CYANIDE DETOXIFICATION:
INCO SULFUR DIOXIDE/AIR PROCESS

DRAFT

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DISCLAIMER AND ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

As a National policy, the Environmental Protection Agency (EPA) is integrating the concept of pollution prevention and waste minimization in many of its activities. Both the Resource Conservation and Recovery Act (RCRA) and the Pollution Prevention Act of 1990 (PPA), encourage the reduction in volume, quantity and toxicity of waste. While RCRA focuses primarily on the reduction in volume and/or toxicity of hazardous waste, the PPA encourages maximum possible elimination of all waste through source reduction.

EPA believes that there are pollution prevention/waste minimization practices currently being implemented by the mining industry. Many of these practices may, in addition to their environmental benefit, realize significant cost savings. It is EPA's intent to identify these practices and foster technology and information transfer throughout the mining industry.

Recognizing that unique issues are associated with the mining industry, such as large volumes of raw material used and waste generated, EPA has conducted research to identify the potential for pollution prevention/waste minimization in the mining industry. This report highlights the INCO Sulfur Dioxide/Air Process which was patented in 1984 to remove cyanide and base metal complexes from industrial wastestreams. Information used to prepare this report was either provided by INCO Exploration and Technical Services Inc. or collected from publicly available documents.

2.0 INCO'S CYANIDE TREATMENT TECHNOLOGY

2.1 INCO Treatment of Tailings Pulps or Slurries

The precious metals mining industry's use of cyanide to extract precious metals from low grade ores is widespread. Cyanidation is the predominant method for precious metals beneficiation and is used on heap leaches or in tank operations to liberate precious metal values from remaining gangue in the ore. Several cyanide detoxification technologies have been developed to treat cyanidation wastes. The International Nickel Company's (INCO) sulfur dioxide/air process is one of two patented sulfur dioxide processes (Devuyst et al., 1992). The other process is patented by Noranda Inc. Both processes are similar with some limited differences in operating procedures. (McGill and Comba 1990)

The INCO process has been commissioned at more than 36 sites in North America. Ten sites are located in the U.S. and are listed in Table 1. Six of these 10 sites, use the INCO process to treat tailings prior to disposal. After treatment, tailings are typically disposed of in a tailings impoundment subject to zero discharge requirements under the Clean Water Act. In addition to Federal Clean Water Act standards, many states have solid waste-related discharge standards for the tailings prior to discharge to the tailings impoundment and the INCO treatment process is used to meet these State requirements.

Table 1. Sites Using INCO Process in the U.S.

Operation	Commissioning Date	Location	Tonnage (MT/D)/CN in Feed	Effluent Type/ CN in Effluent
Colosseum	1987	California	3,600/350	CIP Tails/1
Mineral Hill	1989	Montana	500/150 to 500	Barren/ < 1
Snow Caps	1990	California	Heap	Rinse Water
McCoy/Cove	1990	Nevada	7,500/500-1,000	Thickener U/F / < 10
Kettle River	1990	Washington	1,500/250	CIP Tails/ < 10
Citigold (Ryan Lode)	1991	Alaska	Heap	Pond
Barrick Mercur	1992	Utah	5,000/50	CIP Tails/ < 1
Grant	1992 (Process complete)	Alaska	- - -	Unused cyanide pellets were treated in tanks.
Hayden Hill	1992	California	- - -	Tails
San Luis	1992	Colorado	- - -	Tails

2.2 Treatment Chemistry

In the INCO process, free cyanide and weakly or moderately bound metal-cyanide complexes present in the wastestream are oxidized to cyanate (CNO^-) by the addition of sulfur dioxide and oxygen according to the following stoichiometric reaction:

$$CN^-_{WAD}(1lb) + SO_2(2.64lb) + O_2(1.23lb) + H_2O \text{ yields } OCN^-(1.88lb) + H_2SO_4(3.77lb)$$

(Cyanide + Sulfur Dioxide + Oxygen + Water **yields** Cyanate + Sulfuric Acid)

The reaction usually takes place in a well-mixed and aerated reactor. The aeration provides mixing and oxygen. Sulfur dioxide may be supplied to the reactor in a gas or liquid state, or by the application of sodium sulfite or sodium metabisulfite. INCO has reported actual SO_2 dosages to be 3 - 5 g/g CN_T for barren solutions and 4 - 7 g/g CN_T for tailing slurries. Theoretical reagent consumption for sulphur dioxide was 2.5 mg SO_2/mg WAD cyanide and for lime, 2.2 mg CaO/mg

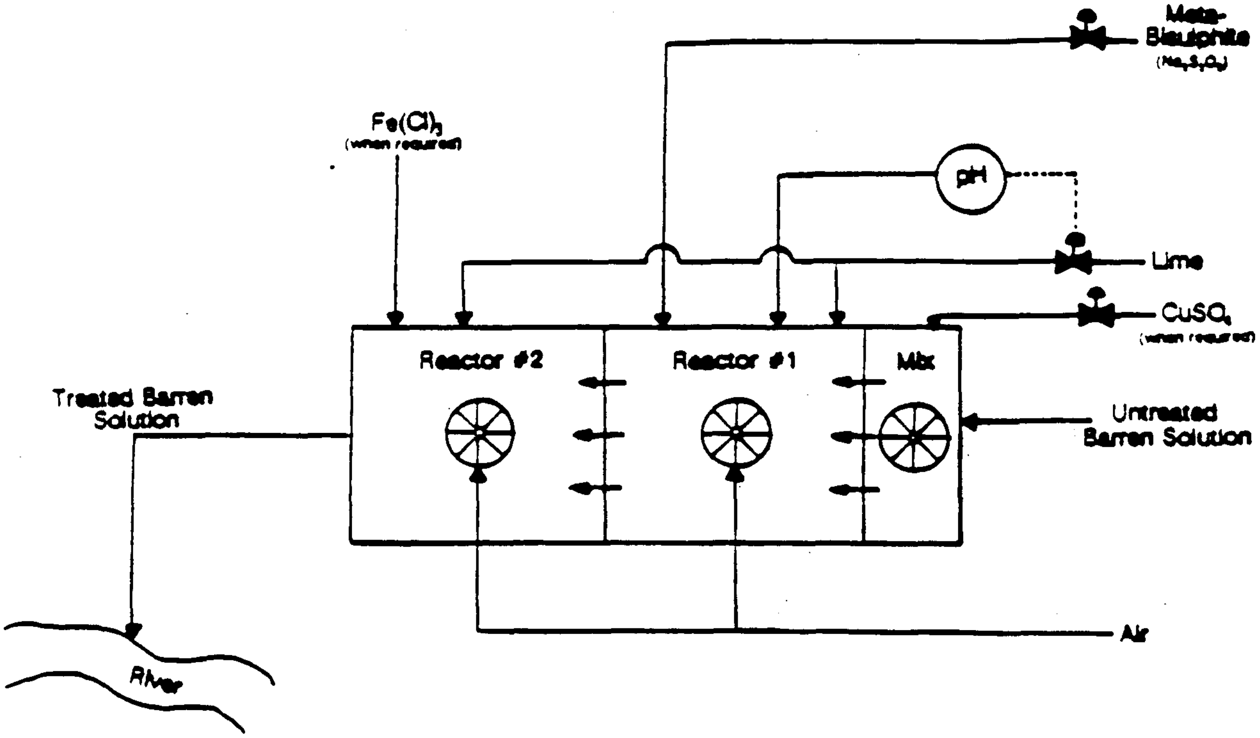
WAD cyanide. (Smith and Mudder, 1991). Higher dosages are reportedly required to treat low concentrations of weak acid dissociable (WAD) forms of cyanide (Vergunst et al., 1991). The reaction is pH dependent: the optimal pH range is 8 - 10. Incomplete oxidation may occur at pH levels > 11. At pH levels below 8, there is a reported reduction in the reaction rates. Since the oxidation reaction results in the formation of sulfuric acid, lime or caustic is added to maintain the optimal reaction pH. The presence of a copper catalyst at an approximate concentration of 50 mg/L is also necessary for the reaction to take place. If the copper concentration naturally present in the wastestream is too low, then supplemental copper may be provided by the addition of copper sulfate solution to the reactor contents.

Although oxygen is also added to the reactor, the literature is not specific as to recommended dissolved oxygen operating levels. This is probably dependent on site specific conditions. The oxidation reaction has also been reported to be temperature dependent. At 25°C, the reaction is rapid and results in a residual cyanide concentration of 0.2 mg/L whereas at 5°C the reaction is slow and results in a residual cyanide concentration of 2.0 mg/L (McGill and Comba, 1990).

In addition to the oxidation of cyanide, metals are also removed from solution by precipitation as metal hydroxides. Unlike the alkaline chlorination oxidation process, the INCO process is capable of removing stable iron-cyanide complexes from solution. Ferricyanides are reduced to insoluble ferricyanide salts and precipitated from solution. The presence of iron-cyanide complexes is undesirable given their ability to decompose in the presence of sunlight, releasing free cyanide. Under typical operating conditions, only 10-20% of thiocyanate is removed. This reportedly results in lower chemical requirements for the SO_2 compared to other oxidation processes and also ensures removal of the more toxic forms of cyanide. Additional removal of thiocyanate is possible by continuing the application of SO_2 following the complete oxidation of the free and complexed forms of cyanide.

The typical INCO treatment system components consist of a single reactor (sometimes two parallel units), SO_2 storage and feed system, lime or caustic chemical feed system, copper sulfate chemical feed system (if needed), and an aeration system. For certain situations where the wastewater contains high nickel concentrations or when arsenic removal is required, multiple stage reactors have been used. (See Figure 1) Since the typical INCO system does not remove significant levels of thiocyanate, cyanate, or ammonia, additional treatment units may be necessary to meet more stringent permit limits for those parameters. Maintaining control of the pH may be difficult due to the formation of a dense slurry in the process of neutralizing the strong acid produced during the process. (Smith and Mudder, 1991)

Figure 1. A Typical Two-Stage Inco Process for Cyanide and Metals Removal
(Source: Smith and Mudder, 1991)



All three parameters, thiocyanate, cyanate, and ammonia, have the potential to contaminate ground water and are toxic to fish. Ammonia may result in increased nitrate levels in ground water assuming nitrification takes place in the upper soil layers. Additional ammonia may be produced by the hydrolysis of cyanate in waters retained in tailings ponds. The retention of precipitated metal hydroxide sludges in tailings ponds may also have undesirable environmental effects. The tailings remaining from the INCO oxidation process may have a considerable heavy metal content. If the sludge is stored for extended periods in unlined (or improperly lined) ponds, there is potential for the metals to migrate into the groundwater.

2.3 Costs

Costs for the installation and operation of INCO's SO_2/Air cyanide destruction facility varies according to the size of the operation, and desired effluent targets. It was not determined how INCO compared to the alkaline chlorination or hydrogen peroxide treatments in similar cases.

Capital Costs

Main equipment components of the INCO process include a reaction tank, a mixer with motor and support, an air compressor or blower with associated piping, an SO_2 reagent system with associated instrumentation and piping, a copper sulfate delivery system (when required) and a lime delivery system. Use of sulfur dioxide roaster gas rather than powdered sodium sulphite or sodium metabisulphite, or burning of pure sulfur, is the least expensive source of sulfur dioxide for this process, and will keep costs down (Smith and Mudder, 1991).

INCO has found that equipment costs for a large installation, a site producing 3300 stpd or more, (requiring 5 to 10 stpd of SO_2), and treating their pulp tailings, may reach approximately $500,000 (Canadian dollars), or about $1.2 million (Canadian dollars) installed. (Devuyst and Robbins, undated)

Operating Costs

Operating costs include cost of reagents, labor, electric power, maintenance, and licensing fees, and may very between $0.09 to $1.58 (Canadian dollars) per standard ton of ore. Average costs for a plant treating CIP tailings using liquid SO_2 is $1.18 (Canadian dollars) per standard ton of ore. Lower operating costs may be realized in pond water treatment, where natural degradation plays a large role in detoxification. Reagent costs tend to be somewhat low, a distinct advantage of the INCO process, compared to the alkaline chlorination and hydrogen peroxide forms of cyanide detoxification.

INCO's process is patented and requires a license to operate. The associated licensing fee is determined on a site specific basis. INCO also offers services to determine process specifications and equipment needs, and provide training and all other assistance to get the process up and running. Services are also negotiable within the framework of the license.

2.4 Benefits

The INCO treatment process treats cyanide (including ferricyanide) contaminated wastes and may be effective to concentrations less than 1.0 mg/L. According to INCO representatives, the process is relatively rapid and can be used to treat both slurries and clear solutions. The process has a flexible design, which permits possible incorporation into existing treatment or production facilities and can be used for either batch or continuous treatment.

According to INCO representatives, the process has one benefit over alkaline-chlorination in that it does not produce cyanogen chloride, as a toxic intermediate reaction by-product. However, other by-products, such as ammonia, cyanate, and thiocyanate may be generated during INCO treatment. Capital and operating costs are comparable with other chemical treatment processes.

2.5 Limitations

Although the INCO process may be effective in treating cyanide concentrations, the process has poor removal efficiency for ammonia, cyanate, and thiocyanate. Tailings treated with INCO may continue to contain ammonia, cyanate, thiocyanate, and metals and additional treatment units may be necessary to meet discharge permit limits for these constituents. Treatment may also result in increased total dissolved solids.

Strict pH control with frequent monitoring is necessary to ensure adequate oxidation of cyanide and metals precipitation. Relatively high reagent consumption (SO_2, lime and copper sulphate) can be expensive.

2.6 Case Study: Echo Bay's Cove-McCoy Mine

INCO completed installation of their largest tailings pulp treatment operation at Echo Bay's Cove-McCoy mine near Battle Mountain in Nevada on September 12, 1990. The INCO sulfur dioxide/air cyanide destruction facility was installed in response to numerous failed and costly efforts to prevent migratory fowl deaths in their 145 hectare tailings pond. (Devuyst, et al. 1992) Installation of the INCO treatment plant detoxified cyanide in the tailings, significantly reducing the numbers of mortalities. (Smith and Mudder, 1991)

The system was designed to treat tailings pulp from CCD underflow at 40 percent solids by weight for a 8,500 short tons per day mill throughput. Tailings pulp containing 268 kg CN_{WAD}/hr at 40% solids is treated with both reactors, (or 134 kg CN_{WAD}/hr per reactor), to a target residual cyanide level of 10 mg/l CN_{WAD}. The SO_2 additions are programmed and controlled by a feed-forward control loop, based on continuous measurement of wt % solids and slurry flow rate, as well as periodical CN_{WAD} analysis. The ratio of SO_2 to CN_{WAD} load is maintained by a feed-back loop in which continuous readings of the treated effluent for pH and cyanide electrode mV's, and periodic readings of residual CN_{WAD}. are performed. The ore usually supplies sufficient copper catalyst so that the addition of copper sulfate is rarely needed.

Laboratory data showed that a dosage of 3.7g SO_2/g CN_{WAD} and 60 minutes retention time, yielded an effluent containing less than 5 mg/l CN_{WAD}. During McCoy-Cove's commissioning, a higher SO_2 to cyanide dosage ratio was used to ensure low residual cyanide in the treated tailings. As effluent levels of CN_{WAD} were reduced to 10 mg/L, SO_2 addition levels were reduced to less than 3 g/g CN_{WAD}. According to facility personnel, the current ratio ranges from 2.6 to 4 SO_2/g CN_{WAD}.

As of October 1990, McCoy-Cove increased the cyanide concentration in their leach circuit to increase their gold recovery rate from 82 percent to 90 percent. During the week of November 17, 1990, the cyanide load was at 150 percent of the design load. Currently the facility has cut cyanide consumption and need for treatment by re-using cyanide.

According to facility personnel, tailings are disposed of in the tailings impoundment where WAD cyanide levels are monitored daily and currently range from 4 to 7 ppm WAD cyanide. According to facility personnel, the INCO system is working well with the major concern being the managment and measurement of SO_2.

3.0 CONTACTS

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5.0 COMMENTS AND RESPONSE

Echo Bay Minerals Company submitted comments to EPA and requested that a number of minor edits to the draft be made. EPA has corrected the text to accommodate the requested changes.