

OVERVIEW OF CYANIDE TREATMENT METHODS

by

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ABSTRACT

For a number of years there has been an increasing interest in methods for treating gold mill effluents for the removal of cyanide prior to discharge to the environment. The recent burgeoning of gold mining in Canada has prompted even greater interest in such methods. However, since it has not been the practice of Canadian gold mines to treat their effluents by any method other than natural degradation, little information is available from actual mill practice on alternative methods for the treatment of effluents.

This report analyzes current gold mining and milling operations and summarizes the data on the volumes and the concentrations of cyanides and other pollutants of the various process streams and the effluents. A projection is made of the anticipated expansion of the industry over the next 5 years and its potential impact on the amounts of cyanide that may be employed. On this basis the indicated increase in volumes of effluents that will be entering the environment make it increasingly important to accelerate the introduction of effluent treatment in the industry.

To assist in the selection of suitable methods, this report reviews and compares the mechanisms, technical capabilities and to some extent the economics of ten processes for cyanide removal or destruction. Some methods for dealing specifically with ferrocyanide are also discussed, since not all of the processes have the capability to eliminate it. In addition, some observations are made on the possibility of reducing the amounts of cyanide to be destroyed, by means of closer process control and by modifications to the gold cyanidation process.

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1 INTRODUCTION

1.1 Scope of the Cyanide Problem

The principle reason for wanting to remove cyanide from gold mill effluents is the potential for harm to aquatic life. Fish in particular are extremely sensitive to minute concentrations of cyanide. In the words of Doudoroff (1976) "Free cyanide concentrations as high as 0.05 mg/L seem to be too close to reported lethal threshold concentrations even for moderately resistant fish, --- to be judged acceptable."

In 1978, some 4,800 tons of cyanide were used in Canada. Although cyanide is used in a number of other Canadian industries, the mining industry, at 3,200 tons per year, is by far the largest consumer, and even at the present time a large part of this consumption, 2,700 tons per year, results from its use in the recovery of gold from its ores. (Harrison 1979).

Gold mines are currently milling 6,240,000 tons of ore per year. Under the impetus of current price levels for the metal, gold mining and cyanide consumption are expected to increase significantly over the next few years. A 50% increase in mill tonnage is in process or planned for 1980 alone, by the expansion of existing mines, reopening of dormant ones and the construction of new facilities. By 1985 it is estimated that the 24 new and planned lode gold mines will be milling an additional 6 million tons of ore per year.

For the most part, existing gold mills had their beginning in the period before environmental consciousness had seriously emerged, when tailings disposal was often guided by convenience, and little thought was given to any effect the effluents might have on the environment. The remote locations, relatively small size and uncertain economic future of most of the mills have until recently worked together in delaying the full implementation of waste treatment measures.

The situation in Ontario has been described in the following terms

"Although accounting for only 11.4 per cent of the total ore milled daily in the province, the gold industry is responsible for virtually 100 percent of all cyanide discharged by active Ontario mine/mill operations, 16 per cent of the suspended solids, 18 percent of the nickel 23 percent of the zinc, 76 percent of the copper and 98% of the arsenic" (Hawley 1978).

The final waste effluents discharged from gold mines vary considerably in their content of free cyanide, metal-cyanide complexes and such cyanide derivatives as cyanate and thiocyanate. Effluent pH is usually close to 8. The acute toxicity to fish of the final effluent also varies considerably but in many instances the effluent itself can kill fish in a very short period. This is not surprising, since a concentration of 0.05 mg/l free cyanide has been shown to be acutely toxic to fish. Table 4 in the report summarizes the volumes and composition of the final effluents from the Canadian gold mines which were operating in 1978.

1.2 Origins of Cyanide and Cyanide Derivatives in Gold Mill Effluents

The cyanide in gold mill effluents results from that used for the hydrometallurgical extraction of gold. Cyanide consumption in Canadian gold mills range from 0.23-2.42 lbs/ton ore and averages approximately 1.0 lbs/ton. Table 1 shows the cyanide consumption at gold mines. Figure 1 depicts the various cyanide and non-cyanide bearing streams which leave a typical gold mine and mill, and eventually enter receiving waters via the tailings pond decant. The largest discharge of cyanide is usually in the barren bleed solution and Table 2 indicates typical chemical composition of such effluents. However, a point worth noting is that considerable cyanide can be discharged from the mill with the filtered leached solids as a result of inadequate filter cake washing with water. Some cyanide may also enter mine water with hydraulically placed tailings backfill or seepage from tailings ponds into the mine workings. An indication of the distribution of cyanide between these various flows is provided in Table 3.

The characteristics of the final effluents (tailing ponds decants) discharged from the Canadian gold mines which were operating in 1978 are shown in Table 4.

Considerable variation exists in some of the metal and cyanide values reported. Uncertainty exists as to the accuracy of the CN_T values presented since the concentrations reported are very method dependent and a variety of methods of analysis are used by the mines. This point will be well appreciated by those familiar with the problems related to cyanide analyses, especially at low levels.

1.3 Liquid Effluent Regulations

When the federal Metal Mining Liquid Effluent Regulations (Environmental Protection Service 1977) were promulgated in 1977, gold mines were specifically exempted and cyanide was not included in the prescribed effluent standards. The reason for this exemption was that Canadian effluent regulations are based on levels attainable through the application of demonstrated "best practicable technology" which takes into

TABLE 1 CYANIDE CONSUMPTION IN CANADIAN GOLD MILLS (1978 Data)

Mine	Ore tpd	lb/ton ore NaCN	lb/ton ore KCN	lb/day NaCN	lb/day KCN
A	1050	2.18	0	2289	-
B	1300	0.40	0	520	-
C	1720	0.73	0	1255	-
D	1860	0.45	0	837	-
E	1425	0.30	0	428	0
F	800	1.57	0	1256	
G	520	0.83*	0	431*	-
H	1985	0.31	0	615	-
I	1300	2.42	0	3146	-
J	3000	0.23	0	690	-
K	3000	-	0.75	0	2250
L	280	1.26	0	353	-
M	650	1.30	0	845	-
N	1200	-	-	945	-
Total				13610**	2250**

* $\text{Ca}(\text{CN})_2$, calculated as NaCN
Ref. - Harrison 1979

** Total 8109 lbs, as CN

account both technical and economic factors. It was judged at the time that no process had been demonstrated to satisfy these requirements with respect to gold-mill effluents, since it was not the practice of gold mines to treat their effluents, other than by natural degradation in tailings ponds. This method has not proved effective in producing acceptable effluents (i.e. effluents non-toxic to fish) in most cases.

The exemption carried with it the challenge to both government and industry to pursue acceptable technology for the treatment of cyanide-bearing effluents, with the aim of the developing practicable effluent limits within a reasonable time frame. As a consequence, an industry-government (federal and provincial) Working Group is in place with the objectives of identifying suitable technology and recommending practical national effluent standards for gold mines. Such standards have been in existence since April, 1977 for base metal, iron ore and uranium mines.

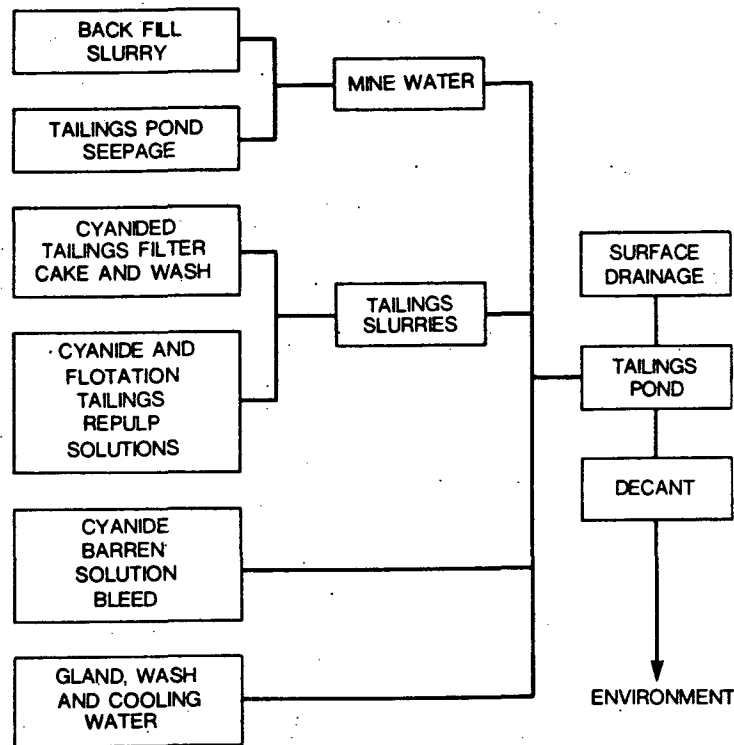


FIGURE 1 SOURCES CONTRIBUTING TO THE GOLD MINE EFFLUENTS

In the past few years there have been significant changes in both the economic and technological aspects of cyanide waste treatment. The price of gold has risen dramatically while at the same time the results of many of the studies on the destruction of cyanide which had begun in the mid-seventies have started to appear. In addition it is expected that the current expansion in the mining and milling of gold ores will result in a substantial increase in the use of cyanide and the discharge of cyanide-bearing effluents, all across Canada.

It is the purpose of this paper, then, to provide an overview of the range of technology available for treating cyanide in wastes and to give an indication of the state-of-the-art of the development of those that appear to be the most promising for ensuring that gold mine effluents are rendered non-toxic.

TABLE 2 SUMMARY OF BARREN BLEED SOLUTION ANALYSES

Mine	Flow IGPM	Mg/L								
		CN _T	CN _F	CNS	Cu	Pb	Zn	Fe	Ni	As
A	28.4	610	N.A.	400	11	0.1	84.1	0.37	1.7	N.A.
B	22.6	220	N.A.	180	73	0.1	17.9	35.7	2.9	0.03
C	6.0	300	N.A.	54	6.7	0.1	62.5	21.4	10.0	0.03
D	85.0	86	N.A.	42	6.1	0.1	13.9	0.06	0.28	0.03
E	41.7	120	N.A.	200	26.2	0.1	10.2	0.07	1.54	0.19
F	41.7	540	N.A.	N.A.	56	N.A.	100	N.A.	79	10.5
G	36.1	220	N.A.	N.A.	50	N.A.	4.1	9.9	14	1.6
H	118	24.4	N.A.	47	12.5	N.A.	5.0	N.A.	2	N.A.
I	97	74	N.A.	50	29	N.A.	31.0	0.1	9	0.005
J	4	750	N.A.	986	140	N.A.	56.0	0.4	200	0.07
K	45.5	310	N.A.	N.A.	300	N.A.	12.0	0.8	3.1	0.001
M	25.0	235	195	180	17.5	N.A.	125	64.5	3.0	3.0
N (1)	42.0	300	195	63.5	80	N.A.	94.5	130	6.0	3.0

N.A. - Not Available
 Ref. - Harrison 1979

5

TABLE 3 SOURCES OF CYANIDE IN GOLD MILL EFFLUENTS

Mine	Waste Barren		Tailings Repulp*		Mine Water	
	Flow IG/D	CN _T Mg/L	Flow IG/D	CN _T Mg/L	Flow IG/D	CN _T Mg/L
A	40,850	610	42,000	150	246,000	0.19
B	32,500	220	195,000	32	230,000	0.6
C	123,300	86	861,300	27	263,000	0.12
D	86,000	300	516,000	90	3,500,000	0.07
E	60,000	120	113,500	70	250,000	0.12
F	150,000	40	1,530,000	19	265,000	< 0.01
G	12,000	170	1,814,000	13	1,000,000	< 0.01
H	14,000	500	800,000	< 0.01	800,000	< 0.01
I	60,000	750	2,125,000	280	330,000	0.30
J	320,000	300	159,000	80	500,000	0

N.A. - Not Available

* - Repulped tailings (slurry) after the final filter

TABLE 4 SUMMARY OF CANADIAN GOLD MILL EFFLUENT DATA - 1978*

Mine	Effluent Volume, IGPD	Analyses Mg/L								
		pH	SS	Cu	Ni	Pb	Zn	Fe	As	CN _T
A	200,000	7.6	17	2.4	0.4	<0.1	0.82	0.6	<0.03	13
B	200,000	8.1	-	0.3	< 0.1	<0.1	0.04	5.1	<0.03	0.29
C	516,000	8.2	37	1.1	0.7	<0.1	0.7	8.2	<0.03	3.3
D	1,500,000	8.3	24	2.3	0.07	<0.1	0.2	0.3	<0.03	6.8
Q	300,000	8.0	8	37	0.7	<0.1	1.6	23	0.04	48
E	390,000	7.2	< 5	0.02	0.03	<0.1	0.1	4.4	<0.03	0.2
F	7,200,000	7.3	10	0.31	0.45	0.05	0.19	N.A.	0.90	0.33
H	1,678,330	7.7	19	0.48	0.16	0.03	0.13	N.A.	0.01	1.15
I	3,171,000	9.0	5	0.91	1.3	<0.01	0.7	N.A.	N.A.	9.6
I	1,000,000	7.8	3	0.04	0.27	<0.01	0.04	N.A.	N.A.	N.A.
J-1	800,000	7.5	3	0.04	0.04	<0.01	0.07	N.A.	N.A.	<0.01
J-2	252,000	7.7	108	0.04	0.41	<0.01	0.05	N.A.	N.A.	N.A.
K	1,600,000	7.7	2.1	9.5	0.10	<0.01	0.07	N.A.	N.A.	<0.01
L	159,000	7.9	123	0.25	0.13	0.02	0.64	N.A.	<0.01	1.8
L	433,000	7.6	159	1.62	< 0.01	0.01	0.17	N.A.	<0.01	N.A.
M	690,000	7-10	13	0.66	0.22	0.11	0.05	N.A.	0.5	1.9
N	915,000	9-10	53	16	1.84	0.10	0.60	N.A.	21.4	26.5

N.A. - Not Available

S.S. - Suspended Solids

Ref. - Harrison, 1979

Ayotte 1979

* Based on grab samples, hence indicative only. Composition of effluents varies widely through the year and particularly in winter.

2 TECHNOLOGY FOR CYANIDE REMOVAL FROM WASTE WATER

2.1 General

The need for the cyanide removal is not, of course, unique to Canadian gold mills. Base metal mines, electroplating and heat-treating facilities, petroleum refineries, steel and coke manufacturers all produce cyanide-bearing wastes. Many of these, particularly the electroplaters, are located in built-up areas, discharging their wastes to municipal sewage systems and thus have been under greater requirement to treat their wastes.

Since the volumes, but not the chemical constituents, of the waste effluents from gold mills are not greatly different from those in metal finishing, the experience gained in the latter industry provides a useful guide to cyanide removal methods possibly applicable in gold milling.

More recently, that is since about 1977, Homestake Gold Mines has carried out extensive investigations of a variety of cyanide destruction methods in an attempt to meet an effluent concentration of 0.02 ppm total CN, in order to comply with the State stream quality standards (Halbe 1980).

In addition, both the Canadian and U.S. environmental protection agencies have funded literature surveys and laboratory and pilot plant studies to evaluate the suitability of a number of the more promising methods and to attempt to overcome problems that might arise due to the peculiarities of gold mill effluents.

Thus, there is a large volume of up-to-date literature dealing with both the technological factors and (but to a lesser extent) the associated economic aspects of cyanide removal.

Table 5 lists most of the known methods for cyanide elimination.

Since the cyanide-bearing waste streams can represent a relatively small fraction of the total mine-mill effluent flow, the most practical approach is to treat them as close to their point of origin and in as concentrated a form as possible, rather than attempting to deal with a total flow of much greater volume and perhaps more complex composition.

Most of the processes are directed to destruction of cyanide, but three of them, Acidification/Volatilization/Reneutralization, the Electrolytic Cyanide Recovery treatment process and the Ion Exchange process, permit recovery of the major part of the cyanide as well as the metals content of the barren solutions. The treatment

TABLE 5 METHODS FOR REMOVING OR DESTROYING CYANIDE

Natural Degradation (Lagooning)

Volatilization
Biodegradation
Oxidation

Oxidation Processes

Alkaline Chlorination

chlorine gas
hypochlorites
electrolytic (in-situ) generation

Ozonation
Hydrogen Peroxide Oxidation

Acidification/Volatilization/Reneutralization

Absorption Processes

Ion Exchange
Activated Carbon
Ion Flotation

Electrolytic Processes

Cyanide regeneration
Cyanide destruction

Conversion to Less Toxic Forms

to thiocyanate
to ferrocyanide

method which is currently receiving the greatest attention, particularly in terms of actual installations, is alkaline chlorination.

2.2 Natural Degradation (Lagooning)

Existing practice is to direct the cyanide-containing streams to a tailings disposal area. Waste barren solution may be pumped to the receiving pond separately, or

used as a transport medium for the solid leach tailings. Thus, there may be a separate pond reserved for receiving barren solution, but in nearly all cases it is discharged into the tailings pond which receives all the mine-mill wastes.

Provided that the pond has a adequate retention time, and short-circuiting is avoided, the operation of natural environmental forces can effect some reduction in the concentration of a number of pollutants, including cyanide. These forces includes photodecomposition by sunlight, acidification by the carbon dioxide in the air, oxidation by oxygen in the air, dilution, adsorption on solids, and seepage into underlying porous media, as well as (but only at long retention times) biological action. Sunlight serves to liberate a fraction of the cyanide contained in the complex ferrocyanide ion. The liberated cyanide, cyanide released from other metal complexes, and any excess cyanide ion are converted to volatile hydrocyanic acid assisted by the progressive lowering of pH in the pond. This depression of pH is due mainly to the action of the carbon dioxide in the air, a reaction favoured by the fact that the initial elevated pH was due to the use of lime as a reagent, although dilution also plays a part. The volatilization of hydrogen cyanide is further accelerated by physical and thermal mixing in the pond and by air currents which remove evolved gas at the surface.

With the reduction in excess cyanide ion, secondary metal precipitation reactions, such as precipitation of zinc hydroxide, copper cyanide and zinc ferrocyanide, may be expected to occur.

Oxidation by oxygen and biological degradation are not likely to be significant factors with the relatively short retention time available in most tailings disposal lagoons.

As is well known, the extent of removal of cyanide is greatly decreased under winter conditions, due to such factors as low temperature and ice cover, which prevent the operation of most of the above-noted forces. These adverse effects could be partly overcome and the cyanide elimination process accelerated by keeping the pond open, improving the extent of mixing and providing increased contact with air and carbon dioxide.

Currently, one gold mine is looking at the implementation of some of these modifications. Some further improvement in natural degradation might be possible by subdividing the treatment lagoon and introducing air containing carbon dioxide-bearing stack gas into the pond for mixing. Also, to obtain the maximum reduction in cyanide concentration the barren solution should be impounded separately from other effluents. This method is practiced by Dome Mines in northern Ontario, where barren solution is impounded during the winter months. The solution is retained until mid-summer, by which

time the cyanide concentration has decreased from approximately 100 ppm to less than 1 ppm. The method may be adequate for lightly polluted effluents, but would probably not, by itself, ensure adequate cyanide elimination from more polluted or complex solutions. It should, however, be considered as a valuable pretreatment to a subsequent treatment method of barren solution.

2.3 Alkaline Chlorination

The use of chlorine and hypochlorite for the treatment of cyanide-containing waste waters is the most highly developed of all the available methods, from the standpoint of background experience, operational simplicity, control techniques, availability of equipment and engineering expertise. In addition, its history for the treatment of cyanide wastes (in the plating industry) dates back 35 years or more so that its strengths and limitations in this application are by now well known.

The first application of chlorination in the Canadian mining industry, to treat the effluent from the Myra Falls operation of Western Mines Ltd, was installed in 1973. It was the subject of a paper presented to the CMP 1977 meeting by A.G. Eccles (1977) who will be bringing us an up-date today.

Since then, its effectiveness and the economic aspects of its application to gold mill effluents have been the subject of laboratory tests and pilot plant investigations (Ritcey, McNamara 1978). (Wiskell, Price, Erkku 1977) and in-plant applications (L.S. Price 1980).

2.3.1 Chemistry of Alkaline Chlorination of Cyanide. The destruction of cyanide by alkaline chlorination may be accomplished by means of chlorine gas, calcium hypochlorite or sodium hypochlorite (White, 1972).

The principal chemical reactions involved are summarized in Table 6.

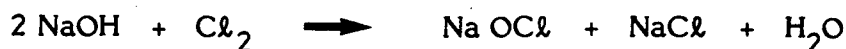
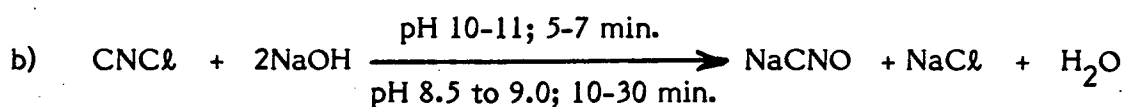
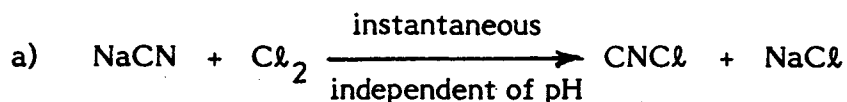
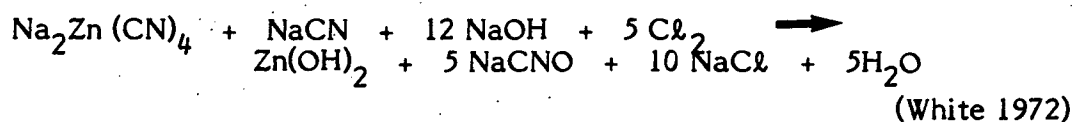
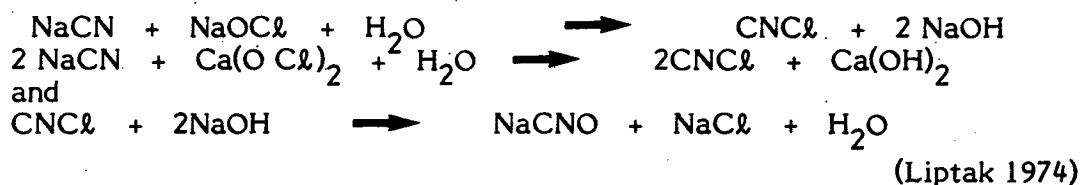
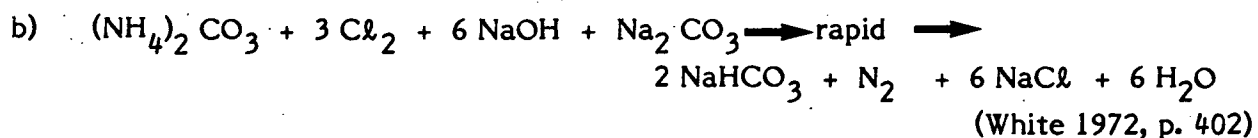
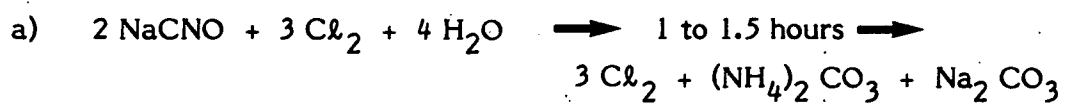
2.3.1.1 Chlorine gas (liquid chlorine). When chlorine gas dissolves in water it hydrolyzes rapidly according to the following equation (White 1972, eq 4.1 p. 183)



This reaction has three consequences with respect to the utilization of chlorine gas:

- 1) only the hypochlorite ion, i.e half of the total chlorine used, is effective as an oxidant
- 2) the acid liberated must be neutralized

TABLE 6 REACTIONS INVOLVED IN THE CHLORINATION OF CYANIDE

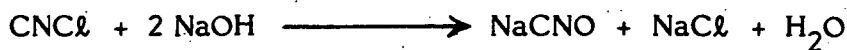
1 Hydrolysis - Dissolution of Chlorine Gas2. Formation of Sodium Hypochlorite from Chlorine Gas3. Oxidation of Cyanide by Chlorine Gas: 1st Stage4. Oxidation of Zinc Complex Cyanide by Chlorine: 1st Stage5. Oxidation of Cyanide by Hypochlorites6. Oxidation of Cyanide by Chlorine: 2nd Stage

- 3) the amount of chloride produced in the effluent is twice the amount that would be present if a chloride-free hypochlorite had been used.

Oxidation of cyanide by chlorine proceeds in two main stages. The first stage has two components, the initial one being oxidation of the cyanide to cyanogen chloride.



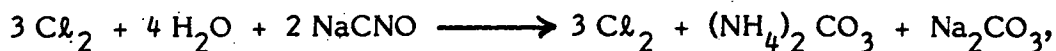
This reaction proceeds almost instantaneously and is independent of pH. The product, cyanogen chloride is highly volatile (b.p. 13.8°C), has limited solubility and its toxicity is of the same order of magnitude as hydrogen cyanide. In the presence of alkali, the cyanogen chloride then hydrolyses to cyanate.



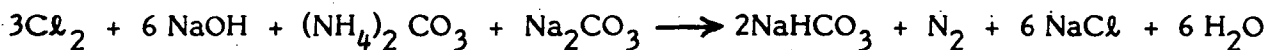
The overall first stage reaction (free cyanide to cyanate) takes 10 to 30 minutes at pH 8.5 to 9.0, dropping to 5 to 7 minutes at pH 10 to 11. If the pH drops as low as 8, cyanogen chloride will persist and in the absence of excess chlorine can continue to persist, at pH 9, for up to 24 hours (White 1972), (American Public Health Assoc. 1976).

The cyanates present as the end product of the reaction at pH 8.5 to 9.0 are not readily decomposed by water or by the excess alkali present in the treated waste unless free chlorine is present.

In the presence of free chlorine, however, the cyanate hydrolyzes to form ammonium carbonate and carbonate ion,

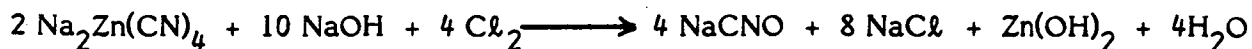


a reaction which takes about 1 1/2 hours. Once the hydrolysis is accomplished the chlorine and caustic rapidly oxidize the ammonium carbonate to nitrogen



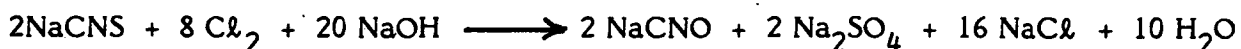
The oxidation of cyanide to cyanate theoretically requires 2.73 parts of chlorine and 3.34 parts of hydrated lime ($\text{Ca}(\text{OH})_2$) per part of free cyanide as CN, while complete destruction to nitrogen gas and carbonate requires 6.82 parts of chlorine and 8.35 parts of hydrated lime. Since complete destruction requires much longer contact time and involves greater reagent consumption, both capital and operating costs are very much higher than for oxidation to cyanate. For this reason, and because the cyanates are at least two orders of magnitude less toxic than cyanide the single stage oxidation to cyanate is usually considered acceptable.

The reaction of the more readily dissociated metal complex cyanides follows a similar path. For example, considering the zincocyanide complex,



the only differences are rate of reaction and formation of the metal hydroxide precipitate. If ferrocyanide is present the metal may precipitate as ferrocyanide instead.

Other oxidizable compounds present in solution also can consume chlorine, and because of the high oxidation potential of chlorine, potential candidates are numerous. The most obvious in gold mill effluents is thiocyanate and because of its labile sulphur atom it is a major chlorine consumer.



This reaction consumes 4.9 parts of chlorine and 6.4 parts of hydrated lime ($\text{Ca}(\text{OH})_2$) per part of thiocyanate as CNS.

Ammonia also consumes chlorine via the reaction already discussed under destruction of cyanate. In simplified form



and the reaction takes 6.3 parts of chlorine and 6.5 parts of hydrated lime ($\text{Ca}(\text{OH})_2$) per part of ammonia as NH_3 .

Chlorine gas requires special transport, handling and storage facilities. Its utilization requires special metering and control equipment, trained operators, and generally careful safety precautions. All of these factors have been well worked out, however, and a properly engineered installation should now present a minimum of problems. The principle disadvantage of liquid chlorine for use in remote locations is that it cannot be transported via aircraft.

Packaged units for generating chlorine electrolytically from salt solutions are available and may be practical if power costs are sufficiently low (Gott 1978).

Figure 2 is a diagram of the alkaline chlorination plant at Western Mines, with details of the various components required.

2.3.1.2 Sodium Hypochlorite. Sodium hypochlorite is made by dissolving chlorine in a solution of caustic soda.



It is usually marketed as a 5%, 10% or 13% solution; with the "available chlorine" content approximately of the same order. It has the advantage that

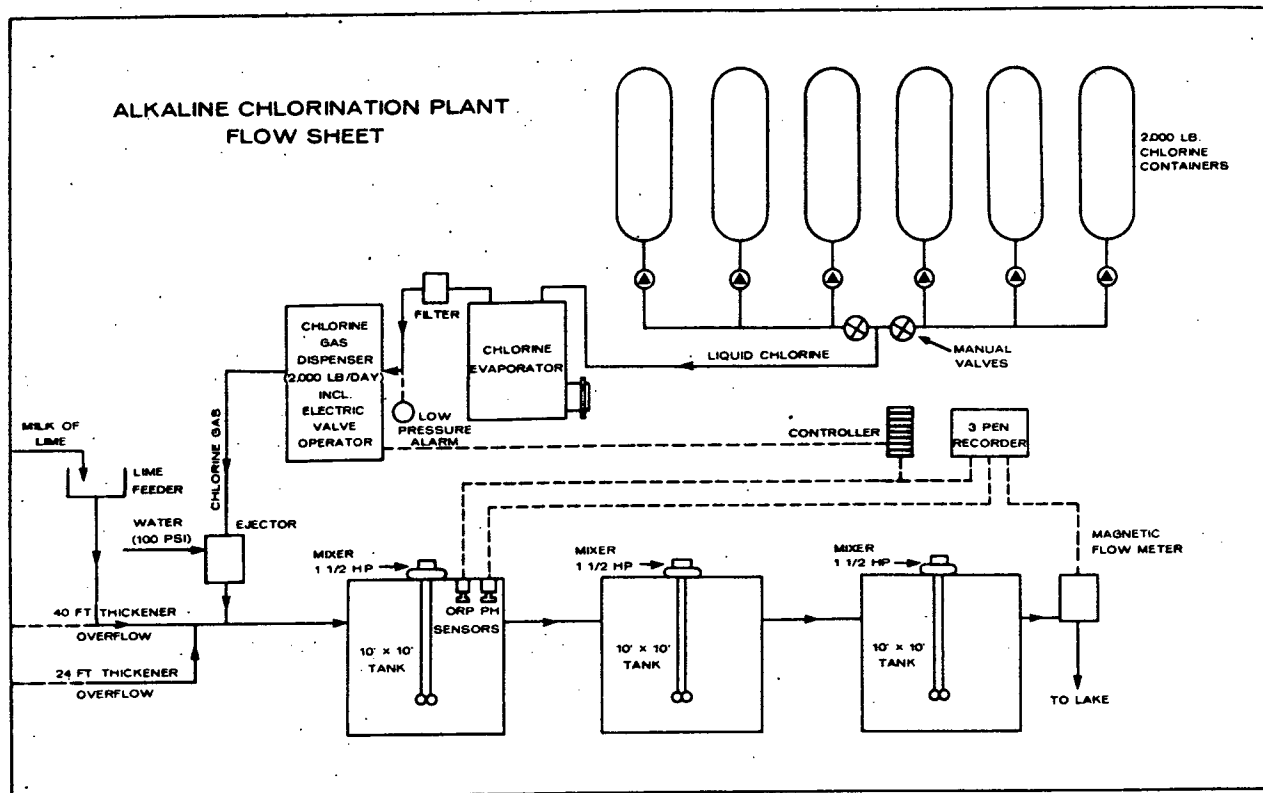


FIGURE 2 ALKALINE CHLORINATION PLANT FLOW SHEET (Eccles 1977)

requirements of hydroxide for neutralization are reduced, it can be metered with solution metering pumps, and it does not pose a fire hazard.

Disadvantages are instability, presence of inert chloride, relatively high cost, and additional expense of transportation.

2.3.1.3 Calcium Hypochlorite. Calcium hypochlorite is available both as bleaching powder (chlorinated lime -35% available chlorine) and HTH (solid calcium hypochlorite containing 3-6% lime and a little calcium carbonate - 70% available chlorine).

HTH has the advantage that its entire chlorine content is available chlorine. As a solid, it is easier to transport and store than liquid chlorine. It is more stable than sodium hypochlorite solutions when properly stored. It is quite soluble in water, so that the solid can be dissolved in water after which it can be metered and controlled in the same way as sodium hypochlorite (Price 1980). Unlike liquid chlorine it can be shipped by aircraft (in 25 kg packages on passenger flights and 45 kg packages on cargo flights). Nevertheless its storage and handling involve major safety considerations, and its cost is about five times that of chlorine at equivalent available chlorine content.

Tables 7 and 8, adapted from those presented by Ritcey (1977), tabulate the advantages and disadvantages of alkaline chlorination.

TABLE 7 ADVANTAGES OF ALKALINE CHLORINATION

Advantages

- 1) Very widely-used method, expertise is available.
 - 2) Influent to process already basic.
 - 3) Reactions complete and reasonably rapid.
 - 4) Toxic metals removed.
 - 5) Chlorine readily available in several different forms.
 - 6) Readily adaptable to either continuous or batch operation.
 - 7) Capital outlay relatively low.
 - 8) Good fail-safe control.
 - 9) Easily controlled to first stage of oxidation, if disposal of CNO^- is permitted.
-

TABLE 8 DISADVANTAGES OF ALKALINE CHLORINATION

Disadvantages

- 1) Reagent costs are high, particularly if complete oxidation is required. Thiocyanate, thio-salts and ammonia are additional heavy consumers of chlorine.
 - 2) Requires careful control of pH to prevent formation of cyanogen chloride which is very toxic.
 - 3) Cyanide is not recovered.
 - 4) Ferro or ferri cyanide are not usually decomposed.
 - 5) Metal content is not recovered.
 - 6) The chloride content of the effluent is increased in direct proportion to the amount of chlorine added.
 - 7) There is a possibility of forming toxic chlorine derivatives (e.g. chlorinated organic compounds) which will require further treatment.
-

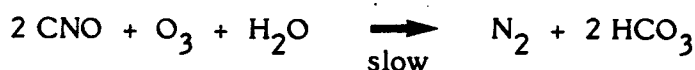
(adapted from Ritcey and McNamara 1978)

2.4 Ozonation

Ozonation tends to be regarded as an exotic technique for waste treatment. However, it is finding increasing application in water and sewage treatment for disinfection and sterilization. It is, for example, being used extensively in the province of Quebec where 19 water treatment plants employ ozone, including Montreal, whose plant is the largest ozone user in the world. World-wide, over 1000 water treatment plants use ozone. With this extensive use, equipment availability and performance are improving and cost is decreasing. Ozone is generated electrically, either from air or from oxygen. Use of oxygen yields twice the ozone concentration at half the power, and there may be some oxidation contribution from the oxygen itself. Hydrogen cyanide, cyanide ion, the complexes of zinc, cadmium and copper as well as thiocyanate are quickly and easily destroyed. The chemical reactions involved are shown in Table 9.

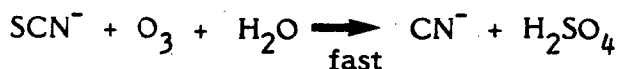
TABLE 9 REACTIONS INVOLVED IN THE OZONATION OF CYANIDE

1. Oxidation of Cyanide by Ozone



(Liptak 1974)

2. Oxidation of Thiocyanate by Ozone



Iron cyanides are more difficult to oxidize with ozone. The combination of ozone with ultra-violet light irradiation is reported to permit complete oxidation of ferrocyanide, but greatly increases cost. (Prober, Melnyk, Mansfield 1977) (Mauk, Prengle, Legan 1976).

Laboratory testing of ozonation on a Canadian gold mill barren was reported by Rowley and Otto (1979) They were able to reduce the total cyanide concentration in a gold mill barren (from Giant Yellowknife Mines Ltd.), which initially contained 450 mg/L total cyanide, to about 2 mg/L in less than 60 minutes. Extending the treatment to 4

hours failed to lower the residual cyanide concentration, a fact which they attributed to the presence of ferrocyanide. Thiocyanate concentration was reduced below the limit of detection. By extrapolating their data, they concluded that first year operating cost would be \$2.35 per kg of ozone generated or \$4.61 per kg of CN plus CNS destroyed.

Homestake Gold Mines has extensively tested ozonation on a large pilot-plant scale at about 100 U.S. gallons per minute. This confirmed that all the cyanides except ferro- and ferricyanide could be destroyed. From an input feed of about 2.5 ppm CN and 13.5 ppm CNS they were able to reduce both cyanide and thiocyanate concentration levels to less than 0.2 ppm, the residual CN being due to the presence of ferrocyanide.

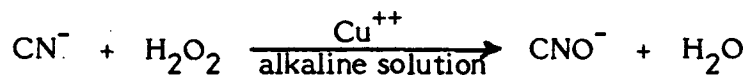
Unfortunately, since their regulatory objective is 0.02 ppm, they have had to consider alternative treatment methods, but given a different feed composition or a less stringent objective, ozonation could be the most suitable process.

2.5 Hydrogen Peroxide

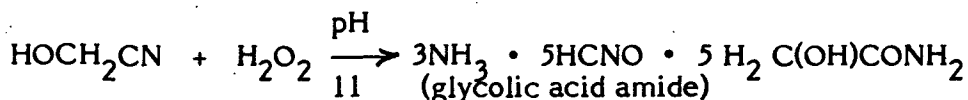
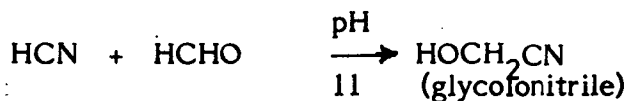
There are two processes employing hydrogen peroxide for cyanide destruction, equations for which are shown in Table 10. The first method employs a catalyst (copper ion) at alkaline pH, as shown in the following equations:

TABLE 10 OXIDATION OF CYANIDE USING HYDROGEN PEROXIDE

1. With Copper Catalyst



2. "Kastone" Process



The second process, known as the "Kastone" process, uses a proprietary formulation containing 41% H_2O_2 with trace amounts of catalyst and stabilizers called the "Kastone® Peroxygen Compound (Dupont)", in conjunction with formaldehyde. The cyanide wastes are heated to 120°F, treated with 3 to 4 parts of the "Peroxygen Compound" and 2 to 3 parts of a 37% solution of formaldehyde per part of sodium cyanide, then agitated for 1 hour. Principle products from the reaction are cyanates, ammonia and glycolic acid amide (Lawes et al 1973). Complete destruction of cyanates does not occur, so acid hydrolysis must be employed if this is required. (Goldstein 1976).

Hydrogen peroxide destroys hydrogen cyanide, cyanide ion and the cyanide in the zinc complex. Higher concentrations decompose most of the cyanide in copper and nickel cyanides. The cyanide in ferrocyanide is not destroyed, nor is thiocyanate. (Ommen 1980). The application of either of the peroxide processes is relatively simple.

Other peroxy compounds such as inorganic or organic peroxy acids may also be used (Zambrunn 1970).

2.6 Other Oxidation Processes

Kandzas et al (1977) have patented a process for destruction of cyanide using oxygen in the presence of PbO_2 catalyst.

2.7 Electrochemical Treatment Processes

Electrochemical treatment of cyanide wastes dates back to 1949. (Sperry, Caldwell 1949, Oylar 1949). In the interval it has been employed in the U.K. for treating plating waste and in Canada for the destruction of cyanide in heat-treating waste (Anon., 1975, Melnichuk, Byerley, Enns 1980). A typical cell used for the former application is shown in figure 3. HSA Reactors Ltd. (of Rexdale) investigated the application of their patented electrochemical technology to on-site treatment of barren solution at the Pamour Schumacher gold mill in a four month, pilot-scale (6 L per min.) campaign. The work included two process options: 1) Metal recovery along with cyanide recovery for recycle and 2) electrochlorination in situ (metal recovery with cyanide destruction). They estimated that process I would recover \$250,000 worth of cyanide per year, provided that the overall mill water balance would accommodate 100% recycle, and both processes would recover about \$90,000 worth of copper and additional gold per year. In actual fact a combination of the two processes would be required, but reagent and metal recovery might significantly offset the operating cost.

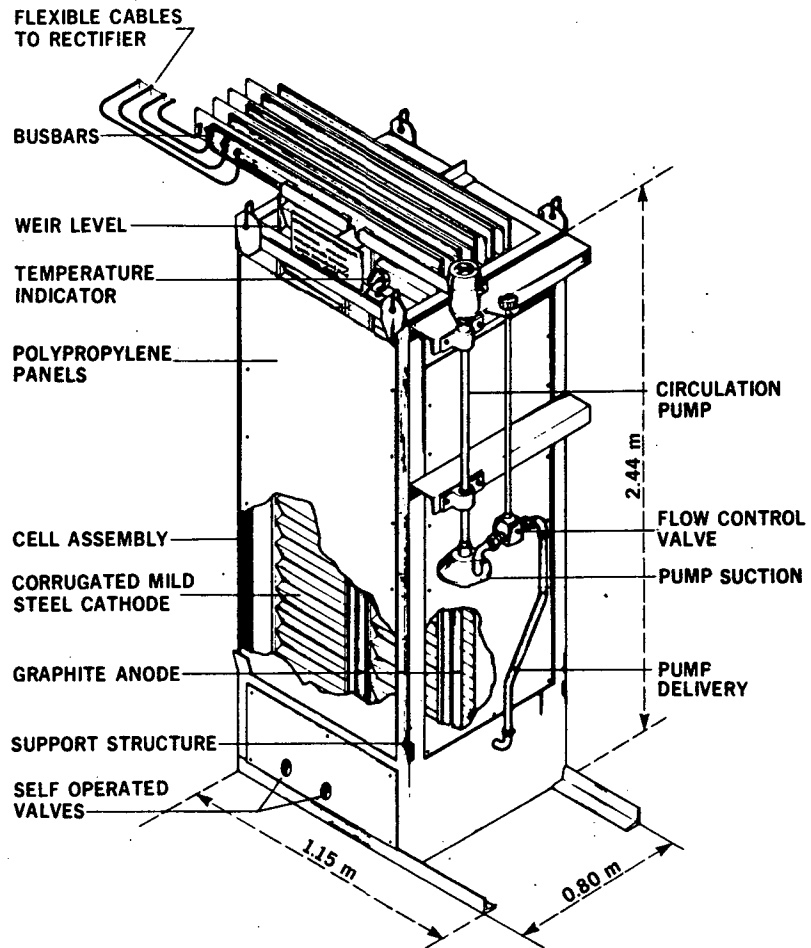
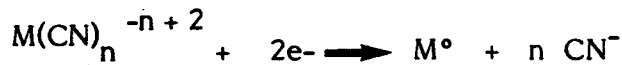


FIGURE 3 ELECTROLYTIC CELL FOR DESTRUCTION OF CYANIDE WASTES

Electrochemical methods fall into three general categories, and the chemical reactions involved are shown in Table 11.

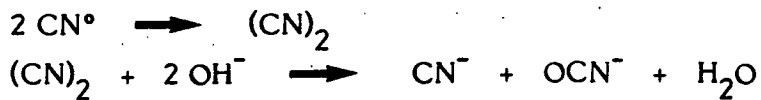
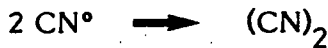
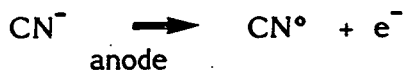
TABLE 11 ELECTROCHEMICAL REACTIONS WITH CYANIDES

1. Electro-reduction



(where M is a divalent metal)

2. Electro-oxidation (Anodic)



3. Electrochlorination

Anode reaction



Cathode reaction



2.7.1 Electroreduction (cathodic): Complex metal cyanide ions undergo reduction at the cathode to deposit or precipitate the metal, regenerating a corresponding amount of cyanide ion, according to the reaction 1 of Table 11.

2.7.2 Electro-oxidation (Anodic): The reactions occurring in anodic oxidation have apparently not been established but the sequence shown in Table 11 may apply (Kuhn 1971).

Thiocyanate is also oxidized, reporting in the effluent as cyanate and sulphate.

2.7.3 Electrochlorination: Introduction of sodium chloride into the solution to be treated gives rise to active chlorine ions either at the electrode or in solution. These react with cyanides to form cyanates, and with thiocyanate to form cyanate and sulphate, as in conventional alkaline chlorination. Chloride ion is regenerated and is therefore again available for charge transfer. The electrolysis should be carried out at 40°-50°C to minimize formation of chlorate at the expense of hypochlorite generation. As with conventional alkaline chlorination, pH control is important.

As far as is known, none of these electrochemical options results in elimination of ferrocyanide.

Option 1, electroreduction, would permit recycle of the regenerated cyanide in the treated barren solution to cyanidation to the extent that the water balance will accommodate it. The advantages of the reduction of fouling constituents (cyanicides) to the metallurgy of the process suggests that it could be advantageous to treat all the barren destined for recycle. This option does not, however, eliminate the necessity to treat that portion of the barren which must be discarded from the mill.

The ability of options 2 and 3 to reduce total cyanide concentration in the effluents to the proposed levels has not yet been demonstrated unequivocally. Electrochlorination appears to approach this goal more closely than electrooxidation. It should be pointed out that if the barren already contains chloride, as is often the case, electrochlorination will in fact be the operative mechanism.

2.8 Acid/Volatilization/Reneutralization

As has been noted already, hydrogen cyanide is extremely volatile, with a vapour pressure of 100 Kpa at 26°C. This phenomenon has been exploited in the Mills-Crowe process for cyanide regeneration. The solution is acidified (0.50-1.0 g/l H_2SO_4 excess) and dropped through a grid-packed tower counter-current to an air stream. The air, which picks up the hydrogen cyanide formed by the acid from the cyanide ion and zinc, copper and nickel cyanide complexes, is swept into an absorber tower where it contacts a weak lime slurry dispersed as a mist. The absorber tower solution is recycled so as to build up useable levels of cyanide concentration for return to cyanidation.

The acid treatment does not liberate cyanide from ferrocyanide or thiocyanate, although much of the cyanide content of the latter could probably be recovered by judicious addition of a strong oxidant after acidification.

A significant amount of solid, consisting of gypsum (from the neutralization of lime by sulphuric acid) and possibly some calcium carbonate from the CO_2 in the air, will form in the depleted cyanide solution. Depending on the composition of the barren feed and the final pH of the treated solution, cuprous cyanide and thiocyanate, and zinc, copper, nickel and iron ferrocyanides may be present as solids, and some zinc, copper, nickel and iron may also be present in solution. In addition the solution is, of course, acid. It is therefore necessary to neutralize and filter the stripped, treated barren before discharging it as effluent.

The acidification/volatilization/reneutralization treatment, like the chlorination process, has been quite thoroughly researched (McNamara 1978, Craigen and Kelly 1977, Ritcey and McNamara 1978,) and has had a significant extent of industrial application by Hudson Bay Mining and Smelting Co. at Flin Flon, Manitoba, where it was used for about 35 years. It was discontinued in 1978 when cyanidation of mill tailings was discontinued. (Mill Staff, 1946, Davis and Coulter 1957)

2.9 Ion Flotation and Precipitate Flotation

Ion flotation has been known for about 20 years now. It resembles conventional froth flotation in that it employs a collector and similar equipment, and the substance to be separated is carried out of the aqueous medium as a froth of air bubbles. (Reed et al 1971, Nagahama 1974) It differs in that the substance to be separated is not usually present initially as a solid. The collectors are ionizable surface-active organic compounds, cationic for the flotation of anions, anionic for floating cations. Since cyanide and its metal complexes are anions, cationic collectors are required. These are usually organic amines similar to those used for liquid-liquid extraction. Thus the mechanism of collection is similar to that of solvent extraction. Since metal cyanide complexes are removed more effectively than cyanide ion, and some of these complexes more effectively than others, it may be desirable to add metal ions to the solution to be treated.

Precipitate flotation differs from ion flotation in that a colloidal precipitate is first formed and then floated, but in the case of cyanides, the one technique merges with the other as a result of interactions between the metals and the cyanide complexes. A laboratory investigation (Reed et al 1971) showed that ferrocyanide and nickelocyanide could be floated effectively, while cuprocyanide has been successfully removed from a zinc concentrate thickener overflow on an industrial scale (2200 m³/day) by a combination of ion, precipitate, and ultra-fine particle flotation, at the Kamioka mine in Japan (Nagahama 1974). The optimum conditions for removal of cyanide from wastes after conversion to ferrocyanide ion and colloidal charged particles of Prussian Blue (poly nucleated $(\text{FeFe}(\text{CN})_6)^-$ and $(\text{FeFe}(\text{CN})_6)^{2-}$ respectively), have been reported by Grieves and Bhattacharyya (1969), using both ion and precipitate flotation. To date it has not been used commercially for the treatment of gold mill effluents.

2.10 Ion Exchange

The ion exchange process for cyanide recovery from gold mill effluents originated with Goldblatt (1956) in South Africa. Its development was prompted as much by concern for recovery of water in a relatively arid region as by loss of cyanide, and was made economically attractive by the availability of discarded ion exchange resin from uranium milling. The system comprised a lead column of the anion exchange resin IRA 400 to adsorb cyanide complexes, followed by a column of the same resin conditioned by precipitation of cuprous cyanide in the resin matrix, to remove free cyanide. The process apparently operated at about pH 11. The process was further refined by Goldblatt (1959) and these studies has served as the basis for most subsequent ion exchange applications.

Application of the method to Canadian gold mill effluents was investigated by CANMET (Gilmore 1976) and it was found to be unnecessary, in the case of the particular barren solution used in the study, to use the cuprous cyanide-saturated resin, satisfactory adsorption being achieved with two identical columns of IRA 400, sulphate form, in series.

Rohm and Haas Ltd, the resin manufacturer, has since investigated a number of resins, both weak-base (Avery, Fries 1974) and strong base (Avery, Waitz 1977), for cyanide removal. The most recent of these, IRA 958, is a strong base acrylic-based resin. It has been used in a pilot-plant study for the removal of cyanides from coke-plant wastes (Bessent, Luther, Eklund 1979) and from gold mill effluents (Halbe 1980).

Rohm and Haas, and Bessent et al note that the resin does not remove free cyanide effectively, and propose that it be converted to ferrocyanide by reaction with ferrous hydroxide prior to ion exchange. The indications are that all the metal complex cyanides are in fact readily adsorbed by anion exchange resins, and since there is often little or no uncomplexed cyanide ions in gold mill effluents, this is not a matter for concern. Where this is not the case, a small amount of any of the metals (zinc, copper or ferrous ion) could be added.

Some advantages of the ion exchange process are: 1) thiocyanate may either be retained or not, as desired, 2) cyanide may be recovered for re-use 3) metals are removed separately 4) engineering expertise is available. The main disadvantage is the fact that "package units" cannot be used and each plant would have to be engineered individually based on solution composition and pilot plant studies.

2.11 Activated Carbon Adsorption/Oxidation

The use of activated carbon for cyanide removal dates back some 14 years and apparently stems from attempts to employ it as a catalyst for the oxidation of cyanide to cyanate by oxygen (Honda, Kondo 1967; Bucksteeg 1966; Bernardin 1973; Kuhn, Wilson 1977). It was found that cyanide was first adsorbed, then catalytically oxidized. The presence of cupric ions results in the formation of copper cyanides, which enhances the adsorption capacity of the carbon. This not only permits faster flow rates but, as with some other methods for cyanide oxidation, adds to the catalytic action. The copper could be impregnated on the carbon or fed with the cyanide solution. Continuous copper feeding causes hydrolysis of cyanate to yield ammonia and carbon dioxide. (Bucksteeg 1966; Bucksteeg, Thiele 1969; Kunz, Casey, Huff 1978; Huff, Bigger 1980)

Reed et al (1971) at Battelle Institute investigated the removal of cyanide using granular activated carbon (20 x 50 mesh) without oxidation. They also found it necessary to add copper (or nickel), this time to ensure removal. The presence of dissolved oxygen thus becomes unnecessary but the bed must then be regenerated. A number of methods for stripping metals and cyanide from the carbon were worked out, but their effect on the life of the carbon was only briefly studied.

More recently the once-through use of powdered activated carbon (along with cupric chloride and dissolved oxygen) has been proposed for the removal of cyanide from petroleum refinery wastes. Aeration was accomplished using conventional activated sludge reactors of the type used in sewage treatment. (Huff, Bigger 1980). The required carbon/cupric chloride doses were quite low and capital cost was said to be small.

The catalytic oxidation option for the use of granulated activated carbon was investigated in the petroleum industry but was unsuccessful because of build-up of organics on the carbon. This would probably not be a problem with gold-mill barrens, and the method might be attractive for a mill already operating a carbon-in-pulp circuit. The once-through powdered activated carbon process would have the disadvantage of increasing the copper load of the waste (Huff, Bigger 1980). Strudgeon, Lewis et al (1980) discuss the safety implications in handling activated carbon.

2.12 Conversion of Cyanide to Less Toxic Forms

Conversion of cyanide to such stable and less toxic forms as ferrocyanide or thiocyanate has been advanced occasionally as a potential solution to the problem of cyanide waste disposal.

2.12.1 Conversion to Thiocyanate. This option was reviewed and critically evaluated by Dodge and Reams (1949). Cyanide reacts with polysulphides in solution at 80° or higher to yield thiocyanate. Lime sulphur (70% calcium sulphide, 5% calcium thiosulphate 5% free sulphur), a commonly used, cheap agricultural fungicide, can be used as the source of polysulphide (Wenlund, Gunick 1940). Dodge and Reams point out that "subsequent contact of the thiocyanate with acid would release hydrogen sulphide, and contact with chlorine or other oxidizing agent (at low pH) would (again) release hydrogen cyanide." This is a somewhat remote possibility in the case of gold mill decants.

2.12.2 Conversion to Ferrocyanide. Addition of excess ferrous sulphate to solutions of cyanide and the complex cyanides of zinc and copper which have been adjusted to pH's between 7.5 and 10.5 converts most of the cyanide to ferrocyanide. This is one of the oldest methods of cyanide disposal (Moir, Gray 1909). It was critically re-evaluated by the U.K. Department of Scientific and Industrial Research in 1947 (DSIR, 1947). The method worked best with samples containing from 10 to 100 ppm as HCN and required a large excess of ferrous sulphate (16 moles per mole of cyanide for cuprocyanide solutions). Cyanide reductions were 88 to 96%.

Reed et al (1971) concluded that the use of iron for complex formation and subsequent cyanide removal required too close control of solution pH to be feasible, and even then was only effective on pure cyanide solutions.

Unfortunately, although ferrocyanide can be considered as almost non-toxic itself, it is quite unstable in the presence of ultra-violet light, dissociating to regenerate cyanide ion. This reaction will occur even on cloudy days and at relatively northern latitudes. Though not rapid under these latter conditions, it sets obvious limits to the amount of ferrocyanide which can be permitted to be discharged. Thus, unless the amount of cyanide to be disposed of is already quite small, its conversion to ferrocyanide would in fact be unacceptable.

2.13 Ferrocyanide destruction or removal

In some cases, generation of ferrocyanide in the gold-milling process may not pose any problem. In other cases, concentration levels of metals such as zinc and copper released from their complexes may be sufficient to result in adequate removal of ferrocyanide by precipitation. In still others, adsorption of ferrocyanide on tailings solids may provide adequate control.

Nevertheless, there may be cases where the ferrocyanide level is such as to render an effluent environmentally unacceptable.

Unfortunately, processes for the elimination of ferrocyanide have not received the same attention as those for the simpler cyanides. As we have seen, natural degradation and acid volatilization leave ferrocyanide untouched in the effluent for disposal. The adsorption processes (ion exchange, activated carbon) yield a ferrocyanide-free effluent but produce in addition a strip solution which is more concentrated in ferrocyanide. The process employing electrochemical regeneration and recycle of barren doesn't remove ferrocyanide either, and hence can result in an ever-increasing build-up which may have to be dealt with.

The oxidation processes - alkali chlorination, electrolytic destruction, hydrogen peroxide and ozonation - as ordinarily employed, are equally ineffective in destroying ferrocyanide, tending instead to oxidize it to ferricyanide.

Complete decomposition with ozone is possible in the presence of ultraviolet light (Mauk, Prengle, Legan 1976) or at elevated temperatures and pH less than 3 (Henderson, Daignault 1973). Chlorination using elevated temperatures, long residence times, and/or in the presence of catalysts has also been proposed. Conditions suggested by Lancy (1,2) were to first chlorinate the waste to oxidize the weaker complexes, then add mercuric chloride catalyst and continue chlorination at 70°F for 24 hours or 180°F for 2 hours. Not only are these conditions unattractive in themselves but the use of mercuric chloride would, of course, be completely unacceptable. Hendrickson and Daignault (1973) found that ferrocyanide (20 g/L $K_4 Fe(CN)_6$) could be decomposed by alkaline chlorination, without a catalyst, in 4 hours at 90°C. None of the catalysts they investigated ($AgNO_3$, $NaNO_3$, $CdSO_4$, steel wool) had any effect. They also investigated acid chlorination. In the acid system maximum decomposition was only 85%, but by making the residue alkaline and rechlorinating, an additional 85% was destroyed, for an overall 98% destruction.

The discussion up till now has indicated that oxidative processes for the destruction of ferrocyanide, while technically possible, are most unattractive. Let us therefore look at some of the alternatives.

The previous investigators (Hendrickson, Daignault 1973) also studied the precipitation of ferrocyanide using heavy metals. Zinc, copper and ferric iron were all effective. Copper and zinc ferrocyanides were the most insoluble but the slowest to settle, and flocculants and centrifugation were used to separate the solids. Final

ferrocyanide levels were 2-3 mg/L $\text{Fe}(\text{CN})_6$. Ferricyanide did not precipitate well with any of the metals, but could be carried down if sufficient ferrocyanide was also present. Ferricyanide is not normally present in barrens or decants, but will be present in effluents treated by oxidation processes. Thus the residual solutions from these processes might have to be treated with a reducing agent prior to addition of the heavy metal precipitant.

Other more attractive alternatives are those proposed by Reed et al (1971), ion flotation and activated carbon adsorption, procedures which have been discussed earlier under these headings.

Methods for disposing of the ferrocyanide sludges would have to be worked out but in view of the relatively small quantities involved, incineration is one possibility.

3 FACTORS INFLUENCING THE CHOICE OF A TREATMENT PROCESS

The factors that influence the selection of the appropriate process for cyanide removal are technical suitability, capability to produce an acceptable effluent, and cost. Evaluation of these factors is greatly hindered at this time because few of the processes have been utilized for treating large volumes and none have been employed to treat gold mill effluents at full scale. The composition of the effluent to be treated is a major consideration in determining both the quality of the treated effluent and the unit cost of treatment. For example, thiocyanate consumes 5 times as much reagent as cyanide in oxidative destruction processes. Many processes either do not remove ferrocyanide adequately, or separate it as a product, usually in more concentrated form, but still necessitating additional disposal steps. Table 12 presents a comparison of most known treatment processes with respect to their effect on the various cyanide-derived compounds found in wastes.

The presentation of a comparison of capital and operating costs is difficult since it is dependent on many interrelated factors, the data that are available represent different years in an era of rapidly increasing costs, and for many of the processes, no applicable costs exist; Table 13 gives some values taken from the literature, qualified as far as possible as to the differences that affect comparability.

It should be emphasized that the goal of effluent treatment is not the specific elimination of cyanide, but the production of an effluent which is non-toxic, particularly to aquatic life. It will be important, therefore, that the overall process include steps for the removal of all other toxic constituents, and not itself introduce toxic components.

TABLE 12

ESTIMATED CAPABILITIES OF PROCESSES FOR CYANIDE REMOVAL FROM GOLD MILL EFFLUENTS*

Process	Suitability for Removal of						Products	Requires further treatment	
	CN ⁻ and HCN	Zinc and Cadmium complex cyanides		Copper and Nickel complex cyanides		Ferro cyanide, Fe(CN) ₆			Thio-cyanate, CNS
		metal	cyanide	metal	cyanide				
Natural degradation	yes	partial	partial	no	no	no	partial	decant	yes
Acidification/Volatilization/Reneutralization	yes	yes	yes	yes	yes	yes	partial	1) treated effluent 2) recycle cyanide solution	yes (a, b) no
Alkaline Chlorination	yes	yes	yes	yes	yes	no	yes	treated effluent	may (b)
Ozonation	yes	yes	yes	yes	yes	with UV irradiation	yes	treated effluent	may (b)
Ion Exchange									
1) untreated resin	no	yes	yes	yes	yes	yes	possible	1) treated effluent	no
2) untreated resin, pretreated solution	yes	yes	yes	yes	yes	yes	possible	2) waste regenerating solution	yes (c)
3) CuCN-treated resin	yes	yes	yes	yes	yes	yes	possible	3) recycle cyanide solution	no
Activated Carbon									
1) granular, fixed bed	no	partial	partial	yes	yes	yes	?	treated effluent	yes (d)
2) granular, copper-treated fixed bed	partial	yes	yes	yes	yes	yes	?	1) treated effluent 2) strip solutions	may (d) yes (d,e)
Activated Carbon, copper-treated, with aeration									
1) granular, fixed bed	yes	yes	yes	yes	yes	partial	?	treated effluent	may (b)
2) powdered, once through	yes	yes	yes	yes	yes	yes	?	1) treated effluent 2) cyanide-free sludge	no no

TABLE 12

ESTIMATED CAPABILITIES OF PROCESSES FOR CYANIDE REMOVAL FROM GOLD MILL EFFLUENTS* (continued)

Process	Suitability for Removal of							Products	Requires further treatment
	CN ⁻ and HCN	Zinc and Cadmium complex cyanides		Copper and Nickel complex cyanides		Ferro cyanide, Fe(CN) ₆	Thio-cyanate, CNS		
		metal	cyanide	metal	cyanide				
Ion Flotation	partial (e)	partial	partial	yes	yes	yes	?	1) treated effluent 2) sludge	may (d) yes
Electrochemical									
1) for cyanide recovery	no (h)	yes	no	yes	no	no	no	1) partially regenerated cyanide solution (for recycle) 2) metal-bearing strip solution	may (f) yes (g)
2) for cyanide destruction	partial to most	yes	partial to most	yes	partial to most	no	yes	1) treated effluent 2) metal-bearing strip solution	may (b) yes (g)
3) Electro-chlorination	yes	yes	yes	yes	yes	no	yes	1) treated effluent 2) metal-bearing strip solution	may (b) yes (g)
Hydrogen Peroxide	yes	yes	yes	partial	partial	no	no	treated effluent	may (b)

a) Extra filtration steps both before and after liming, if copper, nickel and ferrocyanide levels are high.

b) Supplementary treatment (e.g. activated carbon) if ferrocyanide level high.

c) Treatment (e.g. liming) to recover metals for disposal.

d) May require pretreatment to convert all cyanide to copper or iron complexes.

e) Depends on prior conversion to ferrocyanide.

f) Thiocyanate and ferrocyanide build-up, and water-balance considerations will necessitate bleed stream requiring further treatment.

g) Strip solution may be regenerated electrolytically, recovering metals as powder.

h) Cyanide is recycled instead.

* The estimates of performance capability presented in this table are based on literature data for feed solutions from many different sources. The final cyanide concentration that can be achieved, and the cost of treatment in any particular case, can only be determined by actual tests.

TABLE 13 COST DATA FOR SOME CYANIDE DESTRUCTION PROCESSES

Process	Year of Estimate	Location	Size of Plant, IGPD	Solution Composition, mg/L		Cost		Reference
				CN _T	CNS	Capital	Operating (annual) (uncorrected) Note 1	
Alkaline Chlorination (chlorine)	1973 -1977	Western Mines Vancouver Island	200,000	68.3	N.A.	\$107,000	\$96,000*	1
Alkaline Chlorination (chlorine)	1977	Ontario	180,000	40	40	62,000	100,000	2
Alkaline Chlorination (chlorine)	1977	Yellowknife NWT	225,000	117	N.A. (Arsenic 317)	302,000 Note 3	263,000 Note 3	3
Ozonation	1978	Plating Waste U.S.	34,400 Avg	72 (Avg)	N.A.	110,000	4,500	4
Alkaline Chlorination	same	same	68,800 (peak)	260 (peak)	N.A.	42,000	13,250	
Ozonation	1977	Ontario	180,000	40	40	162,000	90,200	2
Ozonation	1979	Yellowknife NWT	66,000	400	100	1,200,000	242,000	5
Ion Exchange	1977	Ontario	180,000	40	40	182,000	193,300	2
Electrochemical (HSA Reactors)								
recovery-recycle	1980	Ontario	97,000	1300	750	430,000	70,590 Note 4	6
destruction	1980	Ontario	same	same	same	550,000	237,000 Note 4	6

TABLE 13 COST DATA FOR SOME CYANIDE DESTRUCTION PROCESSES (continued)

Process	Year of Estimate	Location	Size of Plant, IGPD	Solution Composition, mg/L		Cost		Reference
				CN _T	CNS	Capital	Operating (annual) (uncorrected) Note 1	
Acidification - Volatilization Regeneration								
(Separate acidification)	1977	Ontario	180,000	40	40	346,700	282,600	2
(Integral acidification)	1977	same	same	same	same	242,800	265,800	2
Powdered Activated Carbon, once-through								
one-stage	1980	U.S. petroleum refinery	3.4 x 10 ⁶	0.08	N.A.	N.A.	320,000	7
two-stage	same		same	same	same	(Note 5) same	100,000	7
Granular Activated Carbon, Air oxidation								
	1973	Plating Waste U.S.	200,000	100	N.A.	100,000	100,000 (reagents only)	8

- N.A. - Not Available
- Note 1 - Not adjusted to 1980, no credit for tax incentives
- Note 2 - Recalculated from submitted data
- Note 3 - Recalculated to delete cost of arsenic precipitation
- Note 4 - Not including credits for recovered cyanide or metals
- Note 5 - Assumes activated sludge installation already in place
- * - Actual plant data; others based on laboratory or pilot plant studies.

References

1. Eccles, 1977
2. Craigen, Kelly 1977
3. Erkkku, Price, 1980
4. Cullivan, 1978
5. Rowley, Otto, 1979
6. Mohanta, Jacobs et al 1980
7. Huff, Bigger, 1980
8. Hoffman, 1973

4 **MODIFICATIONS AND IMPROVEMENTS TO THE GOLD CYANIDATION PROCESS AS A FACTOR IN REDUCING EFFLUENT TREATMENT COSTS**

The requirement to eliminate cyanide from effluents means, in effect, that the cost attributable to cyanide consumption now includes all costs related to its ultimate destruction or removal. Some methods of reducing treatment costs include reducing the volume of waste to be treated (thus reducing equipment size and hence capital cost), and minimizing not only its cyanide content but also the content of other solution components that increase treatment cost by consuming reagents or by requiring prolonged contact time.

One method of reducing the cyanide content might be improved feeding and monitoring of cyanide in both cyanidation and precipitation. In the case of ores containing pyrrhotite this might also have the effect of reducing the thiocyanate and ferrocyanide contents in solution. Minimizing thiocyanate formation is particularly important, since not only does it consume much greater quantities of the reagents employed in oxidative effluent treatment processes for cyanide destruction, but it also reduces the gold dissolution rate (McCreedy, Clark, Gow 1961). This, in turn, can lead to the use of higher cyanide concentrations in an attempt to compensate for this negative effect. Thiocyanate formation can be minimized by close pH and temperature control.

Ammonia concentration in the barren should also be minimized if an oxidative process is selected for cyanide destruction, since, as noted, it also consumes oxidant. In the case of chlorine also, it yields chloramines, with possible problems due to their slow decay.

Achieving a reduction in the volume of waste to be treated may require a significant re-routing of water and solutions within the mine-mill complex. As far as possible untreated barren solution should only be recycled to cyanidation and treated barren solution only used for such other purposes as washing of residue filter cake, repulping of tailings or backfill, floor washing, etc. Other methods of limiting cyanide concentration and effluent volume will undoubtedly suggest themselves to the experienced operator.

5 CONCLUSION

This review has attempted to summarize the applicability and shortcomings of the better-known methods for cyanide removal from waste effluents. When technical suitability and costs are taken into consideration, some of these processes will probably prove unsuitable for treating gold mill effluents. It is also apparent that no one process will be applicable to every Canadian gold mill effluents. The information presented here, in conjunction with a knowledge of the range of the composition of a particular waste should assist in the selection of those processes worthy of further consideration and evaluation in any particular case.

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7 REFERENCES AND BIBLIOGRAPHY

- Anon., 1975 "Cyanil unit eliminates CN ion," Can. Chem. Processing, 28-30, Aug. 1975.
- Avery, N.L., Fries, W., 1974 "Removal of cyanide from industrial waste effluents with ion exchange resins," Rohm and Haas Co., 1974.
- Avery, N.L., Waitz, W.H., 1977 "Ion exchange treatment process for the selective removal of cyanide," Amber-Hi-Lites, Rohm and Haas Co. Phila., Pa., Summer 1977.
- Ayotte, C., 1979 "Étude de la qualité des effluents des mines d'or du Québec," Quebec-Canada: SPE-EPS rapport CE-3R-114, Dec. 1979.
- Bernardin, F., 1973, "Cyanide detoxification using adsorption and catalytic oxidation on granular activated carbon," J. Water Poll. Control Fed., 45, No. 2, 221-231, 1973.
- Bessent, R.A., Luther, P.A., Eklund, C.W., 1979 "Removal of cyanides from coke plant wastewaters by selective ion exchange - results of pilot testing program," Proc. 34th Industrial Waste Conf., Purdue Univ., Lafayette Ind., 1979.
- Bucksteeg, W., 1966 "Decontaminating of cyanide wastes by methods of catalytic oxidation and adsorption," Proc. 21st Industrial Waste Conf., Purdue Univ., Lafayette Ind. 1966.
- Bucksteeg, W., Thiele, H., 1969 "Methods for the detoxification of wastewater containing cyanide," German Patent 1,140,963, Jan. 1969.
- Cheremisinoff, P.N., Young, R.A., 1975 "Pollution engineering practice handbook," Ann Arbor Science, Ann Arbor, Mich. 1975. Ultraviolet water purification pp. 404-10.
- Craigen, W.J.S., and Kelly, F.J., 1977 "Economic evaluation of cyanide removal processes," CANMET, Energy Mines and Resources Canada, Lab Report MRP/MSL 77-5 (IR) 1977.
- Cullivan, B., 1978 "Industrial toxics oxidation - an ozone - chlorine comparison," Proc. 33rd Industrial Waste Conf., Purdue Univ., Lafayette Ind., 1978.
- Davis, D., Coulter, R.F., 1957 "Flin Flon Mines" in "The milling of Canadian ores," pp. 189-203, pub. by the 6th Commonwealth Mining and Metallurgical Congress, 1957.
- Dodge, B.F., Reams, D.C., 1949 "A critical review of the literature pertaining to the disposal of waste cyanide solutions, part 2, Plating, 36, 571-577,664, June, 1949.
- Doudoroff, P., 1976 "Toxicity to fish of cyanide and related compound - a review," EPA 600/3-76-038, U.S. Environmental Protection Agency, Duluth Minn., April 1976.
- DSIR., 1947 "Report of the Water Pollution Research Board 1939-1945" Dept. Sci. and Industr. Res., pp. 49-52, His Majesty's Stationery Office, London 1947.

Eccles, A.G., 1977 "Cyanide destruction at Western Mines," Proc. 9th Annual Meeting Canadian Mineral Processors pp. 33-57, 1977.

Environmental Protection Service, 1977 "Metal mining liquid effluent regulations and guidelines," Environment Canada, WPCD, Report EPS 1-WP-77-1, 1977.

Gilmore, A.J., 1976 "The ion exchange removal of cyanide from gold mill wastes for environmental benefit", CANMET, Mineral Sciences Laboratories, Report MRP/MSL 76-26 (IR), 1976.

Goldblatt, E., 1956 "Recovery of cyanide from waste cyanide solution by ion exchange", Ind. Eng. Chem., 48, 2107, 1956.

Goldblatt, E., 1959 "Recovery of cyanide from waste cyanide solution by ion-exchange", Ind. Eng. Chem., 51, No. 3, 241, March 1959.

Goldstein, M., 1976 "Economics of treating cyanide wastes," Pollution Engineering, 8, No. 3, 36-38, March 1976.

Gott, R.D., 1978 "Developments of waste water treatment at the Climax mine", Mining Congress J., 28-34, April 1978.

Grieves, R.B., Bhattacharyya 1969, "Precipitate flotation of complexed cyanide", Proc. 24th Ind. Waste Conf. Purdue Univ., Lafayette Ind., 1969.

Harrison, D., 1979 "Summary of gold mines in Canada; descriptions of processes and effluent streams," Gold Mining Industry Task Force Project 060, Summer 1979.

Hawley, J., 1978 "A water pollution report; active mining operations in the Province of Ontario", Ontario, Ministry of the Environment, July 1, 1978.

Halbe, D., 1980 Homestake Mining Co., Lead, S. Dak., USA, private communication 1980.

Hardisty, D.M., Rosen, H.M. 1977 "Industrial Wastewater Ozonation," Proc. 32nd Industrial Waste Conf., Purdue Univ., Lafayette Ind., 1977.

Henderson, T.N., Daignault, L.G. 1973 "Treatment of complex cyanide compounds for re-use or disposal," U.S. EPA, Office of Research and Monitoring, Washington, D.C., Report EPA-R2-73-269, June 1973.

Hoffman, D.C., 1973 "Oxidation of cyanide adsorbed on granular activated carbon" Plating, 157-162, Feb. 1973.

Honda, S., Kondo, G., 1967 "Treatment of wastewater containing cyanide using activated charcoal," Osaka Kogyo Gijutsu Shikensho Koho, (Japan) 18, No. 4; 367, 1967.

Huff, J.E., Bigger, J.M., 1980 "Cyanide removal from refinery wastewater using powdered activated carbon", Robt. S. Kerr Environmental Research Laboratory, Ada Okla, EPA-600/2-80-125, May 1980.

- Hyatt, D.E., 1976 "Chemical basis of techniques for the decomposition and removal of cyanides," Trans. Soc. Min. Eng., AIME, 260, 204-207, Sept. 1976.
- Kandzas, P.F. et al., 1977 "Removal of cyanides from wastewaters," Russ pat. 456, 507 June 25, 1977, Chem Abstr., 87, 106561 v, 1977.
- Kauffman, G.B., Foust, G.E., Tun, P., 1968, "Pseudohalogens," J. Chem. Ed., 45, No. 2, 141, Feb. 1968.
- Kuhn, A.T. 1971, "Electrolytic decomposition of cyanides, phenols and thiocyanates in effluent streams - a review," J. Appl. Chem. Biotech, 21, No. 2, 29-34, Feb. 1971.
- Kuhn, A., Wilson, C., 1977, "The catalytic air oxidation of cyanides," Oberflache Surf., 18, No. 4, 91, 1977.
- Kunz, R.G., Casey, G.P., Huff, J.E., 1978 "Refinery cyanides, a regulatory dilemma," Hydrocarbon Processing, 98-106, Oct. 1978.
- Lancy, L., 1961 (1), "Chlorination of water-soluble iron compounds using mercuric chloride catalyst," U.S. Patent 2,981,682, 1961.
- Lancy, L., 1961 (2), "Conditioning of cyanide compounds," U.S. Patent 3,101,320.
- Lawes, B.C., Fournier, L.B., Mather, O.B., 1973, "A peroxygen system for destroying cyanide in zinc and cadmium electroplating rinse waters," Plating 60, 902, Sept. 1973.
- Laxen, P.A., Becker, G.S.M., Rubin, R., 1979, "Developments in the application of carbon-in-pulp to the recovery of gold from South African ores," J.S. Afr. Inst. Min. Metall., 79, No. 11, 315-26, 1979.
- Liptak, B.G., 1974, "Environmental engineers handbook," Chilton Book Co., Radnor Pa., 1974. Ozonation pp. 1409-15, 1587-9.
- Mathieu, G.T., 1976, "A preliminary evaluation of ozonation for cyanide destruction of Canadian gold mill effluents," CANMET, Mineral Sciences Laboratories Report MRP/MSL 76-349 (R) 1976.
- Mattock, G., 1977, "Recovery and re-use of metals and chemicals from metal finishing wastes," in "Proceedings, Technology Transfer Seminar on Waste Handling, Disposal and Recovery in the Metal Finishing Industry" EPS, Environ. Canada, Toronto 1975, pub. March 1977.
- Mauk, C.E., Prengle, H.W., Legan, R.W., 1976, "Chemical oxidation of cyanide species by ozone with irradiation from ultra-violet light," Trans. Soc. Min. Eng., 260, 297-300 Dec. 1976.
- McCreehy, H., Clark, C.C., Gow, W.A., 1961 "The use of the gold-leaf test to check the effects of certain possible contaminants of cyanide solutions", Mines Branch, Extraction Metallurgy Division, Investigation Report IR 61-25, 1961.

McNamara, V.M., 1978, "Acidification/volatilization/reneutralization treatment process for decontamination of Canadian gold mill effluents," CANMET, Energy Mines and Resources Canada, Lab Report MRP/MSL 78-223 (IR) 1978.

Melnichuk, P., Byerley, J.J., Enns, K., 1980, "Waterloo Cyanide Recovery Treatment System," Waterloo Centre for Process Development, University of Waterloo, Waterloo, Ont., 1980.

Mill Staff, Flin Flon Concentrator, Hudson Bay Mining and Smelting Co., 1946, "Cyanide and regeneration plant practice at Flin Flon," Trans. CIMM, 49, 130-142, 1946.

Mohanta, S., Jacobs, J., Kennedy, I., Fleet, B., Das Gupta, S. 1980, "Pilot plant investigations of a novel electrochemical treatment of effluents from gold-milling processes", HSA Reactors Ltd. report, prepared for Dept. of Supply and Services and Environment Canada, 1980.

Moir, J., Gray, J., 1909, "The destruction of cyanide" J. Chem. Met. Mining Soc. S. Africa, 10, 433-439, 1909.

Montreal Engineering Co. Ltd., 1973, "A preliminary survey of cyanide-bearing liquid wastes in Canada," Environment Canada, Environmental Protection Service, March 1973.

Murphy, K.L., Robertson, J.L., 1979 "Polysulphides for conversion of cyanides to thiocyanates in gold milling effluents A Literature Review for Fisheries and Environment Canada," Project 2078.2 30, March, 1979, IEC International Environmental Consultants Ltd., 1979.

Nagahama, T., 1974, "Treatment of effluent from the Kamioka concentrator by flotation techniques including development of the Nagahm flotation machine," Bull. CIM, 67, 79-89, April 1974.

Nagy, I., Mrkusic, P., McCulloch, H.W. 1966, "Chemical treatment of refractory gold ores - literature survey," South Africa National Institute of Metallurgy, Report No. 38, Johannesburg, June 1962.

Oeming, L.F., 1946, "Stream pollution problems of the electroplating industry," Sewage Works J. 18, No. 4, 678, 1946.

Ommen, R., 1980, Homestake Mining Co., Lead, S. Dak, U.S.A. private communication.

Oyler, R.W., 1949, "Disposal of waste cyanides by electrolytic oxidation," Plating, 36 No. 4, 341, 1949.

Price, L.S., 1980, Falconbridge Nickel Mines Ltd., Toronto, Ontario, private communication, 1980.

Prengle, H.W., Mauk, C.E., Legan, R.W., Hewes, C.G. III, 1975, "Ozone/U.V. process effective wastewater treatment," Hydrocarbon Processing, Oct. 1975.

Prober, R., Melnyk, P., Mansfield, L., 1977, "Ozone - ultraviolet treatment of coke oven and blast furnace effluents for destruction of ferricyanides," Proc. 32nd Industrial Waste Conf., Purdue Univ., Lafayette Ind., 1977.

Raef, S.F., Characklis, W.G., Kessick, M.A., Ward, C.H., 1974, "Fate of cyanide and related compounds in industrial waste treatment," Proc. 29th Industrial Waste Conf., Purdue Univ. Lafayette Ind., 1974.

Reed, A.K. et al., 1971, "An investigation of techniques for removal of cyanide from electroplating waste," U.S. Environ. Protection Agency, Water Pollution Control Series, Program No. 12010 EIE 11/71, Nov. 1971.

Ritcey, G.M. and McNamara, V.M., 1978, "Treatment of gold mill effluents for removal and recovery or destruction of cyanide - the summary of a joint project with six Canadian gold mills," Proc. 10th Ann. Conf. Canadian Mineral Processors, pp. 152-196, Jan. 24-26, 1978.

Rosehart, R.G., Chu, R., 1974, "Cyanide destruction in mine waste water," Proc. 9th Can. Symp. Water Poll. Res. in Canada, 1974.

Rowley, W.J., Otto, F.D., 1979, "Ozonation of cyanide with emphasis on gold mill waste waters," 29th Can. Chem. Eng. Conf., Sarnia, Oct. 1, 1979.

Seeton, F.A., 1966, "The cyanide process for gold and silver ores," Deco Trefoil, Bull. M3-B-16, Jan. Feb. 1966.

Sperry, L.B., Caldwell, M.R., 1949, "Destruction of cyanide copper solutions by hot electrolysis," Plating 36, No. 4, 343, 1949.

Strudgeon, G.E., Lewis, B.J., Albury, W.W., Clinger, R.C., 1980, "Safety considerations in handling activated carbon," J. Water Poll. Control Fed., 52, No. 10, 2516, 1980.

White, G.C., 1972, "Handbook of chlorination," New York, Van Nostrand Reinhold Co., 1972.

Wernlund, C.J., Gunick, M.J., 1940, "Disposal of waste cyanide solutions," U.S. Patent 2,194,438, 1940.

Wiskel, B.W., Price, L.S., with Erkkku, H., 1977, "Treatment of Giant Yellowknife Mines effluent for reduction of cyanide and arsenic - Pilot plant operation at Giant Yellowknife Mines Ltd. 1976-77," Giant Yellowknife Mines Ltd., Fisheries and Environment Canada, 1977.

Zadra, J.B., Engel, A.L., and Heinen, H.J., 1952, "Process for recovering gold and silver from activated carbon by leaching and electrolysis," USBM R.I. 4843, 1952.

Zambrunn, J.P., 1970, "Destruction of dissolved cyanides," U.S. patent 3,510,424 May 5, 1970.