oxidized.

The cyanide oxidation reaction is catalyzed by the presence of copper ions in solutions. The catalytic effect of copper is not unique to the SO_2/air oxidation process. The presence of copper has also been shown to improve the kinetics and chemical utilization efficiency during ozonation and hydrogen peroxide treatment of cyanide-containing wastewaters (28), and to catalyze the oxidation of cyanide on granular activated carbon (12). Optimal pH conditions for the SO_2/air reaction with cyanide was between 9 and 10. Temperature had no significant effect on the initial cyanide decomposition rate in the range from 5 to 60°C. Cyanide oxidation efficiency was shown to decrease with increasing sulphur dioxide concentration in air over a range from 0.2 volume percent SO_2 in air to 10.0 volume percent SO_2.

Thiocyanate can also be oxidized to cyanate by SO_2 and air, according to the following proposed reaction (11):

$$SCN^- + 4\ SO_2 + 4\ O_2 + 5\ H_2O \longrightarrow CNO^- + 5\ H_2SO_4 \ldots\ldots\ldots\ldots\ldots (9)$$

The decomposition of thiocyanate is catalyzed by nickel, and to a lesser extent by cobalt and copper. However, the kinetics of the thiocyanate oxidation reactions are considerably slower than the cyanide oxidation reactions. Therefore, the presence of thiocyanate in gold mill effluents does not significantly affect the SO_2 requirements of the process in most cases.

The SO_2/air oxidation process also destroys the metal cyanide complexes typically present in metal finishing and gold mining effluents. Based on sequential sampling data from batch experiments, the preferential order of metal cyanide complex removal is:

Zn > Fe > Ni > Cu

The So_2/air oxidation system has been shown to be capable of removing iron cyanide complexes from solution (10,11). During SO_2/air treatment, iron remains in the reduced ferrous state and is not converted to the ferric state as occurs in stronger oxidizing environments. The iron cyanide complexes are removed from solution by precipitation of metal ferrocyanide compounds of the form $Me_2Fe(CN)_6$ (where Me = Cu, Zn and Ni). Metals liberated from the cyanide complexes of copper, zinc and nickel are removed by precipitation of metal hydroxides at the reaction pH.

4. EXPERIMENTAL PROCEDURES

The experimental program involved a series of batch laboratory-scale experiments conducted with synthetic solutions containing cyanide, arsenic and heavy metals, actual gold mill effluents collected from seven operating Canadian mills and rinsewaters from copper cyanide, zinc cyanide and cadmium cyanide plating lines at selected metal finishing plants. The batch experiments were designed to assess the general applicability of the SO_2/air oxidation process as developed by INCO for treatment of a variety of cyanide-containing wastewaters. Subsequently, laboratory-scale continuous flow reactor experiments were conducted on selected gold mill effluents and copper cyanide plating rinsewater.

Details of the experimental program are provided in the following subsections.

4.1 Preparation of Synthetic Solutions

Synthetic solutions containing free and complex cyanide, selected heavy metals including zinc, copper and nickel, iron and arsenic were prepared from distilled water and stock solutions of sodium cyanide (NaCN), potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3\ H_2O$), zinc Chloride ($ZnCl_2$), copper sulphate ($CuSO_4 \cdot 5\ H_2O$), nickel sulphate ($NiSO_4 \cdot 6\ H_2O$), sodium arsenite ($NaAsO_2$) and sodium thiocyanate (NaCNS). The pH of the distilled water was adjusted to 12.0 with sodium hydroxide prior to the addition of the required volume of NaCN stock solution. The pH of the solution was then maintained at 12.0 during each subsequent reagent addition to minimize precipitation of metal hydroxides from the synthetic solution.

The actual concentrations for the synthetic solutions prepared according to this protocol are compared with the design synthetic solution compositions in Table 1. In general, there was good agreement (±20%) between the design and actual concentrations of the specified compounds.

4.2 Collection of Gold Mill and Metal Plating Rinsewaters

Effluent samples were collected from seven operating Canadian gold mills and were shipped to the Wastewater Technology Centre in Burlington for the laboratory-scale treatment studies. Two samples of rinsewaters from

TABLE 1. COMPARISON OF DESIGN AND ACTUAL SYNTHETIC SOLUTION CONCENTRATIONS

SAMPLE #		CONCENTRATION ($mg.L^{-1}$)								
		CN_T*	CN_W†	SCN	Fe	Cu	Zn	Ni	As	CNO
1	Design	202.	61.5	-	50.	50.	-	-	-	-
	Actual	184.	55.4	-	53.4	56.6	-	-	-	-
1A	Design	202.	61.5	-	50.	50.	100.	-	-	-
	Actual	176.	52.4	-	54.2	60.0	92.0	-	-	-
2	Design	202.	61.5	-	50.	50.	100.	-	10.	-
	Actual	170.	56.4	-	51.0	51.4	78.0	-	7.6	-
3	Design	238.	224.	400	5.	50.	100.	2.	1.	-
	Actual	219.	200.	407	5.0	53.4	86.0	2.2	0.65	23.

* Total Cyanide
† Weak Acid Dissociable Cyanide

cyanide-based copper and cadmium plating operations and one sample of rinsewater from a cyanide-based zinc plating operation were also collected for laboratory-scale treatability studies. Operations personnel indicated that plant conditions were typical at the time of sampling; however, it was not possible to verify the representativeness of the samples collected prior to analysis and testing.

4.3 Batch Treatment Procedures

Batch treatments by the copper-catalyzed SO_2/air oxidation process were conducted on the synthetic solutions and wastewater samples using the experimental apparatus shown in Figure 1. The reaction vessel was a 1600-mL beaker continuously stirred with a variable speed mixer equipped with a turbine-type blade. Initial liquid volume for the batch experiments was 1.0 L. All experiments were conducted at room temperature (22°C). Refrigerated effluent samples were allowed to attain room temperature prior to commencement of the batch treatments.

Sulphur dioxide (SO_2) and air were introduced to the reaction vessel through calibrated rotameters by means of a fritted-glass diffuser. The design SO_2 addition rate was 6.0 $g.h^{-1}$ as a 3.4% by volume mixture with air. The experimental apparatus precluded the use of lower SO_2 concentrations ($\leq$ 2.5% SO_2) which have been shown to give significantly better SO_2 utilization efficiency $^{(12)}$.

The reactor pH was automatically controlled at 9.0 Lime slurry (39 $g.L^{-1}$ $Ca(OH)_2$) was used during treatment of synthetics, gold mill effluents and metal finishing rinsewaters. Sodium hydroxide (40 $g.L^{-1}$ NaOH) was used for specific metal finishing rinsewaters as indicated. The reduction-oxidation (Redox) potential and pH of the reacting mixture was continuously monitored and recorded.

Typically, the batch experiments were run for approximately ten minutes after a stable Redox potential had been attained in the reaction vessel and the reactions were considered to be complete. Liquid phase samples were then collected, filtered and preserved for cyanide and metal analysis.

The total mass of SO_2 used during each batch experiment was measured by weighing the SO_2 gas cylinder before and after each experimental run.

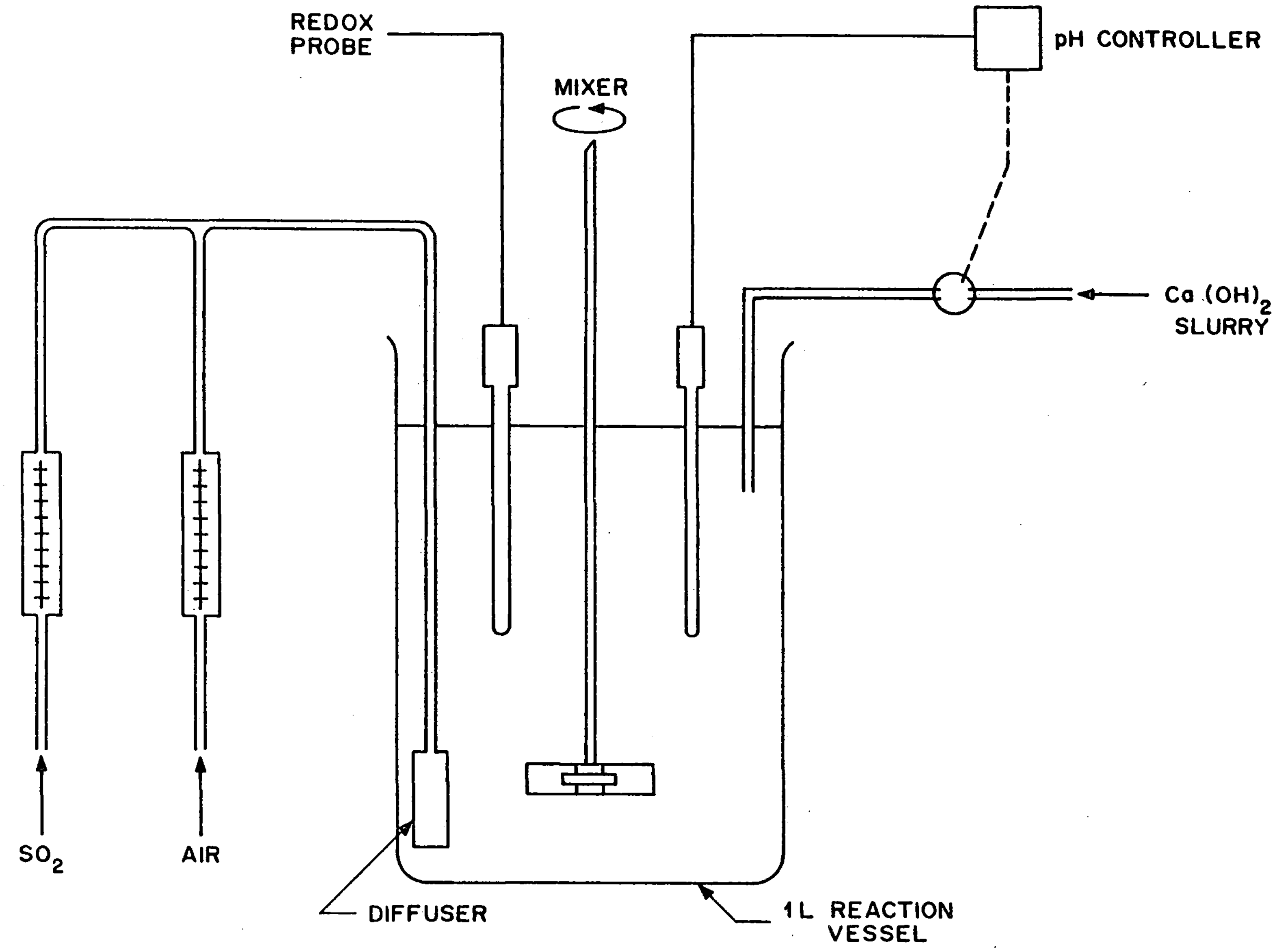

FIGURE 1 — EXPERIMENTAL APPARATUS - BATCH RUNS

Similiarly, the volume of $Ca(OH)_2$ slurry or NaOH solution used for pH control was recorded in order to calculate chemical consumptions and to allow for volume correction when calculating the mass removal of various contaminants.

During two of the batch experiments, on synthetic solution #3 and effluent from gold mill #3, a mass balance on cyanide species and heavy metals was conducted. The mass of precipitated solids generated during the oxidation reactions was quantified and the air-dried solids submitted for laboratory analysis.

4.4 Continuous Flow Treatment Procedures

Effluents from gold mills 3, 6 and 7 and the second rinsewater sample from the copper cyanide plating operation were subjected to continuous flow treatability evaluations.

On the basis of discussions with INCO researchers (29), a two-stage reaction system was utilized during treatment of the effluent from gold mill 3. The two-stage system is shown schematically in Figure 2. All subsequent continuous flow experiments were conducted in a single-stage reactor system of similar design.

In the two-stage system, each reactor was a 1600-ml beaker equipped with an overflow to provide a nominal reactor volume of 1.0 litre. The reactors were equipped with variable speed laboratory-scale mixers similar to those used in the batch experiments. Separate SO_2 and air feed systems were provided for each reactor. The gases were applied through calibrated rotameters by means of fritted glass diffusers. In both cases, the design SO_2 concentration in the air stream was approximately 3.5 percent by volume. The single reactor system consisted of one mixed 1.0 L reaction vessel.

Automatic pH control systems were provided for each reactor to maintain the reaction pH at 9.0. Lime slurry was used for pH control during treatment of all gold mill effluents. Both lime and sodium hydroxide were used during treatment of copper cyanide plating rinsewater. Redox potential in the reactors was continuously monitored and recorded. All experiments were conducted at room temperature (22°C).

To initiate the continuous flow experiments, each reaction vessel was filled with approximately 1.0 L of wastewater and batch treatment of the effluent was conducted according to the same procedures as described in

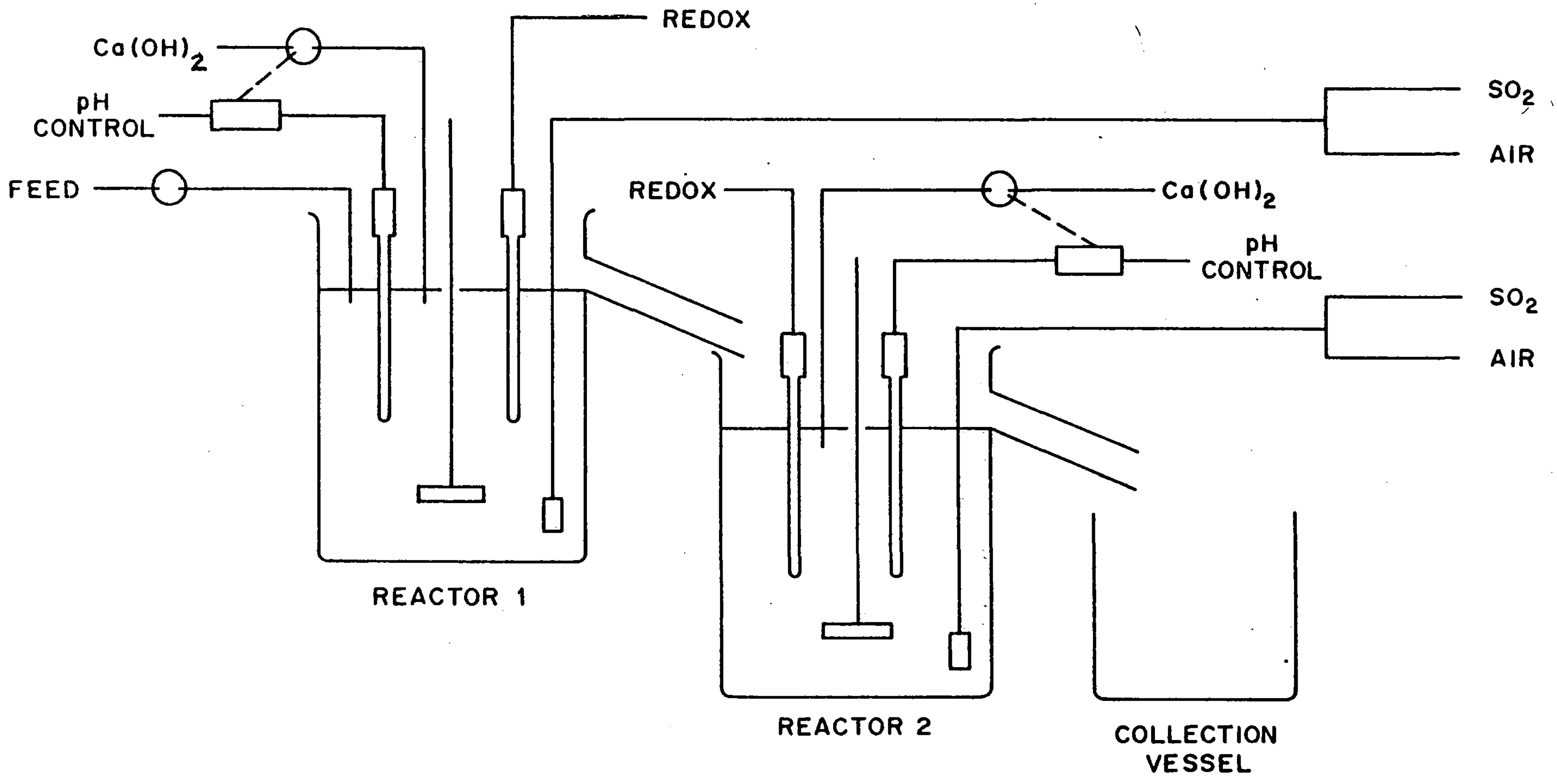

FIGURE 2 — EXPERIMENTAL APPARATUS — CONTINUOUS RUNS

Section 4.3. When the batch reaction was completed, feed to the reaction vessels was then initiated by means of a calibrated peristaltic pump, along with reagent (SO_2, air, $Ca(OH)_2$ or NaOH) addition. The experiment was run for 2.5 to 3.0 times the nominal hydraulic retention time prior to sampling the contents of the reactors.

As in the batch experiments, reagent consumptions were determined by weight difference. Reactor liquid samples were immediately filtered and perserved for laboratory analysis for cyanide species and metals.

4.5 Analytical Procedures

All analyses were conducted according to standard procedures (30). Analyses for cyanide species (total and weak acid dissociable cyanide) were conducted at the Wastewater Technology Centre using the procedures outlined by Conn (31). Analyses for metals were done by atomic absorption spectroscopy, according to the protocols described in Standard Methods (30). In addition, each gold mill effluent was submitted for analysis by the inductively-coupled plasma procedure.

Spiked samples and replicates were submitted to the analytical laboratories as a part of the overall quality assurance/quality control (QA/QC) program. This was in addition to the routine QA/QC program carried out internally by the laboratories. The results and statistical analysis of this QA/QC program are summarized in Appendix I (Tables I-1 and I-2).

Relative standard deviations for the replicate analyses were generally less than 10 percent with the exception of weak acid dissociable cyanide (CN_w) and arsenic (As). The high relative standard deviation for CN_w analysis was related to poor replication of results in one of the five sets of duplicate analysis.

Similarly, recovery of spikes to samples was generally greater than 80 percent, with the exception of CN_w and As analyses. In the case of CN_w analyses, the average recovery is biased by poor results in one of the three spiked samples submitted for analysis.

5. RESULTS AND DISCUSSIONS

The characteristics of the synthetic solutions, gold mine effluents and metal finishing rinsewater samples utilized for the laboratory-scale experiments are summarized in Tables 2, 3 and 4 respectively. The results of the inductively-coupled plasma (ICP) analyses of the effluents from the gold mills 1, 2, 3, 4, and 5 are given in Appendix II.

The composition of the synthetic solutions (Table 2) was designed to assess the effect of metal concentrations (Fe, Cu, Zn, Ni and As) on the cyanide oxidation reactions and the overall removal of metals under batch treatment conditions. All synthetic solutions had similiar initial concentrations of total cyanide (CN_T = 170 to 219 mg. L^{-1}), although the concentration of weak acid dissociable cyanide varied over a four-fold range (CN_W = 52 to 200 $mg \cdot L^{-1}$). The type of metal-cyanide complex present in these synthetic solutions also varied, dependent on the type and concentration of metals (Fe, Cu, Zn, Ni) added.

The gold mill effluents (Table 3) exhibited a widely diverse composition as would be expected considering the range of ore type and mill circuits in use. Total cyanide concentrations ranged from less than 100 $mg \cdot L^{-1}$ to more than 1000 mg. L^{-1}. Similiarly, thiocyanate concentration varied over a range of almost two orders of magnitude (approximately 30 mg. L^{-1} to 2000 mg. L^{-1}). Heavy metal concentrations exhibited similar variation. Only gold mill 2 had an excessively high arsenic concentration (approximately 30 mg. L^{-1}) in the untreated wastewater.

The metal finishing rinsewaters (Table 4) also showed an extreme variation in cyanide content. The first copper cyanide (CuCN) rinsewater evaluted was extremely concentrated (13.5 g $CN_T \cdot L^{-1}$), indicative of an unusually low rate of dilution in the plating circuit. The subsequent sample was more representative of typical rinsewaters, containing approximately 400 mg $CN_T \cdot L^{-1}$. Conversely, the first cadmium cyanide (CdCN) rinsewater was very dilute (15 mg $CN_T \cdot L^{-1}$), indicative of excessive freshwater flow rates in the plating circuit, and the second sample was considerably more concentrated (1,150 mg $CN_T \cdot L^{-1}$). Of the five metal finishing rinsewater samples, the zinc cyanide (ZnCN) sample would be considered most typical in composition. Variation in production rates and product type have a considerable impact on rinsewater quality. Longer term sampling and closer operator

TABLE 2. CHARACTERISTICS OF SYNTHETIC SOLUTIONS

SYNTHETIC #	CONCENTRATION ($mg.L^{-1}$)								
	CN_T	CN_W	SCN	Fe	Cu	As	Zn	Ni	CNO
1	184.	55.4	-	53.4	56.6	-	-	-	-
1A	176.	52.4	-	54.2	60.0	-	92.0	-	-
2	170.	56.4	-	51.0	51.4	7.6	78.0	-	-
3	219.	200.	407.	5.0	53.4	0.65	86.0	2.2	23.

TABLE 3. CHARACTERISTICS OF GOLD MILL EFFLUENTS

GOLD MILL CODE #	CONCENTRATION (mg.L^{-1})								
	CN_T	CN_W	SCN	Fe	Cu	As	Zn	Ni	CNO
1	92.	92.	32.3	<0.1	9.4	0.008	20.6	4.9	4.2
2	680.	514.	112.	68.	126.	30.2	120.	9.2	7.
3	1100.	1005.	436.	19.	186.	0.012	336.	0.2	67.
4	664.	652.	930.	0.9	83.	0.670	81.	116.	29.
5	588.	307.	2076.	97.	5.9	0.106	0.5	0.8	11.
6	770.	616.	1524.	56.	140.	0.5	114.	0.7	38.
7	398.	311.	1844.	29.	186.		80.	1.4	32.

TABLE 4. CHARACTERISTICS OF METAL-FINISHING RINSEWATERS

RINSEWATER TYPE	SAMPLE NO.	CONCENTRATION (mg.L^{-1})							
		CN_T	CN_W	Fe	Cu	Zn	Ni	Cd	CNO
CuCN	1	13,500.	9,500.	328.	8,775.	17.1	7.2	-	19.
	2	405.	373.	7.6	75.	1.1	0.3	-	7.5
CdCN	1	15.	12.2	1.0	0.09	0.41	0.1	0.57	-
	2	1,150.	1,104.	27.	114.	7.2	1.3	160.	-
ZnCN	1	147.	125.	4.1	0.54	60.1	0.1	-	23.

control of freshwater make-up rates would be necessary to ensure that rinsewater samples are representative.

Batch experiments were conducted on the synthetic solutions as prepared. For the gold mill effluents, batch treatments were conducted on each wastewater as received at WTC. In addition, for gold mill 1, copper sulphate (50 mg $Cu.L^{-1}$) was added to catalyze the oxidation reaction and a second batch treatment was conducted. For gold mill 5, copper sulphate was added at two levels of concentration (50 mg $Cu.L^{-1}$) and each spiked wastewater was treated under batch conditions. For gold mill 3, duplicate treatment results were obtained as a result of the batch treatment approach used to initiate the continuous flow experiments.

The copper cyanide rinsewater was treated, under batch conditions, as received. In addition, due to high initial strength of this rinsewater sample, the effluent was diluted 50 times with distilled water to attain a representative concentration of cyanide (approximately 250 mg $CN_T.L^{-1}$) and a second batch treatment was conducted on the diluted sample. Copper, at 50 $mg.L^{-1}$, was added to the zinc cyanide rinsewater and the first cadmium cyanide rinsewater sample. The second cadmium cyanide rinsewater contained adequate copper (114 $mg \cdot L^{-1}$) to catalyze the cyanide oxidation reactions and was treated as received at WTC.

5.1 Results of Batch Experiments

The operating conditions for each batch treatment experiment are summarized in Table 5. The results of the batch tests are discussed in the following subsections.

5.1.1 Batch Treatment of Synthetic Solutions

The results of the batch treatments of synthetic solutions are summarized in Table 6, in terms of the initial and final concentrations of cyanide species and metals. The mass removal efficiencies attained for each synthetic solution are shown in Table 7. In the calculation of mass removal efficiency, the increase in volume of the reaction mixture resulting from the addition of lime for pH control has been taken into account.

The effect of metal concentration on the copper-catalyzed reaction is evident by comparison of the treatment attained for synthetic solution 1

TABLE 5. BATCH REACTION SYSTEM OPERATING CONDITIONS

RUN #	SAMPLE DESCRIPTION	pH CONTROL CHEMICAL	RUN TIME (min.)	INITIAL pH	REDOX (mV, S.H.E.)		FINAL VOLUME (ml)	SO_2 ADDITION	
					INITIAL	FINAL		$g.h^{-1}$	% SO_2
1	Synthetic 1	$Ca(OH)_2$	240.	10.10	292	334	1649	5.0	2.8
2	Synthetic 1A	$Ca(OH)_2$	70.	12.04	420	457	1146	5.4	3.1
3	Synthetic 2	$Ca(OH)_2$	45.	11.90	418	462	1097	6.0	3.4
4	Synthetic 3	$Ca(OH)_2$	60.	12.16	384	499	1140	6.2	3.5
5	Gold Mill	$Ca(OH)_2$	21.	11.96	268	329	1060	6.3	3.6
6	Gold Mill 1 + 50 mg $Cu.L^{-1}$	$Ca(OH)_2$	50.	12.13	324	399	1120	6.1	3.5
7	Gold Mill 2	$Ca(OH)_2$	68.	10.68	262	434	1229	6.6	3.8
8	Gold Mill 3 - Run 1	$Ca(OH)_2$	71.	11.00	326	484	1230	6.6	3.8
9	Gold Mill 3 - Run 2	$Ca(OH)_2$	75.	11.20	333	474	1280	7.1	4.0
10	Gold Mill 4	$Ca(OH)_2$	48.	12.06	144	296	1108	6.3	3.6
11	Gold Mill 5	$Ca(OH)_2$	210.	11.46	270	274	1427	5.8	3.3
12	Gold Mill 5 + 50 mg $Cu.L^{-1}$	$Ca(OH)_2$	145.	11.36	266	319	1450	6.2	3.5
13	Gold Mill 5 + 200 mg $Cu.L^{-1}$	$Ca(OH)_2$	90.	11.53	280	378	1600	7.3	4.1
14	Gold Mill 6	$Ca(OH)_2$	105.	12.25	214	454	1425	7.9	4.5
15	Gold Mill 7	$Ca(OH)_2$	45.	12.05	202	350	1115	6.3	3.8
16	CuCN Rinsewater #1	$Ca(OH)_2$	100.	11.72	254	255	1245	7.6	4.3
17	CuCN Rinsewater #1 - Diluted	$Ca(OH)_2$	38.	12.03	357	407	1100	5.9	3.4
18	CuCN Rinsewater #2	$Ca(OH)_2$	50.	10.50	259	410	1250	6.0	3.4
19	CuCN Rinsewater #2	NaOH	50.	10.50	300	436	1135	5.8	3.3
20	ZnCN Rinsewater	$Ca(OH)_2$	31.	11.98	288	298	1049	5.8	3.3
21	CdCN Rinsewater #1	$Ca(OH)_2$	110.	6.75	415	374	1393	6.0	3.4
22	CdCN Rinsewater #2	$Ca(OH)_2$	90.	11.30	319	404	1420	5.8	3.3
23	CdCN Rinsewater #2	NaOH	120.	11.31	280	300	1300	6.0	3.4

TABLE 6. RESULTS OF BATCH TREATMENTS OF SYNTHETIC SOLUTIONS

SYNTHETIC SOLUTION #	SAMPLE	CONCENTRATION (mg.L^{-1})								
		CN_T	CN_W	SCN	Fe	Cu	Zn	Ni	As	CNO
1	Untreated	184.	55.4	-	53.4	56.6	-	-	-	-
	Treated	38.6	0.33	-	15.0	0.03	-	-	-	-
1A	Untreated	176.	52.4	-	54.2	60.0	92.0	-	-	-
	Treated	0.13	0.05	-	<0.1	0.05	0.36	-	-	-
2	Untreated	170.	56.4	-	51.0	51.4	78.0	-	7.6	-
	Treated	0.42	0.06	-	<0.1	0.05	0.24	-	0.74	-
3	Untreated	219.	200.	407.	5.0	53.4	86.0	2.2	0.65	23.
	Treated	0.30	0.11	276.	<0.1	0.55	2.9	0.3	0.003	328.

TABLE 7. MASS REMOVAL OF CONTAMINANTS AFTER BATCH TREATMENT OF SYNTHETIC SOLUTIONS

SYNTHETIC SOLUTION #		PARAMETER								
		CN_T	CN_W	SCN	Fe	Cu	Zn	Ni	As	CNO
1	Initial Conc.(mg.L^{-1})	184.	55.4	-	53.4	56.6	-	-	-	-
	Removal (%)	65.4	99.0	-	53.7	99.9	-	-	-	-
1A	Initial Conc.(mg.L^{-1})	176.	52.4	-	54.2	60.0	92.0	-	-	-
	Removal (%)	99.9	99.9	-	>99.8	99.9	99.6	-	-	
2	Initial Conc.(mg.L^{-1})	170.	56.4	-	51.0	51.4	78.0	-	7.6	-
	Removal (%)	99.7	99.2	-	>99.8	99.9	99.7	-	89.3	-
3	Initial Conc.(mg.L^{-1})	219.	200.	407.	5.0	53.4	86.0	2.2	0.65	23.
	Removal (%)	99.8	99.9	22.7	>97.7	98.8	96.2	84.4	99.5	+

Note: '+' indicates a net increase in mass after treatment and 1A. These two synthetic solutions were similiar in composition with the exception that approximately 100 mg $Zn.L^{-1}$ was added to synthetic 1A. The treatment of synthetic 1 was incomplete. Although mass removal of free cyanide (CN_w) was approximately 99 percent efficient, there was insufficient copper present to precipitate insoluble metal ferrocyanide compounds such as $Cu_2Fe(CN)_6$. The residual total cyanide remained in solution in the form of a soluble iron cyanide complex.

Upon the addition of zinc to the synthetic solution, the iron precipitation reaction goes to completion as evident from the data generated for synthetic solution 1A. The presence of zinc allows the precipitation of iron and cyanide, probably in the form $Zn_2Fe(CN)_6$ (29). Based on batch treatment data generated by INCO, the ratio of (Cu + Zn + Ni): Fe must exceed 2.0 to allow the complete removal of cyanide and iron from the aqueous phase (29). In synthetic solution 1, this metal ratio was approximately 1.0 compared to a metal ratio of approximately 3.0 in synthetic 1A. Mass removal efficiencies during treatment of synthetic 1A exceeded 99 percent for all components.

Synthetic solution 2 had a similiar composition to synthetic solution 1A with the exception of the addition of 7.6 mg $As.L^{-1}$. Removal efficiencies for cyanide, iron, copper and zinc were comparable for synthetics 1A and 2. In addition, the SO_2/air oxidation process resulted in the removal of approximately 90 percent of the original arsenic in the sample. INCO have not extensively researched the mechanism of arsenic removal during SO_2/air oxidation; however, the removal mechanism may involve oxidation of arsenite to arsenate and subsequent co-precipitation with the metal hydroxides at pH 9.0 (14).

Synthetic solution 3 was the most complex of the synthetic solutions evaluated under batch treatment conditions. As in the treatment of synthetics 1A and 2, adequate copper was present to catalyze the cyanide oxidation reactions and there were adequate levels of Cu, Zn and Ni to ensure complete precipitation of the iron cyanide from the aqueous phase. Removal of arsenic from synthetic solution 3 was virtually complete. Synthetic solution 3 contained approximately 400 mg $SCN.L^{-1}$ and the SO_2/air oxidation process resulted in a net removal of approximately 20 percent of the initial thiocyanate. INCO have shown that in effluents containing copper and nickel, copper catalyzes the oxidation of cyanide and metal cyanide complexes, and nickel catalyzes the oxidation of thiocyanate (11).

Metal concentrations in the treated liquid from synthetic solution 3 were predictably low with the exception of zinc (2.9 $mg.L^{-1}$). There was insufficient cyanide in the aqueous phase to account for the elevated zinc concentration in solution. Zinc solubility at pH 9.0 is approximately 1 $mg.L^{-1}$ (6). It is possible that the elevated levels of cyanate (328 mg $CNO.L^{-1}$) and thiocyanate (276 mg $SCN.l^{-1}$) may effect zinc solubility. Alternatively, the precipitation of zinc hydroxide may be time dependent and insufficient time may have been allowed to ensure attainment of an equilibrium concentration of zinc in the aqueous phase. Considerably more research would be necessary to confirm the chemistry responsible for the high zinc concentration in the treated sample.

The consumption of SO_2 and lime during batch treatment of synthetic solutions is summarized in Table 8. The SO_2 and lime requirements were interpolated from the overall consumption for each experimental run based on the estimated reaction time actually required for completion of the treatment to a stable Redox potential. INCO, during batch experiments, sampled the reaction vessel with time during the reaction and obtained immediate analyses for total cyanide (10,11). Thus, a more precise estimate of reaction time and reagent consumption was obtained. Such intensive sampling and rapid analysis was outside the scope of this investigation.

Based on the data presented in Table 8, reagent consumption during treatment of synthetic 1 was high due to less than optimal composition of the solution in terms of metal concentrations. For synthetic solutions 1A, 2 and 3, SO_2 consumptions were in the range of 14 to 16 g SO_2 per g CN_T removed. The SO_2 requirement was 5 to 6 times the theoretical demand based on oxidation of cyanide to cyanate (Equation 8, Section 3). INCO experimental results have consistently indicated poorer SO_2 utilization under batch treatment conditions compared to continuous flow experiments (10,11). In addition, INCO showed that SO_2 consumption increased with increasing SO_2 addition rates over a range from 0.2 percent to 10.0 percent SO_2 by volume in air (10).

5.1.2 Batch Treatment of Gold Mill Effluents

The results of the batch treatments of gold mill effluents are summarized in Table 9, in terms of the initial and final concentrations of cya-

TABLE 8. REAGENT CONSUMPTION FOR BATCH TREATMENT OF SYNTHETIC SOLUTIONS

SAMPLE TREATED	CN_T $(mg.L^{-1})$		CONSUMPTION (g per g CN_T Removed)		COMMENT
	INITIAL	FINAL	SO_2	$Ca(OH)_2$	
Synthetic 1	184.	38.6	137.8	210.	Incomplete Reaction
Synthetic 1A	176.	0.13	15.4	8.8	Complete
Synthetic 2	170.	0.42	16.2	11.2	Complete
Synthetic 3	219.	0.30	14.2	8.3	Complete

TABLE 9. RESULTS OF BATCH TREATMENTS OF GOLD MILL EFFLUENTS

GOLD MILL #	SAMPLE DESCRIPTION	CONCENTRATION (mg.L^{-1})								
		CN_T	CN_W	SCN	Fe	Cu	Zn	Ni	As	CNO
1	Untreated	92.	92.	32.3	<0.1	9.4	20.6	4.9	0.0008	4.2
	Treated	65.2	39.5	43.	0.6	11.	18.	4.2	0.14	18.0
	+ 50 mg Cu.L^{-1} and Treated	0.06	0.06	36.	0.05	0.84	0.21	0.36	<0.001	111.
2	Untreated	680.	514.	112.	68.	126.	120.	9.2	30.2	7.
	Treated	6.2	0.51	70.	2.1	0.12	0.10	0.2	0.120	623.
3	Untreated	1100.	1005.	436.	19.	186.	336.	0.2	0.012	67.
	Treated - Run 1	0.48	0.22	366.	0.5	5.0	22.	0.1	0.010	1283.
	Treated - Run 2	0.21	0.06	402.	0.08	1.9	9.0	0.05	<0.001	1111.
4	Untreated	664.	652.	930.	0.9	83.	81.	116.	0.670	29.
	Treated	477.	445.	1014.	0.8	79.	74.	104.	0.029	58.
5	Untreated	588.	307.	2076.	97.	5.9	0.5	0.8	0.106	11.
	Treated	197.	17.1	1518.	66.	4.4	0.9	0.4	0.016	19.
	+ 50 mg Cu.L^{-1} and Treated	147.	5.3	1860.	56.	0.11	0.1	<0.1	0.006	181.
	+ 200 mg Cu.L^{-1} and Treated	0.14	0.07	2012.	0.07	0.25	0.09	<0.1	0.005	-
6	Untreated	770.	616.	1524.	56.	140.	114.	0.7	0.50	38.
	Treated	1.16	0.44	1680.	0.2	0.68	0.1	<0.1	-	513.
7	Untreated	398.	311.	1844.	29.	186.	80.	1.4	-	32.
	Treated	0.47	0.33	1596.	0.1	1.0	0.4	<0.1	0.015	420.

nide species and metals. The mass removal efficiencies for each gold mill effluent treatment are summarized in Table 10.

Gold mill 1 effluent contained relatively low concentrations of metals, particularly copper (<10mg $Cu.L^{-1}$). INCO have found inefficient cyanide oxidation under batch treatment conditions in aqueous samples containing less than approximately 50 mg $Cu.L^{-1}$ (29). This observation was confirmed in the batch treatment of gold mill effluent 1. Treatment of the 'as-received' wastewater resulted in a removal of approximately 25 percent of the total cyanide present in the sample. The addition of copper (50 mg $Cu.L^{-1}$) to the wastewater prior to treatment resulted in the virtually complete removal of cyanide (>99.9 percent). Removal of metal contaminants exceeded 90 percent. In this wastewater, after the addition of copper to catalyze the cyanide oxidation reaction, there was virtually quantitative conversion of cyanide to cyanate.

Treatment of gold mill 2 effluent under batch conditions resulted in mass removal efficiencies in excess of 95 percent for all contaminants with the exception of thiocyanate. However, despite high removal efficiencies, the treated effluent contained an elevated concentration of cyanide (6.2 mg $CN_T.L^{-1}$), apparently in the form of an iron cyanide complex. INCO researchers believe that the treatment of wastewaters such as gold mill 2 effluent should be carried out in a two-stage system with an intermediate solid/liquid separation step (34). It appears that high levels of nickel in the effluent create difficulty in achieving low residual CN_T concentrations unless the precipitated solids are removed before the completion of the reaction. Batch treatment time for gold mill effluent 3 was 68 minutes. It is possible that slightly longer treatment time might have produced lower residual cyanide concentrations with this particular wastewater, although copper, nickel and zinc had been virtually eliminated after 68 minutes of treatment. Further work would be required to precisely define the treated effluent quality attainable with this wastewater.

During batch treatment of this particular wastewater, the presence of nickel (9.2 mg $Ni.L^{-1}$) appears to have catalyzed the removal of approximately 25 percent of the thiocyanate present. Of particular interest during treatment of gold mill effluent 2 is the removal of more than 99 percent of the initial arsenic to a treated concentration of 0.12 mg $As.L^{-1}$. Mass balances on nitrogen present in cyanide, thiocyanate and cyanate in the liquid

TABLE 10. MASS REMOVAL OF CONTAMINANTS AFTER BATCH TREATMENT OF GOLD MILL EFFLUENTS

GOLD MILL #	SAMPLE DESCRIPTION	PARAMETERS								
		CN_T	CN_W	SCN	Fe	Cu	Zn	Ni	As	CNO
1	Untreated Conc. (mg.L^{-1})	92.	92.	32.3	<0.1	9.4	20.6	4.9	0.008	4.2
	Treated, Removal (%)	24.9	54.5	+	+	+	7.4	8.2	+	+
	+50 mg Cu.L^{-1} & Treated, Rem.(%)	>99.9	>99.9	+	+	98.4	98.8	91.5	>87.5	+
2	Untreated Conc. (mg.L^{-1})	680.	514.	112.	68.	126.	120.	9.2	30.2	7.
	Treated, Removal (%)	98.8	99.9	23.2	96.2	99.9	99.9	97.3	99.5	+
3	Untreated Conc. (mg.L^{-1})	1100.	1005.	436.	19.	186.	336.	0.2	0.012	67.
	Treated Run 1, Removal (%)	>99.9	>99.9	+	96.7	96.7	91.9	38.5	+	+
	Treated Run 2, Removal (%)	>99.9	>99.9	+	99.5	98.7	96.5	68.0	>89.7	+
4	Untreated Conc. (mg.L^{-1})	664.	652.	930.	0.9	83.	81.	116.	0.670	29.
	Treated, Removal (%)	20.4	24.4	+	1.5	+	+	0.7	95.2	+
5	Untreated Conc. (mg.L^{-1})	588.	307.	2076.	97.	5.9	0.5	0.8	0.106	11.
	Treated, Removal (%)	52.2	92.1	+	2.9	+	+	28.7	78.5	+
	+50 mg Cu.L^{-1} & Treated, Rem.(%)	64.0	97.5	+	16.9	99.7	68.3	>82.0	91.8	+
	+200 mg Cu.L^{-1} & Treated, Rem.(%)	>99.9	>99.9	+	99.8	99.8	71.2	>90.0	92.5	+
6	Untreated Conc. (mg.L^{-1})	770.	616.	1524.	56.	140.	114.	0.7	0.5	38.
	Treated, Removal (%)	99.8	99.9	+	99.5	99.3	99.9	>79.6	-	+
7	Untreated Conc. (mg.L^{-1})	398.	311.	1824.	29.	186.	80.	1.4	-	32.
	Treated, Removal (%)	99.9	99.9	+	99.6	99.4	99.4	>92.0	-	+

NOTE: "+" indicates a net increase in mass after treatment.

phase indicate that only approximately 55 percent of the cyanide removal can be accounted for by oxidation to cyanate. This agrees with the proposed mechanism of precipitation of metal ferrocyanide compounds of the form $Me_2Fe(CN)_6$ (where Me = Cu, Zn and/or Ni) in the presence of iron in the untreated sample.

Duplicate batch treatments of effluent from gold mill 3 yielded comparable results. Removal of total cyanide exceeded 99.9 percent in both cases despite initial concentrations in excess 1 g $CN_T.L^{-1}$. During the second run, treatment time was extended by approximately 4 minutes relative to the first run. This small increase in reaction time resulted in a significant reduction in the treated effluent metal concentrations for all metal species analyzed. However, the residual concentrations for both Cu and Zn in the treated sample exceeded the theoretical solubility of these metals at pH 9.0 (6). The mechanisms discussed in Section 5.1.1 related to the high Zn concentrations after treatment of synthetic solution 3 may also be responsible for the elevated Zn and Cu concentrations in this particular sample after treatment. Alternatively, some complexing agent other than cyanide may be present in this wastewater which is capable of maintaining metals in solution at concentrations in excess of the equilibrium solubility. As noted in Section 5.2.2, SO_2/air treatment of metal rinsewaters resulted in a net generation of ammonia (NH_3-N). Ammonia concentrations were not measured in treated or untreated gold mill effluents. Inco have measured ammonia concentrations up to approximately 20 mg $NH_3\text{-}N \cdot L^{-1}$ in treated gold mill effluents (29). The presence of ammonia would increase the solubility of metals in the treated wastewater. Excessive SO_2 dosages may also keep copper in solution as a sulphite ion complex (34). A more detailed analysis of the treated and untreated wastewater and a review of the chemicals used in the mill circuit would be necessary to confirm the presence of a complexing agent.

The SO_2/air oxidation process resulted in a removal of only approximately 20 percent of the total cyanide from gold mill effluent 4. Discussions with INCO researchers (29) indicated that under batch reaction conditions, wastewaters of similiar composition have relatively slow initial reaction rates. Treatment time for gold mill effluent 4 was approximately 45 minutes at which point the Redox potential appeared to have stabilized, although analytical data indicated incomplete cyanide oxidation. Extended treatment time may have produced improved treatment efficiency in this case.

The effect of copper concentration on the efficiency of the SO_2/air oxidation reactions is evident from the results of batch treatments of effluent from gold mill 5. In the raw wastewater, the (Cu + Zn + Ni): Fe ratio was less than 0.10. As evident from the data in Table 9, there were insufficient concentrations of other metals present to allow precipitation of insoluble metal ferrocyanide complexes. Iron and cyanide remained in solution as a soluble iron cyanide complex under these conditions. The addition of 50 mg $Cu.L^{-1}$ to gold mill effluent 5, increasing the (Cu + Zn + Ni): Fe ratio to approximately 0.6, resulted in an improved removal efficiency of free cyanide due to the catalytic effect of copper. In addition, the percent removal of total cyanide increased from approximately 52 percent to 64 percent due to precipitation of $Cu_2Fe(CN)_6$. A further increase in the concentration of copper in the wastewater sample by the addition of 200 mg $Cu.L^{-1}$ allowed the cyanide removal reactions to continue to completion. At this level of copper addition, the initial metal ratio (Cu + Zn + Ni): Fe was approximately 2.1. Removals of total and weak acid dissociable cyanide exceeded 99.9 percent following the addition of 200 mg $Cu.L^{-1}$ to this wastewater.

Effluents from gold mills 6 and 7 were similar in character. Both contained relatively high concentrations of iron (56 and 29 $mg.L^{-1}$, respectively); however, copper and zinc were present in both samples at adequate concentrations to catalyze the cyanide oxidation reactions and to allow precipitation of insoluble metal ferrocyanide complexes. During batch treatment of both of these effluents, the percent removal of total and weak acid dissociable cyanide exceeded 99 percent. Removal of all metal species (with exception of nickel which was reduced to the level of detection) also exceeded 99 percent. After batch treatment of effluents from both gold mills 6 and 7, the residual weak acid dissociable cyanide concentration was somewhat higher than in the other batch treatments which proceeded to completion (0.44 and 0.33 $mg.L^{-1}$, respectively) despite the high removal efficiency attained. Although the results of single batch experiments are inadequate to precisely define the treated quality attainable for a specific wastewater, an increase in the batch treatment time might result in further removal of the residual cyanide present after treatment of these particular effluents.

The consumption of SO_2 and lime for batch treatment of the gold mill effluents is summarized in Table 11. The experimental runs have been rearranged and presented in order of increasing initial copper concentration

TABLE 11. REAGENT CONSUMPTION FOR BATCH TREATMENT OF GOLD MILL EFFLUENTS

SAMPLE TREATED	INITIAL Cu CONC. (mg.L^{-1})	CN_T CONC (mg.L^{-1})		CONSUMPTION (g per g CN_T Rem.)		COMMENT
		INITIAL	FINAL	SO_2	$Ca(OH)_2$	
Gold Mill 5	5.9	588.	197.	65.8	54.3	Incomplete
Gold Mill 1	9.4	92.	65.2	96.1	102.2	Incomplete
Gold Mill 5 + 50 mg Cu.L^{-1}	55.9	588.	147.	39.6	45.6	Incomplete
Gold Mill 1 + 50 mg Cu.L^{-1}	59.4	92.	0.06	44.4	42.3	Complete Reaction
Gold Mill 4	83.	664.	477.	36.9	31.1	Incomplete
Gold Mill 2	126.	680.	6.2	9.4	11.3	Complete Reaction
Gold Mill 6	140.	770.	1.16	18.1	20.5	Complete Reaction
Gold Mill 7	186.	398.	0.47	11.8	10.7	Complete Reaction
Gold Mill 3 - Run 1	186.	1100.	0.48	6.1	6.9	Complete Reaction
Gold Mill 3 - Run 2	186.	1100.	0.21	7.0	8.6	Complete Reaction
Gold Mill 5 + 200 mg Cu.L^{-1}	205.9	588.	0.14	14.5	24.7	Complete Reaction

to provide an indication of the catalytic effect of copper on the SO_2/air oxidation reactions. In general, the data indicate a reduction in chemical requirements at increasing initial copper concentration, despite an order of magnitude variation in the initial cyanide concentrations and considerable variability in the metal composition of the effluent samples. A similiar trend toward improved chemical utilization at increasing copper concentrations has been reported by INCO (10,11).

Batch treatment of effluent from gold mill 5 at three levels of initial copper concentration (5.9, 55.9 and 205.9 $mg.L^{-1}$) provides a specific example of copper catalysis of the SO_2/air oxidation reactions. Sulphur dioxide utilization efficiency increased more than four-fold upon the addition of 200 mg $Cu.L^{-1}$. The optimal initial copper concentration for a specific wastewater appears to be related to the metal content of the wastewater and independent of initial cyanide concentration over the range of concentrations evaluated in these investigations.

With the exception of the results obtained during treatment of effluents from gold mill 2 and gold mill 3, SO_2 consumption was significantly higher than the theoretical requirement based on Equation (8). The reaction time used to calculate reagent consumptions for the batch tests were estimated based on the time required to attain a stable Redox potential and the inherent inaccuracy in this method of determining SO_2 and lime consumption undoubtedly contributed to the high chemical requirements shown in Table 11. In addition, reagents requirements have been shown to be consistently lower under continuous flow conditions compared to batch conditions (10,11). Continuous flow experiments would be necessary to define the chemical requirements and associated costs for full-scale treatment of these specific wastewaters.

5.1.3 Batch Treatment of Metal Finishing

The results of the batch treatments of rinsewaters from cyanide-based metal plating operations are summarized in Table 12, in terms of the initial and final concentrations of cyanide species and metals. The mass removal efficiencies for each batch treatment are summarized in Table 13.

Treatment of the concentrated copper cyanide (CuCN) rinsewater (batch run 16) did not continue to completion. After approximately 100

TABLE 12. RESULTS OF BATCH TREATMENTS OF METAL FINISHING RINSEWATERS

BATCH RUN #	RINSEWATER TYPE	SAMPLE DESCRIPTION	pH CONTROL CHEMICAL	CONCENTRATION (mg.L^{-1})							
				CN_T	CN_W	Fe	Cu	Zn	Ni	Cd	CNO
16	CuCN	Sample 1 - Untreated	-	13500.	9500.	328.	8775.	17.1	7.2	-	19.
		Sample 1 - Treated	$Ca(OH)_2$	7650.	3770.	107.	8520.	0.2	4.6	-	-
17	CuCN	Sample 1 - Diluted (1:50)	-	264.	225.	8.4	184.	0.47	0.1	-	3.4
		Sample 1 - Diluted & Treated	$Ca(OH)_2$	0.05	0.06	0.03	1.39	0.03	<0.05	-	297.
	CuCN	Sample 2 - Untreated	-	405.	373.	7.6	75.	1.1	0.28	-	7.5
18		Sample 2 - Treated	$Ca(OH)_2$	0.3	-	0.1	7.97	0.12	<0.02	-	376.
19		Sample 2 - Treated	NaOH	0.4	-	0.1	8.44	0.02	<0.02	-	415.
	ZnCN	Untreated	-	147.	125.	4.1	0.54	60.1	0.1	-	23.
20		+ 50 mg Cu.L^{-1} and Treated	$Ca(OH)_2$	0.12	0.11	0.4	3.15	1.1	0.1	-	162.
	CdCN	Sample 1 - Untreated	-	15.	12.2	1.0	0.09	0.41	0.1	0.57	-
21		+ 50 mg Cu.L^{-1} and Treated	$Ca(OH)_2$	0.02	0.02	0.4	20.0	0.57	0.1	0.70	-
	CdCN	Sample 2 - Untreated	-	1150.	1104.	27.	114.	7.2	1.3	160.	-
22		Sample 2 - Treated	$Ca(OH)_2$	5.14	1.74	0.4	1.45	0.06	0.1	6.3	1124.
23		Sample 2 - Treated	NaOH	415.	345.	0.8	81.	5.6	1.5	20.	222.

TABLE 13. MASS REMOVAL OF CONTAMINANTS AFTER BATCH TREATMENT OF METAL FINISHING RINSEWATERS

BATCH RUN #	RINSEWATER TYPE	SAMPLE DESCRIPTION	pH CONTROL CHEMICAL	CONCENTRATION ($mg.L^{-1}$)						
				CN_T	CN_W	Fe	Cu	Zn	Ni	Cd
	CuCN	Sample 1, Untreated Conc. ($mg.L^{-1}$)	-	13500.	9500.	328.	8775.	17.1	7.2	-
16		Treated, Removal (%)	$Ca(OH)_2$	29.5	50.6	59.3	+	99.5	20.5	-
	CuCN	Sample 1, Diluted (1:50) Conc. ($mg.L^{-1}$)	-	264.	225.	8.4	184.	0.47	0.1	-
17		Diluted & Treated, Removal (%)	$Ca(OH)_2$	>99.9	>99.9	99.5	98.9	90.4	>25.0	-
	CuCN	Sample 2, Untreated Conc. ($mg.L^{-1}$)	-	405.	373.	7.6	75.	1.1	0.28	-
18		Treated, Removal (%)	$Ca(OH)_2$	>99.9	>99.9	98.2	86.7	86.4	>91.1	-
19		Treated, Removal (%)	NaOH	>99.9	>99.9	98.4	87.2	97.9	>91.9	-
	ZnCN	Untreated Conc. ($mg.L^{-1}$)	-	147.	125.	4.1	0.54	60.1	0.1	-
20		+ 50 mg $Cu.L^{-1}$ & Treated, Removal (%)	$Ca(OH)_2$	99.9	99.9	89.8	93.5	98.1	+	-
	CdCN	Sample 1, Untreated Conc. ($mg.L^{-1}$)	-	15.	12.2	1.0	0.09	0.41	0.1	0.57
21		+ 50 mg $Cu.L^{-1}$ & Treated, Removal (%)	$Ca(OH)_2$	99.8	99.7	44.3	44.4	+	+	+
	CdCN	Sample 2, Untreated Conc. ($mg.L^{-1}$)	-	1150.	1104.	27.	114.	7.2	1.3	160.
22		Treated, Removal (%)	$Ca(OH)_2$	99.4	99.8	97.9	98.2	98.8	89.1	94.4
23		Treated, Removal (%)	NaOH	53.1	59.4	96.1	7.6	+	+	83.8

Note: "+" indicates a net increase in mass after treatment.

minutes of treatment, little change in the sample Redox potential was observed and the reaction was terminated. Based on the initial cyanide concentration and the theoretical SO_2 requirement, approximately 4.5 hours of batch treatment would have been required under ideal conditions at the SO_2 application rate of the batch tests. On the basis of typical SO_2 utilization efficiencies under batch treatment conditions, more than 8 hours of treatment might have been necessary to reduce the cyanide concentration to low levels. Upon dilution of the concentrated CuCN rinsewater to a cyanide concentration considered typical of normal operation in a metal finishing process, the SO_2/air oxidation reactions continued to completion (batch run 17). Mass removal of cyanide exceeded 99.9 percent. The total cyanide concentration of the treated sample was reduced to less than 0.1 mg $CN_T.L^{-1}$.

Batch treatments of the second CuCN rinsewater were conducted using both lime (run 18) and sodium hydroxide (run 19) for pH control. As shown in Tables 12 and 13, there was no significant difference in the treatment efficiency attained using lime or sodium hydroxide. Total cyanide was reduced to less than 1 $mg{\cdot}L^{-1}$ in both cases, equivalent to a removal efficiency in excess of 99.9 percent. In both cases, however, the residual copper concentration exceeded the equilibrium solubility concentrations at pH 9.0 (6).

The use of sodium hydroxide reduced the dry weight of sludge generated after treatment by approximately 20 percent relative to treatment of the same sample using lime for pH control. In addition, scaling of pH and Redox potential electrodes and gas diffusers encountered when lime was applied to the system were eliminated by the use of sodium hydroxide.

The virtual absence of copper in the zinc cyanide (ZnCN) rinsewater necessitated the supplemental addition of copper to catalyze the SO_2/air oxidation reactions. Batch treatment in the presence of approximately 50 mg $Cu{\cdot}L^{-1}$ resulted in predictable removal efficiencies for all contaminants. Overall removal of cyanide from the ZnCN rinsewater was approximately 99.9 percent complete.

As noted previously, the composition of the first cadmium cyanide (CdCN) rinsewater was atypical in terms of the cyanide and metal concentrations. Although cyanide species were readily reduced to low levels (<0.1 mg $CN_T.L^{-1}$), the feasibility of the SO_2/air oxidation process cannot be adequately defined on the basis of batch treatment of this dilute rinsewater. The second CdCN rinsewater treated effectively using lime for pH control (batch run 22). Although the residual cyanide concentration was approximately 5 mg $CN_T \cdot L^{-1}$, the removal efficiency exceeded 99 percent. A slight increase in the 90 minute reaction time may have reduced the treated cyanide concentration to levels approaching 1 $mg \cdot L^{-1}$. Removal of cadmium from the rinsewater exceeded 94 percent to a treated concentration of approximately 6 mg $Cd \cdot L^{-1}$. When sodium hydroxide was used for pH control (batch run 23) during treatment of the second CdCN rinsewater sample, treatment efficiency decreased significantly. After 120 minutes of treatment, cyanide removal was approximately 50 percent efficient. The addition of calcium carbonate to the reaction vessel after 120 minutes of treatment resulted in a rapid increase in the system Redox potential, attaining a level of +414 mV. (S.H.E.) after a further 30 minutes of treatment with SO_2, approximately equivalent to the final Redox potential in run 22 when lime was used for pH control. No final treated sample was taken for analysis after the addition of $CaCO_3$. It appears that, at least in the case of the CdCN rinsewater sample, calcium ions either catalyze or actively participate in the cyanide oxidation reactions. INCO have not encountered similar problems in treating gold mill effluents using sodium hydroxide for pH control or using sodium sulphite (Na_2SO_3) as the source of SO_2 and for pH control (29). Further work would be required to define the contribution of calcium ions to the cyanide oxidation reactions and to determine if the problems encountered in treating the CdCN rinsewater are specifically related to the constituents of the waste.

Chemical requirements for batch treatment of the metal finishing rinsewaters are summarized in Table 14. Sulphur dioxide consumption during batch treatment of concentrated CuCN rinsewater approached the theoretical requirement of 2.47 g SO_2 per g CN_T removed. Upon dilution, chemical consumptions increased significantly, to approximately 9.5 g SO_2 per g CN_T removed. Treatment of the second CuCN rinsewater resulted in comparable SO_2 consumptions. There was no significant difference in the sulphur dioxide requirements between batch runs conducted with lime and sodium hydroxide addition. Treatment of the ZnCN rinsewater in the presence of supplemental copper resulted in an SO_2 consumption of 13.6 g per CN_T removed.

The extremely high demand for SO_2 measured during batch treatment of the first CdCN rinsewater (915 g per g CN_T) was the result of difficulties in defining the reaction endpoint in a dilute solution on the basis of

TABLE 14. REAGENT CONSUMPTION FOR BATCH TREATMENT OF METAL FINISHING RINSEWATERS

SAMPLE TREATED	CN_T CONC. (mg.L^{-1})		CONSUMPTION (g per g CN_T Removed)			COMMENT
	INITIAL	FINAL	SO_2	$Ca(OH)_2$	NaOH	
CuCN - Sample 1	13,500.	9,500.	3.2	2.4	-	Incomplete Reaction
CuCN - Diluted Sample 1	264.	0.05	9.5	14.8	-	Complete
CuCN - Sample 2	405.	0.03	7.4	13.7	-	Complete
CuCN - Sample 2	405.	0.01	7.1	-	8.0	Complete
ZnCN	147.	0.12	13.6	4.9	-	Complete
CdCN - Sample 1	15.	0.02	915.	N.A.	-	Low Initial pH
CdCN - Sample 2	1,150.	5.14	7.6	13.6	-	Complete
CdCN - Sample 2	1,150.	415.	19.5	-	19.7	Incomplete Reaction

Redox potential, and is not considered indicative of the requirement for treatment of a representative CdCN rinsewater. Subsequent treatment of the second CdCN rinsewater was accomplished with chemical consumptions comparable to those required for treatment of the CuCN rinsewater samples when lime was used for pH control. The effect of using sodium hydroxide for pH control on the efficiency of the oxidation reactions is apparent from these data. The SO_2 consumption increased more than two-fold to 19.5 g per g CN_T removed when sodium hydroxide was used.

5.1.4 Mass Balances on Metal and Cyanide Species

In order to determine the relative distribution of cyanide and metal species in the liquid and solid phases after treatment, analyses were conducted on the precipitates recovered following batch treatment of synthetic solution 3 and following batch treatment of effluent from gold mill 3 (Run 1).

The results of the mass balance generated as a result of analysis of the liquid and solid phases produced from treatment of synthetic solution 3 are summarized in Table 15. Of the fraction of nitrogen accounted for after treatment, less than 1 percent was present in the precipitated solids. Cyanate, generated from the oxidation of cyanide and thiocyanate, and the residual unreacted thiocyanate accounted for virtually all of the nitrogen initially present in the sample as CN_T and SCN. The precipitated solids contained only 85 mg CN_T per gram on a dry weight basis. The ratio of iron to cyanide in the precipitated solids fraction was approximately 40:1, far in excess of the stoichiometric ratio of iron to cyanide in metal ferrocyanide compounds of the form $Me_2Fe(CN)_6$. Of the metals accounted for in the treated synthetic sample, more than 95 percent of the iron, copper and zinc were recovered, probably as metal hydroxides, in the solid phase.

A similiar trend of cyanide and metal distributions upon treatment of effluent from gold mill 3 was noted, as summarized in Table 16. More than 99.9 percent of the nitrogen present in the system after treatment was recovered in the liquid phase as cyanate, generated by oxidation of cyanide, and thiocyanate, which was virtually unaffected by the treatment process. The concentration of cyanide in the precipitated solids was 42 mg $CN_T.g^{-1}$, on a dry weight basis. More than 90 percent of the initial copper and zinc

TABLE 15. DISTRIBUTION OF CYANIDE AND METAL SPECIES IN LIQUID AND SOLID PHASES AFTER TREATMENT OF SYNTHETIC SOLUTION 3

	UNTREATED SAMPLE[1]	TREATED SAMPLE		
		LIQUID PHASE[2]	SOLID PHASE[3]	TOTAL
TOTAL NITROGEN PRESENT IN CN_T, CNO AND SCN (mg)	223.3	181.9	0.2	182.1
PERCENT OF NITROGEN RECOVERED	-	85.1	0.1	85.2
MASS OF METALS PRESENT (mg)				
Fe	5.0	<0.1	6.8	6.8
Cu	53.2	0.6	43.3	43.9
Zn	85.7	3.1	82.6	85.7
Ni	2.2	0.3	1.5	1.8
PERCENT OF METALS RECOVERED				
Fe	-	<2.0	136.0	136.0
Cu	-	1.1	81.4	82.5
Zn	-	3.6	96.4	100.0
Ni	-	13.6	68.2	81.8

NOTE:
1. Initial Liquid Volume = 0.997 L
2. Final Liquid Volume = 1.052 L
3. Final Dry Solid Mass = 1.89 g

TABLE 16. DISTRIBUTION OF CYANIDE AND METAL SPECIES IN LIQUID AND SOLID PHASES AFTER TREATMENT OF GOLD MILL 3 EFFLUENT

	UNTREATED SAMPLE[1]	TREATED SAMPLE		
		LIQUID PHASE[2]	SOLID PHASE[3]	TOTAL
TOTAL NITROGEN PRESENT IN CN_T, CNO AND SCN (mg)	717.7	611.4	0.3	611.7
PERCENT OF NITROGEN RECOVERED	-	85.2	<0.1	85.2
MASS OF METALS PRESENT (mg)				
Fe	18.9	5.4	18.9	24.3
Cu	185.4	6.0	157.5	163.5
Zn	335.0	26.1	235.7	261.8
Ni	0.2	0.1	0.3	0.4
PERCENT OF METALS RECOVERED				
Fe	-	28.6	100.0	128.6
Cu	-	3.2	85.0	88.2
Zn	-	7.8	70.3	78.1
Ni	-	-	-	-

NOTE:
1. Initial Liquid Volume = 0.997 L
2. Final Liquid Volume = 1.184 L
3. Final Dry Solid Mass = 11.33 g

recovered after treatment was present in the precipitate at concentrations of 1.39 percent and 2.08 percent, respectively. The iron to cyanide ratio in the solid fraction was approximately 40:1, indicating that iron hydroxide precipitation was the primary mechanism for iron removal from this sample.

Both synthetic sample 3 and gold mill 3 effluent contained relatively low concentrations of iron, 5 mg $Fe.L^{-1}$ and 19 mg $Fe.L^{-1}$, respectively. INCO has reported the absence of cyanide in the metal hydroxide precipitates generated during treatment of solutions which do not contain iron (10). The low concentration of cyanide observed in the precipitates generated by treatment of these two solutions confirms this observation.

The concentration of metals in the precipitated solids is dependent on the initial concentration of metals in the liquid sample and the quantity of lime required during SO_2/air oxidation reactions. Concentrations of less than 5 percent copper and zinc in the precipitated solids resulted from these batch treatment experiments. INCO have generated metal hydroxide precipitates containing up to 18.8 percent copper and up to 10.7 percent zinc during continuous flow experiments (10,11). The higher concentrations are primarily a result of the lower $Ca(OH)_2$ requirements under continuous flow conditions. In specific instances, these concentrated metal hydroxide precipitates may have a potential metallurgical value.

5.2 Results of Continuous Flow Experiments

5.2.1 Continuous Flow Treatment of Gold Mill Effluents

The results of the continuous flow SO_2/air oxidation experiments conducted on effluent from gold mill 3 are summarized in Tables 17 and 18 for the two hydraulic loading conditions evaluated.

At a nominal hydraulic retention time (HRT) of 40 minutes in each reactor, the cyanide oxidation reactions were virtually complete in the first stage of the two-stage reaction system. Removal of total cyanide exceeded 99.9 percent in the first reactor. Approximately 66 percent of the cyanide was removed by oxidation to cyanate. Thiocyanate was virtually unaffected by the SO_2/air oxidation.

All metal species were removed to concentrations approaching the theoretical solubility at pH 9.0 with the exception of zinc. The high residual zinc concentration confirms the findings of the batch experiments with this particular wastewater (Section 5.1.2).

TABLE 17. RESULTS OF CONTINUOUS FLOW TREATMENT OF GOLD MILL 3 EFFLUENT - RUN 1

CONDITIONS: Two Stage Reactor System
Nominal Hydraulic Retention Time per Reactor = 40 min.
Air Flow: Reactor 1 - 1.00 $L \cdot min^{-1}$
Reactor 2 - 0.43 $L \cdot min^{-1}$
SO_2 Dosage: Reactor 1 - 4.38 $g \cdot L^{-1}$ (3.7% SO_2 in air, by volume)
Reactor 2 - 2.05 $g \cdot L^{-1}$ (4.0% SO_2 in air, by volume)
Temperature: 22°C Reactor pH = 9.0

STREAM	CONCENTRATION ($mg \cdot L^{-1}$)									ORP (mV,S.H.E.)
	CN_T	CN_W	SCN	CNO	Fe	Cu	Zn	Ni	As	
Feed	1076.	1012.	500.	67.	22.	180.	306.	0.15	0.012	353
Reactor 1	0.42	0.33	484.	-	0.11	5.4	33.	<0.02	-	439
Reactor 2	0.13	0.12	496.	1215.	0.07	1.2	16.	<0.05	<0.001	474

CHEMICAL CONSUMPTION	$g\ SO_2 \cdot g\ CN_T^{-1}$	$g\ Ca(OH)_2 \cdot g\ CN_T^{-1}$
Reactor 1	4.06	7.24
Reactor 2	-	-

TABLE 18. RESULTS OF CONTINUOUS FLOW TREATMENT OF GOLD MILL 3 EFFLUENT - RUN 2

CONDITIONS: Two Stage Reactor System
Nominal Hydraulic Retention Time per Reactor = 24 min.
Air Flow: Reactor 1 - 1.00 $L \cdot min^{-1}$
Reactor 2 - 0.43 $L \cdot min^{-1}$
SO_2 Dosage: Reactor 1 - 2.61 $g \cdot L^{-1}$ (3.7% SO_2 in air, by volume)
Reactor 2 - 1.22 $g \cdot L^{-1}$ (4.0% SO_2 in air, by volume)
Temperature: 22°C Reactor pH = 9.0

STREAM	CONCENTRATION ($mg \cdot L^{-1}$)									ORP (mV,S.H.E.)
	CN_T	CN_W	SCN	CNO	Fe	Cu	Zn	Ni	As	
Feed	1076.	1012.	500.	67.	22.	180.	306.	0.15	0.012	353
Reactor 1	130.	120.	484.	1103.	0.07	162.	17.	<0.20	<0.001	434
Reactor 2	0.21	0.19	450.	1422.	0.08	2.1	27.	<0.05	<0.001	454

CHEMICAL CONSUMPTION	$g\ SO_2 \cdot g\ CN_T^{-1}$	$g\ Ca(OH)_2 \cdot g\ CN_T^{-1}$
Reactor 1	2.76	2.47
Reactor 2	9.40	18.0
Overall	3.56	5.03

Chemical consumptions in the first stage reactor were 4.06 g SO_2 per g CN_T removed and 7.24 g $Ca(OH)_2$ per g CN_T removed. The lower chemical requirements under continuous flow conditions relative to the batch treatment results presented in Section 5.1.2 confirm the findings presented by INCO (10,11). The results indicate an SO_2 utilization efficiency of approximately 61 percent relative to the theoretical requirement of 2.47 g SO_2 per g CN_T removed. Chemical consumption in the second stage reactor was high due to small residual concentration of cyanide remaining in solution for oxidation.

At a nominal hydraulic retention time of 24 minutes in each reactor, cyanide destruction was approximately 88 percent complete in the first stage and continued to completion in the second stage. Overall cyanide removal efficiency exceeded 99.9 percent. Treated effluent quality at increased hydraulic loading was similiar to that attained at a nominal HRT of 40 minutes per reactor. As in the initial continuous flow experiment and the batch experiments conducted on wastewater from gold mill 3, elevated zinc concentrations were present in the treated effluent.

Improved SO_2 and lime utilization was achieved in the first stage reactor at a nominal HRT of 24 minutes compared to the utilization efficiency in experiment 1 at a nominal HRT of 40 minutes. Relative to the theoretical requirement, SO_2 utilization efficiency in reactor 1 was approximately 90 percent. In the second stage, chemical consumption was significantly higher; however, overall chemical consumption in the two-stage system at higher hydraulic loading was lower than the consumption in the first stage reactor in experiment 1. More detailed continuous flow experiments would be necessary to optimize the number and type of reactors relative to the chemical consumption during treatment of this wastewater.

Effluent from gold mill 6 was treated under continuous flow conditions in a single-stage reactor system with the results shown in Table 19. Cyanide removal efficiency improved under continuous flow treatment relative to the results attained under batch treatment conditions (Table 9). Total cyanide removal exceeded 99.9 precent to a residual level of less than 1 mg $CN_T \cdot L^{-1}$, despite an elevated concentration of iron in the untreated sample. However, chemical consumptions during continuous treatment were relatively high (16.6 g SO_2 and 23.7 g $Ca(OH)_2$ per g CN_T removed) and did not show a significant decrease compared to the consumptions measured during

TABLE 19. RESULTS OF CONTINUOUS FLOW TREATMENT OF GOLD MILL 6 EFFLUENT

CONDITIONS: One Stage Reactor System
Nominal Hydraulic Retention Time = 90 min.
Air Flow: 1.32 $L \cdot min^{-1}$
SO_2 Dosage: 12.78 $g \cdot L^{-1}$
% SO_2 in Air: 3.7% $^V/v$
Temperature: 22°C   Reactor pH = 9.0

STREAM	CONCENTRATION ($mg \cdot L^{-1}$)								ORP (mV,S.H.E.)	Reagent Consumption ($g \cdot gCN_T^{-1}$)	
	CN_T	CN_W	SCN	CNO	Fe	Cu	Zn	Ni		SO_2	$Ca(OH)_2$
Feed	770.	616.	1524.	38.4	56.	140.	114.	0.65	214	-	-
Effluent	0.61	0.11	-	-	0.09	1.14	-	0.09	452	16.6	23.7

batch treatment of this wastewater (Table 11). The nominal hydraulic retention time for the continuous flow experiment was 90 minutes, selected on the basis of the results of the batch treatment. Further optimization of the SO_2 application rate and reactor retention time would be necessary to precisely define the optimum operating conditions for continuous treatment of this wastewater.

A series of continuous flow experiments were conducted on the effluent from gold mill 7 with the results shown in Table 20. In a one stage reactor system, nominal hydraulic retention times were varied from 15 to 45 minutes at SO_2 dosages in the range from approximately 2 to 5 $g \cdot L^{-1}$. Based on these results, optimum treatment in terms of effluent quality and reagent consumption was attained at an HRT of 30 minutes and an SO_2 dosage of 3.4 $g \cdot L^{-1}$. Process performance appears to be relatively unaffected by reactor HRT over the range of conditions evaluated. Increased SO_2 dosage results in significant improvements in process efficiency, but with substantial increases in chemical consumption.

5.2.2 Continuous Flow Treatment of Metal Finishing Rinsewaters

Continuous flow SO_2/air oxidation experiments were conducted on the second CuCN rinsewater obtained for evaluation. A single stage reactor system was used. Both lime and sodium hydroxide were utilized for pH control in the continuous flow experiments. Results of the continuous flow tests are summarized in Table 21.

As indicated by the results obtained at a hydraulic retention time of 30 minutes, treatment efficiency was not significantly affected by the choice of chemical used for pH control. Total cyanide removal efficiency in both cases exceeded 99 percent to levels approaching 1 mg $CN_T \cdot L^{-1}$. Lime addition resulted in an improvement in the removal of copper from the rinsewater relative to sodium hydroxide addition on the basis of these experimental runs. The SO_2 requirements in both cases were comparable, approximately 7 g SO_2 per g CN_T removed. The use of sodium hydroxide for pH control reduced the mass of solids generated by the treatment process by approximately 25 percent relative to the quantity generated for the same degree of treatment with lime addition.

TABLE 20. RESULTS OF CONTINUOUS FLOW TREATMENT OF GOLD MILL 7 EFFLUENT

CONDITIONS: One Stage Reactor System

RUN #	NOMINAL HRT (Min)	AIR FLOW ($L \cdot min^{-1}$)	SO_2 DOSAGE ($g \cdot L^{-1}$)	% SO_2 ($^v/v$) IN AIR
1	15	1.177	1.97	3.8
2	15	3.534	4.95	3.2
3	45	0.391	2.25	4.4
4	30	1.177	3.40	3.3
5	45	1.177	5.00	3.2

STREAM	CONCENTRATION ($mg \cdot L^{-1}$)					ORP (mV,S.H.E.)	REAGENT CONSUMPTION ($g \cdot gCN_T^{-1}$)	
	CN_T	CN_W	Fe	Cu	Ni		SO_2	$Ca(OH)_2$
Feed	398.	311.	29.	186.	1.4	202	-	-
Effluent - Run 1	46.9	-	2.1	153.	1.0	249	5.61	5.62
Effluent - Run 2	1.99	-	0.22	25.	0.04	339	12.5	15.2
Effluent - Run 3	55.1	-	6.3	93.	<0.02	320	6.57	-
Effluent - Run 4	0.69	0.42	0.18	15.	0.12	344	8.56	3.60
Effluent - Run 5	0.33	0.24	0.15	6.3	0.23	361	12.6	6.98

TABLE 21. RESULTS OF CONTINUOUS FLOW TREATMENT OF COPPER RINSEWATER

CONDITIONS : One Stage Reactor System

RUN #	NOMINAL HRT (Min)	AIR FLOW ($g \cdot L^{-1}$)	SO_2 DOSAGE ($g \cdot L^{-1}$)	%SO_2 ($^{v}/v$) in AIR	pH CONTROL CHEMICAL
1	20	1.00	1.94	3.3	NaOH
2	30	1.00	2.91	3.3	NaOH
3	30	1.00	2.87	3.3	$Ca(OH)_2$

STREAM	CONCENTRATION ($mg \cdot L^{-1}$)									ORP (mV,S.H.E.)	REAGENT CONSUMPTION ($g \cdot g\ CN_T^{-1}$)		
	CN_T	CN_W	SCN	CNO	NH_3-N	Fe	Cu	Ni	Zn		SO_2	$Ca(OH)_2$	NaOH
Feed	405.	373.	4.9	7.5	2.6	7.6	75.	0.28	1.1	330	-	-	-
Effluent - Run 1	0.4	0.16	0.0	479.	22.4	0.1	12.6	<0.10	0.01	404	4.80	-	7.99
Effluent - Run 2	1.13	0.35	0.0	502.	25.6	0.1	11.1	0.10	0.02	494	7.20	-	7.08
Effluent - Run 3	0.71	0.22	0.4	428.	20.5	0.2	2.5	<0.10	0.01	424	7.10	15.3	-

Optimum treatment in terms of effluent quality and reagent consumption was attained at a nominal HRT of 20 minutes. Sulphur dioxide consumption at these operating conditions was 4.8 g SO_2 per g CN_T removed, and the treated effluent cyanide concentration was reduced to 0.4 $mg \cdot L^{-1}$.

A net increase in the concentration of ammonia in the treated rinsewater was noted in all three continuous flow experiments, probably generated as a result of the hydrolysis of cyanate. The presence of ammonia in the treated samples may be partially responsible for the elevated metal concentrations noted in a number of the batch and continuous flow experiments conducted during this investigation. Ammonia (NH_3) has been reported to be acutely toxic to freshwater biota at concentrations ranging from 0.01 $mg \cdot L^{-1}$ (32) to 2.0 $mg \cdot L^{-1}$ (33), depending on the species, system pH and temperature. Therefore, ammonia generation during treatment is of particular concern in instances of direct discharge of treated wastewaters from either gold mills or metal finishing facilities to the receiving waters. Further investigations are necessary to define the mechanisms controlling ammonia generation and the concentrations of ammonia present after treatment of other metal finishing rinsewaters and of gold mill effluents.

6. CONCEPTUAL PROCESS DESIGN AND COSTING FOR GOLD MILL EFFLUENT TREATMENT

Conceptual process design details for an SO_2/air oxidation system to treat wastewater from a model gold mill were developed based on the characteristics and treatability data generated for effluent from gold mill 3. The process flowsheet for the cyanide destruction system is shown schematically in Figure 3.

6.1 Design Basis

Design flow for the model treatment facility was 130 $m^3.d^{-1}$. A single-stage reactor system was selected for the conceptual design based on the data generated in the continuous flow laboratory experiments. Although improved chemical consumption was attained in the two-stage system, the simplified control requirements and significantly reduced capital costs associated with a one-stage system favoured this design approach for this wastewater. In some instances, depending on the characteristics of the wastewater, a two-stage system may be necessary. Hydraulic retention time in the reactor was conservatively designed for 50 minutes to allow for fluctuations in the wastewater strength.

As the majority of gold mills utilize hydrated lime in the mill circuits, a dedicated lime slurry makeup system was not provided for the treatment facility. Automatic pH control equipment was provided. Redox potential in the reactor would be continuously recorded but not utilized as an automatic process control variable for the system. Sulphur dioxide requirements were based on the chemical consumption data for the continuous flow laboratory-scale experiments. For the purposes of the conceptual design, liquid SO_2 would be utilized. In specific instances where roaster gases containing SO_2 are available, utilization in the cyanide destruction process would have considerable environmental and economical advantages. Alternately, SO_2 could be generated on-site by the combustion of elemental sulphur.

Provision for removal of precipitated metal hydroxides was included in the conceptual design for instances of direct discharge to a receiving water. Settling characteristics of the suspended particulate matter were not evaluated during the laboratory-scale experiments. The design was based on conservative estimates of typical settling velocities for metal hydroxide

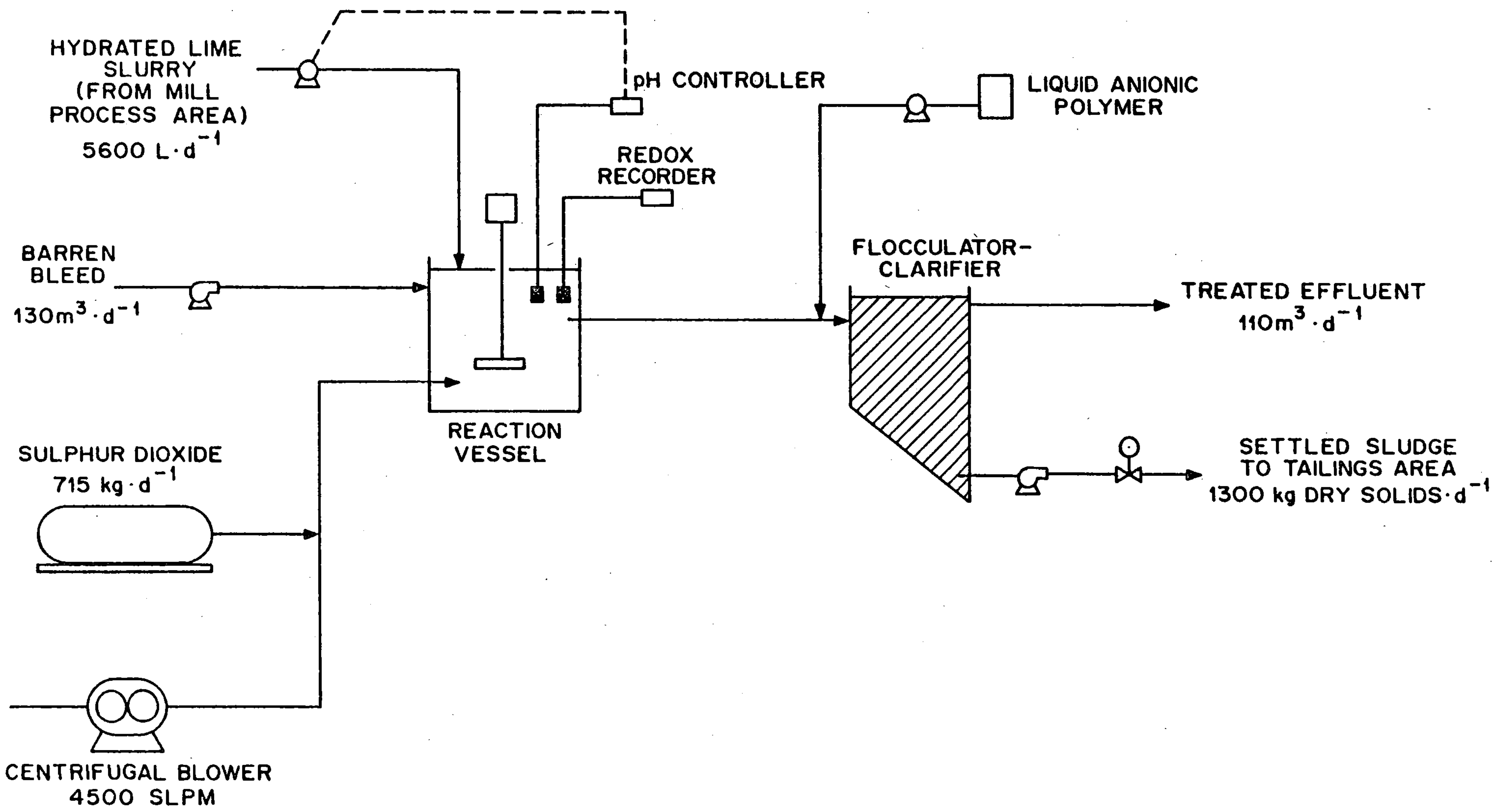

FIGURE 3 — SCHEMATIC FLOWSHEET OF CYANIDE DESTRUCTION PROCESS FOR MODEL GOLD MILL

floc. A feed system for anionic polymer to an integral flocculation zone of the flocculator-clarifier was included in the process flowsheet. Settled solids, in the form of a sludge containing up to 5 percent solids, would be discharged to the tailings impoundment area. No provision was made for dewatering of the settled sludge from the process.

In the conceptual process flowsheet shown in Figure 3, there is no provision for recycle of settled solids to the reactor. In some cases, the recycle of settled metal hydroxide floc improves the SO_2 utilization efficiency (10). In other cases, particularly in wastewaters containing high nickel concentrations, the presence of precipitated metals in the reactor adversely affects process performance (26). The impact of solids recycle on the process would require assessment for each individual wastewater.

6.2 Capital and Operating Cost Estimates

Capital and annual operating costs were developed for an SO_2/air oxidation system with and without the equipment related to solid-liquid separation. Costs for the major capital items are summarized in Table 22. With the exception of the clarification equipment, the major capital cost item for the SO_2/air oxidation system is the reaction vessel. Cost estimates were prepared for two optional reactor configurations as shown in Table 22. INCO have successfully used a flotation cell in a demonstration-scale plant treating gold mill effluent (12); however, capital costs for this reactor configuration are significantly higher than the comparable costs of a reaction tank equipped with a gas sparger and turbine-type mixer similar to the equipment used for water and wastewater recarbonation. Scale-up of the reactor design based on laboratory-scale data is difficult. Pilot-scale studies would be required to determine the optimal reactor configuration. The use of an inclined plate flocculator-clarifier (Lamella) has significant cost advantages over a conventional clarifier design. In addition, the smaller space requirements of the Lamella clarifier may be advantageous in existing gold milling operations. Therefore annual cost estimates were based on the installation of a Lamella flocculator-clarifier for solid-liquid separation. Transportation costs have not been included in the cost estimates.

The total installed costs of the treatment facility are summarized in Table 23 for the two options evaluated. The installed costs range from

TABLE 22. GOLD MILL EFFLUENT TREATMENT SYSTEM ESTIMATED COSTS OF MAJOR CAPITAL ITEMS

ITEM	DESCRIPTION	COST ($)
1	Centrifugal Blower 2.2 kW supplying 4500 SLPM at 120 kPa	3,500.
2	Sulphur Dioxide Feed System including evaporator, piping, manifold and pressure reducing valve.	15,000.
3	Lime slurry metering pump supplying in the range of 50 to 500 LPH.	3,000.
4	Main process feed pump - centrifugal delivering 100 L·min^{-1} at 3 m. head with on/off level-activated control.	1,200.
5	Reaction Vessel Option 1: Dispersed air flotation cell, enclosed four-cell unit equipped with gas dispersion mixers, without skimmers and lauder boxes.	43,000.
	Option 2: 5000 L. mild steel reaction tank, 0.75 kW turbine type mixer equipped with gas sparger ring, turbine shaft and mounting platform.	16,000.
6	Instrumentation and control including ORP sensor and transmitter; pH sensor, transmitter and controller; dual pen recorder.	6,400.
7	Miscellaneous piping and valving, etc.	4,000.
8	Solid-Liquid Separation Option 1: Lamella clarifier Model 125/55 with integral flocculator, plastic plates, mild steel construction.	25,800.
	Option 2: Conventional solids contact flocculator clarifier, 3.0 m diameter with integral 1.2 m flocculation zone, equipped with rake mechanisms.	40,000.
9	Settled sludge pump, variable speed, positive displacement in the range of 5 to 50 L·min^{-1} at 5% solids concentration.	6,250.
10	Polymer feed system - chemical feed pump delivering in the range of 0.01 to 0.1 LPH.	100.
11	Additional miscellaneous piping and valving associated with solid-liquid separation.	6,000.

approximately $80,000 to $180,000, depending on the reactor configuration and the requirement for solid-liquid separation prior to discharge.

TABLE 23. CAPITAL COSTS OF GOLD MILL EFFLUENT TREATMENT SYSTEM

	REACTION SYSTEM EXCLUSIVE OF SOLID-LIQUID SEPARATION	REACTION SYSTEM INCLUSIVE OF SOLID-LIQUID SEPARATION
Major Capital Equipment ($)	49,100 - 76,100	87,200 - 114,200
Installation at 60% of Major Capital ($)	29,500 - 45,700	52,300 - 68,500
Total Installed Cost ($)	78,600 - 121,800	139,500 - 182,700

NOTE: Higher cost figure relates to the dispersed air flotation cell reactor configuration.

The operating costs (labour, chemicals and electrical) associated with the SO_2/air oxidation process are summarized in Table 24. All chemical costs are F.O.B. the supplier. Sulphur dioxide costs shown in Table 24 are based on the availability of bulk liquid SO_2 in shipments of 50 to 90 metric tons at the mill. The use of 1 ton cylinders of liquid SO_2 increases the costs significantly to $180,000, on the basis of a unit price of $0.69 per kg SO_2.

TABLE 24. GOLD MILL EFFLUENT TREATMENT SYSTEM OPERATING LABOUR, CHEMICAL AND ELECTRICAL COSTS

ITEM	DESCRIPTION	ANNUAL COST ($)
1	Lime based on bulk quicklime @ $0.061 per kg.	15,500.
2	Sulphur Dioxide based on liquid SO_2 @ $0.13 per kg.	34,000.
3	Liquid anionic polymer @ $4.50 per kg.	1,100.
4	Electrical @ $0.03 per kwh	1,000. - 3,500.
5	Operator Time...6 hours per day @ $10. per hr	21,900.

The range of electrical costs shown in Table 24 relate to the significantly higher power requirements associated with the diffused air flotation cell compared to the conventional reactor design. Operator time associated with the treatment process were based on 2 hours per 8 hour shift. Preliminary data from pilot-scale operation of an SO_2/air oxidation system indicate that automatic process control based on Redox potential may be feasible (12), in which case the requirement for operator attention to the process could be significantly reduced. However, the feasibility of applying automatic process control based on Redox is dependent on the characteristic Redox curve of the wastewater and would have to be evaluated for each particular waste.

A cost-effective alternative to the purchase of liquid SO_2 may be to burn sulphur and generate SO_2 on-site. Small-scale sulphur burners (approximately 20 $kg \cdot h^{-1}$ capacity) are not readily available on the market; however, it is estimated that the capital cost of such a system would be approximately $25,000, inclusive of all safety requirements and equipped with clean-out capabilities to allow burning of crude sulphur (34). At a unit cost of $0.105 per kg for crude sulphur, the annual chemical costs would be approximately $14,000 compared to an annual cost of $34,000 for the purchase of liquid SO_2. In instances where roaster gases were available at the mill at adequate SO_2 concentrations, the chemical costs associated with the purchase of sulphur or sulphur dioxide could be eliminated. INCO have demonstrated the feasibility of utilizing roaster gases at pilot scale (12).

Total annual cost estimates were determined based on the capital and direct operating costs for the installation of an SO_2/air oxidation process at the model gold mill. Installed capital costs were amortized over 12 years at 15% percent interest.

The range of total annual costs are summarized in Table 25. Total annual costs range from $90,600 to $117,900, equivalent to a cost of between $1.77 and $2.31 per kg CN_T removed. Of this cost per unit cyanide removal, $0.98, or approximately 50 percent, is directly related to the cost of chemicals (SO_2 and lime) for the cyanide destruction process.

TABLE 25. TOTAL ANNUAL COSTS FOR CYANIDE DESTRUCTION FACILITY AT A MODEL GOLD MILL

	REACTION SYSTEM EXCLUSIVE OF SOLID-LIQUID SEPARATION	REACTION SYSTEM INCLUSIVE OF SOLID-LIQUID SEPARATION
Amortized Installed Capital Cost, 12 Years @ 15% ($ per year)	14,200. - 21,900.	25,100. - 32,900.
Annual Operating Costs ($ per year)	72,400. - 74,900.	73,500. - 76,000.
Maintenance @ 5% of Installed Capital ($ per Year)	4,000. - 6,000.	7,000. - 9,000.
Total Annual Cost ($)	90,600. - 102,800.	105,600. - 117,900.
Cost per kg CN_T Removed ($)	1.77 - 2.01	2.07 - 2.31

7. CONCEPTUAL PROCESS DESIGN AND COSTING FOR METAL FINISHING RINSEWATER TREATMENT

Conceptual process design details for an SO_2/air oxidation system to treat copper cyanide rinsewater from a metal finishing facility were developed based the results of the laboratory-scale continuous flow treatability results summarized in Table 21. The process flowsheet for the metal finishing wastewater treatment facility is shown schematically in Figure 4.

7.1 Design Basis

The cyanide destruction process is typically one component of the overall wastewater treatment system required at a metal finishing plant. The overall treatment system might also include chromium reduction, neutralization, flocculation/clarification and sludge dewatering facilities depending on the nature of the plating processes. Cyanide-bearing waste streams after cyanide destruction would typically be combined with other metal-containing wastewaters for sedimentation of metal hydroxides prior to discharge. For the purposes of cost estimation, only the cyanide destruction component of the wastewater treatment system has been considered. The design details and costs associated with subsequent sedimentation and sludge dewatering components of the system would be dependent on the total wastewater flow and metal content of the combined wastewater. Detailed cost breakdowns for these components are available in the literature (22).

Design flow for the cyanide destruction process was 45 $L \cdot min^{-1}$ and operating cost estimates were developed on the basis of an 8-hour per day, 5 day per week production schedule. On the basis of the continuous flow treatability data, a single stage reactor system providing a nominal hydraulic retention time of 20 minutes at design flow was selected.

Liquid sulphur dioxide would be utilized for cyanide destruction. In many metal finishing plants, sulphur dioxide is also used for chromium reduction in the wastewater treatment process. The combined use of SO_2 for both cyanide destruction and chromium reduction could reduce the overall capital cost of the wastewater treatment system by utilizing a common feed system for both functions. It is not considered practical to generate SO_2 on-site by means of a sulphur burner in metal finishing applications.

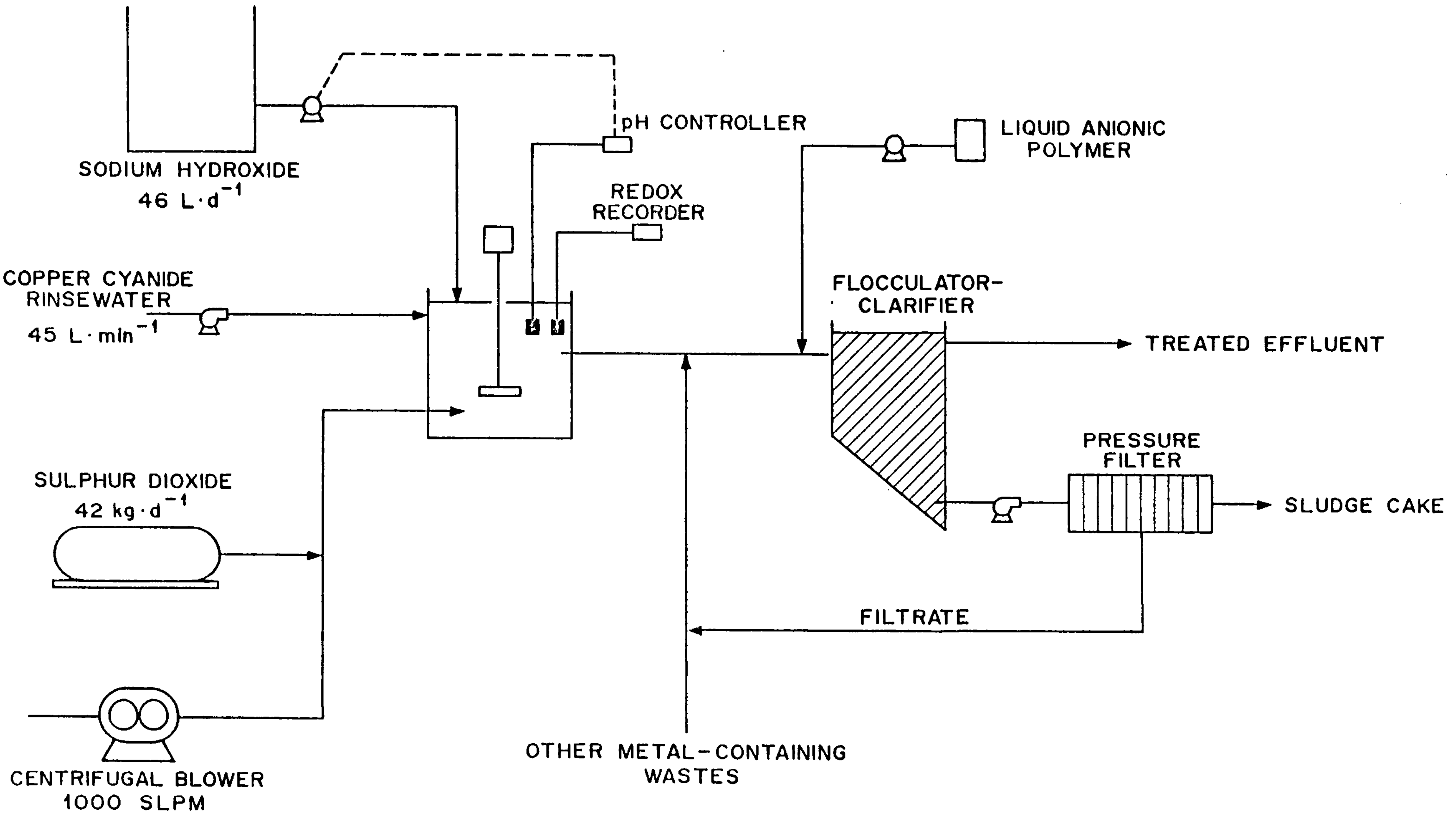

FIGURE 4 — SCHEMATIC FLOWSHEET OF CYANIDE DESTRUCTION PROCESS FOR COPPER CYANIDE RINSEWATER

Sodium hydroxide would be utilized for pH control. The use of sodium hydroxide increases the chemical costs associated with the cyanide oxidation process approximately four-fold relative to the use of lime. However, metal finishing plants use large quantities of sodium hydroxide in the production area and a dedicated sodium hydroxide storage tank would not be necessary. In the case of lime, a dedicated lime slurry makeup system would be required. Furthermore, lime addition increases the net sludge generation rate from the cyanide destruction system by approximately 30 percent relative to that generated by the addition of sodium hydroxide for pH adjustment. Sludge disposal, at an average cost of $5 per tonne, is a significant economic consideration in assessing the economics associated with lime and sodium hydroxide use in the cyanide destruction system.

As was the case in the conceptual design for the cyanide destruction system at the model gold mill, automatic pH control equipment would be provided. Redox potential would be continuously recorded but not utilized as an automatic process control variable for the system.

7.2 Capital and Operating Cost Estimates

Estimated costs for the major capital items associated with the cyanide destruction system are summarized in Table 26. Reactor design was based on a reaction tank equipped with a gas sparger and turbine-type mixer to effect liquid-gas contact. As discussed in Section 7.1, no costs are included in Table 26 for clarification and sludge dewatering facilities as the cost of these components are controlled by the volume and characteristics of the total plant wastewater stream.

Total capital cost of the SO_2/air cyanide oxidation system is approximately $34,000. On the basis of installation costs equivalent to 60 percent of major capital costs, the total installed cost of the system would be approximately $55,000.

The operating costs (labour, chemicals and electrical) associated with the SO_2/air oxidation process are summarized in Table 27. All chemical costs are F.O.B. the supplier. Costs associated with sulphur dioxide requirements were based on the purchase of bulk liquid SO_2 at $0.13 per kg. The use of 1 ton cylinders of liquid SO_2 would increase these costs to approximately $7,250, based on a unit price of $0.69 per kg SO_2. No costs are included for sludge dewatering and disposal in Table 27. Estimated sludge

TABLE 26. COPPER CYANIDE RINSEWATER TREATMENT SYSTEM ESTIMATED COSTS OF MAJOR CAPITAL ITEMS

Item	Description	Cost $
1.	Centrifugal Blower 1.1 kW supplying 1000 SLPM at 120 kPa	3,000.
2.	Sulphur Dioxide Feed System including evaporator, piping, manifold and pressure reducing valve.	15,000.
3.	Sodium hydroxide metering pump supplying in the range of 1 to 10 LPH	1,000.
4.	Main process feed pump - centrifugal delivering 45 $L \cdot min^{-1}$ at 3 m head with on/off level activated control.	750.
5.	Reaction vessel - 1000 L mild steel tank, 0.19 kW turbine type mixer equipped with gas sparger ring, turbine shaft and mounting platform.	5,000.
6.	Instrumentation and control including ORP sensor and transmitter; pH sensor, transmitter and controller; dual pen recorder.	6,400.
7.	Miscellaneous piping and valving etc.	3,000.

TABLE 27. COPPER CYANIDE RINSEWATER TREATMENT SYSTEM OPERATING LABOUR, CHEMICAL AND ELECTRICAL COSTS

Item	Description	Annual Cost ($)
1.	Sodium hydroxide based on 50% NaOH @ $0.46 per kg dry weight.	8,050.
2.	Sulphur dioxide based on liquid SO_2 @ $0.13 per kg.	1,350.
3.	Electrical @ $0.03 per kWh	100.
4.	Operator Time....2 h per 8 h shift, 1 shift per day @ $10. per hr.	5,000.

generation for the case of sodium hydroxide addition for pH control was approximately 0.15 kg dry solids per m^3 of wastewater treated compared to a generation rate of approximately 0.20 kg dry solids per m^3 treated in the case of lime addition. Actual dewatering and disposal costs will depend on the type and size of dewatering equipment, dewatering characteristics, chemical conditioning costs and total quantity of sludge requiring disposal.

The total annual cost associated with the SO_2/air cyanide destruction process is estimated at approximately $26,000, inclusive of amortization of capital, operating and maintenance as shown in Table 28. The unit cost of treatment for the metal rinsewater application is high ($11.95 per kg CN_T removed) relative to that estimated for the gold mill application (Table 25). Amortization of capital contributes approximately $4.52 per kg CN_T destroyed in the rinsewater application compared to approximately $0.28 to $0.64 per kg CN_T in the gold mill application. This difference in costs is directly related to the 8 hours per day, 5 days per week production schedule in the metal finishing application compared to the gold mill system which operates on a 24-hour per day, 7 day per week schedule. Similarly, maintenance requirements per unit cyanide destroyed are higher in the rinsewater application ($0.78 per kg compared to a range of $0.08 to $0.18 per kg for gold mill effluent treatment).

TABLE 28. COPPER CYANIDE RINSEWATER TREATMENT SYSTEM TOTAL ANNUAL COSTS

	ANNUAL COST ($)
Amortized Installed Capital Cost, 12 years @ 15%	9,850.
Annual Operating Costs	14,500.
Maintenance @ 5% of Installed Capital	1,700.
Total Annual Cost	26,050.
Cost per kg CN_T Removed	$11.95

8. CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Based on laboratory-scale batch and continuous flow experiments, the SO_2 / air oxidation process was demonstrated to be a technically feasible alternative to alkaline chlorination and ozonation for treatment of a variety of cyanide-containing wastewaters including gold mill effluents and metal finishing rinsewaters.

Specifically, the following conclusions can be drawn:

- In the presence of adequate concentrations of dissolved copper, the SO_2/air oxidation process was capable of reducing cyanide concentrations from more than 1 g $CN_T.L^{-1}$ to less than 1 mg $CN_T.L^{-1}$. The optimum copper concentration was dependent on the composition of the untreated sample.
- Removal efficiencies exceeding 99 percent in terms of cyanide species and heavy metals were achievable during treatment of synthetic solutions, gold mill effluents and metal finishing rinsewaters.
- Removal of more than 99.5 percent of iron present as iron cyanide complexes was attained in the presence of adequate concentrations of copper and zinc in the wastewater sample.
- Thiocyanate was virtually unaffected by the SO_2/air oxidation process.
- In specific cases, treated samples contained metal concentrations in excess of the theoretical solubility. The cause of elevated dissolved metal concentrations could not be firmly established based on the results of these investigations.
- Based on a conceptual flowsheet for an SO_2/air oxidation process for a model gold mill, total installed costs associated with the cyanide destruction system were in the range from $78,600 to $121,800, dependent on reactor configuration. Equipment related to solid-liquid separation resulted in an additional cost of approximately $60,000.
- Total annual cost associated with the operation of an SO_2/air oxidation process at a model gold mill are in the range of $1.77 to $2.31 per kg CN_T removed. Chemical costs (sulphur dioxide and lime) amount to approximately $0.98 per kg CN_T removed.

- Based on a conceptual flowsheet for an SO_2/air oxidation process for a copper cyanide rinsewater treatment application, total installed costs associated with the cyanide destruction system were approximately $55,000.
- Total annual costs associated with the operation of an SO_2/air oxidation system for copper cyanide rinsewater treatment are approximately $26,050, equivalent to $11.95 per kg CN_T removed. Chemical costs (sulphur dioxide and sodium hydroxide) amount to approximately $4.31 per kg CN_T removed.

8.2 Recommendations

The laboratory-scale studies demonstrated the applicability of the SO_2/air oxidation process for treatment of a range of cyanide-containing wastewaters including gold mill effluents and metal finishing rinsewaters. Further investigations are required to confirm the process chemistry and reaction kinetics and to verify the conceptual design aspects developed as a result of these studies.

Specifically, the following recommendations with respect to the SO_2/air oxidation process are made:

- Further laboratory-scale investigations should be conducted under controlled experimental conditions to assess the following aspects of the SO_2/air oxidation process:
  - (i) the effect of metal species and metal concentration on reaction kinetics and process efficiency,
  - (ii) the effect of recycling metal hydroxide precipitate on the rate of cyanide oxidation and the overall process performance,
  - (iii) the optimum reaction mixing conditions and the impact of reactor design on process performance,
  - (iv) the mechanisms involved in the generation of ammonia during SO_2/air oxidation of cyanide and the concentration of ammonia produced after treatment of gold mill effluents,
  - (v) the contribution of calcium ions to the cyanide oxidation reactions, and
  - (vi) the applicability of the process to slurries.

- Leaching studies should be conducted on samples of precipitate containing elevated cyanide concentrations to determine the stability of the solid fraction.
- The toxicity of treated effluents generated from the SO_2/air oxidation process should be investigated.
- Pilot and/or demonstration-scale treatability investigations should be conducted to optimize process design details, verify the long-term efficiency of the process under actual industrial conditions and confirm the preliminary cost estimates developed as a result of the laboratory-scale studies. Such pilot/demonstration-scale investigations are needed in gold mill and metal finishing applications.

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LIST OF ABBREVIATIONS

As - arsenic
$Ca(OH)_2$ - calcium hydroxide
Cd - cadmium
CdCN - cadmium cyanide (process)
Cl^- - chloride ion
Cl_2 - chlorine
CN_T - total cyanide
CN_W (also CN^-) - weak acid dissociable (free) cyanide
CNCl - cyanogen chloride
CNO (also CNO^-) - cyanate (ion)
CNS (also CNS^-) - thiocyanate (ion)
Cu - copper
CuCN - copper cyanide (process)
°C - degrees Celsius
Fe - iron
g - gram
$g \cdot h^{-1}$ - grams per hour
$g \cdot L^{-1} \cdot h^{-1}$ - grams per litre per hour
HCO_3^- - bicarbonate ion
H_2O - water
HP - horsepower
HRT - hydraulic retention time
IGPM - Imperial gallons per minute
kg - kilogram
$kg \cdot d^{-1}$ - kilograms per day
kPa - kilopascals
kW - kilowatt
L - litre
$L \cdot min^{-1}$ - litres per minute
LPH - litres per hour
m - metre
m^3 - cubic metre
$m^3 \cdot d^{-1}$ - cubic metres per day
$mg \cdot L^{-1}$ - milligram per litre

LIST OF ABBREVIATIONS cont'd

min	-	minute
ml	-	millilitre
mV	-	millivolt
N_2	-	nitrogen gas
NH_3-N	-	ammonia nitrogen
Ni	-	nickel
OH^-	-	hydroxide ion
O_3	-	ozone
ORP (also Redox)	-	oxidation-reduction (potential)
S.H.E.	-	standard hydrogen electrode
SLPM	-	standard litres per minute
SO_2	-	sulphur dioxide
SO_4^{-2}	-	sulphate ion
UV	-	ultraviolet (radiation)
vol.	-	volume
$^v/v$	-	volume (percent)
wt.	-	weight
WTC	-	Wastewater Technology Centre
Zn	-	zinc
ZnCN	-	zinc cyanide (process)
>	-	greater than
<	-	less than

METRIC CONVERSIONS

m x 3.28 = ft

m^3 x 35.314 = ft^3

L x 0.220 = Igal

kg x 2.205 = lb

kW x 1.341 = HP

$m^3 \cdot d^{-1}$ x 220.36 = IGPD

SLPM x 0.0353 = SCFM

kPa x 0.145 = psia

g x 0.002205 = lb

LPM x 0.220 = IGPM

APPENDIX I

RESULTS OF ANALYTICAL QA / QC PROGRAM

TABLE I-1 ANALYTICAL QA/QC RESULTS - REPLICATE ANALYSES

REPLICATE #	ANALYSIS #	PARAMETER (mg.L^{-1})							
		CN_T	CN_W	SCN	CNO	Fe	Cu	Zn	Ni	As
1.	1.	219.	200.	366.	1283.	53.4	60.0	90.0		31.0
	2.	219.	216.	399.	1276.	55.0	60.0	94.0		29.4
2.	1.	147.	5.28	1860.	181.	0.8	79.0	74.0	1040.	0.006
	2.	145.	2.53	1568.	182.	0.8	75.0	74.0	98.0	0.009
3.	1.	1092.	1023.	504.	1215.	66.0	5.04	22.0	0.4	<0.001
	2.	1060.	1000.	496.	1217.	61.0	4.60	26.0	0.4	<0.001
4.	1.	0.33	0.42	484.	297.		20.0	0.09	<0.05	
	2.	0.41	0.47	424.	296.		19.5	0.09	<0.05	
5.	1.	92.				19.	186.	336.	0.20	
	2.	85.				22.	180.	306.	0.15	
6.	1.	0.04	0.04	1.3		<0.1				
	2.	0.06	0.08	1.4		<0.1				
MEAN STANDARD ERROR (%)		8.7	23.5	6.6	0.3	3.6	2.8	4.3	6.1	10.7

TABLE I-2 ANALYTICAL QA/QC RESULTS - RECOVERY OF SPIKES

PARAMETER	CONCENTRATION (mg.L^{-1}) INITIAL	SPIKE	FINAL	PERCENT RECOVERY	MEAN SPIKE RECOVERY % (± Rel. Var.)
CN_T	0.30 0.48 0.06	10.0 10.0 5.0	9.08 9.70 3.05	87.8 92.2 59.8	79.9 (± 22.0%)
CN_W	0.11 0.22 0.06	10.0 10.0 5.0	8.56 8.60 2.51	84.5 83.8 49.0	72.4 (± 28.0%)
SCN	36.0	5.0	41.0	100.00	-
Cu	0.55 4.41 0.25	1.0 4.0 2.0	1.70 8.40 2.27	115.0 99.8 103.5	106.1 (± 7.5%)
Zn	2.90 0.94	2.0 12.0	4.30 13.0	70.0 100.5	85.3 (± 25.3%)
Fe	0.07	2.0	1.3	61.5	-
As	0.65 0.12	1.0 1.0	1.37 0.50	72.0 38.0	55.0 (± 43.7%)

APPENDIX II

RESULTS OF INDUCTIVELY-COUPLED PLASMA ANALYSIS OF GOLD MILL EFFLUENTS

TABLE II-1 RESULTS OF INDUCTIVELY - COUPLED PLASMA (ICP) ANALYSIS OF GOLD MILL EFFLUENTS

PARAMETER	CONCENTRATION (mg.L^{-1})				
	GOLD MILL 1	GOLD MILL 2	GOLD MILL 3	GOLD MILL 4	GOLD MILL 5
Ag	<0.5	<0.5	0.13	<0.5	0.11
Al	<0.3	2.5	2.1	0.4	3.7
Be	<0.001	<0.001	<0.001	<0.001	<0.001
Ca	214.	98.7	182.	1270.	123.
Cd	<0.07	<0.07	<0.07	0.09	<0.07
Co	0.11	0.38	0.15	3.39	0.16
Cr	<0.008	<0.008	<0.008	0.011	<0.008
Cu	8.88	124.	185.	90.9	5.68
Fe	<0.2	70.2	22.7	0.9	113.
K	34.	11.	54.	26.	38.
Mg	<0.04	1.87	0.13	<0.04	0.64
Mn	<0.01	0.04	<0.01	0.03	<0.01
Mo	<0.3	<0.3	1.6	1.9	<0.3
Na	396.	712.	975.	1080.	1660.
Ni	4.24	7.80	0.31	134.	0.70
P	<0.6	<0.6	<0.6	<0.6	<0.6
Pb	<0.05	<0.05	<0.05	<0.05	<0.05
Sr	0.705	0.067	0.447	2.73	0.297
Th	<0.06	<0.06	<0.06	0.25	<0.06
Ti	<0.01	0.03	0.11	<0.01	<0.01
V	<0.003	0.004	<0.003	0.007	<0.003
Zn	16.9	131.	292.	88.6	0.48
Zr	<0.03	<0.03	<0.03	<0.03	<0.03