Mines Branch Information Circular IC 145

CYANIDE RECOVERY FROM GOLD-BARREN WASTE SOLUTIONS: A Literature Review.

by

A. J. Gilmore[*] and W. A. Gow[**]

SUMMARY

The literature has been reviewed to assess the possibilities of economically recovering cyanide from alkaline waste solutions from Canadian gold-milling operations.

The literature cites two possible processes. In one process, now in use in a Canadian plant, the alkaline waste solution is acidified with sulphuric acid to convert the free and combined cyanide to hydrocyanic acid, which is absorbed in a lime slurry. The other process was developed to the pilot plant stage in South Africa. It involves an ion exchange technique. By the use of both anion and cation exchangers, both the cyanide and the base metals, present as metal cyanide complexes, are recovered.

Cyanide recovery by these two processes would be uneconomic in most Canadian operations, mainly because of the small tonnages of cyanide discarded.

---

[*] Senior Scientific Officer and [**] Head, Hydrometallurgy Subdivision, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines

Circulaire d'information IC 145

RÉCUPÉRATION DU CYANURE DES SOLUTIONS DE REBUT DONT ON A EXTRAIT L'OR:

Aperçu bibliographique

par

A. J. Gilmore* et W. A. Gow**

RÉSUMÉ

Les auteurs ont fait l'examen des publications appropriées afin de déterminer s'il serait rentable de récupérer le cyanure présent dans les solutions alcalines de rebut dans les ateliers d'extraction de l'or.

Les ouvrages traitent de deux procédés possibles. Dans le premier, qui est en usage dans une usine canadienne, la solution alcaline de rebut est traitée à l'acide sulfurique afin de transformer le cyanure libre et combiné en acide cyanhydrique, qui est absorbé par une pâte aqueuse de chaux. Quant au second procédé, il a atteint le stade semi-industriel en l'Union sud-africaine. Dans ce dernier cas, on a recours à l'échange ionique. En utilisant des échangeurs tant anioniques que cationiques, on peut récupérer aussi bien le cyanure que les métaux communs, qui sont présents sous forme de complexes métalliques cyanurés.

La récupération du cyanure par l'un ou l'autre des procédés susmentionnés ne serait pas rentable dans la plupart des installations canadiennes, à cause surtout de la faible quantité de cyanure jetée au rebut.

---

*Chargé de recherches principal et **chef, Subdivision de l'hydrométallurgie, Division de la métallurgie extractive, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CONTENTS

Tables

Figures

INTRODUCTION

In the treatment of gold ores by the cyanidation process, gold milling plants are forced to discard a portion of the plant solutions. This waste is necessary to purge the solutions of impurities that interfere with the dissolution of gold by cyanide. These waste solutions contain cyanide, present as free cyanide, thiocyanate, and metal cyanide complexes.

Early in 1962, a group of Canadian gold mill operators asked the Extraction Metallurgy Division of the Mines Branch to investigate the possibility of economically recovering the cyanide being discarded. Data from sixteen operating gold mills, submitted with the request, showed that the value of discarded free cyanide ranged from $0.007 to $0.114 per ton of ore milled. The total value of free cyanide discarded daily by any one of these plants ranged from $5.00 to $80.00. On the basis of these figures, the operators believed that an economic process for the recovery of cyanide from the waste solutions would result in significant savings in the operating costs of some gold mills.

Before beginning a laboratory test program on this problem, a review of the literature was made to evaluate the feasibility of reported techniques for the recovery of cyanide from these waste solutions. This review covered published reports on the disposal of cyanide wastes from both the electroplating industry and the gold milling industry.

The study revealed that the objectives of the two industries are dissimilar. The gold milling industry is interested in the economic recovery of the cyanide from the waste solutions for re-use. The plating industry, because the plants are usually located in urban areas, is interested in the economic removal or destruction of the free cyanide prior to the discharge of waste solutions to streams and natural water courses. As the concentration of cyanide is similar in the waste solutions of the two industries, the techniques proposed for the treatment of plating wastes were studied to see whether any were adaptable to the treatment of gold milling wastes.

The techniques employed or investigated by the plating industry were as follows:

(a) The conversion of the free cyanide to a less toxic metal complex (1) (2), a process referred to as complexation.

(b) The conversion of the free cyanide to the less toxic thiocyanate (1).

(c) The oxidation (1) of the free cyanide to the less toxic cyanate with chlorine (3), hypochlorite (4), ozone (5), peroxides (1), permanganates (1), or electrolysis (6).

(d) The acidification of the cyanide solution to evolve hydrocyanic acid which could be recovered for re-use (7).

(e) The recovery of the free cyanide for re-use by ion exchange techniques (8).

Most of the above methods are of no interest to the gold milling industry as they are either too expensive or result in the destruction of the cyanide. However, the acidification and ion exchange techniques are of interest. Both methods have been developed and used by the mining industry on either full-scale or pilot-plant-scale operations for the recovery of cyanide from gold milling wastes.

This report deals with the information in the literature covering the application of the acid and ion exchange processes for the recovery of cyanide from waste cyanide solutions.

THE ACID PROCESS

When cyanide-bearing wastes are acidified to a predetermined pH in the range of 3 to 7 with low cost sulphuric acid or flue gas (SO_2 or CO_2), most of the cyanide, present as free cyanide and copper or nickel complexes, is evolved as hydrocyanic acid.

$$2NaCN + H_2SO_4 \rightarrow 2HCN\uparrow + Na_2SO_4 \qquad \text{(Eq 1)}$$

and $$Na_2Cu(CN)_3 + H_2SO_4 \rightarrow CuCN\downarrow + 2\,HCN\uparrow + Na_2SO_4 \qquad \text{(Eq 2)}$$

and $$Na_2Ni(CN)_4 + 2H_2SO_4 \rightarrow 4HCN\uparrow + NiSO_4 + Na_2SO_4 \qquad \text{(Eq 3)}$$

or

$$3NaCN + 2SO_2 + CO_2 + O_2 + 3H_2O \rightarrow 3HCN\uparrow + 2NaHSO_4 + NaHCO_3 \qquad \text{(Eq 4)}$$

The evolution of the hydrocyanic acid can be accelerated by heating and either aerating or steam stripping the solution. Several hours are required for decomposition of the cyanide, and the last traces of cyanide are removed with difficulty. Thiocyanate is not converted to cyanide by the sulphuric acid process. The hydrocyanic acid gas can be absorbed in an alkaline solution, as either calcium or sodium cyanide, according to the following reactions:

$$2HCN + CaO \rightarrow Ca(CN)_2 + H_2O \qquad \text{(Eq 5)}$$

or

$$HCN + NaOH \rightarrow NaCN + H_2O \qquad \text{(Eq 6)}$$

At the plant of the Hudson Bay Mining and Smelting Company Limited, Flin Flon, Manitoba, 93 per cent of the cyanide contained in the waste solutions from gold extraction operations is recovered by the acid process (9). The analysis of a solution typical of that treated at the Flin Flon plant is given in Table 1.

TABLE 1

Flin Flon Cyanide Waste Solution (9)(10)

Assay	Concentration
Au	0.00019 oz/ton
Ag	0.003 "
CaO	0.25 lb/ton
Recoverable cyanide	1.75 to 2.0 lb NaCN/ton

Recycle acid, containing 180 g H_2SO_4/litre, from the zinc plant is added at the top of a packed tower (Figure 1) to the barren solution which contains about 2.0 lb recoverable cyanide/ton of solution. The acidified solution containing hydrocyanic acid is dropped counter-current to an air stream, and the effluent solutions are pumped to the top of the next tower, of which there are four series. The hydrocyanic acid gas is air-swept from the towers and absorbed into a spray of a weak lime slurry to convert the hydrocyanic acid to calcium cyanide [$Ca(CN)_2$], as in reaction(Eq 5). The effluent gases from the absorbers are recycled to the acidification step, and the calcium cyanide-lime solution is used to supply cyanide to the gold extraction plant.

The reported acid consumption at Flin Flon is 4.17 lb H_2SO_4/ ton of solution or 2.44 lb H_2SO_4/lb equivalent NaCN. At $0.015/lb for commercial grade acid, the acid reagent cost would be of the order of $0.06/ton of solution or $0.04 lb equivalent NaCN recovered. These estimated reagent costs apply only to the Flin Flon cyanide regeneration and are based on a solution capacity of 3,300 ton/day containing 1.84 lb recoverable equivalent NaCN per ton of solution. The regeneration operation at Flin Flon requires three men per day (10), but no estimate of other operating costs is available.

The major equipment for the regeneration plant at Flin Flon consists of four packed towers with grids, four 40 ft x 4 1/2 ft absorbing ducts with six rotor sprays in each unit, four blowers rated at 36,000 cu ft/min, eight centrifugal pumps, and a storage tank. Every two to four months the packed tower grids are changed, as deposits of gypsum and other insoluble salts accumulate and restrict the air flow.

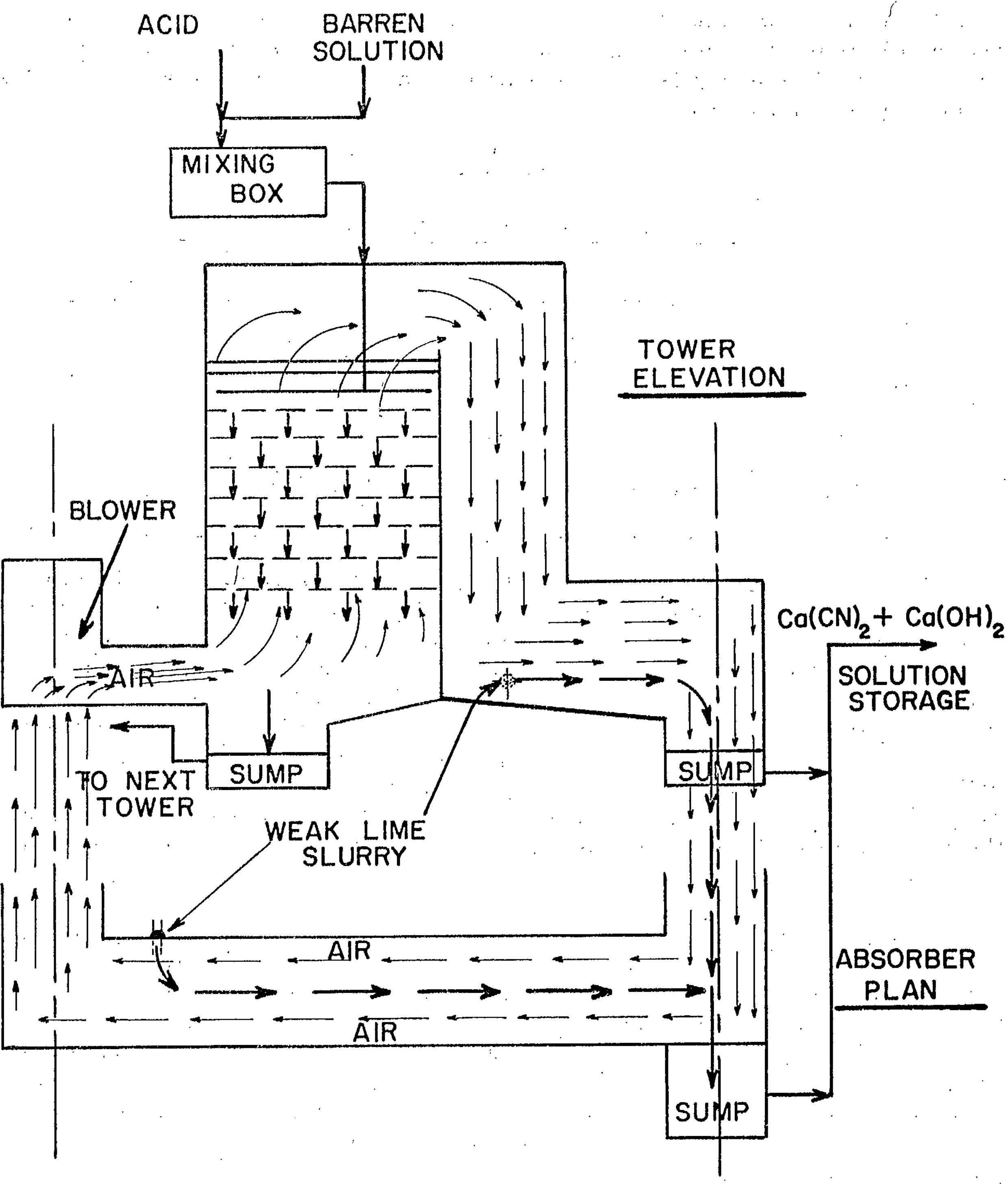

FIGURE I. CYANIDE REGENERATION UNIT.(10)

THE ION EXCHANGE PROCESS

In a South African pilot plant study, water, complexed base metals and 95 per cent of the cyanide in gold mill effluents were recovered by an anion exchange process which utilized poisoned* strong base anion exchange resins (Amberlite IRA-400)** discarded from nearby uranium plants (11). Also, the South African investigators estimated that the cyanide recovery operation would remove temporary poisons from used uranium plant resins, thus allowing their re-use in the uranium plants. The analysis of the gold barren cyanide wastes used as feed solution to the pilot plant is given in Table 2.

TABLE 2

Gold-barren Cyanide Waste from Zinc Precipitation

Assay	Concentration
NaCN (total)	0.20 - 0.32 lb/ solution ton
NaCNS	0.14 - 0.20 " "
Zn	0.02 - 0.06 " "
Ni	0.002 - 0.030 " "
Cu	0.002 - 0.020 " "
Co	0.0002 - 0.002 " "
Au	0.0003 - 0.0013 oz/ ton

Free cyanide and metal cyanide complex anions were adsorbed on two columns in series containing sulphated anion exchange resin (Figure 2). The effluent from the primary column, where the metal cyanide complex anions were adsorbed, flowed to a secondary column, where the free cyanide anions were adsorbed on "conditioned"*** resin. The secondary column effluent, containing thiocyanate and gold, was recycled to the gold extraction plant. The recycling of this solution was an important consideration in the South African operation because the mill water supply is limited in some areas, and also because this procedure reduced gold losses in discarded solutions.

---

*Temporarily poisoned with silica or polythionates.

**Amberlite IRA-400 is a product of Rohm and Haas Company, Philadelphia, Pa.

***The "conditioning" was accomplished by agitating the anion exchange resin in a cuprocyanide solution, followed by a thorough washing. This "conditioning" prepares the resin for adsorption of the free cyanide anion.

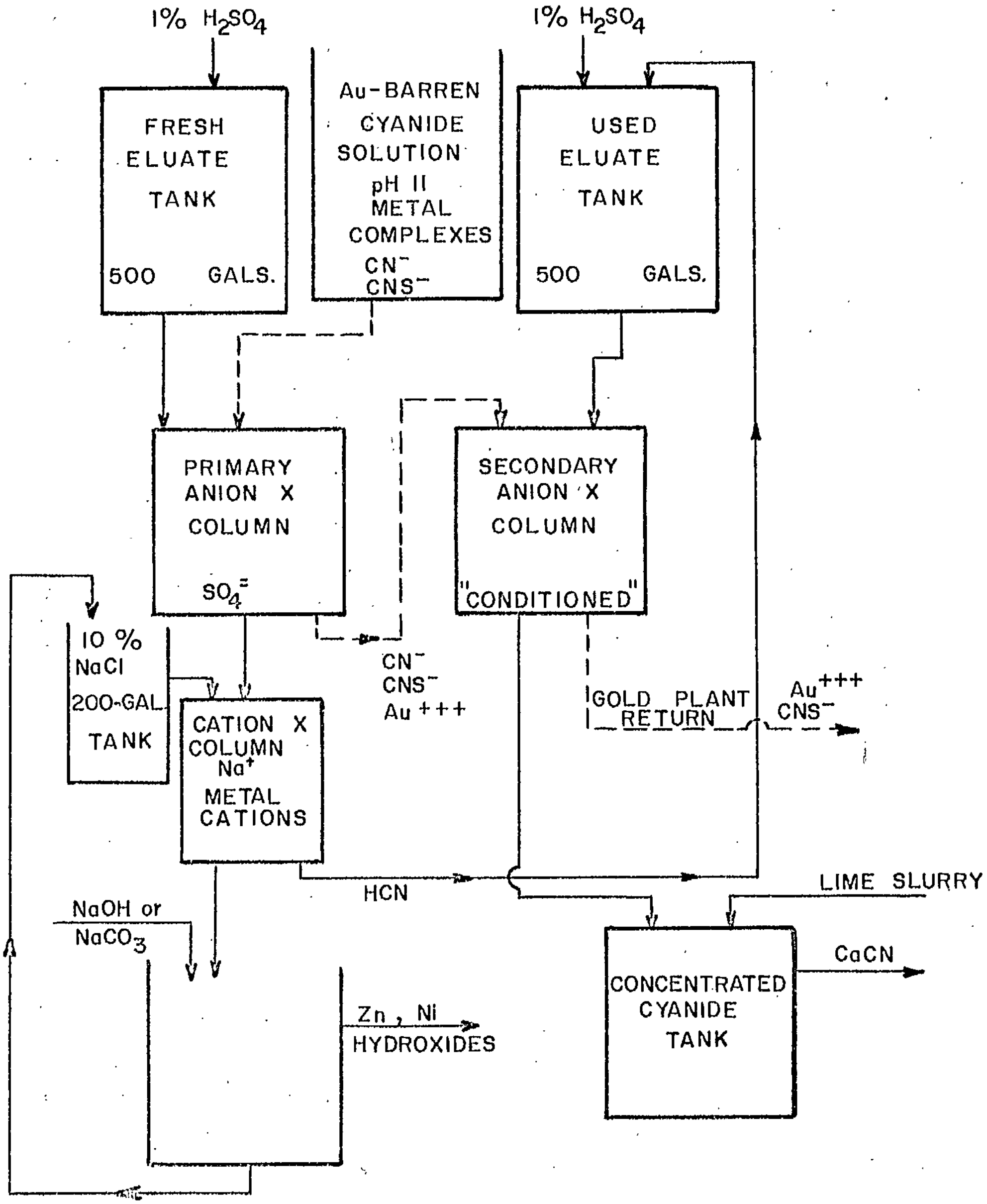

FIGURE 2. A SIMPLIFIED PILOT PLANT FLOWSHEET OF ION EXCHANGE CYANIDE RECOVERY CIRCUIT. (11)

A one per cent sulphuric acid elution decomposed the metal cyanide complex anions on the primary column. The nickel, zinc and cyanide were eluted from the resin as metal sulphates and hydrocyanic acid.

$$R\,[M(CN)_4] + H_2SO_4 \longrightarrow M(CN)_2 + HCN\uparrow + RSO_4 \qquad \text{(Eq 7)}$$

and

$$M(CN)_2 + H_2SO_4 \longrightarrow MSO_4 + 2\,HCN\uparrow \qquad \text{(Eq 8)}$$

where R=resin and M=metal.

The acid eluate from the primary column was fed to a column of cation exchange resin (Amberlite IR 120)*, where the nickel and zinc cations were adsorbed. The hydrocyanic acid passed through the column and was pumped to a used eluate storage tank, where the acid concentration was adjusted to one per cent sulphuric acid. This solution was used to elute the free cyanide anions from the "conditioned" anion exchange resin in the secondary column. The eluate from the secondary column was treated with a lime slurry (as in reaction (Eq 5)) to produce calcium cyanide for use in the gold plant.

The nickel and zinc were stripped from the cation resin with a 10 per cent sodium chloride solution acidified to pH 2 to 3 with sulphuric acid. The acid-sodium chloride eluate was neutralized, precipitating the nickel as hydroxides (12). Ninety-two per cent of the zinc and 77 per cent of the nickel were recovered in this manner. After recovery of the precipitate by filtration, the filtrate was reused in subsequent elutions.

Further details on this process, including the treatment of the copper cyanide complex, may be found in the literature (11)(12).

The South Africans estimate that one skilled and one unskilled operator working one shift per day, during the week and on alternate weekends, could manually operate an ion exchange plant for a daily capacity of 15,000 tons of cyanide waste solutions.

The ion exchange process has considerable appeal for the South African operators, due to the shortage of water in some areas, the availability of 'poisoned' resin from uranium plants which are often integrated with the gold operations, the possibility of regenerating the poisoned resin so it could be reused in the uranium plants, and the relatively high concentration in the cyanide wastes of base metals which can be recovered by the ion exchange technique. In Canada, however, there is rarely any concern regarding water supply, and although a source of used and unused resin exists at uranium-producing centres, due to the cut-back in uranium production, these supplies are at some distance from the gold producing areas. In addition, the problem of resin poisoning is not as serious in Canadian uranium operations as it is in South African plants.

---

*Amberlite IR 120 is a product of Rohm and Haas Company.

The reagent costs for the recovery of cyanide per pound of equivalent sodium cyanide, using approximate Canadian reagent costs, were:

1.77 lb H_2SO_4	at \$0.015	=	\$0.03
1 lb NaCl	at \$0.01	=	\$0.01
Total			\$0.04

These estimated reagent costs are based on reported data from a pilot plant operation on a typical South African cyanide waste solution. No value was given for the personnel requirements or other operating costs of the process.

Based on the adsorption flow, this pilot plant handled an estimated daily capacity of 25.2 solution tons. The five ion exchange columns used were 17 1/2 in. diameter x 6 feet high and made of rubber-lined steel pipe. A 4 in. diameter plastic disc on the bottom of each column supported sized gravel and 3.3 cu ft of resin to give a resin bed depth of 24 in. Other major equipment included two 500-gal, rubber-lined eluate tanks and two 200-gal, rubber-lined tanks for sodium chloride and concentrated cyanide. The columns and tanks were connected with polyethylene tubing.

DISCUSSION

In evaluating the application of either the acidification or the ion exchange process to a specific gold mill, the concentration of recoverable cyanide and the daily solution waste tonnage to be treated must be considered. In the acidification process, the lower the concentration of recoverable cyanides in wastes of the same alkalinity, the higher will be the reagent cost per pound of cyanide recovered, since much of the acid required is consumed in neutralizing and acidifying the solution. In both processes, the lower the daily tonnage of cyanide wastes for the same cyanide concentration, the higher will be the labour cost per pound of cyanide recovered.

Using the available data on reagent costs for the Flin Flon operation, and assuming a rough figure of \$60.00/day for other operating costs and capital write-off, it can be calculated that the Flin Flon operation would cease to be economic when treating 3300 tons of solution/day if the cyanide concentration in the waste solutions dropped to about 0.4 lb NaCN/ton. If the tonnage of waste solution treated by the plant was reduced from the present 3300 tons to 1000 tons per day, the cyanide concentration of the solution would have to be at least 0.7 lb NaCN/ton for the operation to break even. On the basis of these figures, few gold mines in Canada, if any, are discarding sufficient cyanide in waste solutions for the acid process, as used at Flin Flon, to be economic.

In the ion exchange process, the reagent cost per pound of cyanide recovered does not depend on the concentration of cyanide in the solution treated, but only on the amount of recoverable cyanide available. Consequently, using the reagent costs obtained in the South African pilot plant, and assuming again a figure for all other costs of $60.00 per day, a gold plant must recover 500 lb of equivalent NaCN per day to break even. Although this is a minimum figure, only a few gold mining operations in Canada can meet this requirement.

These approximate economic analyses indicate that few Canadian gold mill operators would benefit by either process. Of the two processes, the ion exchange technique appears to be more generally applicable, since its use is not limited by the concentration of recoverable cyanide in the waste solution. In addition, the ion exchange process offers advantages in the conservation of water and the economic recovery of base metals. These advantages were not evaluated in the economic assessment, but they may be worthy of consideration to some Canadian gold mill operators.

Although this discussion is not encouraging with respect to the economic feasibility of cyanide recovery from the waste solutions of Canadian gold mills, each mill would have to evaluate the processes described. Different conditions of labour distribution, reagent costs, and capital write-off would result in different economic assessments. In the final analysis, it is up to each mill operator to decide whether waste cyanide recovery could be advantageous.

ACKNOWLEDGMENTS

Grateful acknowledgment is made of the cooperation of the Mines Branch Library staff under Miss M. Saulter, in particular Miss R. Mills and Mrs. E. Pulker, in assisting the authors with the literature research.

REFERENCES

1. B.F. Dodge and W. Zabban, "Disposal of Plating Room Wastes. I. A Critical Review of the Literature Pertaining to the Disposal of Waste Cyanide Solutions", Plating, May 1949, p. 463; June 1949, p. 571; and July 1949, p. 723.

2. David Milne, "Disposal of Cyanides by Complexation", Sewage and Industrial Wastes, vol. 22, No. 9, p. 1192, September (1950).

3. J.G. Dobson, "The Treatment of Cyanide Waste by Chlorination", Engineering Bulletin, Purdue University, Third Waste Conference, p. 209, May (1947).

4. B.F. Dodge and W. Zabban, "Disposal of Plating Room Wastes. III. Cyanide Wastes: Treatment with Hypochlorites and Removal of Cyanates", Plating, p. 561, June (1951).

5. C.A. Walker and W. Zabban, "Disposal of Plating Room Wastes. VI. Treatment of Plating Room Waste Solutions with Ozone", Plating, p. 777, July (1953).

6. R.W. Oyler, "Disposal of Waste Cyanides by Electrolytic Oxidation", Plating, p. 341, April (1949).

7. B.F. Dodge and W. Zabban, "Disposal of Plating Room Wastes. IV. Batch Volatilization of Hydrogen Cyanide from Aqueous Solutions of Cyanides", Plating, p. 1133, October (1952).

8. C.A. Walker and W. Zabban, "Disposal of Plating Room Wastes. V. Treatment of Cyanide Waste Solutions by Ion Exchange", Plating, p. 165, February (1953).

9. R.F. Coulter, "Beneficiation of Ores at the Flin Flon Concentrator", Transactions, Canadian Institute of Mining and Metallurgy, vol. 55, p. 200 (1962).

10. D. Davis et al., "Cyanide and Regeneration Plant and Practice at Flin Flon", Transactions, Canadian Institute of Mining and Metallurgy, vol. 49, p. 130 (1946).

11. E. Goldblatt, "Recovery of Cyanide from Waste Cyanide Solutions by Ion Exchange --Pilot Plant Studies", Industrial and Engineering Chemistry, vol. 51, p. 241, March (1959).

12. E. Goldblatt, "Recovery of Cyanide from Waste Cyanide Solutions by Ion Exchange", Industrial and Engineering Chemistry, vol. 48, p. 2107, December (1956).

===

AJG:WAG/im