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**TREATMENT OF PLATING WASTEWATERS  
CONTAINING METAL CYANIDE COMPLEXES  
BY A GAS MEMBRANE-ION EXCHANGE PROCESS**

**M.J. Semmens, C.F. Kenfield, Y. Chang, R. Qin, and E.L. Cussler**



minnesota water resources research center



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This publication constitutes the final report for a WRRC project directed by Michael J. Semmens of the Department of Civil and Mineral Engineering, and Edward L. Cussler of the Department of Chemical Engineering, University of Minnesota, entitled: An Innovative Process for Inexpensive Cyanide Concentration and Recovery from Dilute Wastewaters. This project was completed in June, 1988.

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Patrick L. Brezonik, Director

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## ABSTRACT

A novel gas membrane-ion exchange process (GM-IX) is described to treat metal plating wastewaters containing zinc cyanide and recover usable forms of zinc and cyanide. The process uses a strongly basic anion exchange resin to selectively concentrate the metal cyanides from dilute plating wastes. Following exhaustion, the resin is regenerated under acidic conditions. The metal cyanide complexes are broken down as a result of HCN production under these acidic conditions, and the acidic regenerant containing the HCN is recirculated through a gas membrane module that is supplied with a caustic stripping solution. Volatile HCN migrates across the gas permeable membranes to be absorbed and neutralized in the NaOH solution.

The products of the process include concentrated sodium cyanide solution containing some excess sodium hydroxide, and concentrated acidic zinc sulfate solution that can be treated by an electrowinning process to recover zinc metal and a re-usable acid for regeneration.

Results of mass transfer studies indicate that the rate of HCN transfer across the gas permeable membrane is rapid and complete. The transfer is largely limited by diffusion within the lumen of the hollow fibers but also is influenced by the reaction rate of HCN with base outside the fibers.

The gas permeable membrane provides the basis for effective separation and recovery of cyanide from zinc and cadmium plating wastes. Initial ion exchange is necessary to concentrate dilute metal cyanide solutions such as rinsewaters, but if the wastewater is already concentrated, only acidification is required.

The zinc cyanide precipitate formed in the resin during regeneration was found to be  $Zn(CN)_{2(s)}$ . Recovery of cyanide from acidified zinc and cadmium cyanide solution is fast and complete when the solution pH is sufficiently acidic to convert the cyanide to the HCN form; above pH 2.0 the rate of cyanide recovery was slowed by the low percentage of HCN present at equilibrium. In concentrated zinc cyanide solutions such as may be encountered during regeneration a lower pH is required to convert all the complexed cyanide to HCN. To achieve good regeneration, a strong acid solution and sufficient contact time must be provided to ensure complete cyanide removal. A kinetic model interfaced with a chemical equilibrium model successfully predicted the rate of cyanide recovery as a function of operating pH. Agreement between the predicted and the observed cyanide recovery rates indicated that the dissolution rates of  $Zn(CN)_{2(s)}$  does not appear to limit the cyanide recovery rate. Rather, the rate is controlled by the cyanide speciation equilibria.

Solutions containing copper and silver cyanides are less readily treated. The use of organic acids to catalyze the breakdown of these metal cyanides may aid these less tractable solutions. Cyanide cannot be completely recovered simply by acidification of concentrated copper cyanide solutions because of the formation of a cuprous cyanide precipitate. With addition of  $FeCl_3$ , cuprous cyanide precipitate can be oxidized and cyanide can be completely recovered in the NaCN form.

## CHAPTER 1 - INTRODUCTION

### 1-1 Occurrence of Metal Cyanide Wastewaters

Cyanide has been widely used by many industries in processes such as electroplating, metal finishing, printing circuit, mining and photographic bleaching as a complexing agent to hold metal ions in the solution phase. During the manufacturing process, metal cyanide wastewater may be generated either from accidental spills, leaks and drips of process solutions or from the rinse water that is contaminated in the initial cleaning, drag-in, drag-out, and final rinse steps. However, the accidental contributions are irregular, unpredictable and small when compared with the rinse water contributions.

Among these industry-induced metal cyanide wastewater sources, electroplating and metal finishing waste streams are significant generators. There are more than 15,000 metal finishing facilities in the United States. The waste volume and the concentrations of metals and cyanide vary greatly with the shop sizes and the design of drag-out and rinsing systems. The rinse waters from the smaller establishments are extremely variable from shop to shop, and perhaps from day to day within a specific shop. For the intermediate-size and the large plants, the volumes of the cyanide-bearing wastewater could range from 11,000 gallons/day to 410,000 gallons/day<sup>(1)</sup>. The composition of the contaminants in the rinse wastewaters may also vary widely. Concentrations of each component can be as small as less than 0.1 ppm or as concentrated as several hundred ppm. Table 1 shows a sample result of a recent EPA's survey of effluent from 22 electroplaters in the Cleveland area<sup>(2)</sup>.

Table - 1. Effluent Characteristics of 22 Cleveland Electroplating Shops

Pollutant	Effluent concentration (mg/L)		
	Minimum	Maximum	Average
Cyanide, total .....	< 0.1	95.9	14.4
Copper .....	0.1	47.2	4.7
Nickel .....	< 0.1	52.2	5.7
Chromium, total .....	0.1	178.0	20.2
Zinc .....	0.4	101.4	19.3
Lead .....	< 0.1	3.0	0.4
Cadmium .....	< 0.1	24.3	4.3

For each particular metal plating line, for example the zinc or cadmium plating, the major contribution to effluent metal concentration is the metal being plated, zinc or cadmium. However, most job shops operate several plating lines that contain different types of cleaning and electroplating baths, such as zinc, copper, nickel, cadmium, and chromium. Many job shops combine all their rinse waters for the purpose of diluting the metals concentrations and creating a single waste for treatment. In these combined wastewaters many metals and cyanides may require removal to meet discharge regulations.

## 1-2 Environmental Regulations on the Metal Cyanide Wastewaters

Untreated metal cyanide wastewaters have a tremendous impact on natural aqueous environments due to the high toxicity of the heavy metals and cyanide. In addition, discharged into the municipal wastewater system, these wastes may create hazardous conditions for sewer workers as a result of HCN gas production. Finally, the metal content of these wastes may accumulate in biological sludges and limit sludge disposal practices.

In 1972, the Federal Government became responsible for a wide range of regulations related to water pollution control with the enactment of the amended Federal Water Pollution Control Act (FWPCA). For industries discharging wastewater to waterways, the most far-reaching feature of the 1972 FWPCA amendments was the requirement that all such industries install a base level of pollution control technology by July 1, 1977, and a more stringent level by July 1, 1983. The pretreatment standards for both direct and indirect dischargers were set up by EPA in 1979<sup>(3)</sup> and some aspects were amended in 1980<sup>(4)</sup>. Table 2 provides the pretreatment standards of the major pollutants generally found in metal cyanide wastewaters<sup>(5)</sup>.

Table - 2. Pretreatment Standards for Existing Indirect Dischargers

Pollutant	Pretreatment standard ( mg / l )	
	Daily maximum	4-d average
Plants discharging < 10,000 gallons / day:		
Cyanide, amenable .....	5.0	2.7
Lead .....	0.6	0.4
Cadmium .....	1.2	0.7
Plants discharging > 10,000 gallons / day:		
Cyanide, total .....	1.9	1.0
Copper .....	4.5	2.7
Nickel .....	4.1	2.6
Chromium .....	7.0	4.0
Zinc .....	4.2	2.6
Lead .....	0.6	0.4
Cadmium .....	1.2	0.7
Silver .....	1.2	0.7
All metals .....	10.5	6.8

Federal legislation is aimed primarily at maintaining the quality of federal controlled interstate and other natural waters as they may affect the public health and welfare. The laws also allocate the authority and responsibility for maintaining water quality to the individual states. In all cases, the state is authorized to impose requirements more stringent than the Federal guidelines if they desire to do so.



### 1-3 Treatment Methods

Both the technical and patent literature describe a multitude of processes for the destruction or recovery of free cyanide and metal cyanide complexes from solutions<sup>(1)(6-13)</sup>. Some of the most widely known technologies are tabulated in Table 3.

The oxidation of cyanide either completely decomposes cyanide to nitrogen and carbon dioxide or partially oxidizes cyanide to the less toxic cyanate compound. The residual metal hydroxide sludge then becomes a solid waste. Among these oxidation methods conventional alkaline chlorination is most widely used by the electroplating industry because operation of the process is easy to control and the results are quite reliable<sup>(14)(15)</sup>. However, large amount of chemicals are required in this process and the disposal of metal sludge is expensive. The electroplaters and metal finishing industries are therefore seeking a cheaper and more efficient way to deal with their wastewaters.

Complete cyanide destruction by hypochlorites is also used commercially<sup>(16-19)</sup>. Advantages of hypochlorite process over the chlorination process are: (1) handling and metering of the hypochlorites is relatively simple and non-hazardous, (2) the reaction is more rapid than that with chlorine, (3) sludge production is minimized if sodium hypochlorite is used. However the direct hypochlorite treatment is stated to be about twice as expensive as chlorination.

Ozonation has been employed to treat a cyanide waste at the Boeing Airplane (Wichita, Kansas) metal working plant<sup>(20)</sup>. Complete oxidation of cyanide to cyanate is reported, with partial oxidation of cyanate to final end products. Reaction time for ozonation is relatively slower in comparison with chlorination. Under favorable conditions, complete oxidation of cyanide by chlorination takes about 3 minutes<sup>(1)</sup>, while ozonation needs about 60 minutes for completion<sup>(21)</sup>. But if the wastewater has a high chlorine demand, such as ammonia, then ozonation would be cheaper than chlorination.

Electrolytic decomposition is used primarily for the destruction of cyanide in concentrated spent metal plating solutions<sup>(22)</sup>. Although Easton<sup>(23)</sup> indicated that low levels of residual cyanide (0.1 ~ 0.4 mg/L) can be achieved, the reaction time required is 7 to 18 days. In practical use, treated effluent containing normally less than 100 mg/L of cyanide can be further treated by chlorination.

Photolysis has been shown to be able to decompose iron cyanide, which is a stable metal complex species that resists the alkaline chlorination process<sup>(24)</sup>. Ultraviolet irradiation decomposes iron cyanide complex to free cyanide and iron hydroxide<sup>(25)</sup>, but no further decomposition of cyanide was reported.

Reverse osmosis has been investigated to be able to effectively concentrate nickel cyanide solution to certain degree for In-Plant recovery. However, membrane performance generally degrades with time and membrane module requires to be replaced periodically. Current commercial membranes have shown good nickel cyanide rejection. New membrane materials have to be developed to expand its applicability to major plating bath other than nickel<sup>(26)</sup>.

Chemical precipitation is usually applied after removal of cyanide<sup>(37)</sup>. Adsorption of cyanide and complexed cyanide on ferrous sulfide is strongly pH dependent and the

operating pH of this process is limited to around 7.5<sup>(38)</sup>. Most of the plating metal cyanide wastewaters, such as zinc and cadmium cyanide solutions, have pH values that are much higher(> pH 11) than 7.5 and this process is not feasible for these wastewaters.

Ion exchange is a potential technology for the cyanide recovery. Goldblatt<sup>(27)(28)</sup> employed a strong anion exchange resin to remove free cyanide and complexed cyanide from solution. Followed by 0.2N of sulfuric acid regeneration, metals are removed by a cation exchange resin and cyanide is recovered in an alkaline solution. Although accumulation of cuprous cyanide precipitate inside the resin during acid regeneration reduced the ion exchange capacity in consecutive service cycles, this precipitate species was removed by passing 144 bed volume of 0.4% ferric sulfate solution.

Research works on activated sludge treatment of inorganic, organic and metal complexed cyanide started at 50 years ago(29-35). Current investigators are still researching the design and optimization of biological treatment systems to increase their removal efficiency and reliability. Although this process greatly reduces the treatment cost in dealing with low cyanide content solutions(less than 60 mg/L), the uncertainty of its results gives this technology very little practical application.

Numerous additional technologies have been developed for metal cyanide treatment; however, they have been found either technically or economically infeasible. As a result, many platers are waiting for further development of new technologies before they make final decisions on the selection of wastewater treatment processes.

Table - 3. Metal Cyanide Wastewater Treatment Methods

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Chemical Treatments :

- Alkaline chlorination
- Oxidation with sulphur dioxide-air
- Oxidation with hydrogen peroxide
- Oxidation with hypochloride
- Ozonation
- Electrolytic Oxidation
- Photolysis

Physical Treatments :

- Ion exchange
- Reverse osmosis
- Chemical precipitation
- Adsorption on ferrous sulfide

Biological Degradation

---

#### 1-4 GM-IX Process

In this study a novel metal cyanide separation technique - the GM-IX process - was evaluated in laboratory tests. This process, which will be described in detail below, combines a gas membrane module and an ion exchange column as shown in Figure 1 to recover the cyanide and metal content of metal cyanide-bearing wastewaters.

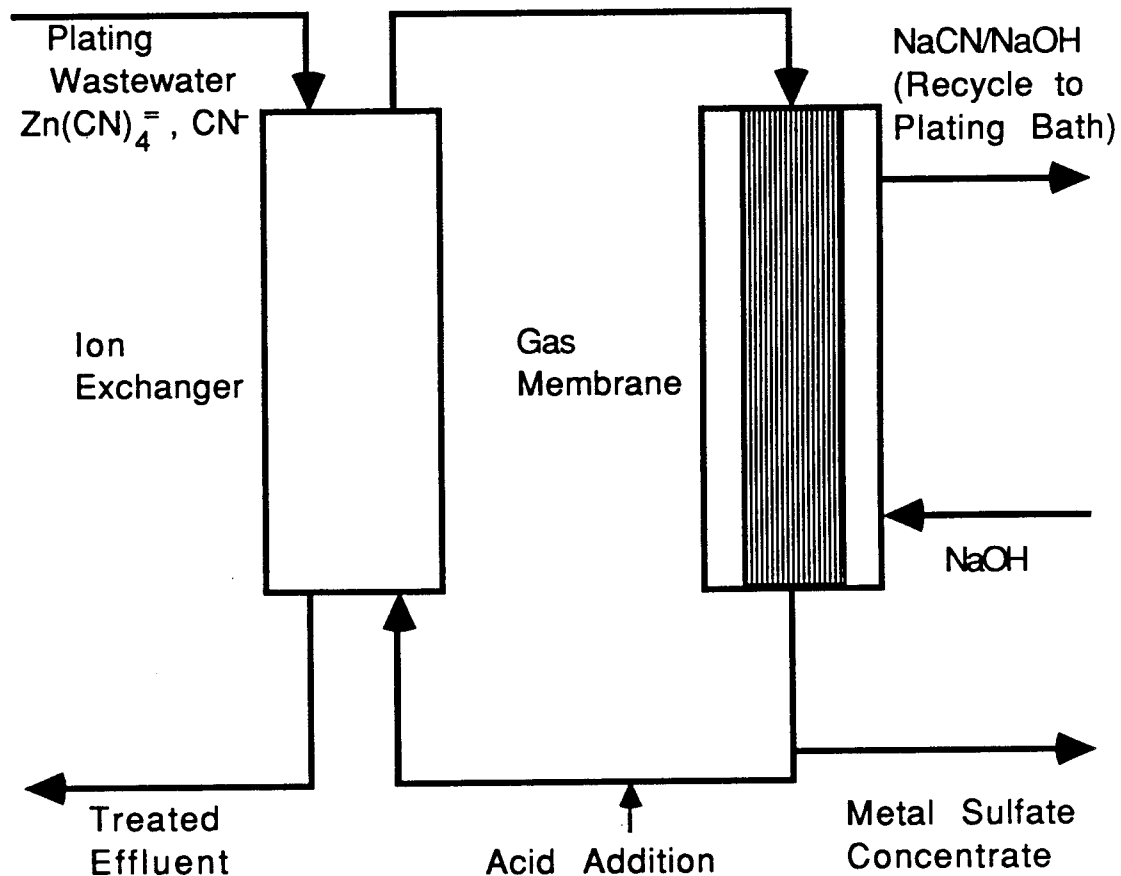


Figure 1. Schematic of the GM-IX Process

Usually metal cyanide wastewaters have an alkaline pH above 11 and under these conditions cyanide ions bind the metals present to form complex anions such as  $Zn(CN)_4^{=}$  and  $Cd(CN)_4^{=}$ . These anionic complexes are readily removed by a strongly basic anion exchange resin. The metal cyanide-free effluent may then be recycled or discharged to a municipal wastewater system after pH adjustment if necessary. When the metal or cyanide concentration in the effluent of the ion exchanger exceeds the wastewater discharge standards, the resin is regenerated with an acid which breaks down the metal cyanide complexes to form free metal ions and HCN. This HCN-rich acidic regenerant is recirculated through the lumen of hollow fibers of a gas membrane, and the gas membrane (which is hydrophobic) allows HCN gas to transport rapidly across the membrane wall while the free metal ions remain in the acid eluent. Outside the hollow fiber membranes,

sodium hydroxide solution is used to absorb and neutralize the transferred HCN to form NaCN. The recovered sodium cyanide can be recycled to the plating bath.

This process produces a small volume of highly concentrated sodium cyanide. In addition the volume of the residual acidic metal solution that is left after regeneration is also small and the metals are quite concentrated, this makes it easier to handle either by chemical precipitation or recovery techniques if the metals can be properly separated. Thus the process has great potential for practical application.

### 1-5 Objectives of this Project

The objective of this project was to study the feasibility of the GM-IX process and to develop an effective operating strategy and optimize the operating conditions for the process. During the project, three papers were published. Each paper presented experimental results and a discussion of a selected part of the process. These papers are discussed below.

Paper 1 focussed on the feasibility study including the mechanisms and the kinetics of HCN transfer across hollow fiber membranes. The mass transfer coefficient of HCN was measured and the influence of acid and base flowrates, base concentration and temperature on the mass transfer coefficient were characterized.

Paper 2 provides the important design criteria for the GM-IX process and discusses topics such as resin selection, membrane surface area requirements, reaction time, chemical doses and the operating flowrates of acid and base. A preliminary cost analysis was also presented in this paper.

Paper 3 presents the MINEQL generated species distribution diagrams of zinc and cadmium cyanide complexes over the pH range from 1-13. A kinetics model was also developed and this was successfully employed to predict the rate of cyanide recovery from zinc and cadmium cyanide solutions as a function on pH. It was shown that the dissolution rate of zinc cyanide precipitate did not appear to limit the rate of cyanide recovery. Complete cyanide recovery was achieved not only in zinc and cadmium cyanide solutions, but also in cuprous cyanide solution with the addition of ferric chloride.

Details of experimental procedures used in the ion exchange and membrane processes are presented in the M.S. Theses of Carol F. Kenfield and Yuyuen Chang. Papers summarizing the major experimental results are presented below.

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## Chapter 2

### CYANIDE RECOVERY ACROSS HOLLOW FIBER GAS MEMBRANES

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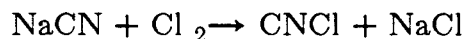
#### (ABSTRACT)

Solutions of certain metal cyanides can be treated with a new, four step process described here. First, the cyanide complexes are concentrated by anion exchange. Second, they are eluted with acid to release small amounts of prussic acid (HCN). Third, the prussic acid is removed with a hollow fiber gas membrane. Fourth, the metal ions released in this way are removed by cation exchange. The prussic acid removal is rapid, so the amount of acid present at any given time can be small while the amount of solution treated per time can be large. Data given here show how the process works and elucidate the mechanisms involved.

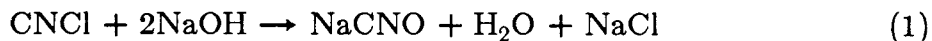
## Introduction

This paper describes a new method for recovering cyanides and certain metals from plating wastes. Cyanide is widely employed in the electroplating industry to hold metallic ions such as zinc and cadmium in solution. Some of these plating solutions contaminate rinse waters which later require treatment. Typical cyanide concentrations, listed in Table I (1), must be reduced to less than 1.0 mg/L (4 day average) prior to discharge.

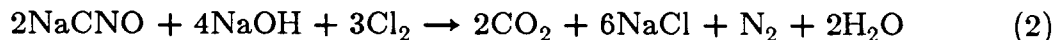
Cyanide removal is most commonly achieved by alkaline chlorination. The first step in the chlorination reaction is instantaneous



The volatile cyanogen chloride then reacts to form sodium cyanate:



While this reaction is slow below pH 8.0, it goes to completion in 30 minutes at pH 8.5. Further chlorination oxidizes the cyanate to carbon dioxide and nitrogen:



The large chlorine and caustic requirements make this common process expensive.

Anion exchange resins have been employed for the removal of cyanides from dilute rinsewaters. Regeneration of these exchangers is difficult because rinsewaters contain not only free cyanides but also metal-cyanide complexes such as  $\text{Zn}(\text{CN})_4^{2-}$  or  $\text{Cu}(\text{CN})_4^{3-}$ . These cyanide complexes are held strongly by the anion exchange resin and are not displaced during normal regeneration. The use of a cation exchanger and a weakly basic anion exchanger ahead of the strongly basic resin can reduce but not avoid these problems (2).

We propose here a new, potentially inexpensive approach for metal and cyanide recovery. The process, shown schematically in Fig. 1, has four parts. First, an anion exchanger concentrates cyanides and metal cyanide complexes. Second, an acid regenerant splits the metal cyanide complexes and releases HCN. Third, the eluate from this exchanger is pumped through a gas membrane module to remove the HCN. Caustic flowing countercurrently through this module reacts with the HCN, producing a concentrated sodium cyanide solution which can be recycled to the plating baths. Fourth, the cations coming out of the gas membrane module are captured on a cation exchanger.

The novel feature of the new process is the use of a gas membrane module for cyanide recovery. In this module, gas membranes  $3 \times 10^{-5}$  m thick separate two aqueous solutions. The gas layer is stabilized within the pores of a hydrophobic microporous membrane (3, 4, 5). Solutes which are volatile can pass across these membranes; non-volatile solutes are completely excluded. Such gas



Table I – Typical Concentrations of Cyanide  
in Plating Wastewaters (14)

Process	Range (mg/L)
Plating rinse	1.4-256 (56 avg)
Bright dip	15-20
Alkaline cleaning bath	6,000
Plating bath:	45,000-100,000
Brass	16,000-48,000
Cadmium	20,000-67,000
Zinc	4,000-64,000

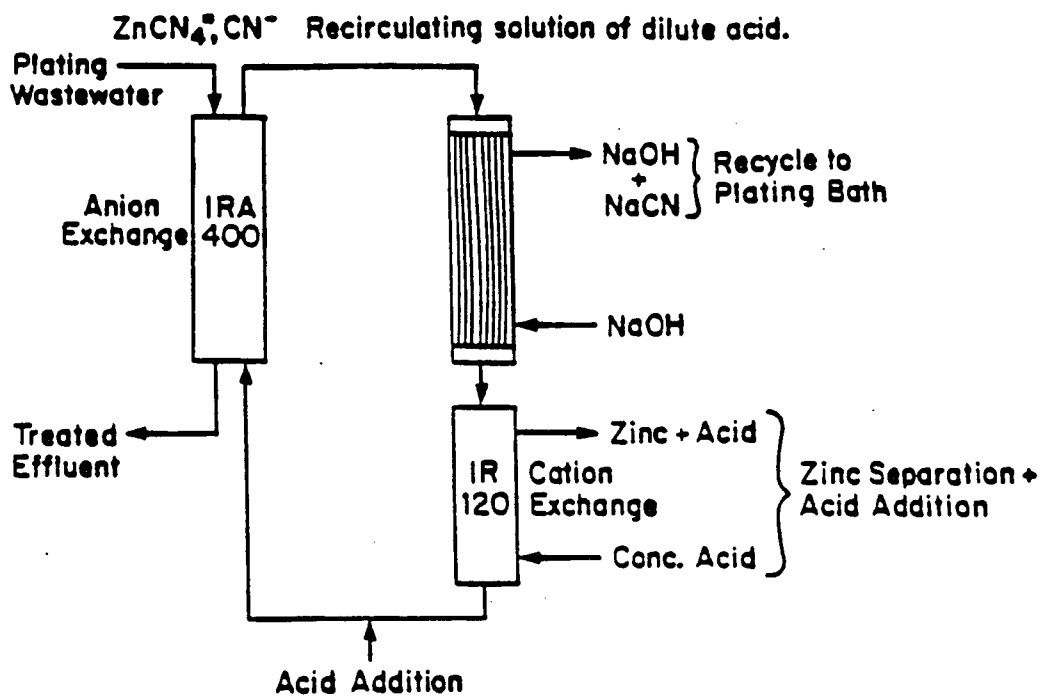


Figure 1 – A New Process for Cyanide Recovery Cyanide complexes, captured by ion exchange, are later eluted with acid. The cyanides in this eluate are recovered for reuse in the membrane module; any cations are captured by cation exchange.

membranes are stable for at least months, even when they are separating solutions whose acid concentrations differ by more than 10 pH units. In this paper the factors influencing the recovery of cyanide across the gas membrane module are considered. Data are discussed in terms of a mass transfer theory and the probable rate controlling mechanism.

### Theory

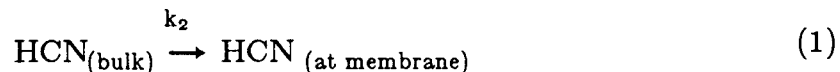
The gas membrane is the key to separating the cyanide. The way in which this membrane will operate is more complicated than previous gas membrane studies. This operation alone involves four steps. To illustrate these steps, we consider the special case of an anion exchanger which has been employed to treat a zinc cyanide stream. The exhausted anion exchanger will contain  $Zn(CN)_4^-$ ,  $CN^-$ ,  $CO_3^-$ , and  $OH^-$  ions. For this case, we consider the four steps sequentially:

#### Step 1

In the first step, a strong acid is pumped through the anion exchanger. Because the  $pK_a$  for HCN is 9.31, HCN will become the predominant cyanide species, liberating the zinc as a divalent cation. The anion exchange resin is left in the acid salt form ( $Cl^-$  or  $SO_4^-$ ). This release is rapid and stoichiometric.

#### Step 2

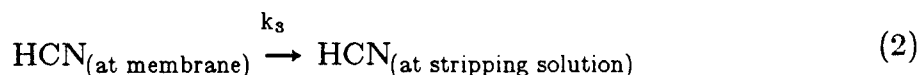
In the second step, the eluate containing the HCN is fed to the gas membrane module where the HCN diffuses from this feed to the membrane wall:



This step is slow because diffusion in liquids is slow. We can expedite it by minimizing the distance for diffusion, but we will still find it one of the slowest steps in the process.

#### Step 3

The HCN dissolved at the wall now volatilizes and diffuses across the gas filled pores of the membrane:

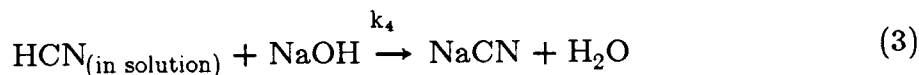


This step is fast because diffusion in gases is fast. In many ways, this is unusual, for most membranes have a substantial resistance to mass transfer. This one does not.

#### Step 4

In the fourth and final step, the HCN diffuses into the stripping solution of

concentrated sodium hydroxide and reacts to form NaCN:



This overall equation is perhaps misleading, for diffusion and chemical reaction occur simultaneously, not sequentially.

The rate of this four step process can be found in terms of the rates of the individual steps using conventional theories of mass transfer. This rate is most easily described as the flux  $j$ , the amount of HCN transferred per area per time:

$$j = K[\text{HCN}] \quad (4)$$

The concentration  $[\text{HCN}]$  is that present in the bulk feed and is controlled by the acid concentrations employed during regeneration in step (1). The rate constant  $K$  is an overall mass transfer coefficient given by

$$\frac{1}{K} = \frac{1}{k_2} + \frac{1}{k_3} + \frac{1}{k_4} \quad (5)$$

where each  $k_i$  is the rate constant of the  $i^{\text{th}}$  step. Because step (1) occurs rapidly,  $k_1$  is large and does not affect the results. It will not be considered further in this analysis.

From past experiments on other systems, we know five characteristics of the mass transfer coefficients,  $k_i$ , which can be checked experimentally:

- 1) The flux  $j$  should vary linearly with  $[\text{HCN}]$ , as stated by Eq. 4.
- 2) The coefficient  $k_2$  will vary with the cube root of the feed velocity.
- 3) The coefficient  $k_3$  should vary inversely with the membrane thickness.
- 4) The coefficient  $k_4$  will vary linearly with the base velocity if the reaction of HCN with base is instantaneous, but be independent of this velocity if the reaction is fast.
- 5) The coefficient  $k_4$  will vary with the base concentration to the first power if the reaction is instantaneous, but with the square root of this concentration if the reaction is fast.

These five characteristics are basic to our analysis of how this process works, and so merit additional discussion.

The first characteristic, the linear variation of flux with [HCN], will be true if the species actually being separated is HCN. The second characteristic implicitly assumes that feed is flowing within the lumen of the hollow fibers. In this case, the rate coefficient  $k_2$  can be accurately predicted from (6):

$$\frac{k_2 d}{D_F} = 1.64 \left( \frac{d^2 v_F}{l D_F} \right)^{1/3} \quad (6)$$

in which  $D_F$  is the diffusion coefficient in the feed;  $d$  and  $l$  are the fiber's diameter and length, respectively; and  $v_F$  is the velocity of the feed. This prediction has been widely tested for both heat transfer and for diffusion in hollow fibers. For heat transfer, the corresponding empirical equation uses a numerical coefficient of 1.86 instead of 1.64 (7).

The third characteristic reflects the expectation that  $k_3$  is given by

$$k_3 = \frac{\epsilon D_M H}{\delta} \quad (7)$$

where  $\epsilon$  and  $\delta$  are the void fraction and the wall thickness of the hollow fiber membrane, respectively;  $D_M$  is the diffusion coefficient in the gas within the membrane's pores; and  $H$  is a partition coefficient which relates the HCN concentration in the gas in equilibrium with the HCN concentration in the liquid. The best tests of Eq. 7 involve changing the membrane thickness, which is experimentally difficult in the hollow fibers used here. As a result, we report a second brief set of experiments using flat membranes.

The fourth and fifth characteristics, the variation of  $k_4$  with the flowrate of the basic stripping solution and with the base concentration, reflect the most subtle behavior. The subtlety hinges on the definitions of an instantaneous reaction and a fast reaction which are used in analyzing mass transfer (9). If the reaction considered here is instantaneous, then HCN and NaOH can not coexist. As soon as they encounter one another, they react. In this case,

$$\frac{k_4 d}{D} = 1.0 \left( \frac{dv_s}{v} \right)^{0.9} \left[ 1 + \frac{[\text{NaOH}]}{[\text{HCN}]_i} \right] \quad (8)$$

where  $[\text{NaOH}]$  is the bulk base concentration and  $[\text{HCN}]_i$  is the liquid phase acid concentration at the interface between membrane and base solution. This equation has a much weaker experimental foundation than that of Eq. 6. We will not use it quantitatively; we note only that if the reaction is instantaneous,  $k_4$  will be proportional to the stripping velocity to the 0.9 power, and to the base concentration to the first power.

We now turn from the limit where the reaction is instantaneous to that where the reaction is fast. By this, we mean that the reaction between HCN and NaOH is extremely rapid, but the reactants can coexist. For simplicity, we discuss only the special case involved here, where the base is present in much

higher concentration than the HCN. In this limit, the mass transfer coefficient of the fourth step is

$$k_4 = \sqrt{D_B \kappa [\text{NaOH}]} \quad (9)$$

where  $\kappa$  is a second order rate constant for the fast reaction. Note that under these conditions  $k_4$  depends on the square root of the base concentration but is independent of the stripping velocity.

The mechanism by which the cyanide separation occurs can be inferred by comparing these characteristics with the experimental results described next.

### Experimental

All chemicals were reagent grade and were used as received. Solutions were prepared by weight by adding sodium cyanide, hydrochloric acid, and any appropriate metal salts with the desired amount of distilled, deionized water. The concentrations of these solutions were measured by titration with silver nitrate standard solution (Baker) or with a cyanide electrode (Orion model 9406). The stripping solutions were prepared by weight by adding sodium hydroxide pellets (Mallinckrodt) to the desired amount of water.

Because the apparatus is similar to that used previously (10,11), only a synopsis will be given here. The apparatus consisted of three parts, an acidic feed reservoir, a basic stripping solution reservoir and the hollow fiber membrane module. The feed reservoir had 100 cm<sup>3</sup> of feed solution and the stripping reservoir contained of 100 cm<sup>3</sup> of basic, stripping solution. The acidic feed reservoir was connected through a Cole Palmer Masterflex peristaltic pump (T-7553-00 Drive and T-7014-20 Head) to the ends of the module, so feed flowed from the reservoir through the lumen of the hollow fibers and back into the feed reservoir. The reservoir containing base was connected through a similar pump to the shell surrounding the fibers, so that the base solution was continuously recycled past the outside of these fibers. The fiber module itself, housed in a glass tube 1 cm inside diameter, contained 120 polypropylene fibers (Celgard 2400 Questar, Charlotte, N.C.) 16.5 cm long, and .0413 cm inside diameter. The fibers were sealed in place with Amicon T674 epoxy potting compound. Several modules made with this geometry yielded experimentally indistinguishable results (7).

The experiments were started by filling both reservoirs. Each solution was sampled for later analysis. The acidic feed pump was turned on and then the basic stripping pump. The base solution was sampled periodically and both solutions were sampled at the conclusion of the test; the sample volumes and concentrations were measured. The overall mass transfer coefficient  $K$  was calculated from these data by means of the equation:

$$K = \frac{V_F}{At} \ln \frac{[\text{HCN}]_o}{[\text{HCN}]} \quad (10)$$

where  $V_F$  is the volume of the feed solution,  $t$  is the time,  $A$  is the total internal

surface area of the hollow fibers, and the subscript "o" indicates the feed concentration at the start of the experiment. This equation, a special case of a more general result derived from Eq. 4, is valid when the stripping solution contains excess base and the recirculation rate of the feed is fast relative to the rate of mass transfer (9). This is the case in the experiments reported here. Thus a plot of  $\ln([HCN]_o/[HCN])$  vs.  $t$  should be linear with a slope proportional to  $K$ . These values of  $K$  were measured as a function of different operating parameters to identify the mechanism of HCN transfer across the membrane.

## Results and Discussion

The object of this paper is the development of a new method of metal cyanide recovery involving HCN diffusion across a gas membrane. To demonstrate this development, we first show that our experimental results do in fact fit Eq. 10, so that we can effectively summarize our data by means of overall mass transfer coefficients. We then examine the characteristics of these coefficients.

All of the data do in fact fit Eq. 10. A typical result collected at pH 2.0 is presented in Fig. 2. All experiments were made at the same feed and base velocities of 2.0 and 2.4 cm/sec, respectively. The scatter in these results is typical of earlier measurements of this type (e.g., 5, 6, 7). Experiments conducted at pH 7 yield essentially identical data, as expected since the  $pK_a$  of HCN is 9.3. A semilogarithmic plot like that in Fig. 2 implies a first order exponential decay. As a result, it will always take the same length of time to reduce the concentration an order of magnitude. If in the first ten minutes, the cyanide concentration drops from 5,000 ppm to 500 ppm, it will then drop to 50 ppm after twenty minutes, and to 5 ppm after thirty minutes.

The results in Fig. 2 justify the first of the five characteristics discussed above, that the flux is proportional to the HCN concentration. In fact, there is a small but significant non-linear variation of flux with  $[HCN]$ . This appears as a variation of  $K$  with  $[HCN]$ , as shown in the inset of Fig. 2. We are not sure of the origin of this effect; it may be due to local ionization. Still, since  $K$  varies less than two times for a one hundred-fold variation with  $[HCN]$ , we assume the flux is linear in  $[HCN]$ . This in turn implies that Eq. 4, the basis of Eq. 10, is very nearly correct.

We now turn to the other characteristics of the overall mass transfer coefficient. The second of these is that  $k_2$  should vary with the cube root of the feed velocity  $v_F$  (cf. Eq. 6); as a result,  $K^{-1}$  should vary linearly with  $v^{-1/3}$ . That this is true is shown in Fig. 3. The slope on this plot, equal to  $2500 (\text{sec/cm})^{2/3}$ , can be compared with that estimated from Eq. 5 and 6. To make this estimate, we take the diffusion coefficient of HCN to equal  $1.0 \times 10^{-5} \text{ cm}^2/\text{sec}$ . The estimated slope is then  $1200 (\text{sec/cm})^{2/3}$ , comparable with the observed value. Thus  $k_2$  does significantly influence the rate of cyanide transfer.

The data in Fig. 3 show that the reciprocal of the mass transfer coefficient is still finite at infinite flow, i.e., when  $v^{-1/3}$  equals zero. In other words, when the flow of feed becomes fast, the flux apparently approaches a maximum value. This maximum value must reflect the resistances of the membrane and the

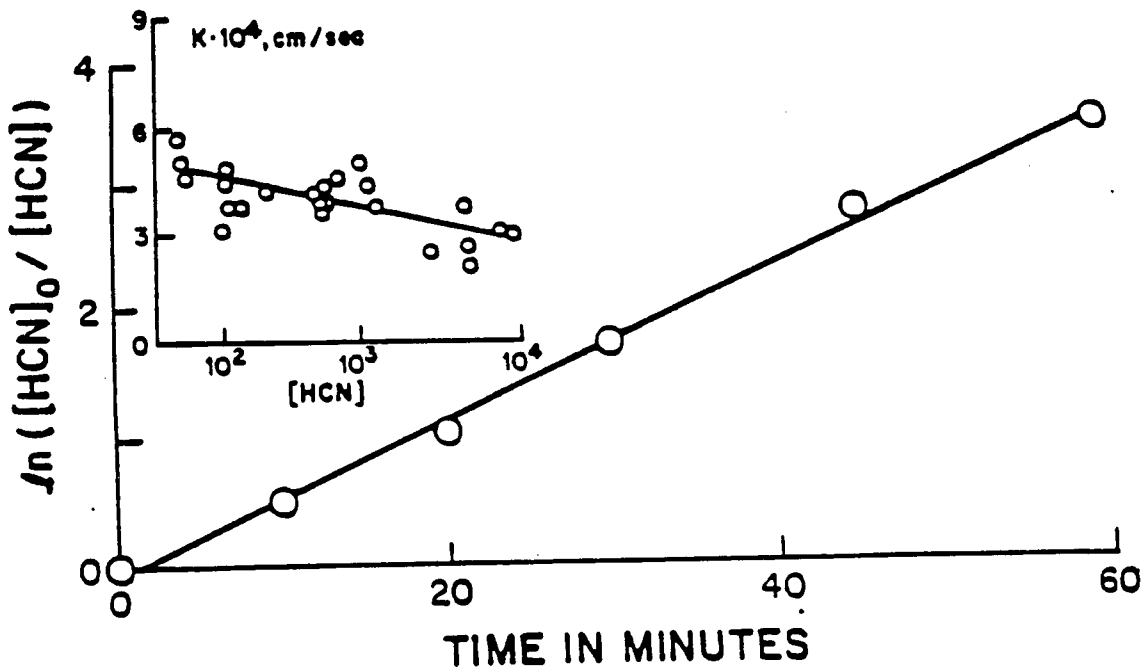


Figure 2 — Cyanide Concentration vs. Time The semilogarithmic variation suggested by Eq. 10, allows calculation of the mass transfer coefficient  $K$ . This coefficient varies only slightly with cyanide concentration, as shown in the inset.

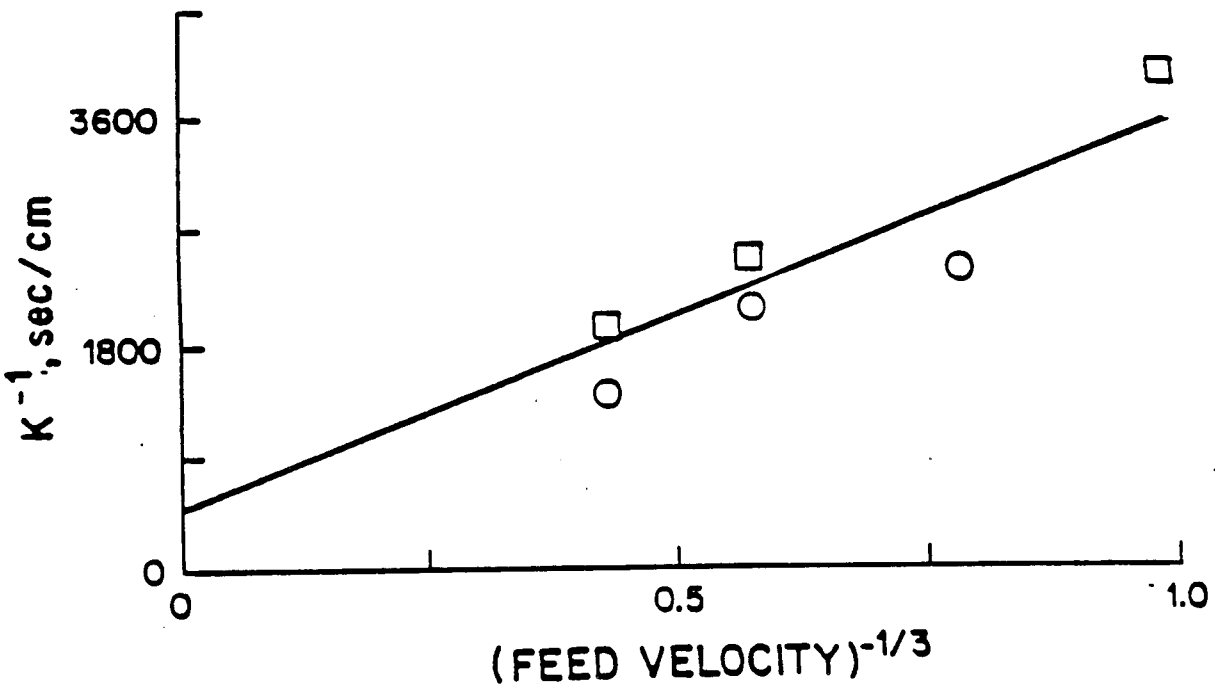


Figure 3 — Mass Transfer vs. Cyanide Feed Velocity This variation shows that diffusion in the feed is a significant resistance to the rate of cyanide stripping. The squares and circles refer to initial feed concentrations of 500 and 5000 ppm, respectively.

stripping solution, which are incorporated into the third and fourth characteristic of this process.

The third characteristic of the process, signaled by Eq. 7, concerns the resistance of the membrane. We want to know whether this resistance is significant, whether the value of  $k_3$  is so small that it contributes a major fraction of the intercept in Fig. 3. Unfortunately, it is difficult to gain this knowledge working only with hollow fibers. Instead, we made two experiments with a diaphragm cell, following a procedure published earlier (5). In both experiments, we allowed HCN from a solution containing 5000 ppm to diffuse across a membrane into 1.0 M NaOH. In the first experiment, the membrane consisted of one sheet of polypropylene film (Celgard 2400); but in the second experiment, two sheets were used. In both experiments, the stirring was rapid, about 300 rpm. In both, the measured mass transfer coefficients are equal within experimental error. Thus the membrane resistance is negligible and  $k_3$  does not contribute significantly to  $K$ .

The fourth and fifth characteristics of the process concern the variation of  $K$  with  $k_4$ , i.e., with the base flow and concentration. If the reaction is instantaneous,  $k_4$  should vary with the 0.9 power of base flow and the first power of base concentration. If the reaction is fast,  $k_4$  should be independent of base flow and vary with the square root of base concentration.

In fact,  $K$  does not vary much with base flow, as shown in Fig. 4. It appears to vary with the square root of base concentration, at least at low base concentration, as shown in Fig. 5. At higher base concentrations, the variation may be closer to linear. This suggests that mass transfer into the base lies in the region between instantaneous and fast reaction, probably closer to the latter (12).

We recognize that plating wastes do not contain pure cyanides, but rather cyanides complexed with metal ions. Indeed, as Fig. 1 shows, we must routinely treat wastes containing these complexes. As a result, we want to test the feasibility of treating these solutions. To do so, we studied cyanide recovery from solutions containing zinc, cadmium, copper and silver cyanide complexes. In each test, the total cyanide concentration varied between 400 and 5000 mg/L, and metal concentrations were also varied as shown in Table II.

The tests conducted on the zinc cyanide solution are important since zinc plating represents the greatest use of cyanide in the metal finishing industry. The results for zinc cyanide and free cyanide, compared in Fig. 6, show that the presence of zinc had no apparent impact on cyanide transfer at pH 2.0. This result may be anticipated from consideration of the zinc cyanide stability constants (13). At pH 2, essentially all of the cyanide in a solution containing zinc is present as HCN. Tests on the removal of HCN from cadmium cyanide solutions, also presented in Fig. 6, show similar behavior.

Tests on other metal cyanides yield less favorable results. For example, little free cyanide can be recovered from the acidified copper cyanide solution. The solutions containing copper cyanide complexes, prepared by dissolving known weights of cuprous cyanide into sodium cyanide solutions, precipitate CuCN when acidified, consistent with other reports (14). In other transfer experiments at pH 5.5, the copper formed a stable complex with cyanide in the molecular ratio of approximately 1:3. Only the free cyanide in excess of that complexed by



Table II – A Summary of Studies Conducted on  
Metal Cyanide Solutions

Metal	Concentration Range mg/L	pH Range	Cyanide Concentration Range mg/L	No. Tests
Zinc	300-3000	2-8	500-5000	10
Cadmium	400-5000	2-5	3000-5000	3
Copper	400-5000	5-8	400-5000	8

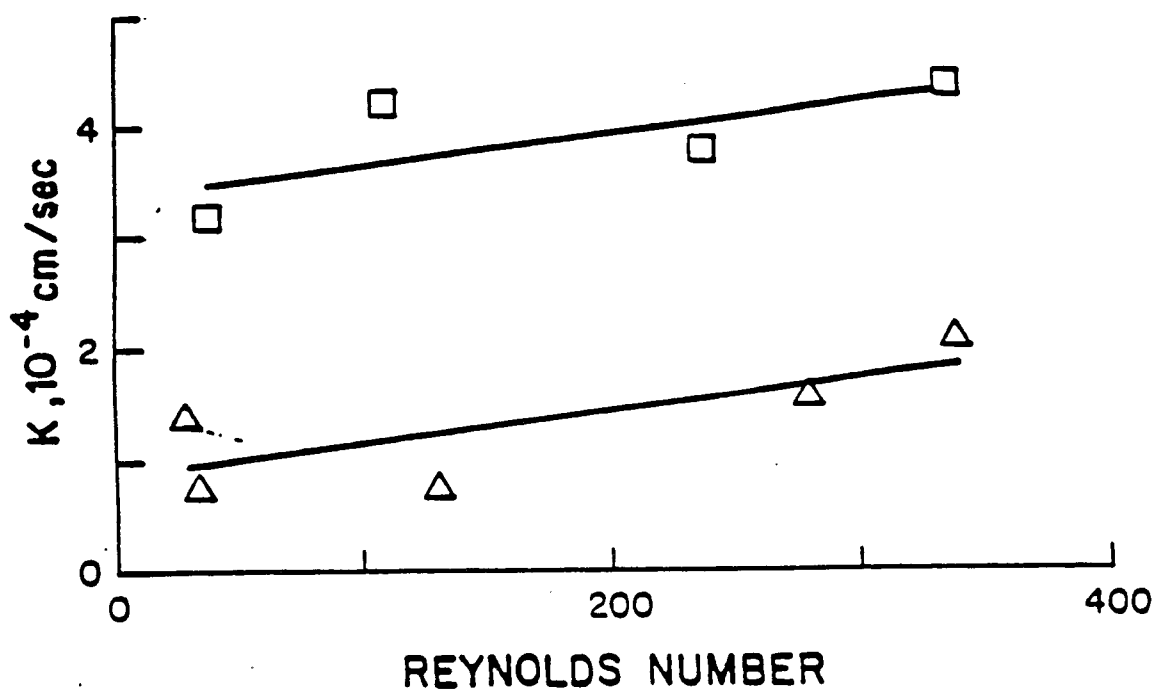


Figure 4 – Cyanide Mass Transfer vs. Stripping Flow The squares and triangles represent base concentrations of 1 M NaOH and 0.1 M NaOH, respectively. The variation with base concentration seems stronger than the variation with the Reynolds number.

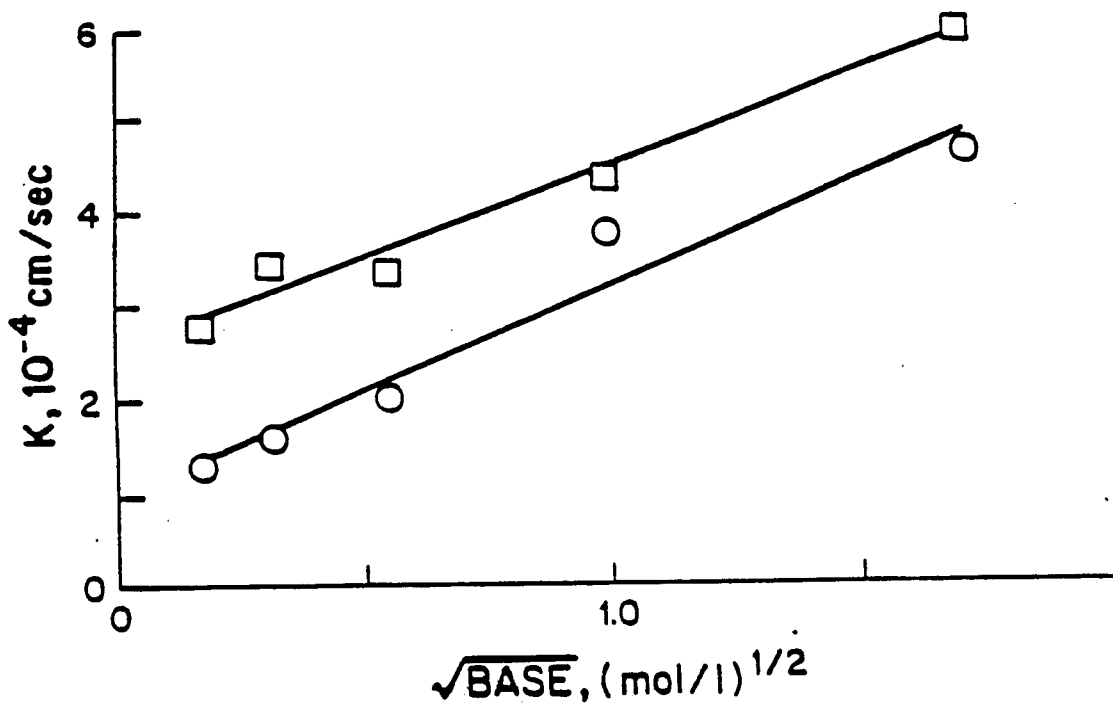


Figure 5 — Cyanide Mass Transfer vs. Base Concentration in the Stripping Solution  
 The squares and circles refer to feed concentrations of 500 and 5000 ppm HCN.  
 This variation is characteristic of mass transfer with fast reaction.

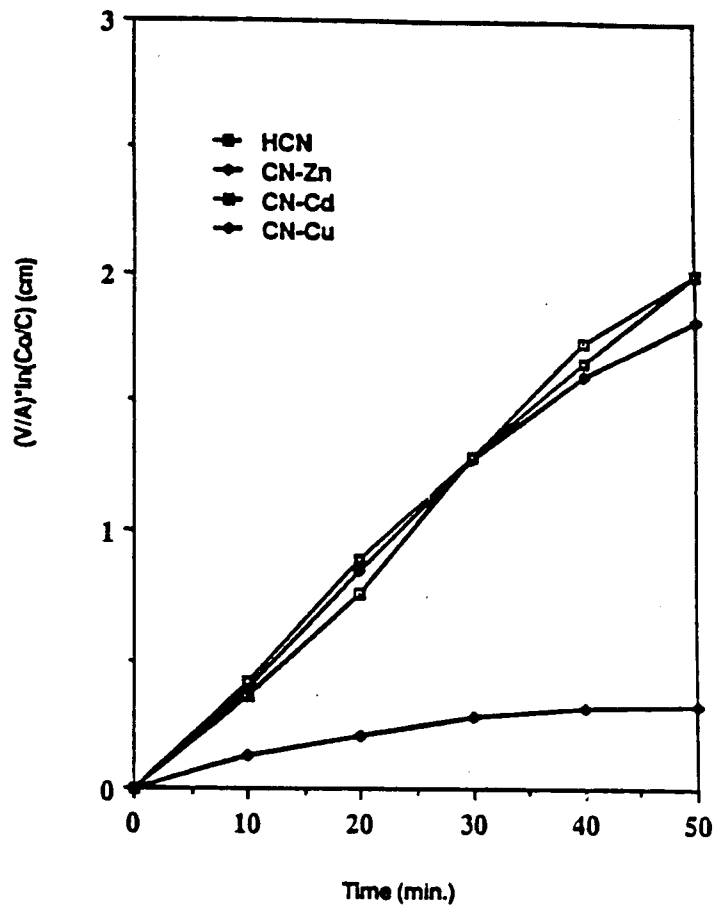


Figure 6 — A Comparison of Cyanide Removal from Metal Cyanide Solutions  
 The rate of cyanide recovery from zinc and cadmium cyanide solutions is equal to the rate from acidified NaCN solution, but recovery from copper cyanide solution is much poorer.

the copper can be removed by the gas membrane. Silver also formed a stable cyanide complex and could not be broken down under acidic conditions. Although nickel was not tested, its chemistry suggests that it will not break down under acidic conditions as well.

Some additional tests were conducted to evaluate the use of organic acids such as acetic acid for the breakdown of copper cyanide complexes. Cuprous cyanide is broken down in the presence of acetic acid and an oxidant (15). Even in the absence of an oxidant, acid appears to improve the breakdown of CuCN and the recovery of free cyanide. Further studies are needed to evaluate the best conditions for this copper cyanide recovery.

### Conclusions

The results of the mass transfer studies on HCN indicate that the rate of transfer across a gas permeable membrane is rapid and complete. The transfer is largely limited by diffusion within the lumen of the hollow fibers but is also influenced by the rate of reaction of the HCN with the base outside of the fibers.

The gas permeable membrane can provide the basis for effective separation and recovery of cyanide from zinc and cadmium plating wastes along the lines of Fig. 1. In certain applications, we can even avoid the initial ion exchange, which is necessary to concentrate dilute metal cyanide solutions such as rinsewaters. If the wastewater is already concentrated, acidification is all that is required. Solutions containing copper and silver cyanides are less readily treated. The use of organic acid to catalyze the breakdown of these metal cyanides may aid these less tractable solutions.

### Acknowledgements

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## Chapter 3

### The GM-IX Process: A Novel Metal Cyanide Treatment and Recovery Technique

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#### Abstract

A novel gas membrane-ion exchange process (GM-IX) is described that is capable of treating metal plating wastewaters containing zinc cyanide and recovering usable forms of zinc and cyanide. In the process a strongly basic anion exchange resin is employed to selectively concentrate the metal cyanides from dilute plating wastes. Following exhaustion, the resin is regenerated under acidic conditions. The metal cyanide complexes are broken down as a result of HCN production under these acidic conditions, and the acidic regenerant containing the HCN is recirculated through a gas membrane module that is supplied with a caustic stripping solution. The volatile HCN migrates across the gas permeable membranes to be absorbed and neutralized in the NaOH solution.

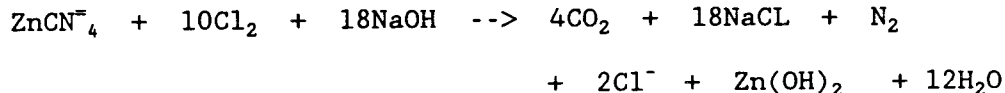
The products of the process include a concentrated sodium cyanide solution containing some excess sodium hydroxide, and a concentrated acidic zinc sulfate solution that can be treated by an electrowinning process to recover zinc metal and a re-usable acid for regeneration.

#### Introduction

This paper describes a novel technology for the economical separation and recovery of metals and cyanides from dilute wastes that contain free and complexed cyanide. As such the process appears to have application in a variety of industries, such as iron and steel manufacturing, photographic bleaching and metal plating and finishing, which generate substantial volumes of cyanide bearing wastewater.

A major effort has been made to develop processes for the destruction or recovery of cyanide from industrial waste waters, and the literature is replete with patents and processes that relate to the treatment of cyanide wastes<sup>1</sup>. Most of these processes have been rejected as either technically or economically unacceptable however,

Currently, the alkaline chlorination process is most commonly used for cyanide removal in practice and the overall chemical equation that describes the reaction between chlorine and zinc cyanide is shown below.



There are two major problems with this process: firstly, the large chlorine and caustic requirements make the process expensive; and secondly, the hydroxide sludge generated must be dewatered and landfilled which is expensive and expected to increase in cost in the near future. There is a need for a more economical process that can be employed to separate and recover the metals and cyanide from dilute wastewaters such that landfilling operations are not required.

The GM-IX process is a novel two step process that responds to this need. The first step is an ion exchange process which serves to selectively concentrate the free and complexed cyanide from dilute rinse waters. The second step involves the acid regeneration of the resin, following exhaustion, with the regenerant being pumped through a gas membrane module to selectively recover pure cyanide. These steps are discussed separately below.

#### Ion Exchange (IX)

A typical rinsewater composition for a zinc cyanide plating operation is shown in Table 1. It is noteworthy that the zinc is present as an anion ( $ZnCN_4^-$ ), as is cyanide, and that the water is strongly alkaline. If the rinsewater is pumped through a cation exchanger in the hydrogen form the zinc can be removed because, in the acidic environment of the resin, the zinc cyanide complex is hydrolyzed and divalent zinc cations are generated which are held by the anionic functional groups of the resin. Unfortunately, the removal is only effective while the cation exchanger retains some  $H^+$  exchange capacity. As soon as the hydrogen ion complement of the cation exchanger is exhausted the effluent from the resin rises back up to the influent pH and no further zinc removal takes place. Since the influent is highly alkaline, the neutralization of the  $H^+$  cation exchange capacity occurs rapidly. This behavior is illustrated graphically in Figure 1. This Figure depicts the breakthrough curves for zinc and sodium, for Amberlite IR-120 (Rohm and Haas, Philadelphia, PA) in the  $H^+$  form, and the curves are compared with the effluent pH profile. Zinc and sodium breakthrough clearly coincide with the increase in effluent pH which heralds the exhaustion of the hydrogen ion capacity of the resin. These breakthrough curves indicate that the resin was only effective in treating an alkaline zinc cyanide rinsewater for approximately 15 bed volumes (approximately 112 gallons/cu. ft.) of throughput.

The use of a cation exchanger in the  $H^+$  form has two additional disadvantages:

- i) Cyanide is not removed by the cation exchanger, and the effluent from the ion exchanger is an acidic solution containing toxic HCN. The cation exchanger must therefore be followed by an anion exchanger in the  $OH^-$  form to neutralize the HCN and remove the cyanide anion.
- ii) Some precipitation occurs in the cation exchange column. Zinc cyanide ( $ZnCN_2$ ) precipitation occurs when the pH of the rinsewater is decreased in the resin column, but the conditions are not acidic enough ( $pH > 1-2$ ) for free zinc production. If the resin is backwashed the backwash water will be contaminated with zinc cyanide.

Since the zinc cyanide complex is labile it is better to apply the zinc cyanide rinsewater directly to a strongly basic resin. In our studies we evaluated the performance of Amberlite IRA 400 (Rohm and Haas, Philadelphia, PA) in the  $OH^-$  form for complexed and free cyanide removal. A typical breakthrough curve is depicted in Figure 2. The IRA 400, an inexpensive gel type resin, was effective in removing both zinc and cyanide for 65-75 bed volumes of throughput (490-565 gall./cu. ft.) when treating the same water as the cation exchanger. The anion exchanger therefore had approximately 5 times the capacity of the cation exchanger for zinc removal and it removed cyanide at the same time. The effective capacities of the resin for zinc and cyanide were 3.6 and 2.3 lbs./cu. ft. for zinc and cyanide respectively. For these reasons cation exchange was not considered further and studies concentrated on the direct

TABLE 1

Typical Zinc Cyanide Rinsewater Composition  
Tested in This Study

Zinc = 320 mg/L  
pH = 12  
Calcium < 5 mg/L  
UVA = 1.59 @ 254 nm

Cyanide = 500-550 mg/L  
Sodium = 1150 mg/L  
TOC = 150 mg/L

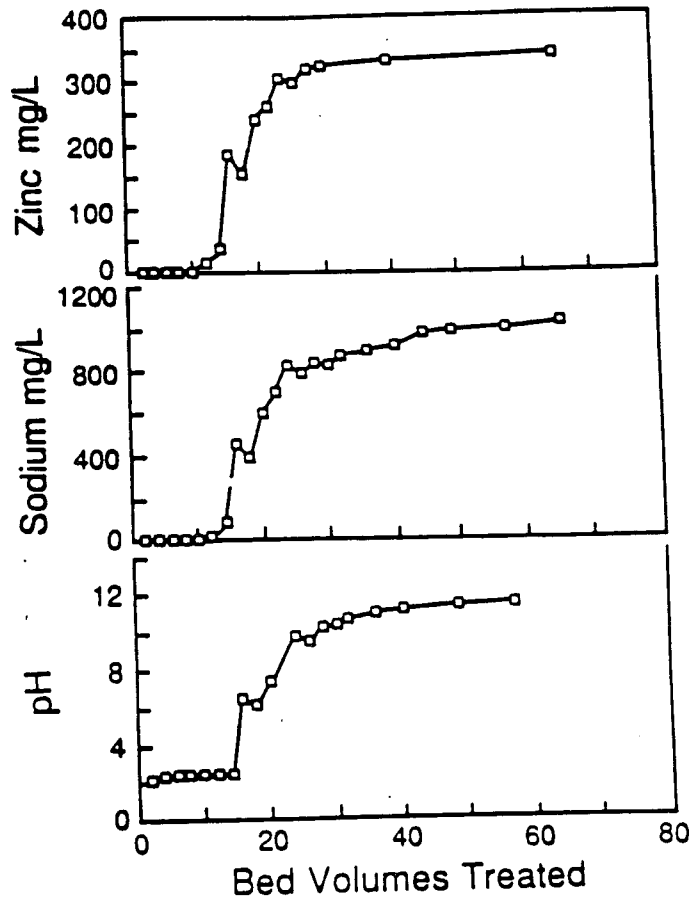


Figure 1: Breakthrough Curves Obtained for IR-120 in Hydrogen form.



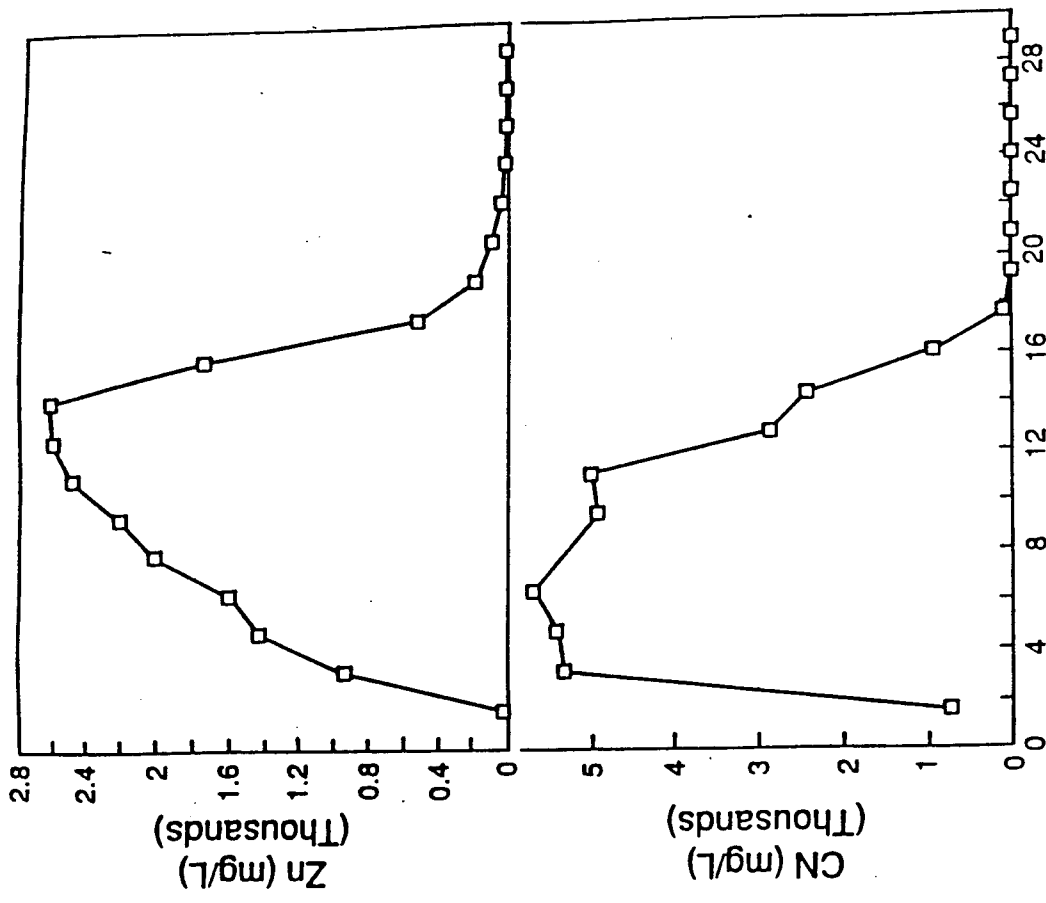


Figure 3: The Release of Zinc & Cyanide from IRA 400 During Regeneration with 0.2N H<sub>2</sub>SO<sub>4</sub> at a Flow rate of 10 BV/hr.

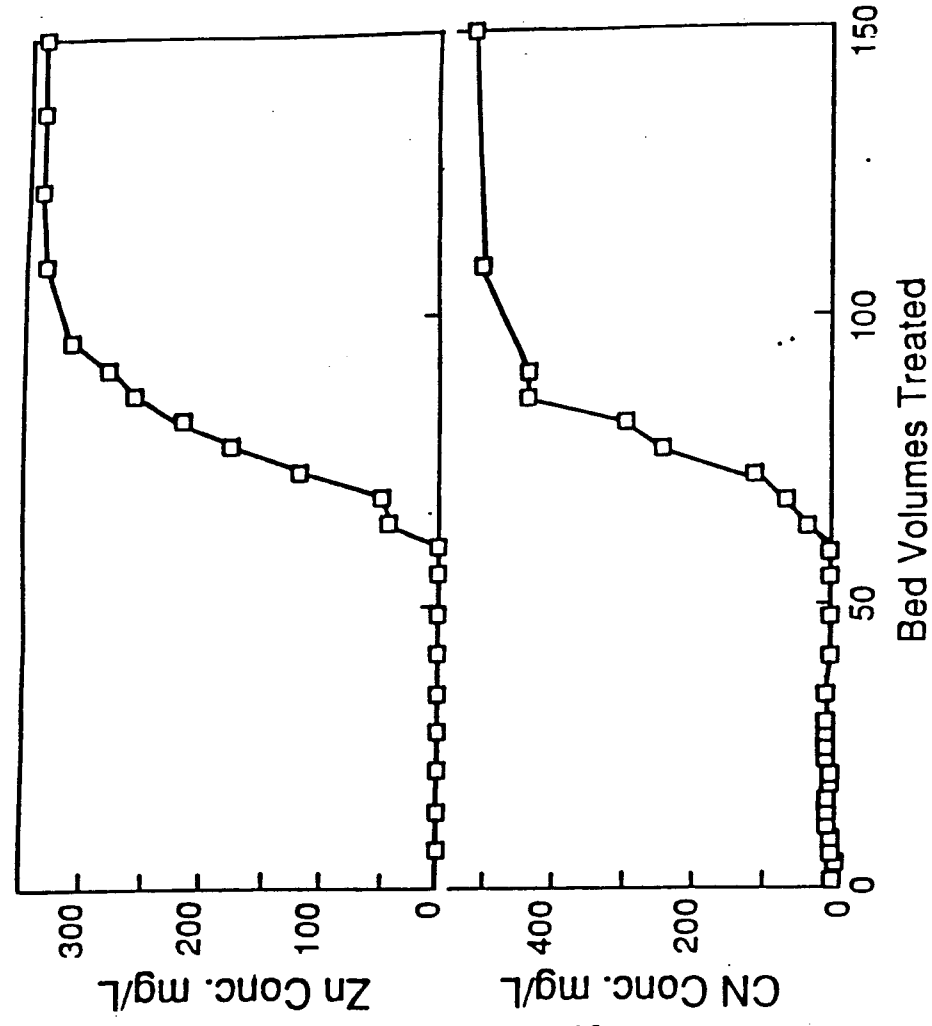


Figure 2: Typical Zinc & Cyanide Removal Performance Curves for IRA 400 (6.1 BV/hr, Zn<sub>0</sub>=340 mg/l, CN<sub>0</sub>=441 m/l)

use of strongly basic resins.

### Regeneration

Metal cyanide complexes such as  $ZnCN_4^{2-}$  are very strongly held by basic resins and simple displacement by  $OH^-$  using a caustic regenerant is ineffective. Studies demonstrated that even with extended caustic regeneration (32 lbs. NaOH/cu. ft. resin) less than 40% of the zinc cyanide was eluted from the resin.

A more effective means of regeneration employs an acid to encourage hydrolysis of the cyanide complex. This approach was employed successfully by previous investigators (Goldblatt<sup>2</sup>).

In our studies both sulfuric acid and hydrochloric acid were tested for their effectiveness in regenerating the resin. Hydrochloric acid was found to be effective in removing the cyanide from the resin but the high chloride concentrations promoted the formation of anionic zinc chloride complexes that were selectively retained by the anion exchanger. To remove the zinc chloride complexes it was necessary to elute the resin with large volumes of rinsewater and this was clearly unacceptable.

Sulfuric acid was more attractive as a regenerant and extensive tests were conducted to evaluate the strength, volume and flowrate of acid required for effective regeneration.

Goldblatt<sup>2</sup> found that it was possible to regenerate IRA 400 with 30 bed volumes of 0.2 N  $H_2SO_4$  at a flowrate of 4 bed volumes/hr for 7.5 hours. A study was conducted to test the effectiveness of sulfuric acid under similar conditions except that the flowrate was increased to 10 Bv/hr in order to complete regeneration in less than 3 hours. The elution of zinc and cyanide from IRA 400 is depicted in Figure 3, and at first glance it appears that the zinc and cyanide are released completely in just over 20 bed volumes of regenerant. However, when, after 30 bed volumes of regenerant had been applied the resin was rinsed and returned to service, the breakthrough curves shown in Figure 4 were obtained. These data indicate that the resin removed cyanide satisfactorily but zinc removal was characterized by a large leakage level (approximately 10-15 mg/L zinc).

Numerous additional experiments were conducted with different regenerant strategies and it became clear that the complete release of zinc from the resin was accomplished slowly regardless of the acid strength (0.2 - 1.0 N) and flowrate (1-6 bed volumes per hour) employed. It appears that under the acidic conditions some zinc cyanide,  $ZnCN_2$  precipitates and the release of zinc from the resin is governed by the rate at which  $ZnCN_2$  re-dissolves<sup>5</sup>. It was found that the initial release of zinc cyanide from the resin was most rapid and extensive with the higher strength acid (10%) but a long contact was then required to complete the removal of residual zinc and cyanide.

### Discussion

The strongly basic resin was shown to be effective in selectively concentrating zinc cyanide complexes and free cyanide from plating wastewater. The resin was readily regenerated with concentrated sulfuric acid (10%) and the process concentrated the metal cyanides from 10 to 80 times from the feed composition shown in Table 1.

Unfortunately, the acidic spent regenerant is high in toxic HCN and zinc content and must be treated appropriately. The regenerant could be neutralized with caustic and treated by alkaline chlorination but if this were the case the ion exchange process would only have served as a means of concentrating the waste. Since the high chemical costs of alkaline chlorination would still be incurred, the additional expense of ion exchange could not be justified. The

ion exchange option can only be justified if we can process the spent regenerant less expensively.

Research was therefore conducted to evaluate the use of a gas permeable membrane to selectively separate and recover the cyanide content of regenerant in a reusable form.

#### Gas Membrane (GM)

Gas membranes are thin ( $3 \times 10^{-5}$  m) microporous hydrophobic polymeric membranes that can be employed to separate two aqueous solutions without wetting. The pores of the membrane, which are approximately  $0.02 \mu$  in diameter, remain dry and gas filled. Only volatile species such as dissolved gases may transfer across the membrane through these gas filled pores; non-volatile dissolved species are rejected by the membrane<sup>3</sup>.

The gas membrane can be employed to advantage in the treatment of the acidic ion exchange regenerant. The acidic regenerant is pumped on one side of the membrane while an alkaline stripping solution (NaOH) is recirculated on the other side of the membrane. The HCN is volatile and may pass through the membrane. When the acidic gas reaches the stripping solution it is neutralized and forms non-volatile sodium cyanide. In this way the HCN content of the regenerant can be recovered as reusable sodium cyanide.

Studies have been conducted on the use of polypropylene microporous hollow fibers manufactured by (Questar, Charlotte, NC 28224). Small scale hollow modules were manufactured in our laboratory. An example module is shown in Figure 5 together with typical design data. Studies were conducted by pumping acid cyanide solutions through the inside of the fibers and a sodium hydroxide solution around the outside of the fibers. An illustration of the experimental system employed for evaluating the rate of cyanide transfer is also shown in Figure 6. The acidic and alkaline solutions were recirculated on either side of the membrane and the extent of transfer was monitored by measuring the concentration of cyanide in the caustic stripping solution with time. Since the original concentration of HCN in the acid solution was known,  $[\text{HCN}]_0$ , the actual concentration  $[\text{HCN}]$  could be evaluated from a mass balance at any time and the mass transfer coefficient,  $K$ , could be determined from the relationship<sup>4</sup>:

$$K = \frac{V}{At} \ln \frac{[\text{HCN}]_0}{[\text{HCN}]} \quad (1)$$

where  $V$  = the volume of the acid,  $A$  = the area of the membrane, and  $t$  = time. Thus, a plot of  $\ln[\text{HCN}]_0/[\text{HCN}]$  versus time should be linear with a slope proportional to  $K$ . An example of the data collected during a test run are presented in Figure 7 and demonstrate the good linearity expected. Numerous tests were conducted to evaluate the influence of operating conditions on the rate of cyanide transfer and to determine mass transfer coefficients that could be used for scale up.

The experiments are reported elsewhere in detail<sup>4</sup> and only a summary is presented here. Our studies showed that HCN transport across the membrane is rapid and complete. The transfer rate may be limited by the base concentration or by film diffusion control in the acidic stream within the fibers. The sodium hydroxide concentration tends to be limiting when the HCN concentration is very high or the base concentration is low. This is because the HCN migrates across the membrane faster than the NaOH can neutralize it. Under these conditions the rate of transfer of HCN is governed by the rate at which NaCN can diffuse away from the membrane and the rate at which either the NaOH diffuses to the membrane,

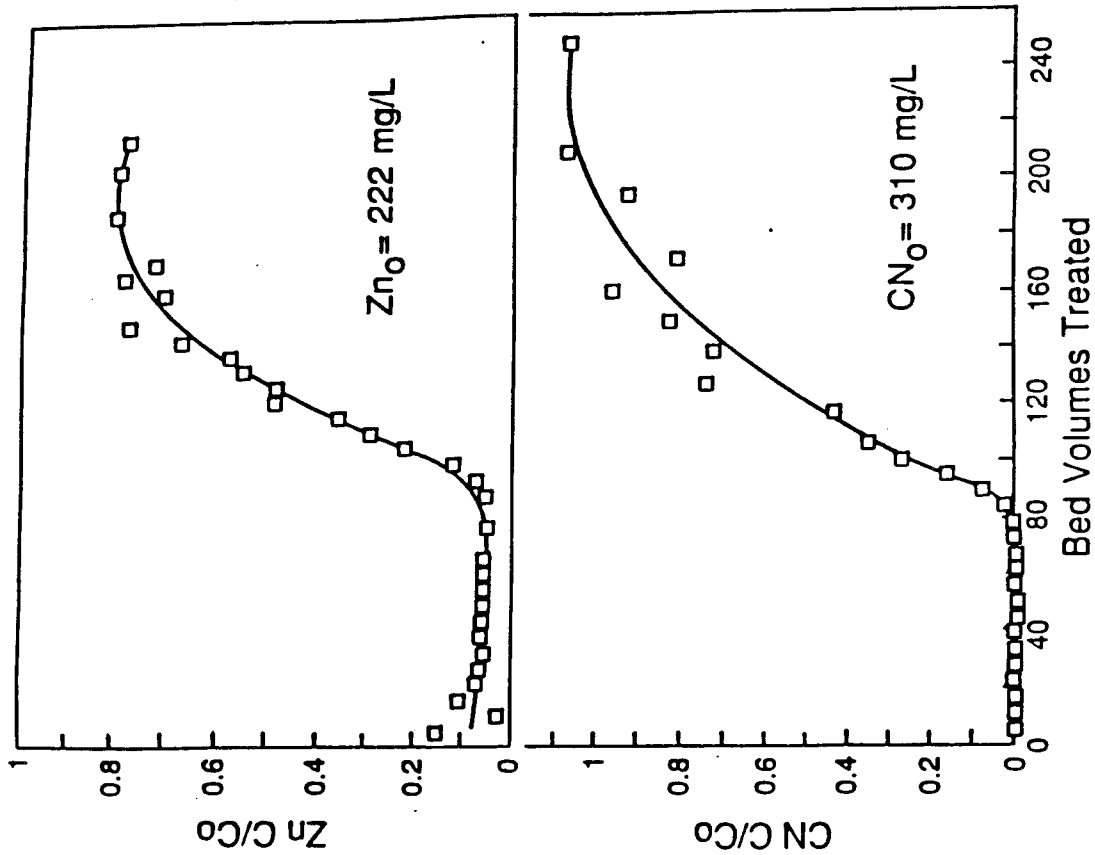
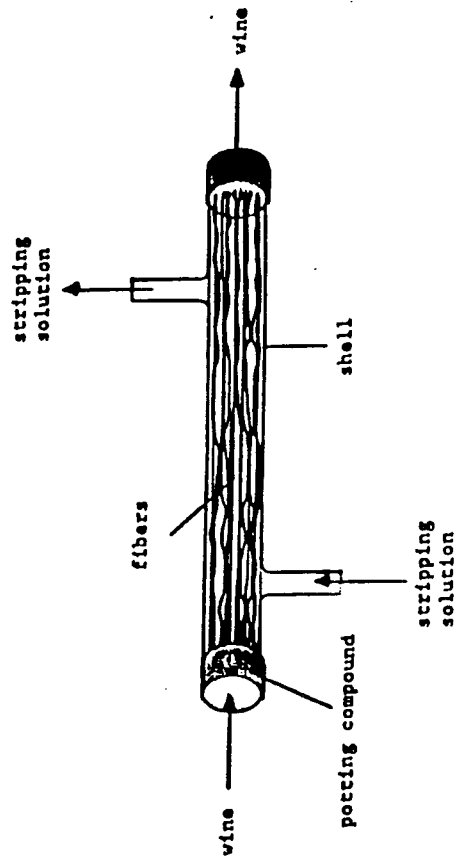


Figure 4: Performance Curves Obtained for IRA 400 Following Regeneration  
 30 BV with 0.2N H<sub>2</sub>SO<sub>4</sub>.



Module Dimensions

Length = 17 cm.  
 Inside diameter = 1 cm.  
 Material of construction = glass  
 No. of fibers = 120  
 Diameter of fibers - inside = 400 μ  
                                   outside = 425 μ  
 Fiber material = polypropylene

Figure 5: Gas membrane modules tested in laboratory studies.

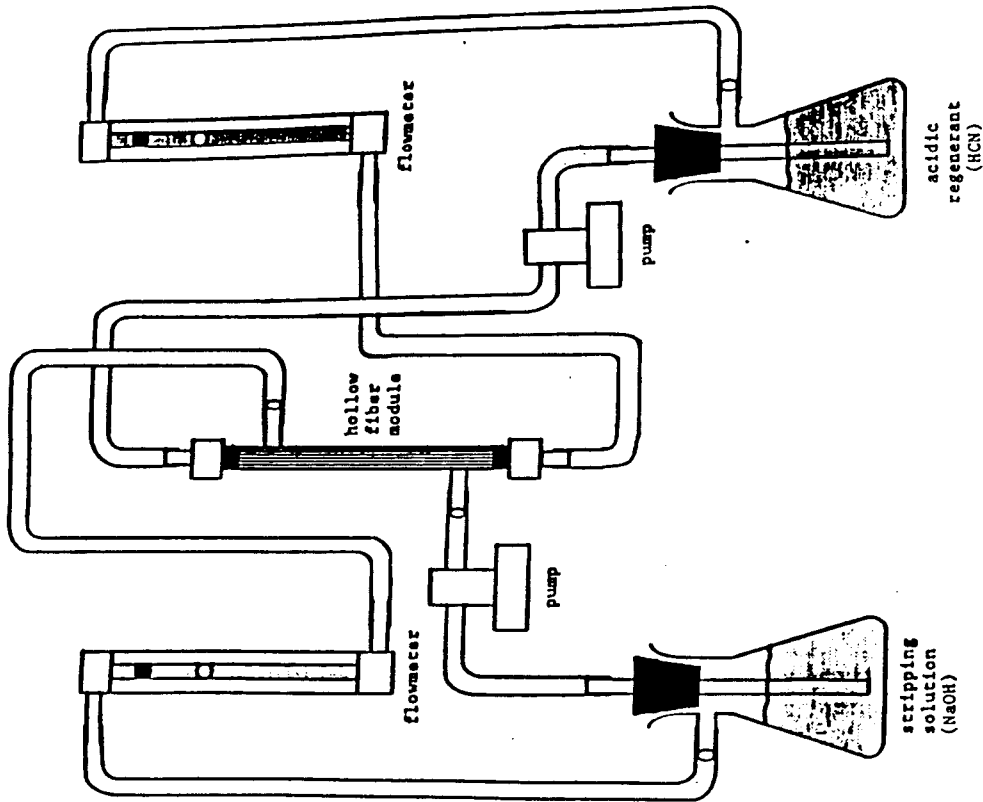


Figure 6: A schematic of the experimental apparatus employed to measure cyanide transfer rates.

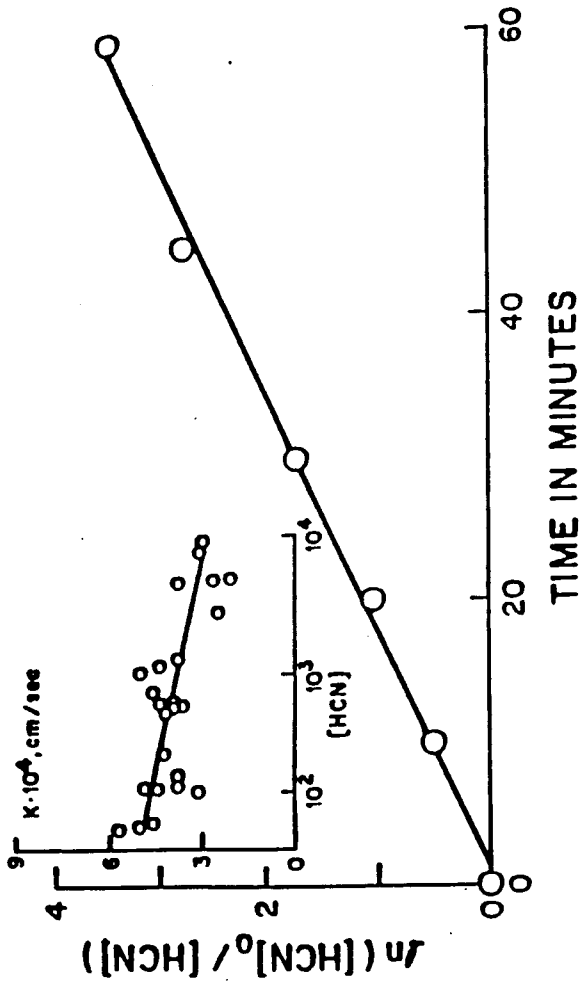


Figure 7: Cyanide Concentration vs. Time  
 The semilogarithmic variation suggested by Eq. 1, allows calculation of the mass transfer coefficient K. This coefficient varies only slightly with cyanide concentration, as shown in the inset.

or reacts with the incoming HCN. When the base stripping solution is concentrated relative to the HCN concentration, the neutralization reaction can be considered instantaneous, and then the rate is governed by the rate of HCN diffusion to the inside of the membrane.

Figure 8 illustrates the influence of the acid velocity within the membrane fibers upon the measured mass transfer coefficients and provides evidence of a film diffusion control mechanism. The overall mass transfer coefficient should vary linearly with the velocity raised to the third power if film diffusion is controlling<sup>5</sup>, and Figure 8 supports such a mechanism. Figure 9 illustrates the influence of sodium hydroxide concentration and flowrate on the measured mass transfer coefficients for HCN. The data clearly indicate that the transfer is significantly faster in the presence of higher concentrations of NaOH, and show that the rate increases slightly with higher base flowrates.

#### The GM-IX Process

By combining the two processes of ion exchange and gas membrane transfer, a novel technique for separating and recovering cyanides from dilute metal cyanide waste waters has been developed. The GM-IX process is depicted schematically in Figure 10. In this process the dilute cyanide waste is pumped through a strongly basic ion exchanger, such as IRA 400, until the resin is exhausted or until the effluent guidelines are exceeded. The resin is then regenerated with approximately 2 bed volumes of 10% H<sub>2</sub>SO<sub>4</sub> that is recirculated between the ion exchanger and the gas membrane module. The acid causes the free cyanide to form un-ionized HCN which is readily released from the ion exchanger. As the regenerant is recirculated through the gas membrane module the HCN is removed from the regenerant and captured in the sodium hydroxide stripping solution that is recirculated on the other side of the membrane. The removal of free cyanide from the resin under acidic conditions also encourage the breakdown of weak metal cyanide complexes such as zinc and cadmium cyanides. Over time, the continued removal of HCN from the acid regenerant forces the hydrolysis of the metal cyanides to completion and results in a metal rich acidic solution.

The design of the module can be estimated simply by assuming the acid regenerant is completely mixed and that the residence time in the gas membrane module is short relative to the mass transfer rate such that only a small fraction of the cyanide is removed from the water during each pass through the fibers.

In this case the concentration of HCN in the regenerant at any time can be calculated from equation 2:

$$\ln \left[ \frac{C_0}{C} \right] = \frac{K.A.t}{V_F} \quad (2)$$

If it is assumed that that hydrolysis of ZnCN<sub>4</sub><sup>=</sup> to Zn<sup>++</sup> and HCN is rapid and complete upon exposure of the ion exchanger to 10% H<sub>2</sub>SO<sub>4</sub>, then the initial HCN concentration in the regenerant may be estimated. For example, the effective capacity of IRA 400 for cyanide removal from zinc cyanide plating wastewater was 2.3 lbs. cyanide cu. ft. If this cyanide content is completely released into 2 bed volumes (15 gallons/cu. ft.) of regenerant an initial concentration, (C<sub>0</sub>), of approximately 18,500 mg/L of HCN would be generated. If the desired final HCN concentration, C, is approximately 2 mg/L then ln C<sub>0</sub>/C = 9.13.

From our studies it appears that a HCN mass transfer coefficient of approximately 4 x 10<sup>-6</sup> m/sec is reasonable for the microporous hollow fibers.

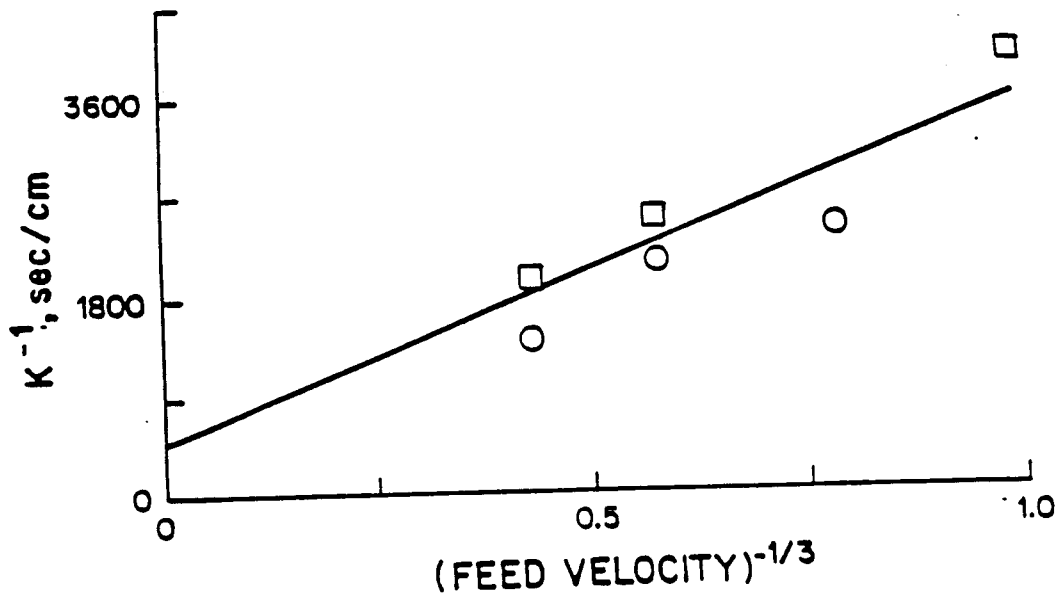


Figure 8: Mass Transfer vs. Cyanide Feed Velocity  
 This variation shows that diffusion in the feed is a significant resistance to the rate of cyanide stripping. The squares and circles refer to initial feed concentrations of 500 and 5000 ppm, respectively.

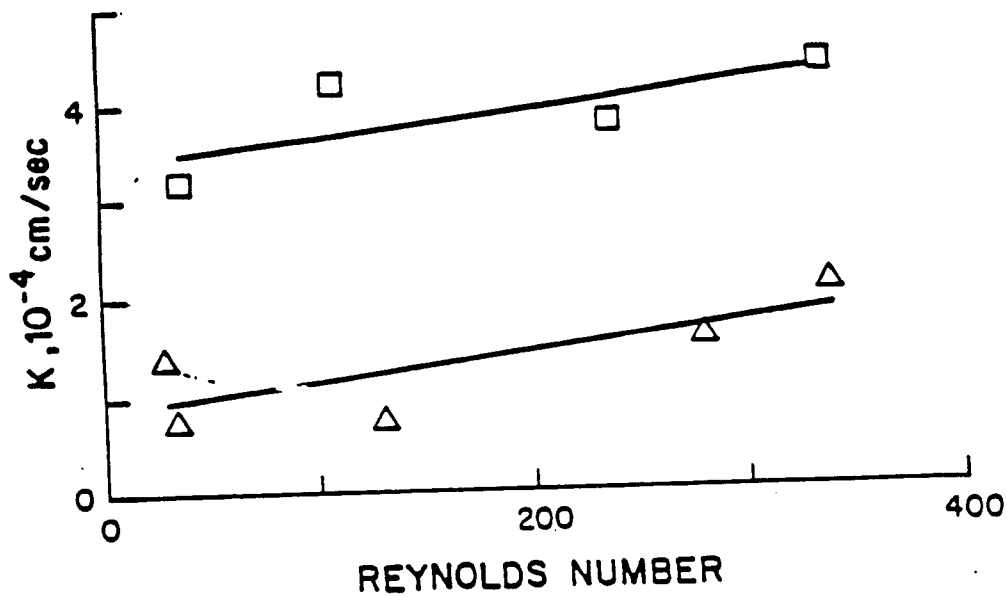


Figure 9: Cyanide Mass Transfer vs. NaOH Flow  
 The squares and triangles represent base concentrations of 1 M NaOH and 0.1 M NaOH, respectively. The variation with base concentration is stronger than the variation with the Reynolds number (velocity of base).

## THE GM-IX PROCESS

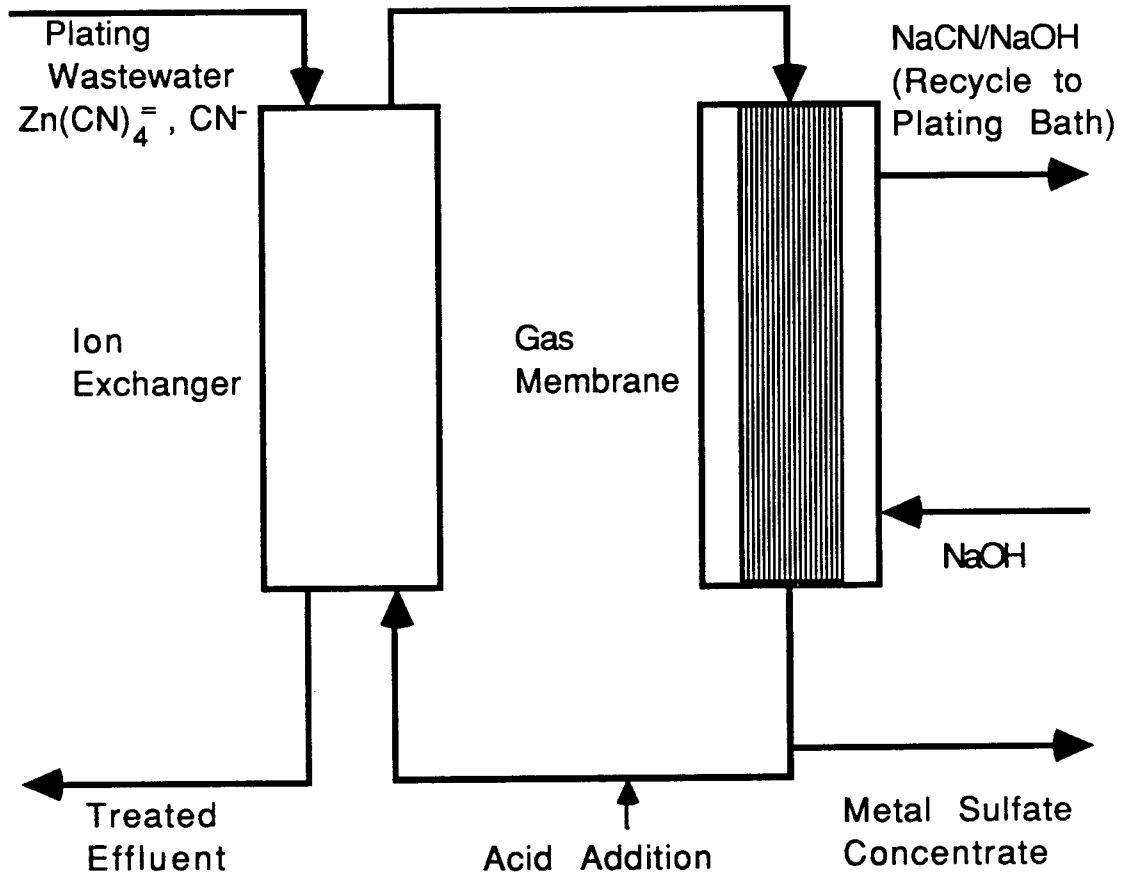


Figure 10. Schematic of the GM-IX Process



Inserting those numbers into equation 2 we obtain:

$$9.13 = \frac{4 \times 10^{-6} A t}{15 \times 3.78 \times 10^{-3}}$$

where A = area of membrane required in m<sup>2</sup> and t = time required for HCN removal in seconds. Thus, if we desire complete regeneration in 6 hours t = 21,600 seconds and A = 6 m<sup>2</sup>. Therefore 6 square meters of membrane surface area are required for complete regeneration of the resin in this time frame. More area would speed the process and less area would prolong it. The design of the process is determined by the operating constraints of the ion exchange system, and the membrane area and time need to be selected with these constraints in mind.

Some tests have been completed on a bench scale GM-IX process. An ion exchange module containing 200 mL of IRA 400 was employed to treat a real zinc cyanide plating wastewater. The ion exchanger was then regenerated with 1.5 bed volumes of 10% H<sub>2</sub>SO<sub>4</sub> which was recirculated through a module of the design shown in Figure 5 having an active surface area of 250 cm<sup>2</sup>. In two hours, 94% of the cyanide content of the resin was captured in the base stripping solution. Calculations similar to those presented above indicated that approximately 96% of the cyanide should be captured by the base in this time period. The agreement is excellent and indicates that the simple analysis described above can be employed for the preliminary design of the GM-IX process for specific applications.

### Conclusions

By interfacing a strongly basic anion exchanger and gas membrane module an effective and efficient means of separating and recovering pure cyanide from dilute cyanide plating wastes has been developed. The process will work effectively for weak metal cyanide complexes such as zinc and cadmium complexes. Preliminary bench scale tests of the GM-IX process indicate that the process performance may be predicted on the basis of the mass transfer data presented in this paper.

### Cost Analysis

A simple cost analysis was conducted to evaluate the comparative costs of the GM-IX and Alkaline Chlorination processes. The comparison was made on the basis of zinc cyanide wastes generated annually by a number of plating operations in the Minneapolis/St. Paul Metropolitan area. The amounts of waste zinc and cyanide generated are approximately 45,000 and 37,500 lbs. respectively. This simple analysis was based on the following assumptions:

- 1) The capital costs and labor costs for GM-IX and alkaline chlorination are approximately equivalent.
- 2) Sludge disposal costs \$200/55 gallon drum.
- 3) Ion exchanger losses 5% of capacity per cycle (conservative).
- 4) Gas membranes have a useful life of 2 years.
- 5) Ion exchanger cost = \$200/cu. ft.  
Membrane cost = \$400/m<sup>2</sup>.
- 6) Chemical costs:  
Chlorine = \$.30/lb.  
Sodium hydroxide = \$.15/lb.  
Sulfuric acid = \$.07/lb.

Sodium cyanide = \$.75/lb.

Zinc = \$.55/lb.

- 7) The zinc rich regenerant could be sent to an electrowinning operation once the cyanide removal was complete. Electrowinning could be employed to recover 50% of the acid for additional regeneration.
- 8) Product zinc, sodium cyanide and acid could be re-used by the plating shops.

The overall costs for the two processes are shown below:

Alkaline Chlorination = \$276,650/year

GM-IX Process = \$164,700/year

Clearly, the GM-IX process is an attractive alternative to conventional alkaline chlorination and, as such, the process warrants further investigation, field testing and development.

#### Acknowledgment

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## Chapter 4

### SELECTIVE CYANIDE RECOVERY FROM WASTEWATER CONTAINING METAL CYANIDE COMPLEXES

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and  
Yu-yuen Chang

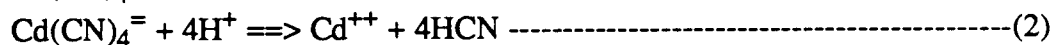
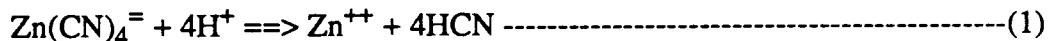
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#### INTRODUCTION

A novel metal cyanide separation technique has successfully combined a gas membrane and an ion exchanger to recover the metal and cyanide content of metal cyanide-bearing wastewaters<sup>(1)</sup>. These wastewaters have an alkaline pH generally above 11 and under these conditions cyanide ions bind the metal to form complex anions such as  $Zn(CN)_4^-$  and  $Cd(CN)_4^-$ . These anionic complexes are readily removed by a strongly basic anion exchange resin. The resin is regenerated with an acid which breaks down the metal cyanide complexes to form free metal ions and HCN. This HCN-rich acidic regenerant is recirculated through the lumen of hollow fibers of gas membrane and the gas membrane (which is hydrophobic) allows HCN gas to rapidly transport across the membrane wall while the free metal ions remain in the acid eluent. Outside the hollow fiber membranes, sodium hydroxide solution is used to absorb the transferred HCN to form NaCN. The recovered sodium cyanide can be recycled to the plating bath. We have reported on this process in earlier publication<sup>(1)</sup> and the intent of this paper is to focus on some operating problems observed in practical application of this process to real metal cyanide rinsewater.

During the regeneration of zinc cyanide saturated ion exchange resin, we observed that white zinc cyanide precipitate formed in the column. And when this regenerated column was rinsed and reused, we found significant zinc leakage in the effluent while no cyanide leakage was detected, as shown in Figure 1 and 2. Our studies also showed that an insoluble precipitate was formed when an anion exchanger containing copper cyanide complex was regenerated with acid. These metal cyanide precipitates are important in both ion exchange and membrane separation processes because the amount present at equilibrium and the kinetics of their dissociation are important factors that may influence the efficiency of acid regeneration and the rate of cyanide recovery.

If enough acid is added the anionic metal cyanide complexes of zinc and cadmium can completely break down to form  $Zn^{++}$ ,  $Cd^{++}$  and HCN as follows:



However the formation of CuCN precipitate that is formed when copper cyanide solutions are acidified cannot be broken down under more acidic conditions. At intermediate pH values, which are necessarily generated during the regeneration process, metal cyanide complexes such as  $Zn(CN)_3^-$ ,  $Zn(CN)_2$ ,  $Cd(CN)_3^-$ ,  $Cd(CN)_2$  and  $Cd(CN)^+$  will also form and retard cyanide separation. If insoluble metal cyanides are formed as is

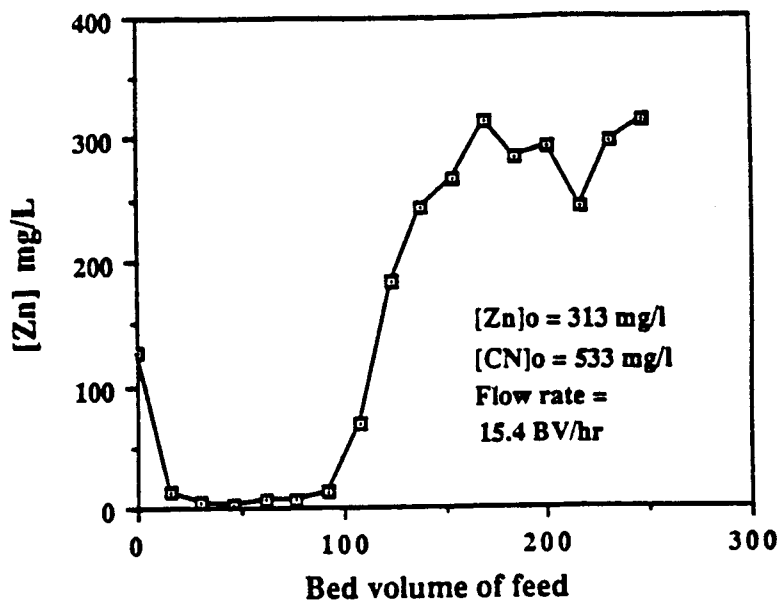


Figure 1 - The Zn Concentrations in the Treated Effluents When the IRA-400 Resins Were Regenerated, Rinsed and Re-used.

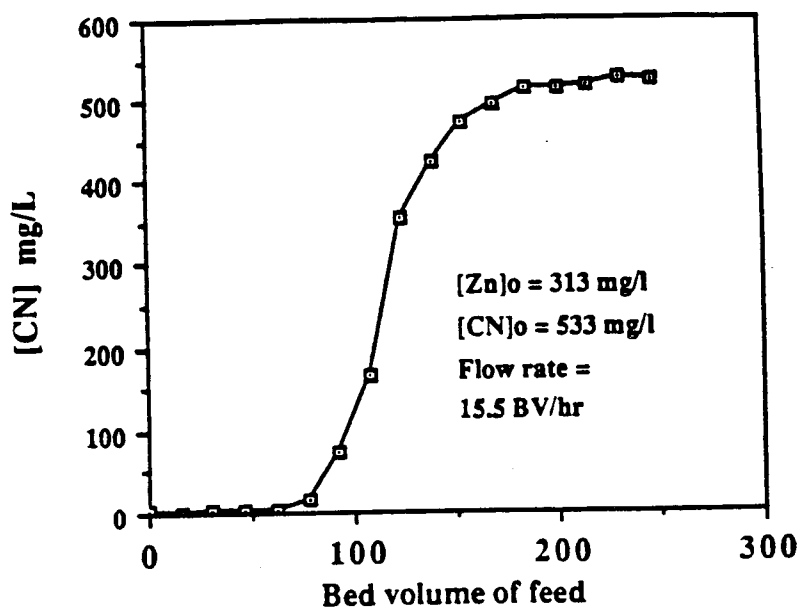


Figure 2 - The CN Concentrations in the Treated Effluents When the IRA-400 Resins Were Regenerated, Rinsed and Re-used.

the case for zinc and copper, these precipitates may retard cyanide recovery dramatically. The kinetics of cyanide release may become controlled by the rate of dissolution of the precipitate, rather than by chemical equilibria.

The regeneration behavior of zinc, cadmium and copper cyanide complexes was evaluated in this study. The objectives of the study were to determine what forms of zinc were retained in the column; what limited the rate of metal and cyanide removal; what caused the zinc leakage when the regenerated resins were reused and how the system could be modified to improve metal removal from the resin. In addition the copper cyanide system was investigated to determine if the regeneration procedure could be modified to break down the CuCN precipitate and allow complete cyanide recovery. Zinc and cadmium behavior are discussed together because of their chemical similarity, and copper cyanide recovery is addressed separately at the end of the paper.

## EXPERIMENTAL

### Materials and Analysis

The synthetic metal cyanide solutions were made from analytical grade reagents. Sodium cyanide and cuprous cyanide solid were dried in the oven at a temperature of 120°C and then stored in the desiccator. Other chemicals were used as received.

Metal cyanide solutions were prepared by adding the metals in the form of zinc oxide, cadmium chloride and cuprous cyanide solid to an alkaline sodium cyanide solution. Sulfuric acid was used to acidify the the synthetic metal cyanide solution, and to control pH. Cyanide concentrations were analyzed by titration<sup>(2)</sup> with standard silver nitrate (Baker).

### Apparatus

The experimental apparatus is depicted schematically in Figure 3. The acid reservoir was filled with a known volume of concentrated metal cyanide solution to simulate the concentrations experienced in a regenerant and this was acidified and sealed immediately. This solution was pumped through the lumen of the hollow fiber membrane in a specially constructed module. Simultaneously, a known volume of concentrated NaOH was recirculated from the base reservoir through the membrane module on the outside of the fibers. The HCN released from the metal cyanide solution following acidification was transported across the membrane and neutralized in the base. By monitoring the cyanide concentration in the base solution as a function of time the rate and extent of cyanide recovery could be calculated.

The hollow fiber membranes (Celgard 2400, Questar Charlotte, N.C.) that were employed are made of hydrophobic microporous polypropylene having a 30 µm wall thickness, approximately 0.02 µm diameter pores and a 400 µm inside diameter. This type of membrane is not wetted by water and the pores remain dry and gas filled. With these gas filled pores, the membrane itself can be viewed as a thin film of gas by which the solutions on each side of the membrane are isolated; gas transfer may take place across this gas film. The hollow-fiber modules were made by potting 120 fibers having a length of 17 cm into a cylindrical glass shell as illustrated in Figure 4.

## CHEMICAL EQUILIBRIA FOR ZINC AND CADMIUM CYANIDE COMPLEXES

In a sodium cyanide solution, the equilibrium between  $\text{CN}^-$  and HCN is a function of the pH and the pK value of HCN which is 9.21 at 25°C. If the solution pH value is

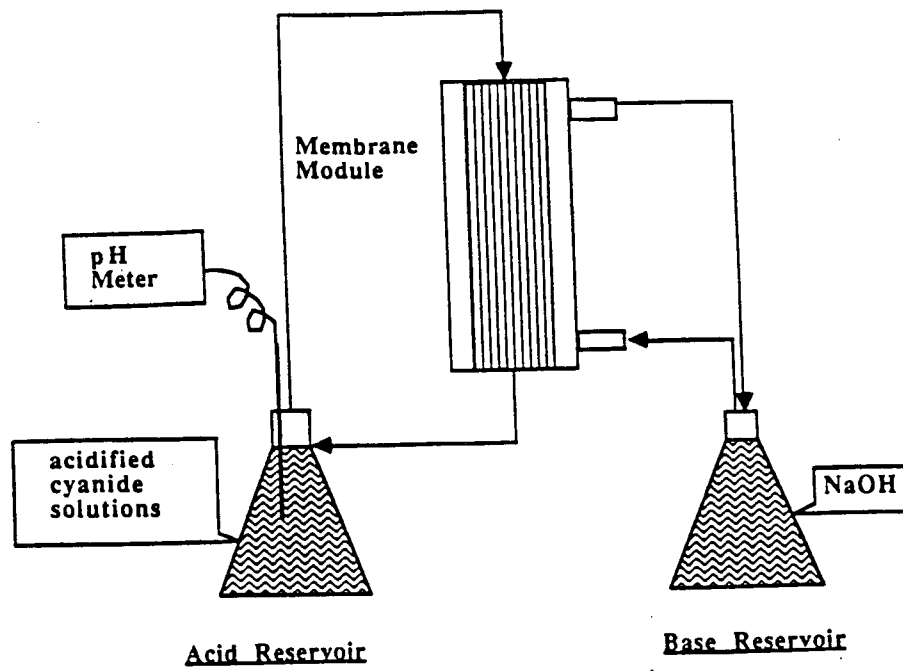


Figure 3 - Experimental Apparatus Employed in the Kinetics Studies

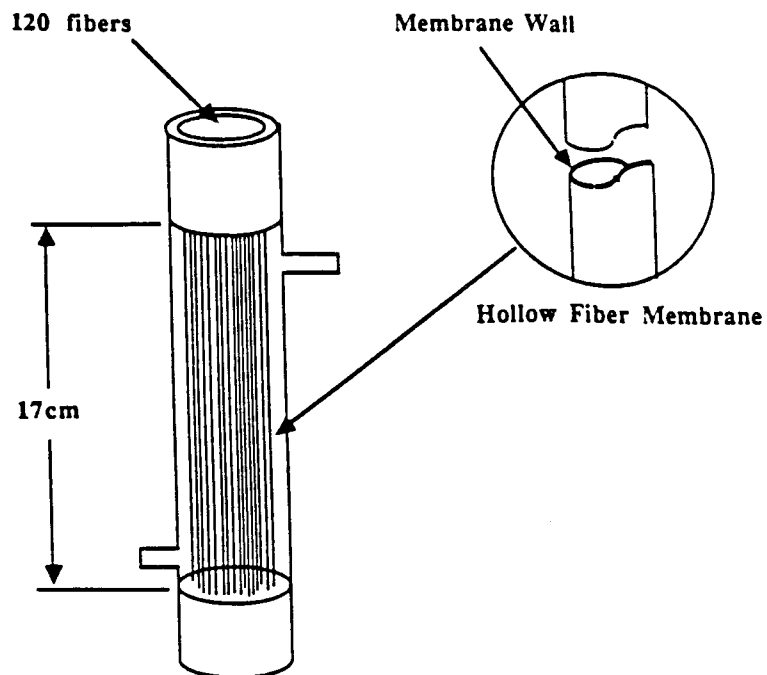


Figure 4 - Detail of the Hollow Fibers Module Tested

above 9.21, free CN<sup>-</sup> ion predominates while below 9.21 HCN predominates. Addition of zinc ions to a cyanide solution creates a variety of zinc cyanide complexes which reduces the concentration of free CN<sup>-</sup> ions in solution. The equilibrium composition is now determined not only by the pK of HCN and pH, but also by the stability constants of each of the complexes that may form, the total concentration of cyanide and the total concentration of zinc. During regeneration pH is the only practical control variable.

The speciation of a given zinc cyanide solution under different pH conditions may be determined by employing a chemical equilibrium model such as MINEQL<sup>(4)</sup>. The thermodynamic information for zinc and cadmium cyanide complexes employed in this study are listed in Table 1.

Table 1 - Stability Constants of Zinc Cyanide Complexes  
and Cadmium Cyanide Complexes

<u>Species</u>	<u>Log K*</u>	<u>Species</u>	<u>Log K*</u>
Zn(CN) <sup>+</sup>	5.30	Cd(CN) <sup>+</sup>	5.55
Zn(CN) <sub>2</sub>	11.70	Cd(CN) <sub>2</sub>	10.70
Zn(CN) <sub>3</sub> <sup>-</sup>	16.70	Cd(CN) <sub>3</sub> <sup>-</sup>	15.50
Zn(CN) <sub>4</sub> <sup>=</sup>	21.60	Cd(CN) <sub>4</sub> <sup>=</sup>	19.00
Zn(CN) <sub>2</sub> (s)	15.50	Cd(CN) <sub>2</sub> (s)	2.60**

\*  $K = \frac{[ML_n]}{[M][L]^n}$ , at 25 °C, ionic strength = 3.0, adapted from Reference (5).

\*\* at 25 °C, ionic strength = 0.1, adapted from Reference (6)..

These stability constants were input to the MINEQL data base. Then, by setting a desired solution pH and fixing the total concentrations of the major ions, such as Na<sup>+</sup>, Zn<sup>++</sup>, H<sup>+</sup>, CN<sup>-</sup> and SO<sub>4</sub><sup>=</sup>, the MINEQL program calculated the concentrations of each cyanide species present. By repeating the computation at different pH values the distribution of cyanide species over the whole pH range was obtained. Figure 5 shows an example of the species distribution in a zinc cyanide solution for the pH range from 1 to 12. In this example, the total concentration of cyanide was 5000 mg/l and total concentration of zinc was 3000 mg/l. When the pH value is higher than 10, all the zinc is present in the Zn(CN)<sub>4</sub><sup>=</sup> form and excess cyanide is present as free CN<sup>-</sup> ions; no HCN is present at this alkaline pH. As pH decreases, H<sub>3</sub>O<sup>+</sup> ions associate with free CN<sup>-</sup> to form HCN first. The Zn(CN)<sub>4</sub><sup>=</sup> gives way to Zn(CN)<sub>3</sub><sup>-</sup> and Zn(CN)<sub>2</sub> forms with the formation of additional HCN. It is noteworthy

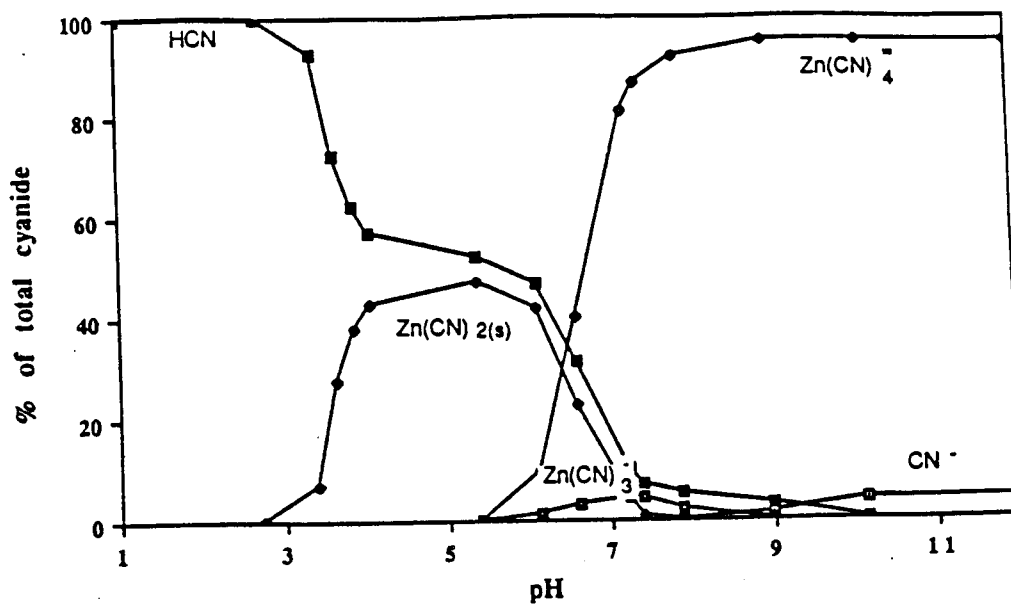


Figure 5 - Zinc Cyanide Complexes and Free HCN Distribution as a Function of pH

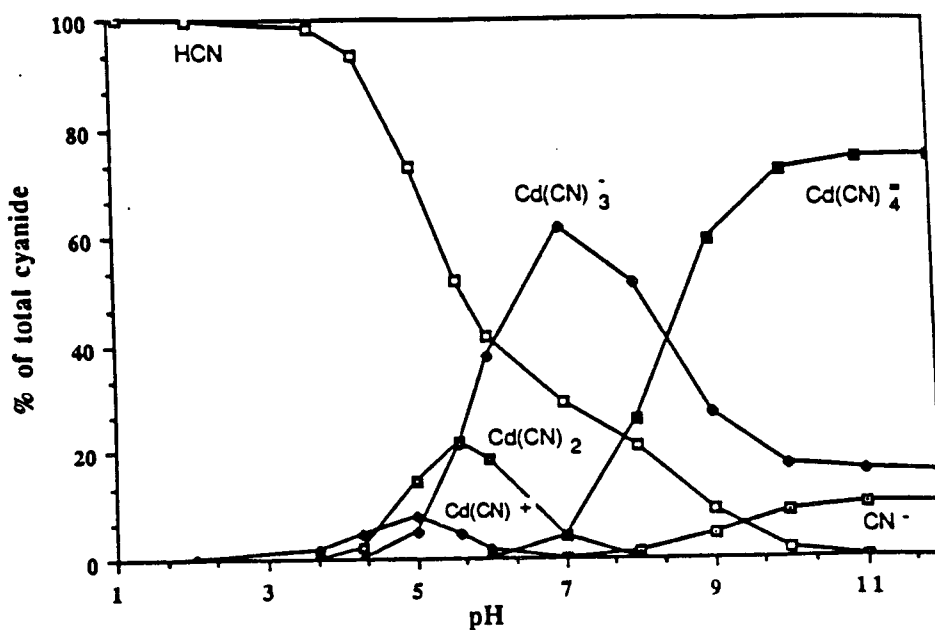


Figure 6 - Cadmium Cyanide Complexes and Free HCN Distribution as a Function of pH



that the model predicts a significant amount of  $Zn(CN)_2$  precipitate should form in the neutral pH range (pH 3-7). At pH 5 almost half of the cyanide is retained in the precipitate and the other half is present as HCN.

Cadmium cyanide exhibits a very similar species distribution with pH as shown in Figure 6. At alkaline pH (above pH 11),  $Cd(CN)_4^{=}$  predominates and no HCN is present. Other cadmium cyanide complexes, such as  $Cd(CN)_3^-$ ,  $Cd(CN)_2$  and  $Cd(CN)^+$  bloom in the neutral pH range. Hydrogen cyanide concentration increases as pH decreases and reaches its maximum concentration below 2. In the case of cadmium, however, no precipitate is formed; all the cyanide species are soluble.

## RESULTS

Initial tests were conducted using sodium cyanide solutions to measure the rate of HCN separation from acidified solution at a variety of pH values. Since the rate of HCN transfer across the membrane follows first order kinetics<sup>(3)</sup> the data were plotted in semilog form as shown in Figure 7. The data obtained indicated that as long as the pH was significantly less than the pK of the HCN, mass transfer across the membrane was independent of pH. From the slope of this curve the overall mass transfer coefficient of HCN was calculated to be  $8.33 \times 10^{-4}$  cm / sec which agrees well with the reported values of Kenfield et al.<sup>(3)</sup>

The following testes were conducted on the zinc and cadmium cyanide solutions. These tests were all conducted at the same temperature and flowrates as the free cyanide tests reported above. Zinc cyanide solutions were tested at pH values of 2.0, 5.0 and 8.0, while the cadmium cyanide was tested at pH 2.0 and 5.6. The concentration profiles obtained in these tests are depicted in Figures 8 and 9. It is clear from these figures that the cyanide separation slowed dramatically for both metal solutions when the pH was raised to values of 5.0 and above. In addition it was observed that during the test with zinc cyanide a large quantity of white precipitate formed. Analysis of the precipitate showed it to be  $Zn(CN)_2$  as expected.

### Discussion and Analysis

Comparison of the cyanide separation rates from sodium cyanide solution and the metal cyanide solutions at pH 2.0 reveals that the HCN mass transfer rate is unaffected by the presence of zinc and cadmium as illustrated in Figure 10. This is not surprising since examination of Figures 5 and 6 indicates that at pH 2.0 100% of the cyanide is present as HCN for both the zinc and cadmium solutions.

On the other hand it is apparent from Figures 5 and 6 that in the less acidic range of pH 5 - 8, metal cyanide speciation reduces the free HCN concentration dramatically. Since the removal rate is first order with respect to HCN concentration this may be expected to reduce the rate of cyanide recovery as observed in Figures 8 and 9. What is not clear from these data is whether the rate of HCN transfer is controlled by chemical equilibria or the kinetics of dissolution of  $Zn(CN)_2$  precipitate formed during acidification. The kinetics of zinc cyanide dissolution may control the formation rate of HCN and thus the rate of HCN removal. The data shown in Figure 8 at pH 5.0 for example indicate that the rate of HCN removal was approximately constant after 50 minutes of contact time and at pH 8.0 the rate of removal was essentially constant from the beginning of the test. This could only result if the concentration of HCN was approximately constant and controlled by a formation rate that was equal in value to the removal rate.

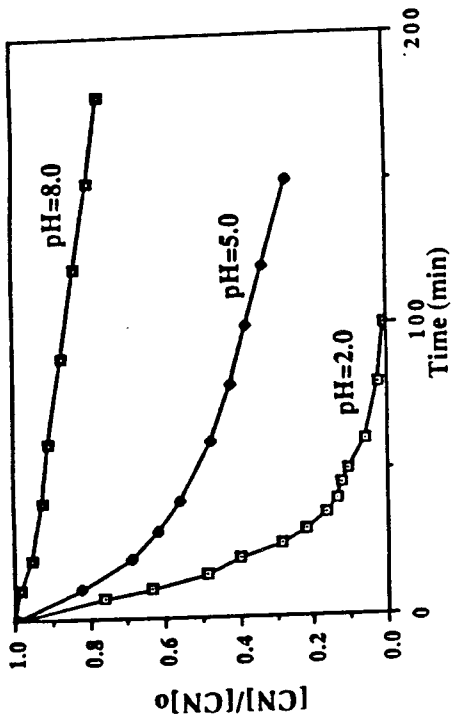


Figure 8 - The Observed Kinetics for Cyanide Removal from Zinc Cyanide Solution at pH 2.0, pH 5.0 and pH 8.0 ( $[Zn]_0=3000\text{mg/l}$ ,  $[CN]_0=5000\text{mg/l}$ )

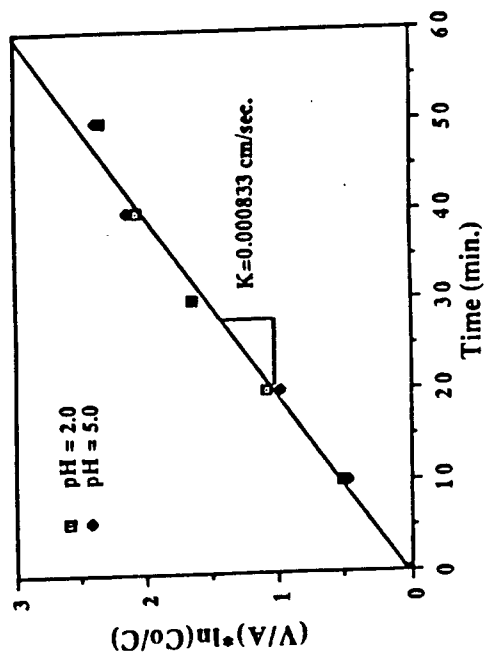


Figure 7 - The Observed Behavior for HCN Separation from Acidified NaCN as a Function of pH

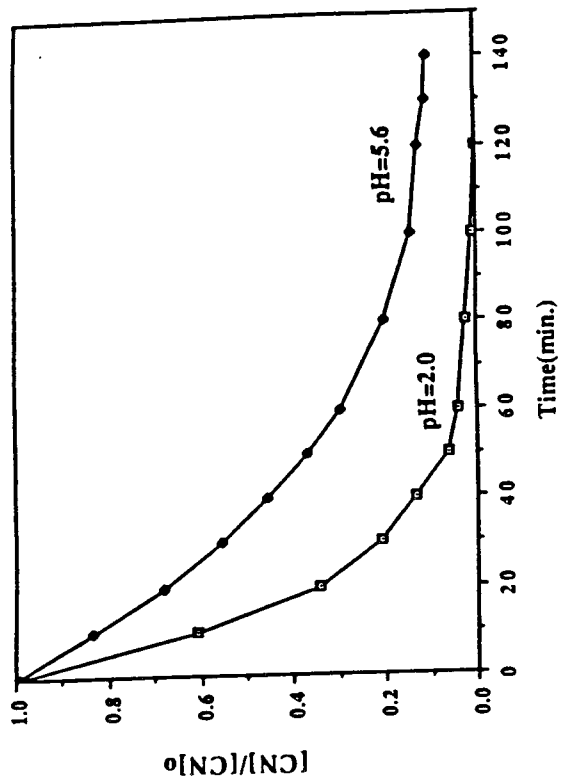


Figure 9 - The Observed Kinetics of Cyanide Removal from Cadmium Cyanide Solution at pH 2.0 and pH 5.6 ( $[Cd]_0=5157\text{mg/l}$ ,  $[CN]_0=5000\text{mg/l}$ )

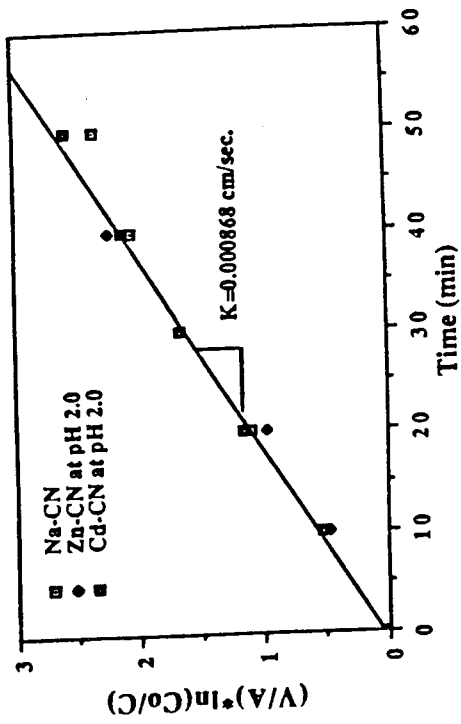


Figure 10 - A Comparison of the Rate of HCN Mass Transfer from Acidified Na-CN, Zn-CN (pH 2.0) and Cd-CN (pH 2.0), Showing that the Overall Mass Transfer Coefficient Was the Same in All Cases.

To determine whether the rate of HCN removal was controlled by chemical equilibria or dissolution kinetics in this case, a program was developed to interface the chemical equilibrium speciation routine with a mass transfer rate model for the membrane apparatus tested. The program computes the rate of cyanide recovery rate as a function of operating conditions and the predicted removal rate can be compared to the experimentally observed results. Good agreement between the predicted and observed behavior would indicate that cyanide recovery is simply controlled by chemical equilibria. If on the other hand the observed rate of recovery is slower than the predicted recovery rate, it would suggest that the rate is controlled by dissociation kinetics.

The interfaced computer model is depicted schematically in Figure 11. The metal cyanide speciation and free HCN concentrations were calculated by the MINEQL program once the feed wastewater composition and the amount of acid added were specified. The output from this program was then fed to the HCN removal model. The rate of HCN transfer across the membrane has been modeled in detail by Kenfield et al.<sup>(3)</sup>. The process may be expressed simply in the following kinetic form when a high acid recycle rate is employed such that  $K_L \cdot a \cdot L/v \ll 1$ :

$$-\frac{dC}{dt} = \frac{K_L A}{V} (C - C^*)$$

where  $K_L$  = overall mass transfer coefficient for HCN transfer.

$A$  = total internal surface area of the hollow membrane fibers.

$V$  = volume of acidified cyanide solution.

$C^*$  = equilibrium concentration of HCN at the membrane interface in contact with the NaOH (which is assumed to be zero in this case since the neutralization reaction is rapid and complete).

$a$  = specific surface area,  $\frac{A}{V}$

$v$  = velocity of acid inside the hollow fiber membranes.

Integrating and rearranging:

$$\frac{V}{A} \cdot \ln \frac{C_0}{C} = K_L \cdot t$$

The value of  $K_L$  ( $8.33 \times 10^{-4}$  cm / sec) was obtained from the free cyanide transfer rate data shown in Figure 7.

With the initial HCN concentration and  $K_L$  value as inputs, the model was employed to calculate the concentration change over an incremental time step. The product composition was then input back to MINEQL to calculate the change in cyanide speciation and the exercise was repeated. In this way the rate of cyanide removal was determined as a function of time and pH.

The agreement between the experimental and predicted rate curves for zinc and cadmium cyanide are presented in Figures 12 and 13 respectively. It is immediately apparent that for these metals the agreement is excellent. It is therefore concluded that the recovery of cyanide is controlled by chemical equilibria and not by the dissolution/dissociation rate of the precipitates or intermediates. Thus the formation of a precipitate during the acidic regeneration process should not be cause for alarm. The process is reversible and the kinetics of dissolution are rapid in relation to the cyanide separation process. Thus the provision of sufficient acid to ensure complete conversion of

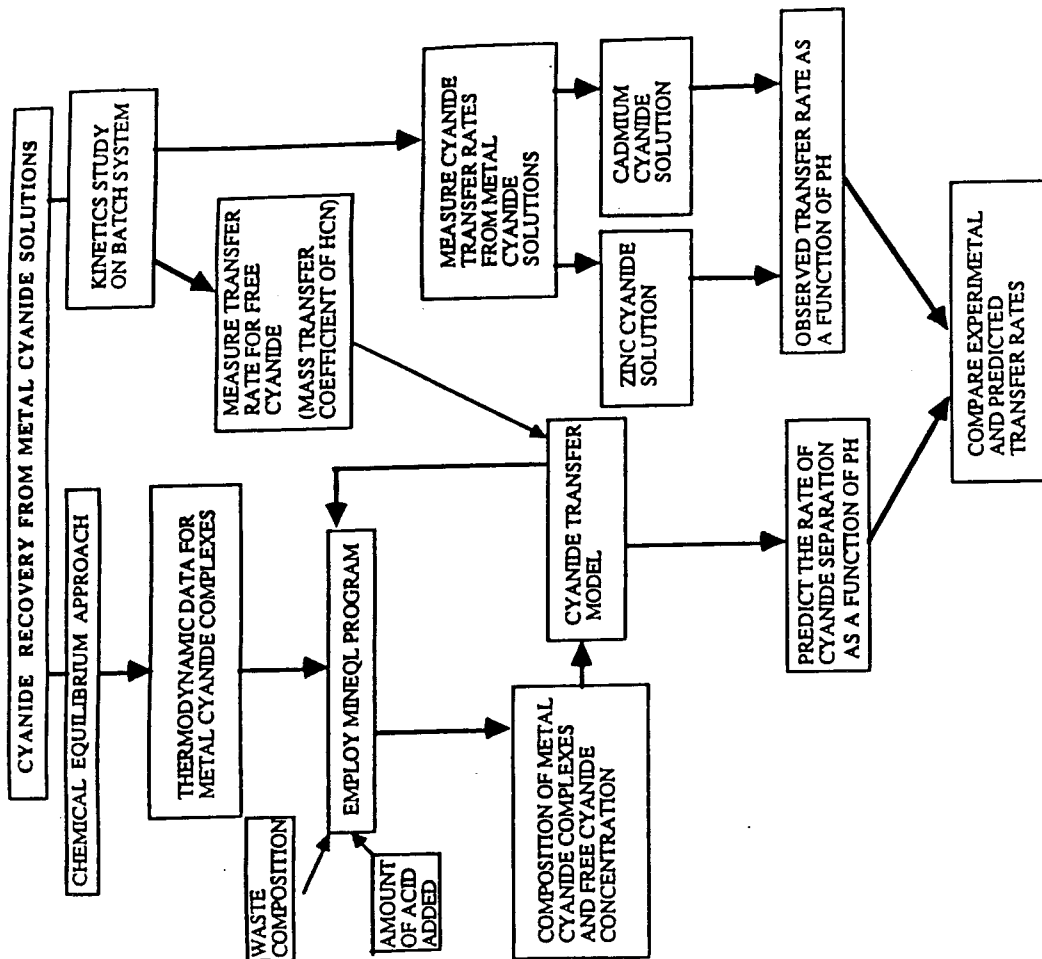


Figure 11 - A Schematic Representation of The Approach Employed in This Study

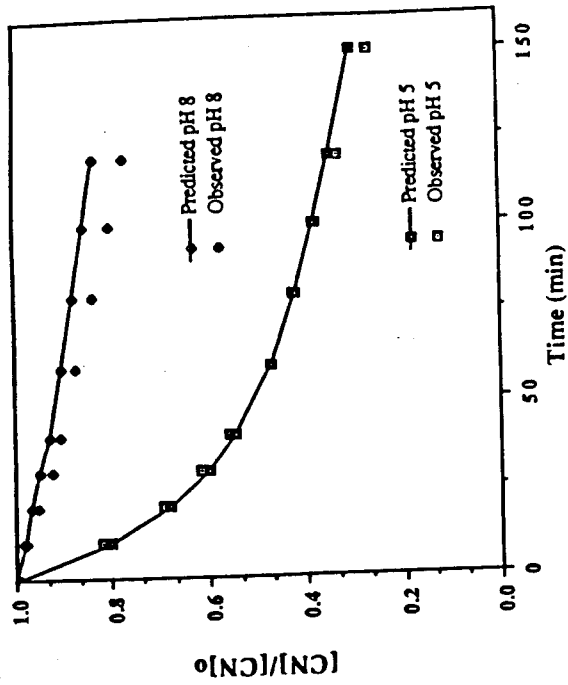


Figure 12 - A Comparison of Observed and Predicted Cyanide Removal from Zinc Cyanide Solution at pH 5.0 and pH 8.0

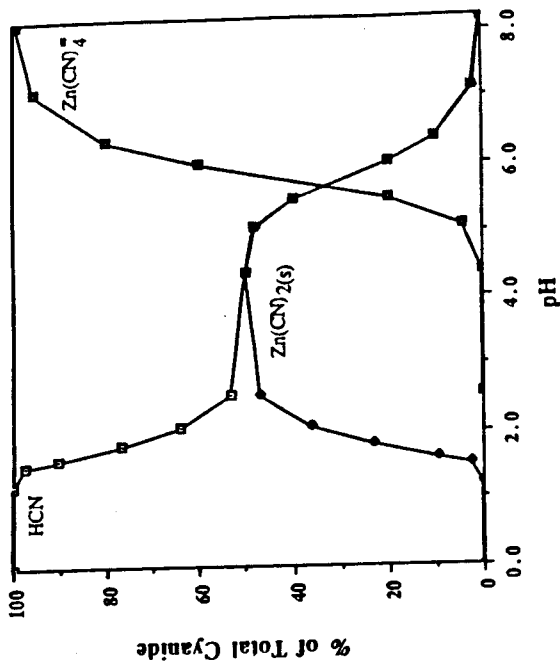


Figure 14 - Cyanide Speciation at High Concentrations Typical of Those Found During Ion Exchange Regeneration. ( $[Zn]_0=2.5M$ ,  $[CN]_0=10M$ )

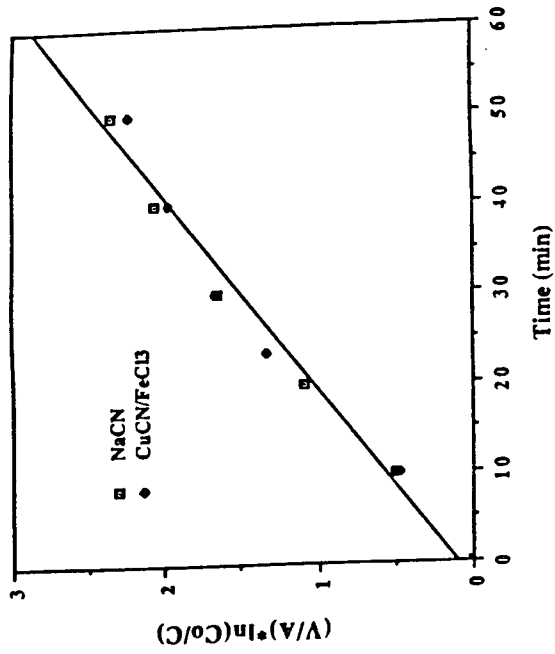


Figure 16 - A Comparison of the Rate of the Transfer Gas from  $CuCN/FeCl_3$  Solution and  $NaCN$  Solution

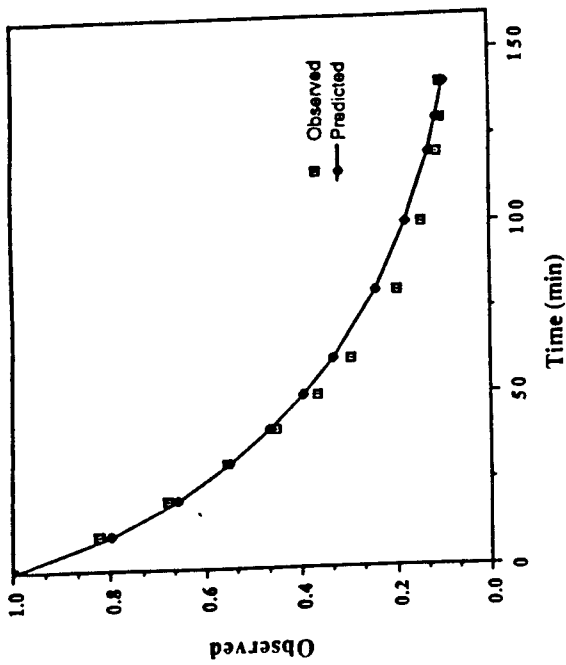


Figure 13 - A Comparison of Observed and Predicted CN Removal from Cadmium Cyanide Solution at  $pH=5.6$

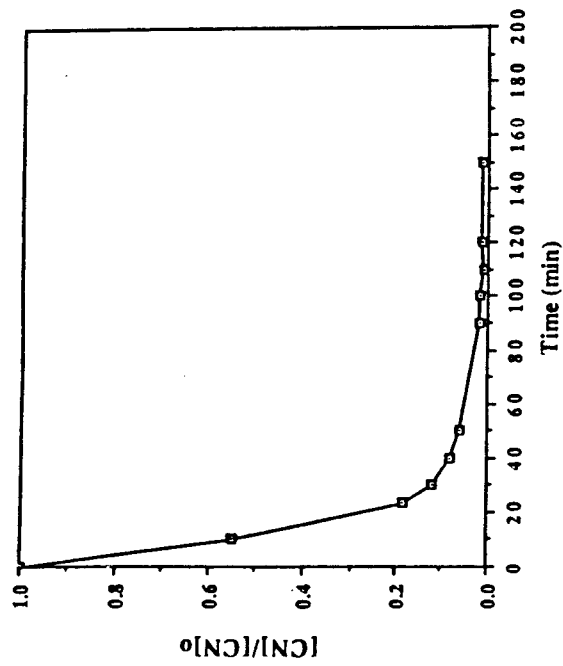


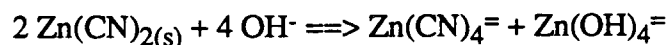
Figure 15 - Cyanide Removal from Cuprous Cyanide/Ferric Chloride Solution ( $[CN]_0=1,190$  mg/l,  $[FeCl_3]_0=10,330$  mg/l)

the cyanide species to HCN should result in complete regeneration if sufficient time is provided for cyanide separation.

#### Zinc Leakage from Ion Exchange Column

In an ion exchange column the resin phase can be considered as a concentrated electrolyte solution. During the regeneration of an anion exchanger that is saturated with  $\text{Zn}(\text{CN})_4^{=}$  the internal resin phase concentrations may exceed 2.5 M zinc and 10 M cyanide. These concentrations are an order of magnitude greater than the concentrations employed to calculate the cyanide species distribution in Figure 14. The use of MINEQL for such concentrated solutions becomes inaccurate since the estimation of activity coefficients is not possible at these ionic strengths. Nevertheless the output of the MINEQL program indicates that zinc cyanide species are stable at lower pH values as concentration increases as shown in Figure 14. Comparison of Figures 5 and 14 indicates that lower pH values must be maintained at higher zinc and cyanide concentrations for complete conversion of cyanide to HCN. Similarly it may be expected that the increasing ratio of zinc to cyanide that develops as cyanide is removed during regeneration will exacerbate this situation.

These results demonstrate that the complete regeneration of anion exchange resins require the provision and maintenance of a highly acidic environment, otherwise the residual zinc cyanide precipitates will be confined in resin matrix. And when the regenerated ion exchange resins were reused, the residual zinc cyanide precipitates confronted an alkaline zinc cyanide wastewater. Reaction between  $\text{Zn}(\text{CN})_{2(s)}$  and hydroxide ion converts  $\text{Zn}(\text{CN})_{2(s)}$  to anionic  $\text{Zn}(\text{CN})_4^{=}$  and gives off  $\text{Zn}(\text{OH})_4^{=}$ .



Selectivity of  $\text{Zn}(\text{CN})_4^{=}$  and  $\text{Zn}(\text{OH})_4^{=}$  to anion exchange resin can be determined either experimentally or by their hydration energies. Since no hydration energy of both species is available and our research at this moment has not proceeded to the ion exchange selectivity study, the discussion in this section only tries to propose a reason to explain the zinc leakage problem.

In anion exchange resin phase, due to the high density of charges, water molecules are somewhat oriented by the fixed cationic functional group of the resin matrix. In addition there is not sufficient room in the resin pores to allow as complete secondary solvation of the ion as in the dilute solution phase. As a result, the strongly hydrated ion prefers the external dilute solution phase and the weakly hydrated ion can lose less hydration energy on passing into the resin phase<sup>(16)</sup>. Both  $\text{Zn}(\text{CN})_4^{=}$  and  $\text{Zn}(\text{OH})_4^{=}$  have similar ion size, same charges and same central metal. It seems the way to judge their hydration abilities is from their complexed ligands. The stronger hydrogen bond of O--H-O than N--H-O makes  $\text{CN}^-$  ion less hydrated and  $\text{OH}^-$  ion. The higher selectivity of  $\text{CN}^-$  to quaternary ammonium functional group than  $\text{OH}^-$  has been demonstrated by Marcus<sup>(17)</sup>. The same idea can be extended to the complexed  $\text{Zn}(\text{OH})_4^{=}$  and  $\text{Zn}(\text{CN})_4^{=}$ . Stronger ion hydration of  $\text{Zn}(\text{OH})_4^{=}$  than  $\text{Zn}(\text{CN})_4^{=}$  holds the former preferentially in the external aqueous phase, giving the observed zinc leakage in the effluent with absent of cyanide.

## COPPER CYANIDE

Solution containing copper cyanide complexes, produced stable cuprous cyanide precipitates upon acidification. Indeed the precipitation of CuCN is the basis of quantitative analysis for copper in the early literature on cyanides in mineral extraction<sup>(15)</sup>. This species not only tends to foul ion exchange resins during the acid regeneration<sup>(7)</sup>, but it also retains a certain amount of cyanide in the acid stream and therefore decreases the efficiency of cyanide recovery. Several techniques have been documented to decompose cuprous cyanide precipitates using ozone<sup>(8)</sup>, hydrogen peroxide<sup>(9)</sup> or SO<sub>2</sub><sup>(10)</sup> as oxidizing agents. In these reactions cyanide was converted into the less toxic cyanate form. However such a process is not amenable to the gas membrane separation process, and a reaction was sought that would enable cyanide recovery to be achieved.

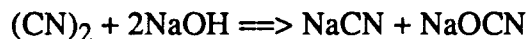
Early literature<sup>(11)</sup> on copper cyanide chemistry showed that stable cuprous cyanide solid could be oxidized by ferric chloride to form cyanogen viz:



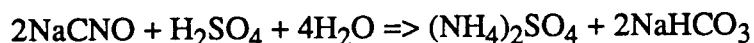
However thermodynamically this reaction is impossible, since  $\Delta G = + 233.3 \text{ KJ / mole}$ <sup>(12)</sup>. From the redox reaction point of view, ferric ion is more likely to oxidize the cuprous copper to the cupric form rather than the cyanide to cyanogen. Although Cu(II) can oxidize free cyanide(CN<sup>-</sup>) to cyanogen gas<sup>(13)(14)</sup>, under acidic condition there won't be free cyanide present and the reduction of cupric copper by free cyanide is thwarted.

The addition of 0.82 g of dry cuprous cyanide solid to 200 ml of 0.185 M ferric chloride solution with an initial pH of 1.34, caused the pH to increase to 1.70 and it was obvious that hydrogen ions participated in the reaction. Also, we didn't observe any CuCl precipitate at the end of the reaction. Although cuprous cyanide can be decomposed by ferric chloride, the reaction was very slow taking approximately 1 hour to complete. An increase in the amount of ferric chloride or the concentration of hydrogen ion significantly accelerated the reaction rate however. By circulating the FeCl<sub>3</sub> treated solution through the hollow fiber membrane module, over 99 percent of the cyanide was recovered in the base reservoir as shown in Figure 15. Plotting the data in semilog form(Figure 16), it can be seen that the mass transfer coefficient of the transfer gas is very close to that obtained with free HCN.

The pH dependence and mass transfer data supported our suspicion that hydrogen cyanide was formed in the reaction rather than cyanogen. To determine the species of the gas that transferred across the membrane we conducted an experiment to determine the cyanide species absorbed in the base reservoir. If the transfer gas was HCN, the base reservoir should contain only NaCN. On the other hand, if the transfer gas was cyanogen, the base reservoir should contain equimolar concentrations of NaCN and NaOCN as shown by the neutralization reaction:



The difference between these two cyanide-bearing base solutions can be easily distinguished by an acidification and cyanide recovery procedure. The solution containing only NaCN will be completely converted to HCN upon acidification. Acidifying the solution containing both NaCN and NaOCN however only converts NaCN to HCN; reaction between sodium cyanate and acid forms the ammonium salt of that acid and sodium bicarbonate<sup>(2)</sup>:

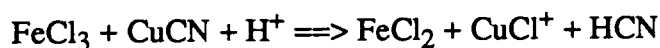


The recovered base/cyanide solution obtained from iron treated copper cyanide in the first test was acidified again and circulated inside the hollow fiber membranes while a fresh sodium hydroxide solution was circulated outside of the fibers to absorb the liberated HCN. The results are listed in Table 2.

<u>Table 2. Total Cyanide Concentrations</u>		
1.	2.	3.
In the original <u>CuCN/FeCl<sub>3</sub> solution</u>	In the Base reservoir <u>after complete recovery</u>	Obtained by acidifying <u>the previous base solution</u>
238.1 mg	238.1 mg	237.0 mg

As may be seen from Table 2, total cyanide recovery was accomplished on the second acidification test confirming that it was HCN that was formed in the original acidified CuCN/FeCl<sub>3</sub> solution.

Thus cuprous cyanide was decomposed by ferric ion under acidic conditions with the formation of HCN. On the basis of our experimental observations we propose the following reaction.



Thermodynamically, this reaction is possible with an the overall free energy change of -2.84 KJ / mole.

### CONCLUSIONS

1. Formation of zinc cyanide precipitate in the resin during regeneration was identified to be Zn(CN)<sub>2(s)</sub>.
2. Recovery of cyanide from acidified zinc and cadmium cyanide solution is fast and complete when the solution pH is sufficiently acidic to convert the cyanide to the HCN form.
3. Above pH 2.0 the rate of cyanide recovery was slowed by the low percentage of HCN present at equilibrium.
4. In concentrated zinc cyanide solutions such as may be encountered during regeneration, the pH required to convert all the complexed cyanide to HCN will decrease. To achieve good regeneration, a strong acid solution and sufficient contact time must be provided to ensure complete cyanide removal.
5. A kinetic model interfaced with chemical equilibrium model successfully predicted the rate of cyanide recovery as a function of operating pH.
6. Agreement between the predicted and the observed cyanide recovery rates indicated that the dissolution kinetics of Zn(CN)<sub>2(s)</sub> do not appear to limit the cyanide recover rate. Rather, the rate is controlled by the cyanide speciation equilibria.
7. Cyanide can not be completely recovered simply by acidification of concentrated copper cyanide solutions because of the formation of cuprous cyanide precipitate.
8. With addition of FeCl<sub>3</sub>, cuprous cyanide precipitate can be oxidized and cyanide can be completely recovered in the NaCN form.



9. Under acidic conditions it is not possible to oxidize cuprous cyanide to cyanogen gas with  $\text{FeCl}_3$  (as proposed by earlier investigators) The ferric ion appears to oxidize copper to cupric form with the release of HCN.

#### ACKNOWLEDGEMENT

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