HOLLOW FIBER MEMBRANE TECHNOLOGY FOR REMOVAL AND RECOVERY OF CYANIDE FROM PROCESS SOLUTIONS

by

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ABSTRACT

Removal of cyanide from process solutions and wastewater is important to maintain the quality of water resources. Cyanide, one of the most toxic of compounds, is widely used in gold leaching operations due to its ability to form water soluble complexes with gold, silver, copper and other metals. Several methods being used in the industry, such as alkaline oxidation, photochemical dissociation, sulfur dioxide catalyzed oxidation, and others, destroy cyanide present in the process solutions before their surface discharge, except the Acidification-Volatilization-Reneutralization (AVR) technique, which recovers cyanide by acidification of cyanide-containing solutions, causing generation of hydrogen cyanide gas, which is reneutralized in sodium hydroxide solution. A similar technique for removal and recovery of cyanide using hollow fiber membrane modules has been investigated to study the effect of operating parameters upon its performance in cyanide removal.

Hollow fiber membrane modules consisting of hydrophobic polypropylene hollow fibers were tested for their performance in cyanide removal under varying conditions of pH, the flow rates of the acidified feed and the alkaline acceptor solutions, and the temperature of operation and cyanide concentration in the feed solution to determine the optimum conditions of operation. The technology has been tested using a larger module under the optimum conditions derived, with the higher flow rates of the feed and the acceptor solution. The performance of the membrane modules for cyanide removal with synthetic and actual process solutions, namely the Reverse Osmosis permeate and the Barren solutions, supplied by Newmont Mining Corporation, are compared and the overall and individual mass transfer coefficients are determined and found to be in reasonable agreement with the values reported in literature. The removal of cyanide over 90 % from the feed solution could be achieved when the pH value for the feed solution was 3 with both the synthetic and the actual solutions. Design considerations, including selection of the feed and the acceptor solutions, their flow rates, total membrane surface area required and geometry of modules for the application of hollow fiber membrane technology for removal and recovery of cyanide at industrial scale are discussed. Also, calculations for the requirement of the number of membrane modules for treatment of a typical process solution in a gold cyanidation plant are performed.

It appears that the hollow fiber membrane technology has a good potential for its application in various industries, including mining and mineral processing, food and beverages, and wastewater treatment. Further investigation is required to improve the efficiency of cyanide removal by increasing the mass transfer coefficients of the membranes, which could be achieved by using the efficient designs of modules and the smarter membrane materials with optimum pore size and porosity. Good operating procedures and cleaning practices would enhance the life of these membranes, and this has to be investigated in future for successful application of hollow fiber membrane technology in gold cyanidation plants.

To my family and God

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CHAPTER 1

INTRODUCTION

Water is an important resource to sustain life on the planet Earth. The mining and metals industries extensively use water for process solutions, water being the universal solvent for the processing of all mineral commodities. Cyanide salts, one of the most toxic of compounds, are widely used in gold leaching operations. Cyanide has a great ability to form complexes with gold, silver, copper and other metals, most of which are water soluble. Therefore, cyanide is present in leach pads, processing plants, electrowinning plants and water treatment plants for surface discharge. Fig. 1 shows the use of cyanide in the mining industry in different parts of the world and Fig. 2 provides a comparison of the uses of cyanide in mining and other industries. From Fig. 2, only 13 % of cyanide out of 1.4 million tons hydrogen cyanide produced is used by the mining industry in the form of sodium cyanide, whereas the rest is used in the production of adhesives, paints, nylon, fire retardants, cosmetic, dyes, and computer electronics. Fig. 3 shows the distribution of major mining-related environmental incidents by location, mine type, cause and involving cyanide since 1975 [1]. From Fig. 3, it can be seen that incidents involving cyanide contribute to 27 % of the total of 33 major mining-related environmental incidents.

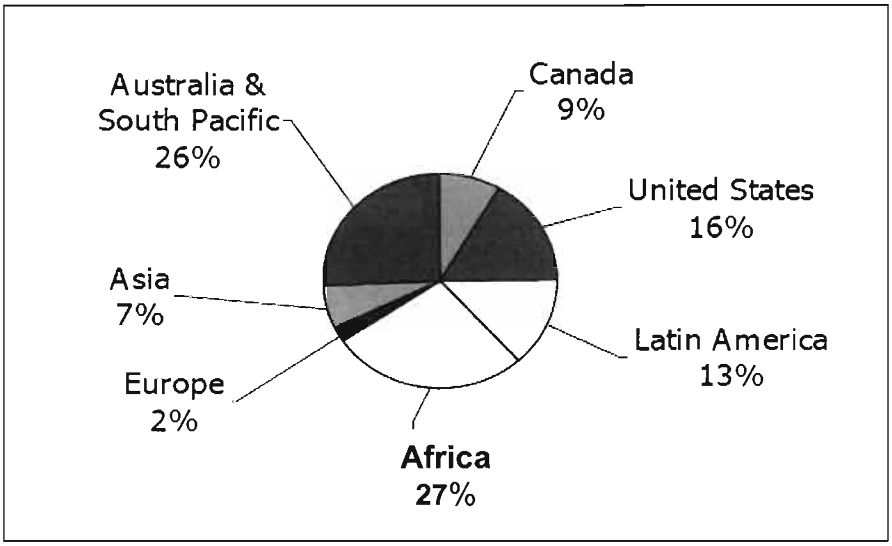

Fig. 1. Distribution of World Mines and Plant Operations That Use Cyanide [1]

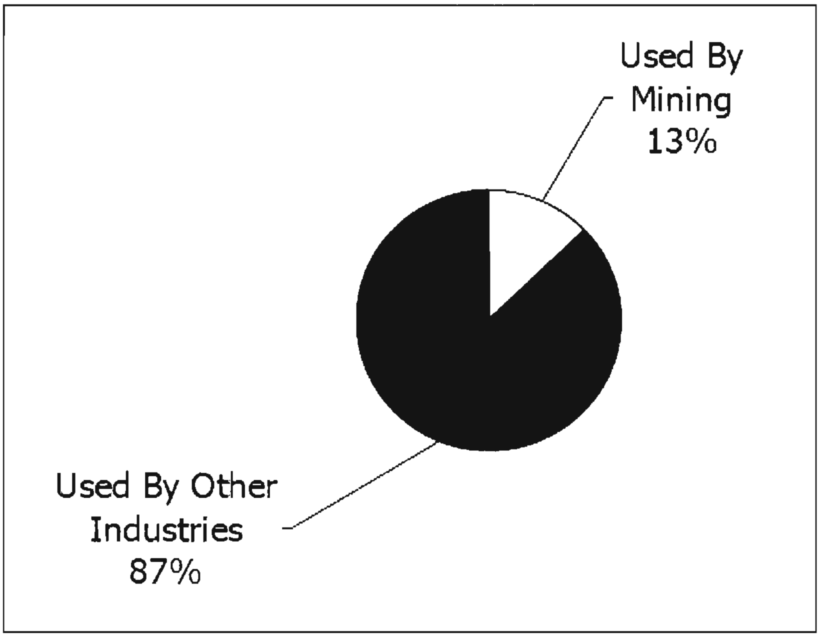

Fig. 2. Industrial Uses of Hydrogen Cyanide [1]

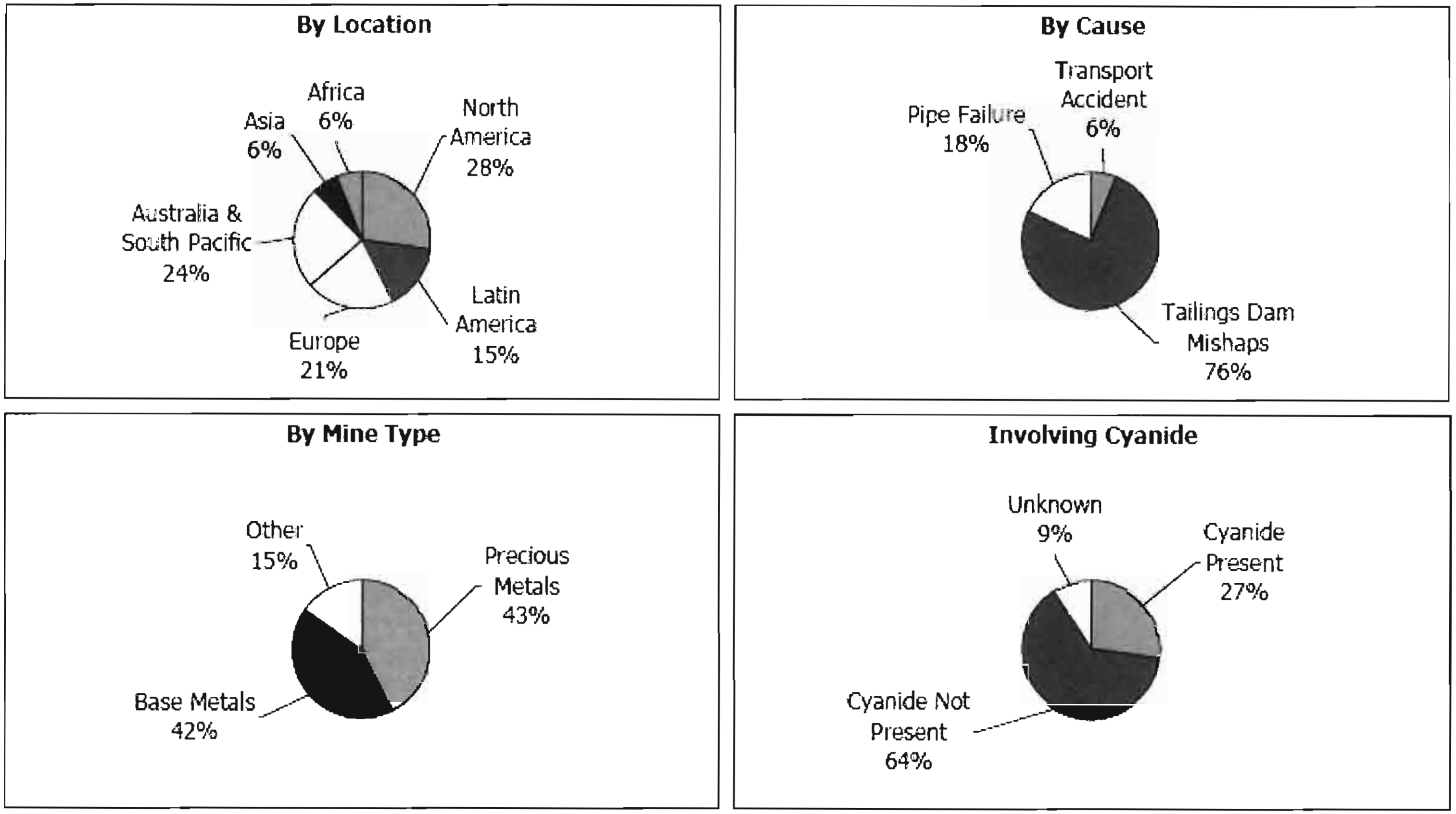

Fig. 3. Distribution of Major Mining-Related Environmental Incidents since 1975 [1]

Cyanide is acutely toxic even in small quantities. Exposure to cyanide can be by inhalation, ingestion, and/or absorption through the skin or eyes. Once into the body, cyanide is rapidly distributed to tissues and organs. It combines with iron present in the cytochrome, a component of the cytochrome oxidase complex in mitochondria, and inhibits this enzyme, preventing the use of intracellular oxygen [2]. This disturbs the balance of production and hydrolysis of adenosine triphosphate (ATP). As a consequence, metabolic acidosis develops because the cells are forced to perform anaerobic metabolism and accumulate hydrogen ions and lactate. The result could be a serious respiratory problem leading to death. Cyanide can have a serious effect on wildlife, aquatic organisms, birds and mammals as it is toxic to many organisms even at very low concentrations. If cyanide present in process solutions and tailings from industries is liberated untreated into the environment, it will contaminate surface and ground water and soil. This will pose a serious threat to the life of living organisms and animals. Therefore, process solutions and tailings must be treated to remove cyanide before their surface discharge and disposal to protect life. Table 1 displays the recent cyanide spills and their impacts in different parts of the world.

As per the current drinking water standards, cyanide ion concentration in surface discharge water should not exceed 0.2 parts per million (ppm) of free cyanide. Hence, water treatment plants destroy and /or separate the excess cyanide in process solutions by alkaline chlorination, reverse osmosis, ion exchange, biological processes, and oxidation by oxidizing agents such as hydrogen peroxide, chlorine dioxide, Caro's acid, ozone and sulfur dioxide. All these processes involve further addition of reagents, chemicals and organisms in water, thus degrading the water quality. Consequently, other processes

Table 1. Recent Cyanide Spills and Their Impacts [3]

Year	Name	Place	Incident	Impact
August, 1995	Omai Gold Mine	Guyana	3.2 billion cyanide laden tailings released into Essequibo river.	All aquatic life in the 4 km range long creek that runs from the mine to the Essequibo river, was killed.
Januray, 2000	Baia Mare Gold Mine	Romania	130,000 cubic yards of cyanide tainted water discharged from a reservoir into river systems in Romania, Hungary and Yugoslavia.	Thousands of tons of fish died in the Tisza and Danube rivers from a cyanide spill.
June, 2000	Lihir Mine	Papua New Guinea	Cyanide spilt into ocean.	-
October, 2001	Tarkwa Gold Mine	Ghana	Spillage of thousands of cubic meters of mine wastewater contaminated with cyanide and heavy metals when a tailings dam ruptured at a mine operation.	All life forms in the river Asuman and its tributaries were decimated, and people's livelihoods were endangered.
November, 2001	Luohe Mine	China	Eleven tons of liquid sodium cyanide leaked into a tributary of the Luohe river over the weekend after a traffic accident.	Livestock animals were poisoned and atleast one person sickened by contamination.
May, 2002	Twin Creeks Mine	Nevada, USA	Twenty-four thousand gallons of cyanide solution was spilled at a mining facility.	-
June, 2002	Denton-Rawhide Mine	Nevada, USA	Approximately 40,000 gallons of dilute cyanide process solution spilled into the environment when the leaching process solution overflowed containment structures from a ruptured pipe caused by a failure of a weld on a 16-inch diameter pipeline carrying process solution from a lined storage pond to a lined heap leach pad.	-
December, 2003	Briggs Mine	Balleratt, USA	A cyanide spill.	-

Table 1. continued

Year	Name	Place	Incident	Impact
January, 2003	HEMCONIC Mine	Bonanza, North Atlantic Autonomous Region	A cyanide solution spill took place dumping cyanide into Bambana river.	Health workers from local indigenous communities reported the death of twelve children who were suspected of having poisoned by drinking water from the Bambana river.
January, 2003	San Andres Mine	Western Honduras	A massive cyanide spill contaminated the Lara river, which feed into the river providing drinking water for the town of Santa Rosa de Copan.	The chemicals killed off fish in the Lara river, which flows into the Higuito, the main supply of potable water for the Santa Rosa de Copan region, one of the cradles of the ancient Maya civilization.
May, 2003	Tarkwa Gold Mine	Ghana	A cyanide spillage occurred when the dangerous chemical spilled from one of the three newly constructed pipelines.	-
January, 2004	Karlgoorlie Gold Mine	Australia	Cyanide-leak into the surrounding groundwater.	-
March, 2004	Siret River	Romania	10 tons of toxic substances leaked into the river from a deactivates chemical processing plant	-
March, 2004	Lower Hutt Transit Depot	New Zealand	Two 180-liter drums of cyanide solution were damaged inside the main freight depot, possibly by a forklift.	Thirty-five people were evacuated.
August, 2004	Misima Mine	Papua New Guinea	Cyanide was discharged during decommissioning of the mine site.	The discharge resulted in poisoning of marine life, with reports of dead fish found floating in the oceans confirmed by the company as linked to the discharge.

Table 1. continued

Year	Name	Place	Incident	Impact
October, 2004	Bogoso Gold Limited	Ghana	A cyanide spill occurred from a new tailings dam into the river Aprepre, which serves as drinking water for surrounding communities, as well as other rivers including Egya Nsiah, Benya and Manse.	Hundreds of dead fishes, crabs, shrimps, and other life forms found floating on the river.
January, 2005	Wexford Ghana Limited at Akyempim	Ghana	Spilled cyanide into the river Kuberko.	-
June, 2005	Phu Bia Gold Mine	Laos	A cyanide spill.	The cyanide killed fish in the nearby rivers and poisoned villagers within atleast 3 km of the mine site. Atleast 60 villagers fell ill as a result of poisoning after eating contaminated fish and drinking contaminated water.
October, 2005	Rapu Rapu Polymetallic Project	Philippines	Spills of process treatment water allegedly causing cyanide contamination of nearby waters.	Caused a small fish-kill.
November, 2005	Bursa Mining	Romania	A cyanide spill.	Contaminated the Hungarian section of the Tisza river.
January, 2006	Draslovka Chemical Company	Czech Republic	Spilled 2 cubic meters (71 cubic feet) of toxic cyanide into the Labe river.	Local fishermen began reporting thousands of dead fish in the river.
June, 2006	Bogoso Gold Limited	Ghana	A cyanide spillage at tailings dam polluted Ajoo stream. A joint on the main tailings returning pipe was disengaged and cyanide laden tailings poured into the external environment.	Killed fish and lobsters. 30 community members who drank water or ate fish and lobsters suffered from dizziness, headaches, stomach aches, loss of appetite, itching tongue and skin itches.
December, 2006	Fort Knox Mine	Alaska	Cyanide found seeping from a hillside next to the dam that holds back waste.	-

might be required to remove these added reagents. Moreover, cyanide once destroyed cannot be reused, and further addition of cyande in the leaching pads and process solutions is required to maintain the process efficiency. Both the destruction and additon of cyanide involve costs associated with them that might affect the overall production cost of the metal produced. For example, Newmont mining operation at Mineral Yanacocha in Peru uses Reverse Osmosis (RO) membrane technology to separate dissolved contaminants from process solutions. The remaining cyanide present in the treated water is destroyed by alkaline chlorination before discharge. The cost for reverse osmosis treatment of the solution is $ 0.38 per cubic meter, whereas the cost for reverse osmosis treatment and alkaline chlorination is $ 0.45 per cubic meter of solution. Therefore, the cost for destruction of cyanide present in the product obtained from the reverse osmosis plant, called the Reverse Osmosis Permeate solution, is $ 0.07 per cubic meter of solution. The cost for treatment of the solution with a conventional plant at the same mine, primarily using chlorination for cyanide destruction and sodium hydrosulfide for mercury precipitation, is $ 0.81 per cubic meter, which makes a substantial difference when huge volumes of solutions are generated. The Reverse Osmosis plant installed at the mine has been in operation since January 2004, without the replacement of membranes, therefore providing a membrane life of over 4 years. Table 2 provides a list of mines and metallurgical plants using various cyanide treatment and recovery techniques with the cyanide concentration in the influents and the effluents of the treatment plants.

Under these circumstances, a technology which would enable removal and recovery of cyanide from such solutions would be quite useful. Membrane technology could be used

Table 2. Different Cyanide Removal and Recovery Technologies Applied at Various Mines and Plant Operations [4]

Industry	Place	Scale	Application	Constituents, mg/l *			Technology	Sources
					CN_t	CN_w		
Baker Mine	British Columbia, Canada	Full	Tailings	Influent	2000	1900	Alkaline Chlorination	Scott and Ingles, 1987
				Effluent	8.3	0.7		
				% Removal	99.6	99.9		
Carolin Mine	British Columbia, Canada	Full	Tailings	Influent	1000	710	Alkaline Chlorination	Scott and Ingles, 1987
				Effluent	170	0.95		
				% Removal	83	99.9		
Mosquito Creek Mine	British Columbia, Canada	Full	Tailings	Influent	310	226	Alkaline Chlorination	Scott and Ingles, 1987
				Effluent	25	0.49		
				% Removal	91.9	98.8		
Giant Yellowknife Mine	Northwest Territories, Canada	Full	Tailings	Influent	7.5	7.1	Alkaline Chlorination	Scott and Ingles, 1987
				Effluent	0.15	0.09		
				% Removal	98	98.7		
Homestake Mine	South Dakota, USA	Full	Solutions	Influent	6.5	-	Biological Treatment	Scott and Ingles, 1987
				Effluent	0.35	-		
				% Removal	94.6	-		
OK Tedi Mine	New Zealand	Full	Tailings	Influent	110-300	90-200	Hydrogen Peroxide	Scott and Ingles, 1987
				Effluent	1-10	< 0.5		
				% Removal	-	-		
Beaconsfield Gold Mine	Tasmania	Full	Tailings	Influent	200	-	Acidification Volatilization Reneutralization	Mudder and Goldstone, 1989
				Effluent	2-4	-		
				% Removal	-	-		
Kerr Addison Mine	Ontario, Canada	Bench	Solutions	Influent	60	-	Acidification Volatilization Reneutralization	McNamara, 1978
				Effluent	< 0.1	-		
				% Removal	> 99.98	-		
Dome Mine	Ontario, Canada	Bench	Solutions	Influent	23	-	Acidification Volatilization Reneutralization	McNamara, 1978
				Effluent	< 0.1	-		
				% Removal	> 99.96	-		
Giant Yellowknife Mine	Northwest Territories, Canada	Bench	Solutions	Influent	260	-	Acidification Volatilization Reneutralization	McNamara, 1978
				Effluent	< 0.1	-		
				% Removal	> 99.996	-		
Hollinger Ross Mine	Ontario, Canada	Bench	Solutions	Influent	610	-	Acidification Volatilization Reneutralization	McNamara, 1978
				Effluent	4.16	-		
				% Removal	>99.3	-		
Pamour Mine	Ontario, Canada	Bench	Solutions	Influent	990	-	Acidification Volatilization Reneutralization	McNamara, 1978
				Effluent	< 0.1-3	-		
				% Removal	> 99.7	-		

Table 2. continued

Industry	Place	Scale	Application	Constituents, mg/l *			Technology	Sources
					CN_t	CN_w		
Dome Mines	Porcupine, Ontario, Canada	Full	Tailings	Influent	100	98.6	Natural Attenuation	Simovic 1985
				Effluent	0.04	0.02		
				% Removal	100	99.98		
Lupin Mines	Contwoyto, NWT, Canada	Full	Tailings	Influent	223	186	Natural Attenuation	Reid, 1985
				Effluent	0.2	0.02		
				% Removal	99.91	99.99		
Cullaton Lake Gold Mines	Keewatin Dist, Canada	Full	Tailings	Influent	800	140	Natural Attenuation	Robinson, 1984
				Effluent	-	< 0.1		
				% Removal	-	> 99.93		
Con Mine	Great Slave Lake	Full	Solutions	Influent	750	-	Precipitation using Iron salts	Scott and Ingles, 1987
				Effluent	0.75	0.35		
				% Removal	99.90	-		
Collosseum Mine	California, USA	Full	Tailings	Influent	364	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	0.4	-		
				% Removal	99.89	-		
Ketza River Mine	Yukon Territory, Canada	Full	Tailings	Influent	150	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	5	-		
				% Removal	96.67	-		
Equity Mine	British Columbia, Canada	Full	Tailings	Influent	175	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	2.3	-		
				% Removal	98.69	-		
Casa Berardi Mine	Quebec, Canada	Full	Tailings	Influent	150	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	1	-		
				% Removal	99.33	-		
Westmin Premier Mine	British Columbia, Canada	Full	Tailings	Influent	150	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	< 0.2	-		
				% Removal	> 99.87	-		
Golden Bear Mine	British Columbia, Canada	Full	Tailings	Influent	205	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	0.3	-		
				% Removal	99.85	-		
McBean Mine	Ontario, Canada	Full	Solutions	Influent	370	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	0.2	-		
				% Removal	99.95	-		
Lynngold Mine	British Columbia, Canada	Full	Solutions	Influent	106	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	0.6	-		
				% Removal	99.43	-		

Table 2. continued

Industry	Place	Scale	Application	Constituents, mg/l *			Technology	Sources
					CNt	CNw		
Mineral Hill Mine	British Columbia, Canada	Full	Solutions	Influent	350	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991
				Effluent	0.5	-		
				% Removal	99.86	-		
Lac Shortt Mine	Quebec, Canada	Full	Solutions	Influent	10	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991)
				Effluent	0.5	-		
				% Removal	95.00	-		
Citadel Mine	Canada	Full	Solutions	Influent	350	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991)
				Effluent	5	-		
				% Removal	98.57	-		
St. Andrew Mine	Ontario, Canada	Full	Solutions	Influent	15	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991)
				Effluent	1	-		
				% Removal	93.33	-		
Sunshine Snow Cap Mine	California, USA	Full	Solutions	Influent	180	-	Sulfur dioxide oxidation	Devuyst et al. 1991)
				Effluent	4	-		
				% Removal	97.78	-		
Kuntz Electroplating	Ontario, Canada	Full	Electroplating wastes	Influent	150	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991)
				Effluent	0.2	-		
				% Removal	99.87	-		
Precious Plate	New York, USA	Full	Electroplating wastes	Influent	30300	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991)
				Effluent	60	-		
				% Removal	99.80	-		
Superfinish	Ontario, Canada	Full	Electroplating wastes	Influent	640	-	Sulfur dioxide oxidation	Devuyst et al. 1989b and 1991)
				Effluent	1.3	-		
				% Removal	99.80	-		

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* CN_t = Total Cyanide and CN_w = WAD Cyanide

for this objective, and could not only eliminate further addition of reagents, but also make the process more economical by recovery of cyanide when conducted at a large scale. Different types of membranes that could be used to remove and recover cyanide are spiral wound membranes, hollow fiber membranes, tubular membranes, flat sheet membranes and ceramic membranes. All these membranes have their own advantages and disadvantages. Hollow fiber membranes contactors have received more attention than others in this application due to added advantages such as higher efficiency, modular design, straightforward scale up, low solvent hold up and constant surface area available for mass transfer independent of flow rates.

1.1 Review of the Literature

Hollow fiber membranes have been used in a variety of applications in the industry such as degasification of process solutions, separation of carbon dioxide and other gases from flue gas streams and waste water treatment. Many researchers have studied the application of hollow fiber membrane technology in various operations such as liquid-liquid extraction, gas separation by absorption and stripping, ozonation of water and removal of volatile components from water. Gabelman and Hwang [5] and Stanojevic et al. [6] reviewed various applications and design considerations for the hollow fiber membranes. Sirkar [7, 8, 9] reviewed the application of hollow fiber membranes for membrane distillation, in which transfer of solvent occurs across a nonwetted membrane, due to temperature difference on two sides of the membrane, and membrane pertraction, in which more than one component of a liquid feed solution diffuse through the nonporous membrane into a stripping liquid. Reed et al. [10], Basu and Sirkar [11] and

Keurentjes et al. [12] used the membranes to study the extraction of chlorinated and aromatic compounds from wastewaters, citric acid from water and fatty acids from soyabean oil, respectively, whereas Matsumura [13] used the membranes to study the extraction of alcohols such as ethanol, isopropanol and n-butanol. Similarly, Lopez and Matson [14], Ding et al. [15], Frank and Sirkar [16,17] and Coelhoso et al. [18] used the hollow fibers for enzymatic transformation, selective extraction of d-leucine from a racemic mixture in water, fermentation of glucose to ethanol, and extraction of lactate from aqueous solution, respectively. Also, Dahuron and Cussler [19] and Dekker et al. [20] studied the extraction of protein using membrane contactors. Semmens et al. [21, 22, 23] studied the air stripping of volatile organic compounds from wastewater and bubbleless aeration of water using membrane contactors. McGrath and Ergas [24] and Aziz et al. [25] demonstrated the removal of toluene and biodegradation of trichloroethylene using polypropylene hollow fiber membrane contactors.

In addition, Carroll et al. [26], Yang et al.[27], Yun et al. [28] and Yoshizuka et al. [29] studied the extraction of metal ions such as chromium, copper, palladium, mercury, zinc and cadmium from aqueous solutions. Sastre et al. [30] studied the extraction and stripping of gold using hydrophobic polypropylene hollow fiber membranes. Wikol et al. [31] and Cornelissen et al. [32] investigated the ozonation of tap and deionized water, respectively. Kunz et al. [33] and Hogan et al. [34] reviewed the process of osmotic distillation using hollow fiber membranes. Tan et al. [35] and Cabral et al. [36] investigated the removal of ammonia from aqueous solutions, whereas Kartohardjono et al. [37] and Ito et al. [38] demonstrated the removal of dissolved oxygen from water using these membranes. Peng et al. [39] studied the pilot scale degassing of water using polypropylene hollow fiber membrane contactors.

Other researchers studied various design aspects of the hollow fiber membrane contactors. Prasad and Sirkar [40] provided an equation for the membrane mass transfer coefficient. They suggested the use of the Wilson plot method to determine the membrane resistance and to gain insight into the effect of fluid velocities on individual mass transfer coefficients. Cooney and Poufos [41] and Cussler [42] presented their own equations for mass transfer coefficients with their own sets of arguments. Prasad and Sirkar [40], Yang and Cussler [27], Wickramasinghe et al. [43], Dahuron and Cussler [19], Lemanski and Lipscomb [44], Seibert et al. [45], Costello et al. [46] and Rogers and Long [47] proposed their equations for mass transfer coefficients in the shell side and tube side flow, in terms of Sherwood number, Reynolds number, Schmidt number and membrane geometry. Wickramasinghe et al. [48] and Wang and Cussler [49] used woven fabrics of hollow fiber to strip oxygen and toluene, whereas Bhaumik et al. [50] used woven fabrics of hollow fiber to strip carbon dioxide. Wickramasinghe et al. [48] and Wang and Cussler [49] provided the equations for the mass transfer coefficients for different modules built with individual fibers, woven fabric of hydrophobic fibers, and the rectangular modules.

Basu and Sirkar [7, 8, 9, 51], Hoq et al. [52], Lopez and Matson [14], and Yang and Cussler [27] discussed the mass transfer coefficients in liquid-liquid system with chemical reactions. Similarly, mass transfer coefficients in gas-liquid systems were discussed by Qi and Cussler [53, 54], Karoor and Sirkar [55], Semmens et al. [56], and Kreulen et al. [57]. Cussler [42] demonstrated that the mass transfer correlation depended on whether the reaction is fast or instantaneous. Yang and Cussler [27] derived the mass transfer correlation for the flow of nonreactive strip, outside and parallel to the hollow fibers. Astarita et al. [58] found that the rate of mass transfer significantly accelerated in the presence of chemical reaction in the strip side.

Prasad and Sirkar [59], and Reed et al. [60] suggested the design procedure and examples for practical applications. Wickramasinghe et al. [61] compared the cost per unit mass transfer with different fiber diameter in gas stripping operation. Wang and Cussler [49] looked at the effect of the number of baffles in the module on the mass transfer performance and the effect of co-current, countercurrent and cross flow configurations on efficiency of membrane.

Semmens et al. [62, 63], Shen et al. [64] and Wickramasinghe et al. [65] conducted research on removal of cyanide from artificial wastewater at laboratory scale. Semmens et al. [63] and Shen et al. [64] demonstrated that in the presence of excess sodium hydroxide, the strip side mass transfer coefficient was much larger than the feed side mass transfer coefficient. Wickramasinghe et al. [65] investigated the removal of cyanide at pilot scale and determined the mass transfer coefficients for solutions containing other volatile components in addition to cyanide.

1.2 Summary

Cyanide is used extensively in many industries such as metallurgical processing, electroplating and chemical synthesis. In the mining and electroplating industries, cyanide is employed to complex dissolve interested metals, gold, silver and copper in aqueous solutions. Due to the extreme toxicity of cyanide, it becomes important to consider technologies for removal from wastewater and its recycle to develop green process technologies. With water quality standards for surface discharge getting stricter as the time passes, studies for removal of contaminants from water must be carried out aiming at the drinking water standards. In order to meet the drinking water standards set by United States Environmental Protection Agency (USEPA), cyanide concentration in wastewaters must be reduced to less than 0.2 mg/L of free cyanide.

Various cyanide removal methods have been developed by researchers throughout the world. A few of the most common cyanide removal methods are described in Table 3. For a method to be successfully implemented for industrial use, it must be simple in operation and maintenance, with low energy and chemical requirements, and must yield economical benefits to the user. Most of the methods presented in the table use further chemical addition to destroy cyanide, further requiring methods to remove unused reagents and products. At present, alkaline chlorination, sulfur dioxide/air copper catalyzed and photochemical dissociation are being widely used in the industry. Each has its own advantages and disadvantages. Common disadvantages for these are their inability to recover cyanide and the low efficiency for cyanide removal. These problems could be overcome by the use of hollow fiber membrane technology.

1.3 Research Objectives

The objective of the study is to evaluate the use of hollow fiber membrane technology for removal of cyanide from process solutions and to investigate and identify the different factors that affect the removal process to determine the optimum operating conditions. The research includes the comparison of performance of the membrane modules with

Table 3. Cyanide Removal Methods [65]

Method	Process Description	Advantages	Disadvantages	Remarks
Acidification--Volatilization--Reneutralization (AVR)	The pH of a cyanide solution is lowered by addition of acid to generate HCN gas. The HCN gas is then stripped using air and absorbed into a NaOH solution.	Cyanide can be recovered.	More complex and hazardous than other processes. Sealed mixing vessels and packed columns are required.	The economics may vary depending on the value of the recovered cyanide.
Activated carbon adsorption	Cyanide is removed by activated carbon adsorption.	-	Regeneration of activated carbon is difficult.	-
Alkaline chlorination	Cyanide is oxidized to cyanate using chlorine or hypochlorite.	Rapid for clear solutions.	Less effective for iron cyanide and slurries. Remaining chloramines and free chlorine lead to secondary contamination.	Most commonly used.
Gas-filled membranes	HCN transfer through a gas-filled hydrophobic microporous membranes to striping solution containing NaOH.	Cyanide can be recovered. No secondary pollutants produced. Energy and chemical requirements are low. Simple operation.	Complexed cyanide is hard to remove.	-
Hydrogen peroxide oxidation	Cyanide is oxidized to cyanate using hydrogen peroxide in the presence of copper ion.	Low residual chemicals and effective in ponds.	Hydrogen peroxide is hazardous and expensive. Requires specialized equipment increasing the total capital cost. The treatment process generates ammonia, which is toxic to fish.	-
Ion exchange	Cyanide is removed by anion exchange resin.	-	Regeneration of resin is difficult since there are cyanide complexes besides free cyanides.	-
Microbiological degradation	Microbial transformation of cyanide to ammonia or nitrate.	Avoids using toxic or hazardous chemicals.	May not be possible to treat wastewaters containing high concentrations of cyanide. Process may be adversely affected by cold temperatures. Capital costs may be higher than for the oxidation processes.	System response to a sudden change in cyanide or nutrient concentration may be sluggish.
Ozonation	Cyanide is oxidized using ozone.	-	Not effective for removing the iron-cyanide complex and is expensive.	-
Photochemical dissociation	Cyanide is dissociated using ultraviolet (UV) irradiation.	Avoids using toxic or hazardous chemicals.	Usually inadequate by itself, and requires chemical treatment or catalysts.	-
Sulfur dioxide/air copper catalyzed oxidation	Cyanide is oxidized to cyanate using sulfur dioxide and air in the presence of copper ions. Sulfuric acid formed is neutralized with lime.	-	Reaction is slow at low temperatures leading to larger tank volumes. Generally does not remove thiocyanate, cyanate, or ammonia.	Cyanate can be transformed into toxic ammonia and nitrate by microbial action.

synthetic and actual process solutions and discussion of the engineering aspects for scale up.

CHAPTER 2

HOLLOW FIBER MEMBRANE TECHNOLOGY

Membranes are used in many industrial applications such as waste water treatment in the mining, mineral and electroplating industries, large scale desalination plants to obtain pure water from the sea, separation of whey and proteins from milk in the dairy industry, separation of oil and water from emulsions, separation of enzymes and antibiotics in the medical industry, and removal of gas from water and process solutions in the silicon wafer industry. Different membrane processes are microfiltration, ultrafiltration, nanofiltration and reverse osmosis in decreasing order of particle size rejected, in other words, the pore size of membranes used. Fig. 4 shows the size ranges of the membrane processes and the contaminants. These processes utilize different membrane modules and shapes such as flat sheet, spiral wound, tubular and hollow fibers. These membranes are made up of different materials such as cellulose acetate (CA), polyvinylidene fluoride (PVDF), polysufone (PSO), polypropylene (PP), polyacrylonitrile (PAN) and silica (SiO_2). These membrane materials have different applications depending on the nature of feed solution handled, size of the particle to be separated, pressure, pH and temperature conditions, nature of the membrane required (hydrophobic or hydrophilic), porosity, and many other operating parameters. Out of these modules, spiral wound and hollow fiber membranes are widely used because of ease and lower cost of manufacturing, larger

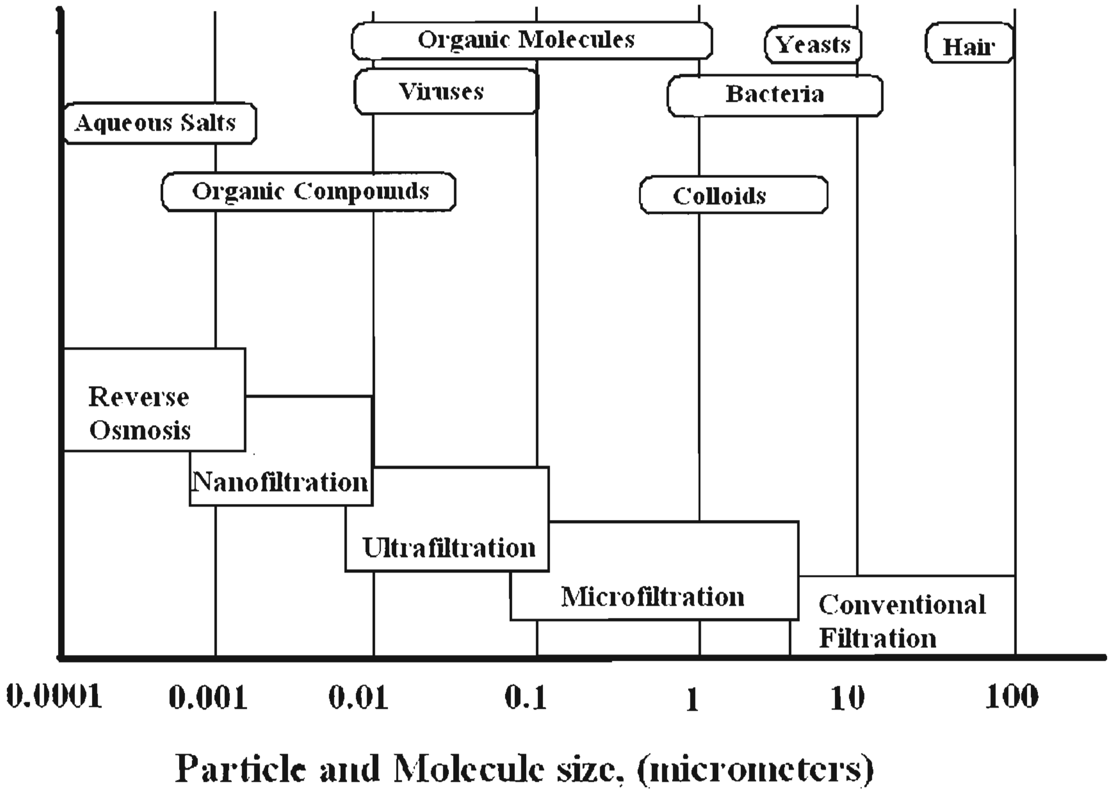

Fig. 4 Size Ranges of the Membrane Processes and the Contaminants [66]

surface area available per volume of the module, modular design of units and straightforward scale up.

2.1 Principles of Separation

The basic principle of membrane separation is the same for all the membrane modules and processes. The separation of interested species is achieved by transport of different species form one side of the membrane to the other, under the influence of a driving force, which is mostly difference in pressure or concentration. Fig. 5 explains the membrane separation process under different driving forces. The membrane acts as a barrier between two phases that allows mass transfer of the species that can be transported through the membrane [33].

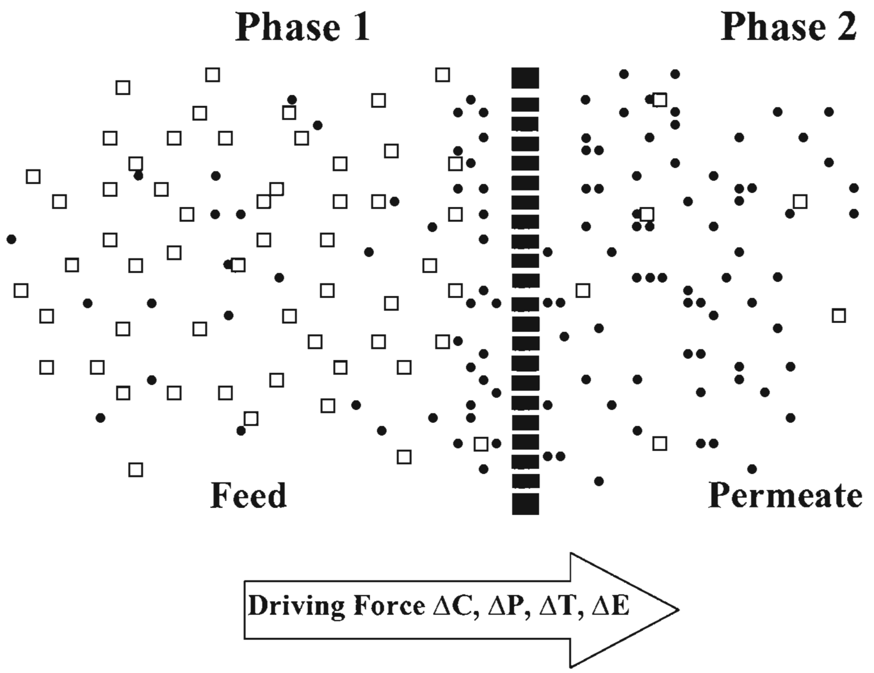

Fig. 5. Schematic of Membrane Separation Process with Different Driving Forces That Could Be Present [6].

The solution containing the species of interest to be removed or recovered flows into the membrane module and is called the feed solution. The liquid flowing on the other side of the membrane that accepts the transported species, and hence, becomes rich in the species of interest, is called the stripping solution or the acceptor solution. The clean water free of the species is called the discharge.

The flux force relationship can be described by a linear phenomenological equation between flux (J) and the driving force:

$$\mathbf{J = - A \frac{dX}{dx}} \tag{1}$$

where A is the phenomenological coefficient and dX/dx is the driving force, expressed as the gradient of X (concentration, pressure, temperature) along the thickness of the membrane [6].

The hollow fiber membranes are used in different modes, wetted and nonwetted. In the case of the wetted mode, the pore space is filled by one of the phases, and the process is called 1) perstraction, when the mass transfer occurs from liquid feed phase to liquid strip phase, due to pressure or concentration gradient across the membrane, and 2) membrane distillation, when the mass transfer results due to temperature difference in the feed and the strip side. Under the nonwetted or gas-filled mode, the pore space is filled by gas or air, or with a liquid which is not miscible with either the feed or the strip phases. The process is called osmotic evaporation or osmotic distillation when there is air or gas in pores, and the liquid supported membrane process when an immiscible liquid fills in pores. The separation here occurs due to different osmotic pressures on both sides of the membrane, and the volatile specie evaporates at the higher osmotic pressure side, crosses the membrane as a vapor, and condenses on the other side where the osmotic pressure is lower [33].

Many researchers have used the hollow fiber membrane technology in a variety of applications to study their performance and mechanism of transport of various species across the membrane. These membrane modules have been used in 1) liquid-liquid extraction of metals such as gold, cobalt and plutonium, 2) gas absorption and stripping to remove carbon dioxide, sulfur dioxide, nitrogen dioxide, ammonia, cyanide, and other volatile organic compounds (VOCs), and 3) pharmaceutical applications to extract important compounds from industrial streams, waste water treatments, blood oxygenation, fermentation and enzymatic transformation, ozonation of water and protein extraction. Other potential applications in which the hollow fiber membrane technology could be used is in the preparation of artificial lungs, underwater breathing units, dialysis, blood plasma separation, emission control units for automobiles, dispersion free solvent extraction, etc.

The hollow fiber membrane can be used in different configurations and with various materials. Different materials used to prepare membranes are polypropylene, Teflon (PTFE), polyvinylidene fluoride, and perflouroalkoxy (PFA) polymers. Researchers like Leveque [67], Prasad and Sirkar [40] and Wickramasinghe [43] studied the different configurations of membrane modules and proposed equations describing the mass transfer coefficients using Sherwood number, Reynolds number and the viscosity of the fluid together with membrane dimensions for tube side flow, shell side flow and shell side cross flow configurations. Wang and Cussler [49], Wickramasinghe et al. [48] and others proposed the mass transfer correlations for hand-built modules from axially wound individual fibers, axially wound fabric of micropores hydrophobic polypropylene fibers, the rectangular modules and cylindrical modules with baffles. Wang and Cussler [49] also studied the co-current and countercurrent flows of feed and strip phases in parallel flow configuration with feed flowing in the tube side, also called the lumen side, and compared with feed flowing in the shell side of the module. They found that the flow perpendicular to the fibers rather than parallel resulted into a higher mass transfer coefficient at the cost of efficiency, when compared to the countercurrent designs.

2.2 Fundamental Considerations

Cyanide, in aqueous solutions, is present mainly in the form of free cyanide and complex cyanide. Cyanide complexes readily with many metals such as gold, silver copper, nickel, cobalt, iron, zinc, etc. Metal cyanide complexes are classified into two groups in regard to their reactivity with acids. Complexes with cadmium, nickel, zinc etc., which are rapidly and completely decomposed by acids, with all CN^- ion converted to HCN, are called Weak Acid Dissociable (WAD) cyanide complexes. On the other hand, complexes that are resistant to decomposition by acids, such as cyanide complexes of cobalt and iron, are termed as "non-WAD" cyanide complexes. The uncomplexed cyanide ion CN^-, and the molecular hydrogen cyanide, HCN, are called the free cyanide. Fig. 6 shows the percentage of free cyanide as CN^- anions and molecular HCN as a function of pH at 25 °C. At low pH, most of the free cyanide is present in the form of molecular hydrogen cyanide. Therefore, by adding a small amount of acid in the waste

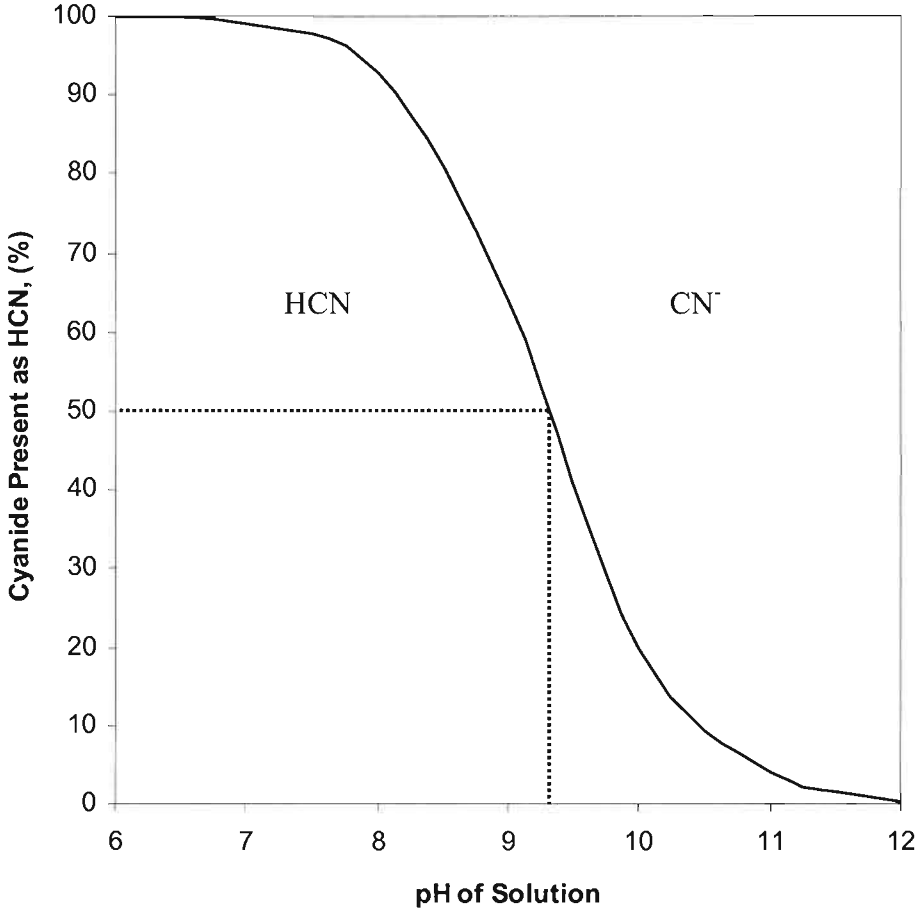

Fig. 6. Relationship Between Cyanide Anion (CN^-) and Molecular Hydrogen Cyanide (HCN) as a Function of pH (25°C) [68]

water containing cyanide, free and weak acid dissociable cyanide can be converted into molecular hydrogen cyanide, which being volatile, forms gas. Hydrogen cyanide gas can then be absorbed in sodium hydroxide solution, where it forms sodium cyanide. Reaction Equations (2) and (3) describe the reactions for the waste water feed, whereas reaction Equations (4) and (5) describe the reactions for the acceptor sodium hydroxide solution.

$$CN^- + H^+ \rightarrow HCN_{aq.} \tag{2}$$

$$HCN_{aq.} \rightarrow HCN_{gas} \tag{3}$$

$$HCN_{gas.} \rightarrow HCN_{aq.} \tag{4}$$

$$HCN_{aq.} + NaOH \rightarrow NaCN + H_2O \tag{5}$$

These reactions are the basis for the Acidification-Volatilization-Recovery (AVR) method for cyanide removal. In this method, the pH of cyanide solution is lowered by addition of sulfuric acid to generate hydrogen cyanide gas, which is then air stripped from the solution and absorbed into sodium hydroxide solution. Since hydrogen cyanide, an acutely toxic gas, is generated in the process, the reaction has to be carried out in sealed mixing vessels to avoid any leakage. However, this process suffers from several disadvantages, such as being more complex and hazardous than other cyanide removal methods and requiring sealed vessels and packed columns [65].

Hollow fiber membrane technology is similar to the traditional AVR method. The hollow fiber membrane technology can be used to remove cyanide present in water by addition of acid in a more effective and less hazardous way and the process is called Osmotic Distillation. Osmotic Distillation is a separation process in which a liquid mixture containing a volatile component is contacted with microporous, nonwettable hydrophobic membrane, with another liquid, capable of absorbing the volatile compound, on the opposite side of the membrane [34]. The membrane functions as a vapor gap between the two liquid phases which are potentially miscible with each other. The hydrophobic nature of the membrane material prevents the liquid from penetration and passage into the membrane pores as long as the pressure exerted by solutions on the two sides is less than the breakthrough pressure, Δp, described by Equation (6). The volatile component is free to migrate across the membrane by convection or diffusion. The driving force for transport of volatile components is the difference in vapor pressure of components over the contacting liquid phases.

$$\Delta p = \frac{(2\gamma\cos\theta)}{r} \tag{6}$$

where $\Delta \mathbf{p}$ is the breakthrough pressure for liquid-liquid contacting, γ is the surface tension, $\boldsymbol{\theta}$ is the contact angle between the wetting fluid and membrane pore and $\mathbf{r}$ is the radius of the pore [34].

Cyanide removal from waste water by osmotic distillation using hollow fiber membranes is proposed, in which hydrogen cyanide gas, generated by addition of acid to the feed solution containing cyanide, transports through the membrane under the driving force, vapor pressure difference between the two sides of the membrane. Removal of cyanide from aqueous solution has been studied, using artificial wastewater prepared by addition of sodium cyanide salt in deionized water under different experimental conditions to find the optimum condition for operation.

Kunz et al. [33] studied the process of osmotic evaporation through microporous hydrophobic membranes and maintained that the driving force for transport of volatile components was the difference in chemical potential or the osmotic pressure between the two liquids on different sides of membrane. The chemical potential of the solvent in a solution can be given as:

$$\mu_s = \mu_s^* + RT \ln a_s \tag{7}$$

where μ_s is the chemical potential of the solvent in a solution at pressure **P** and temperature **T**, μ_s^* is the chemical potential of the pure solvent at pressure **P** and temperature **T**, **R** is the gas constant, and $\mathbf{a_s}$ is the solvent activity [Kunz et al., 1996].

Also, the solvent activity can be related to osmotic coefficient ϕ, and vapor pressure P^o of the pure solvent and vapor pressure P of the solvent in solution as:

$$-\frac{1}{M_s \sum_i v_i m_i} \ln a_s = \phi = \frac{1}{M_s \sum_i v_i m_i} \ln \frac{P^o}{P} + \frac{B - V_s^{0(1)}}{M_s RT \sum_i v_i m_i} (P^o - P) \tag{8}$$

where m_i is the molality (in mol/kg of solvent) of the solute component i, v_i is $v_+ + v_-$ in the case of an electrolyte $C_{v+}^{z+} A_{v-}^{z-}$ and M_s is the molecular weight of the solvent. B is the second virial coefficient of the solvent and $V_s^{0(1)}$ is the molar volume of the pure liquid solvent [33].

The osmotic pressure is defined as :

$$\pi = \frac{RT\phi}{m_s V_s^{(1)}} \sum_i v_i m_i \tag{9}$$

where m_s is the molality of the solvent, $\mathbf{V}_s^{(l)}$ is the partial molar volume of the solvent [33].

From Equations (7), (8) and (9), it is seen that the driving force for the vapor flux, the gradient of the chemical potential, is primarily proportional to the vapor pressure difference, ΔP, on the two sides of membrane.

$$\mathbf{\Delta P = P_1 - P_2} \tag{10}$$

where P_1 and P_2 are the respective vapor pressures on two different sides of the membrane.

According to Raoult's Law, the vapor pressure of an ideal solution is dependent on the vapor pressure of each chemical component and the mole fraction of the component present in the solution. Mathematically,

$$\mathbf{P_s = \sum_i (P_i)_{pure}\, x_i} \tag{11}$$

where $(P_i)_{pure}$ is the vapor pressure of the pure component i, and x_i is the mole fraction of the component i, in the solution.

Therefore, in case of solutions containing molecular hydrogen cyanide, the driving force for the transport of hydrogen cyanide would be the difference in vapor pressure of the two solutions due to water and molecular hydrogen cyanide. In other words, if the difference in water vapor pressure on two sides of membrane is negligible, the driving force is primarily due to the difference in vapor pressure of molecular hydrogen cyanide on two sides. Hence, under equilibrium conditions, the driving force for transport of hydrogen cyanide is the difference in concentration of hydrogen cyanide in feed and acceptor solutions.

The microporous hydrophobic membrane consists of pores initially filled with air. For a simple diffusion process across the membrane, the vapor flux, J_D, which is the rate of mass transfer per unit area of membrane, can be described by :

$$\mathbf{J_D = \frac{1}{Y_{ln}} \frac{D\varepsilon}{l} \frac{M_s}{RT}(P_2 - P_1)} \tag{12}$$

where, Y_{ln} is the molar fraction of air (log mean), D is the vapor diffusion coefficient, ε is the porosity of membrane, l is the pore length obtained by the product of the turtuosity factor, τ, and membrane thickness, d. This model does not take into consideration the interactions between the vapor molecules and the membrane pores and regards air entrapped in the pore as a motionless medium [33].

Different diffusion models can be considered when the interaction between the membrane pores and the diffusing molecules are to be considered. When the pore size is larger than the mean molecular path of diffusing molecules, Poiseuille capillary model could be used to describe the flux through the membrane, as the diffusing molecules will collide with each other more frequently than with pore walls and the pressure drop across the membrane would be primarily due to the shear stress within the fluid. The flux in this case can be described as:

$$\mathbf{J_P = \frac{1}{8} \frac{r^2\varepsilon}{l} \frac{M_s}{\eta} \frac{P_m}{RT}(P_2 - P_1)} \tag{13}$$

When the pore size of the membrane is smaller than the mean molecular path of the diffusing molecules, flux through membrane can be described using Knudsen diffusional model as:

$$\mathbf{J}_{\mathrm{K}} = \frac{2}{3}\frac{\mathbf{r\varepsilon}}{\mathbf{l}}\sqrt{\left(\frac{8}{\pi}\frac{\mathbf{M}_{\mathrm{s}}}{\mathbf{RT}}\right)}\,(\mathbf{P}_2 - \mathbf{P}_1) \qquad (14)$$

From Equations (12), (13) and (14), it can be seen that the flux is proportional to the driving force, $(P_2 - P_1)$.

$$\mathbf{J} = \mathbf{C}\,(\mathbf{P}_2 - \mathbf{P}_1) \qquad (15)$$

In other words, flux is proportional to the concentration difference across the membrane.

$$\mathbf{J} = \mathbf{K}\,(\mathbf{C}_2 - \mathbf{C}_1) \qquad (16)$$

where K is the overall mass transfer coefficient for the diffusing molecules, and C_1 and C_2 are the concentrations of volatile specie in solutions on the two sides of the membrane.

In the case of cyanide removal from the feed solution, by acidification and absorption by the alkaline acceptor solution, whose pH is adjusted by addition of sodium hydroxide, the hydrogen cyanide gas diffuses through the membrane immediately reacting with the sodium hydroxide molecules to form sodium cyanide. Thus, the hydrogen cyanide concentration in the acceptor solution can be considered negligible throughout the length of the membrane module. Also, if the osmolarities of the feed and acceptor solution are different, water vapor transport will occur from the region of high osmolarity to the region of low osmolarity.

The rate of change of hydrogen cyanide concentration in the feed solution in the membrane module would be equal to the rate of mass transfer of hydrogen cyanide from the tube side to the shell side. The mass balance around the membrane module on the feed side flow results in Equations (17) and (18).

$$\mathbf{QdC + \alpha(C - dC) = -K\,(C - C_a)(2\pi rn)dx} \tag{17}$$

$$\mathbf{dC + \frac{\alpha}{Q}(C - dC) = -K\frac{(2\pi rn)}{Q}(C - C_a)dx} \tag{18}$$

where Q is the volumetric flow rate of feed solution, C is the concentration of hydrogen cyanide in feed solution at a distance x from the entry to the membrane, α is the rate of water vapor transfer, K is the overall mass transfer coefficient, C_a is concentration of hydrogen cyanide in acceptor solution at the same point, r is the inner radius of the membrane fiber and n is the number of fibers in the membrane module. Since the change in volume due to water vapor transport would be small, the ratio **α/Q** would be very small and hence negligible.

Under these conditions Equation (18) can be rewritten as :

$$\frac{dC}{(C - C_a)} = -K\frac{(2\pi rn)}{Q}dx \tag{19}$$

Integrating Equation (19), with boundary conditions, we obtain

$$\int_{C_f}^{C_d} \frac{dC}{(C - C_a)} = -K\frac{(2\pi rn)}{Q}\int_0^L dx \tag{20}$$

$$\ln\frac{C_d - C_a}{C_f - C_a} = -K\frac{(2\pi rn)}{Q}L \tag{21}$$

where C_f and C_d are the concentrations of hydrogen cyanide in the feed solution and the solution leaving the membranes (discharge), respectively, and L is the length of the hollow fiber membranes.

The concentration of hydrogen cyanide in acceptor solution, C_a, can be assumed to be zero as reaction between hydrogen cyanide and sodium hydroxide is rapid, and if sodium hydroxide is in excess, there is essentially no hydrogen cyanide present in acceptor solution. Also, if the total surface area of the membrane in the tube side is denoted by A, the Equation (21), in a simplified form, can be written as :

$$\ln\frac{C_d}{C_f} = -K\frac{A}{Q} \tag{22}$$

The overall mass transfer coefficient for diffusing molecules can be calculated using Equation (22), for the known values of C_d, C_f, A and Q.

The velocity of fluids flowing in the shell side and the tube side of the membrane can be determined using Equations (23) and (24).

$$\mathbf{v_s = \frac{Q_s L}{V}} \tag{23}$$

where,

v_s = Fluid velocity in the shell side

Q_s = Flow rate of fluid in the shell side

L = Length of hollow fiber membranes in the shell side

V = Shell side volume

$$\mathbf{v_t = \frac{Q_t}{n\pi r_i^2}} \tag{24}$$

where,

v_t = Fluid velocity in the tube side

Q_t = Flow rate of fluid in the tube side

n = Number of hollow fiber membranes in the module

r_i = Inner radii of hollow fiber membranes

For a membrane module with fixed number of fibers and their dimensions, the velocity of fluid flowing in the tube side is proportional to the flow rate of the fluid. Similarly, the velocity of fluid flowing in the shell side of the membrane module is proportional to the flow rate of the fluid for modules with fixed dimensions of the shell side.

The overall mass transfer coefficient consists of different components for the feed side mass transfer, mass transfer through membrane, and the acceptor side mass transfer. The overall mass transfer coefficient, K, can be written as :

$$\frac{1}{K}=\frac{1}{k_f}+\frac{1}{k_m}+\frac{1}{k_a} \qquad (25)$$

where k_f, k_m and k_a represent the individual mass transfer coefficients describing the transfer of diffusing molecules across the feed side or tube side concentration boundary layer, through the membrane and across the acceptor side or the shell side concentration boundary layer. The individual mass transfer coefficients can be estimated by preparing the Wilson plots for different K values obtained at different flow rates of solutions in the tube side and the shell side. An important assumption in the Wilson plot method is that the tube side and the shell side mass transfer coefficients are proportional to the velocity of the fluids flowing in the tube side and the shell side of the membrane module. Fig. 7 shows a hypothetical Wilson Plot with 1/K and $1/v^{\alpha}$ plotted on the y and x-axes respectively. From the plot of overall mass transfer coefficient with respect to the variations in velocity of the feed solution, the y-intercept, I_f, provides the sum of the membrane and the acceptor side resistances, because at infinite feed velocity, the feed side resistance would be zero.

$$I_f=\frac{1}{k_m}+\frac{1}{k_a} \qquad (26)$$

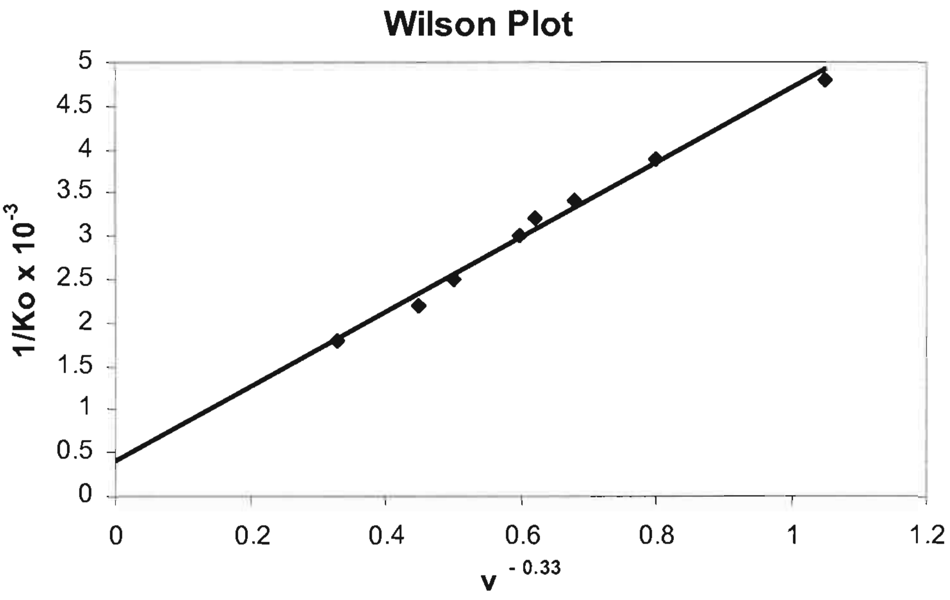

Fig. 7. A Typical Wilson Plot [5[

Similary, from the plot of overall mass transfer coefficient with respect to the variations in velocity of the acceptor solution, the y-intercept, I_a, provides the sum of the membrane

$$I_a = \frac{1}{k_f} + \frac{1}{k_m} \qquad (27)$$

and the feed side resistances, because at infinite velocity of the acceptor solution, the acceptor side resistance would be zero. Using the information obtained from the two intercepts, I_f and I_a, and the overall mass transfer coefficient at certain velocities of the feed and the acceptor solution, the individual mass transfer coefficients for the feed side, the membrane and the acceptor side can be calculated.

The removal of cyanide from the feed solution is calculated as the fraction of cyanide that was removed from the feed solution, or in other words, the ratio of the difference of cyanide concentration in the feed solution and the cyanide concentration in the discharge solution to the cyanide concentration in the feed solution. The recovery of cyanide is calculated as the ratio of mass of cyanide recovered in the acceptor solution to the mass of cyanide present in feed solution in unit time. The removal of cyanide from the feed solution and the recovery of cyanide in the acceptor solution can be calculated using Equations (28) and (29), respectively.

$$\mathbf{Removal, R_1 = \frac{C_f - C_d}{C_f}} \tag{28}$$

$$\mathbf{Recovery, R_2 = \frac{C_a * Q_a}{C_f * Q_f}} \tag{29}$$

Q_a is the flow rate of the acceptor solution and Q_f is the flow rate of the feed solution.

CHAPTER 3

MATERIALS AND METHODS

3.1 Identification of Factors Expected to Affect Cyanide Removal

Removal of cyanide from aqueous solutions using hollow fiber membrane technology is driven by the difference in vapor pressure of the solutions on the different sides of the membrane. Factors affecting the vapor pressure of a solution such as temperature, pressure, concentration of volatile component, and ionic strength, are expected to cause a change in the flux of the diffused molecules. Properties of the membrane such as pore size, porosity, membrane material, membrane dimensions, and the active surface area of the membranes are expected to influence the mass transfer across the membrane.

Various factors that are expected to influence the removal of cyanide using hollow fiber membranes, and would be useful in considering for the industrial application of this technology, are identified as follows:

a) pH of the feed solution, pH_f.

b) pH of the acceptor solution, pH_a.

c) Flow rate of feed solution, Q_f.

d) Flow rate of acceptor solution, Q_a.

e) Concentration of cyanide in feed solution, C_f.

f) Temperature of operation, T.

In addition to these factors, total dissolved solids (TDS) in acceptor solution, cyanide concentration in acceptor solution, C_a, use of lime in place of sodium hydroxide to elevate the pH of acceptor solution and effect of mode of flow of feed and acceptor solutions were also identified as important factors, from the point of view of industrial application, which might affect the transport of hydrogen cyanide. The difference in temperature of feed and acceptor solution is an important factor to be studied as the transport and chemical kinetics on the two sides of the membrane are expected to change with temperature.

Cyanide, in aqueous solution, is present in the form of cyanide ions (CN^-) and molecular hydrogen cyanide (HCN). Molecular hydrogen cyanide dominates in a system when the pH is less than 9.31, whereas cyanide anion dominates in the system when the pH of the solution is greater than 9.31, as the pK_a for dissociation of hydrogen cyanide is equal to 9.31 [65]. For the maximum removal of cyanide from feed solution, it would be desirable that most of the cyanide present in solution is in the form of hydrogen cyanide, which diffuses through the membrane. Thus, feed solution must be kept at pH lower than 9.31 so that hydrogen cyanide dominates. On the other hand, in the acceptor solution, it would be desirable to have most of the cyanide collected in the form of cyanide anion, or in other words, molecular hydrogen cyanide should be minimum, so that the driving force, the difference in vapor pressure of volatile components (Equation (15)) or the difference in concentration of hydrogen cyanide (Equation (16)), on the two sides, is always maintained. Therefore, the pH of acceptor solution must be kept higher than 9.31 so that cyanide anion dominates in the acceptor side.

Previous investigators have shown that the individual mass transfer coefficients for the tube side and the shell side are dependent on velocity of fluids on either side of the membrane. For a fixed dimension of membranes, the flow velocity changes with change in volumetric flow rate, and hence, the individual mass transfer coefficients in the tube side and the shell side also change. Optimum flow rates of the feed and the acceptor solutions have to be determined for the maximum removal of cyanide at minimum cost.

The concentration of cyanide in the feed and the acceptor solutions affect the concentration of hydrogen cyanide in them. Also, from Equation (16), the flux of molecules diffusing through the membrane is directly proportional to the difference in concentration of volatile components. Therefore, it is important and interesting to investigate the performance of the membrane module at different concentrations of cyanide in the feed solution. Modules with different designs might be required for different feed solutions.

The solubility of volatile components in solution varies with temperature. Generally, at higher temperatures, the solubility of volatile components decreases, and at lower temperatures, the solubility is much higher. Osmotic pressure and flux through the membrane under diffusion are also dependent on temperature, thus making temperature an important factor to investigate the performance of the membranes.

In industry, the process solutions have a wide range of total dissolved solids present in them. The knowledge of effect of total dissolved solids present in the acceptor solution would be helpful in selecting the area of application of this technology and the process solutions that could be used as acceptor.

The effect of cyanide concentration in acceptor solution appears to be important in order to observe how the membrane performance changes with increase in cyanide concentration in acceptor solution. It might be important from the point of view of industrial application for cyanide recovery where the acceptor solution could be recirculated to achieve the desired level cyanide concentration for other uses, without affecting the removal efficiency.

Lime is widely used in industries, especially in mining, to control the pH of the process solutions. Lime is preferred over sodium hydroxide and other reagents, due to its lower cost, easier availability and storage. It would be interesting to investigate whether lime could be used to raise the pH of acceptor solution, for use in cyanide removal by hollow fiber membranes. Lime could be a better alternative to sodium hydroxide for the industrial application, if the performance is not marred by its use. Cyanide removal is expected to change, if sodium hydroxide is substituted by lime, if the rates of reaction of hydrogen cyanide with lime and sodium hydroxide are different. Also, due to resulting suspended solids by addition of lime, acceptor solution may require pretreatment to prevent the clogging of membrane pores.

In parallel flow modules, two types of flow of feed and acceptor solutions could be achieved, namely co-current and countercurrent flow modes. In co-current flow mode, the feed and acceptor solutions flow in the same direction, but on different sides of the membrane. On the other hand, in countercurrent flow mode, the feed and acceptor solutions flow in different directions. It would be interesting to know the effect of mode of flow of the two solutions on the removal efficiency of cyanide by membranes.

Previous researchers have suggested countercurrent flow mode for better mass transfer coefficient [6, 49, 69]

The processing plants in industries have a variety of solutions present at different temperatures. The solutions at different temperatures are expected to have different solubilities of volatile components, and hence different vapor pressures. Also, the transport and chemical kinetics are expected to change with temperature, affecting the removal efficiency. If some of these solutions are to be used as feed and acceptor solution, it would be important to know the changes in removal efficiency resulting due to the difference in temperatures of the two solutions.

3.2 Design of Experiments

Statistical design of experiments was conducted to study the effects of various factors that were identified to have some effect on the removal of cyanide by the hollow fiber membrane method. Different levels for selected factors were chosen based upon the conditions existing in unit processes. Important factors that could be studied by statistical analysis of results from Factorial Design of experiments were selected. The selected factors are:

a) pH of the feed solution, pH_f.
b) pH of the acceptor solution, pH_a.
c) Flow rate of feed solution, Q_f.
d) Flow rate of acceptor solution, Q_a.
e) Concentration cyanide in feed solution, C_f.
f) Temperature of operation, T.

Two Level Six Factor Full Factorial Design of experiments with two replicates was conducted to study the effect of the mentioned factors on the removal of cyanide from aqueous solutions. The different levels of these factors are presented in Table 4. A total of 128 experiments were conducted to carry out the statistical analysis of results obtained from the experiments. The experiments were conducted at low and high levels of the selected factors: the low level for each listed under column marked -1 and the high level for each listed under column marked 1. The low level for pH of feed solution was chosen as pH 3, because at this pH, almost all of the cyanide present in the solution is expected to be in the form of molecular hydrogen cyanide (Fig. 6). The high level was chosen to be 9.5 as this is close to the pH value 9.31, at which cyanide anion and molecular hydrogen cyanide are present in equal proportion. It would give us the insight into the removal process, when hydrogen cyanide was dominating and when both cyanide ions and hydrogen cyanide are present in equal proportion, in the feed solution. The low and high values of acceptor solution were chosen to be 9.5 and 12, to observe the removal process, when the acceptor solution has equal proportions of cyanide anion and molecular hydrogen cyanide, and when cyanide anion is dominating in the solution.

Table 4. Factors and Levels of Factors Selected for Design of Experiments

Factors		**Levels**		**Units**
		-1	1	
pH of Feed Solution	pH_f	3	9.5	pH units
Temperature of Feed Solution	T	5	35	Degrees C
Flow Rate of Feed Solution	Q_f	20	80	ml/min
Cyanide Concentration in Feed Solution	C	10	1000	PPM CN^-
Flow Rate of Acceptor Solution	Q_a	10	60	ml/min
pH of Acceptor Solution	pH_a	9.5	12	pH units

Similarly, the low and high levels for flow rates of feed and acceptor solution were chosen as 20 milliliters per minute and 80 milliliters per minute, and 10 milliliters per minute and 60 milliliters per minute, respectively. The different values were chosen for flow rates of feed and acceptor solution to observe how the removal process varied with different ratios of flow rates of these solutions.

The effect of concentration of cyanide was studied at two levels, 10 parts per million of cyanide anion at low level and 1000 parts per million of cyanide anion at high level, to observe the removal efficiency by the method. The performance of membrane in removal of cyanide from solution, at these two different levels of cyanide concentration, would help us to ascertain the possibility of application of this technology in two different areas, where cyanide removal is desired in both dilute and concentrated streams of process solutions.

The effect of temperature was studied at 5 ^{0} Celsius and 35 ^{0} Celsius. Different processes have different temperature requirements, and the solutions emanating from these processes are at different temperatures. The two values were chosen to decide if the technology could be used for solutions at different temperatures in the processing plant. Also, the temperature varies geographically on Earth. The application of this technology for industries situated in different parts of world, having different temperature conditions, could be explored. Experimental conditions for different experiments obtained from various combinations of levels of selected factors are presented in coded form in Appendix A, where code -1 indicates low level of the factor and code 1 indicates high level of the factor.

The experiments involving Liqui-Cel® Extra-Flow 2.5 x 8 module were conducted at different flow rates than those for the Liqui-Cel® MiniModule 1 x 5.5, because of the difference in size of the two modules. The experiments to determine the mass transfer coefficients for the Extra-Flow module was conducted with the flow rates of the feed and the acceptor solution varying from 200 milliliter per minute to 800 milliliters per minute and 100 milliliters per minute to 600 milliliter per minute, respectively. These values were selected based on the flow per unit available area of the membrane, flux. The available membrane active area for the Extra-Flow modules was about 10 times that of the MiniModule. Hence, the flow rates of the feed and the acceptor solutions in experiments involving the Extra-Flow modules were raised by the factor of 10 when compared to the flow rates of these solutions in case of the MiniModule. Similarly, the flow rates for the feed and the acceptor solutions using the Extra-Flow module were assumed to be 200 milliliters per minute and 600 milliliters per minute, respectively, based on the results obtained from the experiments conducted with the MiniModule.

3.3 Experimental Set-up

Experiments to investigate the removal of cyanide from aqueous solutions using hollow fiber membranes were conducted using Liqui-Cel® MiniModule 1 x 5.5 and Liqui-Cel® Extra-Flow 2.5 x 8 Membrane Contactors, supplied by Membrana-Charlotte. The co-current configuration, with the feed solution flowing in the tube side and the acceptor solution flowing in the shell side, was used to study the performance of membrane in removal of cyanide at different operating conditions for the factorially designed experiments. Fig. 8 provides the schematic diagram for the hollow fiber membrane experiments. Fig. 9 presents a photograph of the actual laboratory set up used for the experiments.

The Liqui-Cel® MiniModule 1 x 5.5 membrane module consisted of 2300, X50 hollow fibers, with inner and outer diameters of each fiber, as 220 micrometers and 300 micrometers, respectively. The pore size, porosity and active surface area values of the membranes as provided by the supplier in the data sheet were 0.04 micrometers, 40 percent and 0.18 square meter, respectively. The Liqui-Cel® MiniModule 1 x 5.5 Membrane Contactor comes with polypropylene hollow fibers enclosed in a polycarbonate housing with polyurethane as the potting material. The membrane module allows the parallel flow pattern of the solutions for both the tube and the shell sides. The hollow fibers are potted on each end of the device and the feed solution flows inside the fibers, the acceptor solution flowing in the shell side, outside the fibers. Fig. 10 shows a photograph of the Liqui-Cel® MiniModule 1 x 5.5 Membrane Contactor used in the experiments. The priming volumes for the lumen side, also called the tube side and the shell side, were 16 milliliters and 25 milliliters, respectively. The maximum temperature, pressure and flow guidelines as provided by the supplier are 4.2 kilogram per square centimeter at 23 ° Celsius and 2.1 kilogram per square centimeter at 35 ° Celsius, with flow less than 500 milliliters per minute in the lumen side.

The Liqui-Cel® Extra-Flow 2.5 x 8 membrane module consisted of 10200 X50 hollow fibers. The Extra-Flow membrane module comes with polypropylene hollow fibers enclosed in a polypropylene housing with polyethylene potting. The pore size, porosity and active surface area values of the membranes as provided by the supplier in the data sheet were 0.04 micrometers, 40 % and 1.4 square meters, respectively. The priming

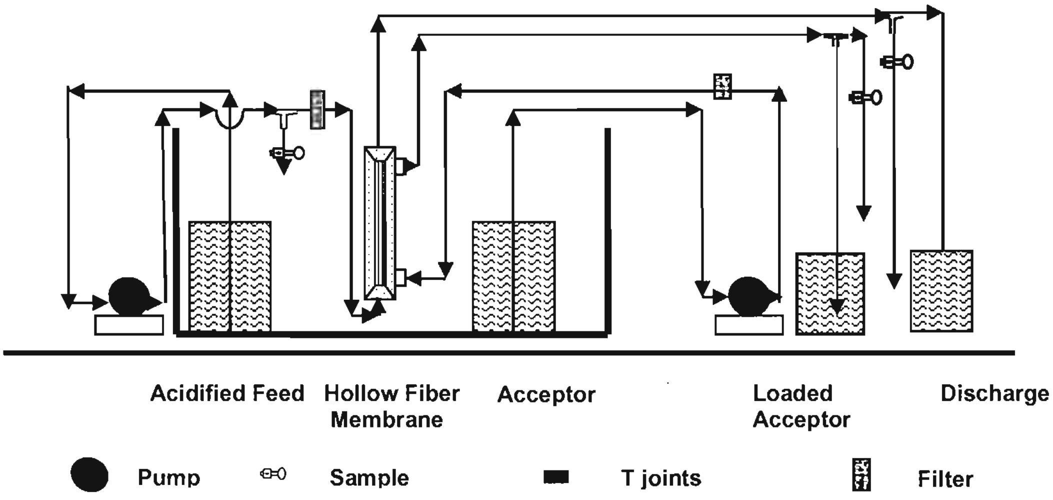

Fig. 8. Schematic Diagram for the Removal of Cyanide from Aqueous Solutions Using Hollow Fiber Membranes with Co-current Configuration.

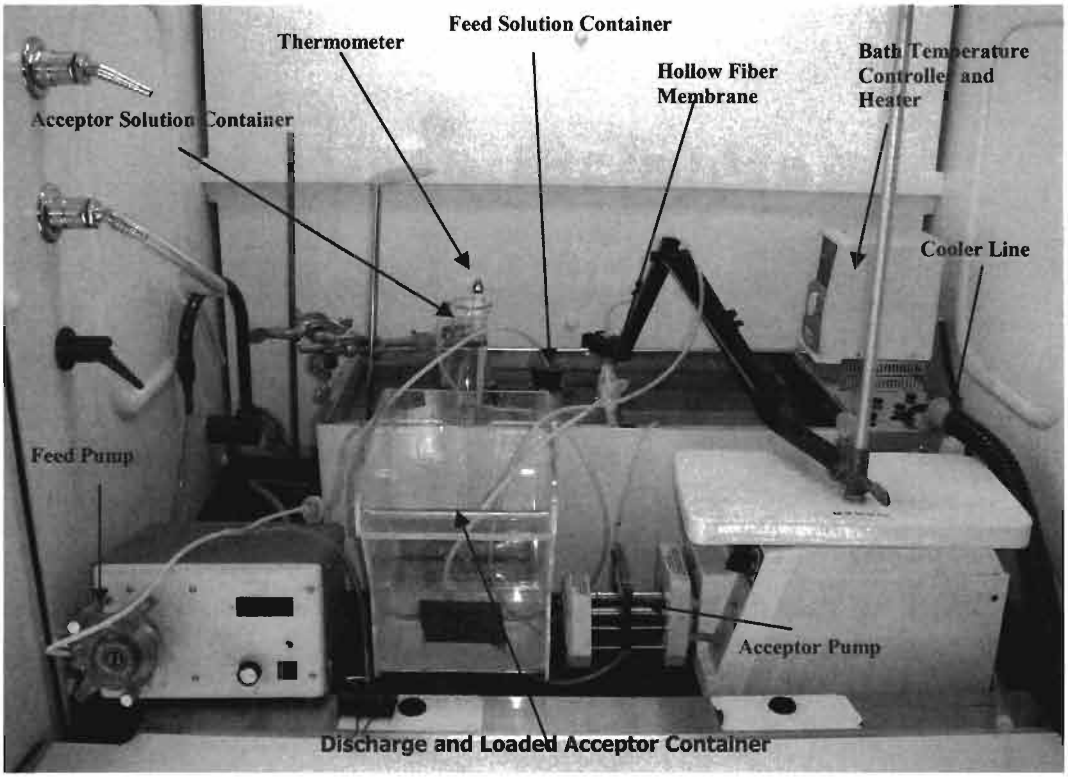

Fig. 9. Laboratory Set-up for the Removal of Cyanide from Aqueous Solutions Using Hollow Fiber Membranes with Co-current Configuration

Fig. 10. A Picture of Liqui-Cel® MiniModule 1 x 5.5 Membrane Contactor, Supplied by Membrana, Supplier Item Number : G543.

volumes for the lumen side, also called the tube side and the shell side, were 150 milliliters and 400 milliliters, respectively. The maximum temperature, pressure and flow guidelines as provided by the supplier are 7.4 kilogram per square centimeter at 40 ^{0} Celsius and 2.1 kilogram per square centimeter at 70 ^{0} Celsius, with flow of 0.1 to 0.7 m^3 per hour in the shell side. The Extra-Flow module allows the flow of the feed solution on the outside of the fibers, whereas the acceptor solution flows in the fibers, maximizing the surface are for larger flow rates of the feed solution. The Celgard® Hollow fiber is knit into a fabric which is wound around a distribution tube. The feed solution is forced radially across the fibers by using a central baffle within the module, hence, providing the element of crossflow pattern and the counter current mode when the acceptor solution flows in a direction opposite to the flow of feed solution. The picture and the design in detail of the Liqui-Cel® Extra-Flow2.5 x 8 Membrane Contactor used in the experiments are presented in Fig. 11.

The temperature of the membrane module and the feed and the acceptor solutions were maintained constant by placing the membrane and the containers holding solution in a thermostatic water bath (S-38), supplied by Grant. The digitally-controlled Grant heater and temperature controller (GD100) was used to achieve the desired temperature of water bath. The temperature of water bath was brought below the ambient room temperature using the Grant Cooler (C2GL) controlled by the same temperature controller.

Peristaltic pumps were used to pump the feed and acceptor solutions through the membrane module. The flow of the two solutions was controlled by adjusting the speed of the motors driving the pumps. The pump speed was controlled by the electrical speed controller attached to the pump assembly.

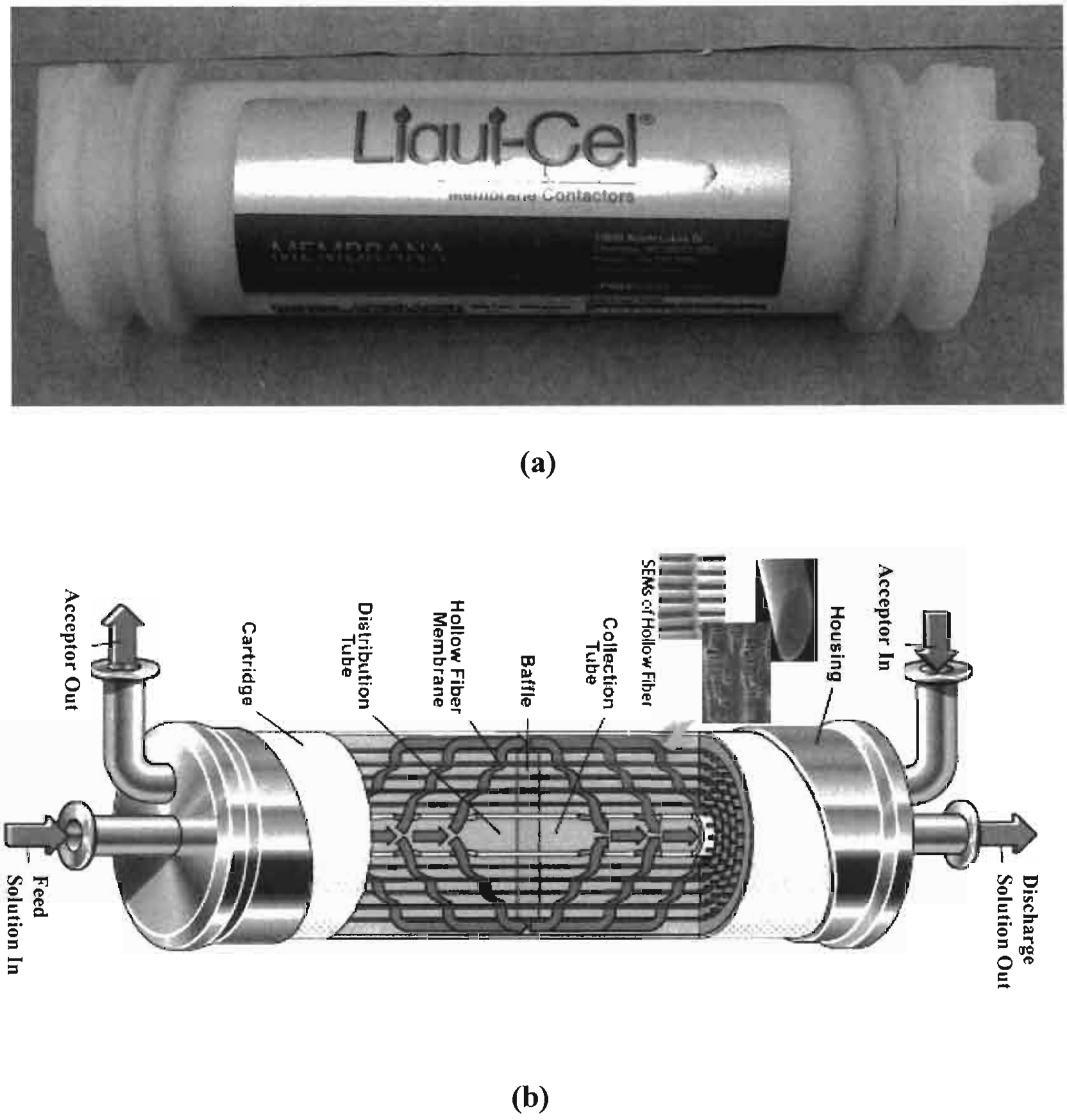

Fig. 11. Liqui-Cel® Extra-Flow 2.5 x 8 Membrane Contactor

(a). A Picture of Liqui-Cel® Extra-Flow 2.5 x 8 Membrane Contactor, Supplied by Membrana. Supplier Item Number: G501

(b). Design* of Liqui-Cel® Extra-Flow 2.5 x 8 Membrane Contactor, Supplied by Membrana [70]

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* Modifications have been made to the diagram as per the application in this research work. Liqui-Cel is a registered trademark of Membrana, A division of Celgard LLC. Celgard is a registered trademark of Celgard LLC.

3.4 Experimental Procedure

Different experiments were conducted to study the removal of cyanide under different operating conditions. All the experiments were conducted under the ventilated hood to avoid any health problems that could arise by exposure to cyanide. The solutions were pumped into the respective sides, using peristaltic pumps, which were placed outside the water bath to avoid electrical hazards. The pumps were calibrated prior to the experiments for the flows corresponding to the different speed (RPM) using deionized water as fluid. The flow mode was changed from co-current to counter current by interchanging the acceptor solution inlet and outlet pump tubings.

The feed solutions were prepared by dissolving 0.0191 grams and 1.913 grams of sodium cyanide, in deionized water, to make up to 1 liter for 10 parts per million and 1000 parts per million solutions, respectively. Reagent grade sodium cyanide chemical, of 98.5 % purity, supplied by Fischer Chemicals, was used for the purpose of the experiments. The pH of feed solution was adjusted by addition of few drops of concentrated hydrochloric acid, of 12.1 M strength, and sodium hydroxide solution of 4 M strength, as and when required, the container being placed on the heater and magnetic stirrer, with a magnetic stir bar in the solution to facilitate mixing. The pH of the acceptor solution was adjusted in a similar manner. The pH and the total dissolved solids in the solutions, while being adjusted, were monitored and measured by the bench top pH and conductivity meter, pH/CON 510, supplied by Oakton Instruments.

During each experiment, the samples of feed, acceptor and discharge solutions were collected from the sample valves, after allowing the solutions to flow for 5 min., and were stored in scintillation vials of 25 milliliters capacity. The sample vials were properly labeled according to the experiment number and the type of solution it stores. The samples were preserved, by adding 200 microliters of 4 Molar sodium hydroxide solution, in sample vials, to prevent the subsequent loss of cyanide.

The concentration of cyanide in each sample was determined by analyzing the samples with the Alpkem Cyanide Analyzer, connected to a computer and supported by CN Lab Solutions software (CN Lab Version 1.27). The analyzer works with the flow injection technique followed by the amperometric detection by a silver reference electrode. The analyzer was calibrated with standard solutions with known concentration of cyanide and then the samples were analyzed using the preset cyanide analysis methods on the computer and the analyzer. The samples were fed directly to the analyzer through a sample probe for analysis. In the case of samples with high concentration of cyanide, the samples were appropriately diluted so that the cyanide concentration in the sample was within the range of detection. The cyanide concentration values in different solutions obtained from the analyzer were recorded and later analyzed, to determine the performance of the membranes in removal of cyanide from feed solution.

Investigation of the effect of total dissolved solids on removal of cyanide was carried out by adding sodium chloride salt, reagent grade, supplied by EM Science, in deionized water in varying amounts, to change the total dissolved solids, and the pH was then adjusted by addition of 4 M sodium hydroxide solution. The total dissolved solids levels in the solutions were measured using the bench top pH and conductivity meter, manufactured by Oakton, and the experiments were conducted at optimum conditions as determined from the statistical analysis of data from two level six factor design of experiments. Similarly, to find out the effect of cyanide concentration in the acceptor solution, varying amounts of sodium cyanide was added in the acceptor solution, for different experiments. For experiments to investigate the use of lime as a substitute for sodium hydroxide to adjust the pH of the acceptor solution, calcium hydroxide, reagent grade, of 97.7 % purity, supplied by Mallinckrodt Baker Inc., was added in deionized water, until the desired pH was achieved, and the experiments were then conducted in the counter-current mode to study cyanide removal and recovery.

Experiments to investigate the effect of various factors such as total dissolved solids and cyanide concentration in acceptor solution, use of lime as a substitute for sodium hydroxide to elevate the pH of acceptor solution, mode of flow of feed and acceptor solutions, and the effect of difference in temperatures of feed and acceptor solutions and to estimate the overall and individual mass transfer coefficients were studied after the most important factors and the optimum conditions for operation were determined from the statistical analysis. Except for the factorially designed experiments, in which the temperatures of both the feed and the acceptor solutions were kept at 35 °C and the temperatures of the solutions were kept at 30 °C, due to the supplier's updated maximum operating temperature recommendations. Also, the temperature of the acceptor solutions was varied from 5 °C to 30 °C in the experiments to investigate the effect of difference in temperatures of feed and acceptor solutions. Experiments to investigate the use of lime in place of sodium hydroxide in acceptor solution, estimation of overall and individual mass transfer coefficients, and the effect of difference in temperatures of feed and acceptor solutions were conducted with countercurrent mode of flow of these solutions.

The membrane module was washed prior to and after the end of the experiments by circulating the deionized water on both the shell side and the tube side of the module, for at least 20 min. at low level flow rates to render it clean and suitable for use in the following experiments. The pH of the discharge solution was regularly monitored to confirm that the membrane module was working properly. Any leakage or damage in membranes would change the pH of discharge solution, as there was a significant difference in pH of feed and acceptor solution in all experiments, except for a few cases in which the pH of both the solutions was the same. A change in pH of the discharge solution was observed occasionally, which indicated that the hollow fiber membranes had failed. Under these conditions, the damages, if any, were confirmed by flowing different acidic and alkaline solutions in the tube side and the shell side of the membrane, without cyanide, and monitoring the pH of discharge solution. Upon confirmation, the experiments were conducted with new membrane modules. Damage or wetting of the membrane pores resulting in a higher pH of the feed/discharge solution was observed twice when the experiments were conducted with MiniModule. The first incident of membrane damage or wetting was observed in the middle of the factorially designed experiments, after sixty experiments using approximately 60 liters of the feed solution, including replicates, were conducted. The membrane was replaced with a new one that lasted for the rest of the factorially designed experiments and the other experiments to investigate the effect of dissolved solids and cyanide concentration in the acceptor solution, for about eighty experiments using approximately 80 liters of the feed solution under different conditions. A new membrane module was used to carry out the remaining experiments and was undamaged until the end of the research. No such damage or wetting was observed with the Extra-Flow module during the research.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Statistical Analysis of Factors Investigated

The results of the experiments conducted under the Two Level Six Factor Factorial Design were statistically analyzed using Design Ease and Matlab computer softwares. The fraction of cyanide removed from feed solution, calculated from the concentration of cyanide in feed and discharge solution, was considered as the response for all experiments. The Half Normal and Normal Probability plots of effects were prepared to identify the significant factors and the interactions affecting the removal of cyanide. The Analysis of Variance (ANOVA) was conducted to support the findings from the two plots. The Half Normal and Normal Probability plots of effects derived from the factorial experiments are presented in Appendix B. Table 5 provides the ANOVA results showing the main effects of individual factors and the effects due to interaction of factors that were found to be significant in removal of cyanide from aqueous solutions.

The f-values at 95 % confidence level ($\alpha = 0.05$), $f_{0.05,\ 1,\ 115}$, for all the factors and interactions were 3.92. Since the f-values at the 0.05 level of significance, $f_{0.05,\ 1,}$ are smaller than the calculated f-test statistics values in Table 5, all the factors and the interaction combinations are considered to have a significant effect on removal of cyanide. Also, for all the factors and the interaction combinations displayed in Table 5,

Table 5. Analysis of Variance for the Factorial Experiments

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-values	Probability
Model	7.54	12	0.63	57.56	< 0.0001
pH of the feed solution, pH_f	0.37	1	0.37	33.53	< 0.0001
Temperature of operation, T	0.16	1	0.16	14.64	0.0002
Flow rate of feed solution, Q_f	1.3	1	1.3	119.09	< 0.0001
Concentration of cyanide in feed solution, C_f	1.12	1	1.12	102.75	< 0.0001
Flow rate of acceptor solution, Q_a	1.05	1	1.05	96.6	< 0.0001
pH of the acceptor solution, pH_a	1.56	1	1.56	142.59	< 0.0001
$pH_f * T$	0.4	1	0.4	37.1	< 0.0001
$pH_f * C_f$	0.24	1	0.24	22.03	< 0.0001
$Q_f * C_f$	0.16	1	0.16	14.69	0.0002
$Q_f * pH_a$	0.28	1	0.28	25.76	< 0.0001
$C_f * pH_a$	0.71	1	0.71	65.43	< 0.0001
$Q_f * C_f * Q_a * pH_a$	0.18	1	0.18	16.48	< 0.0001
Residual	1.25	115	0.011		
Cor. Total	8.79	127			

the probability value (P-value) was less than the level of significance, α, which implied that all the factors and interaction combinations mentioned in the table are significant.

The statistical analysis of the data obtained yielded a model to predict the response, cyanide removal (R1), incorporating the main effects and the interaction effects of the significant factors. Equation (28) describes the model obtained for the removal of cyanide.

$$\begin{aligned} R1 = {} & 0.30 - 0.053 * pH_f + 0.035 * T - 0.10 * Q_f - 0.094 * C_f + 0.091 * Q_a + 0.11 * pH_a \\ & - 0.056 * pH_f * T - 0.043 * pH_f * C_f + 0.035 * Q_f * C_f - 0.047 * Q_f * pH_a - 0.07 * C_f * pH_a \\ & - 0.037 * Q_f * C_f * Q_a * pH_a \end{aligned} \tag{28}$$

The R^2 and the Adjusted R^2 values for the data were 0.8573 and 0.8424. These values can be considered reasonable for the statistical design of experiments. The f-values at 95 % confidence level ($\alpha = 0.05$), $f_{0.05,\,12,\,115}$, for the model was 1.84, which was much smaller than the calculated f-test statistics value. Also, the P-value for the model was much lower than the level of significance, α. These facts indicate that the model correctly represents the findings.

The optimum operating conditions for maximum removal of cyanide was obtained from the model. The model suggested that the removal of cyanide was maximum when the feed pH was low, acceptor pH was high , feed flow was low, acceptor flow was high, cyanide concentration in feed was low and the temperature of operation was high. The different levels of factors for which the maximum removal of cyanide could be obtained, as suggested by the model, are presented in Table 6.

Table 6. Optimum Operating Condition for Maximum Removal of Cyanide

Factors	pH_f	T	Q_f	C_f	Q_a	pH_a
Coded Values	-1	1	-1	-1	1	1
Experimental Values	3	30 °C	20 ml/min	10 ppm	60 ml/min	12

The straight line trend of residuals in the Normal Probability Plot (Appendix C) confirmed that the assumption of normality of the residuals held true. Although there were a few outliers in the plot, the overall plot nearly represented a straight line. Residual analysis of the data showed that the residuals were evenly distributed across the levels of factors studied and did not show any specific trend, indicating the equality of variance. The plots of residuals against predicted response, predicted response against actual response and residuals against factors, and the response surfaces incorporating different factors are presented in Appendix D.

From the statistical analysis of the removal of cyanide from water under different operating conditions, it can be concluded that all six factors, namely, pH of feed solution, pH of acceptor solution, flow rate of feed solution, flow rate of acceptor solution, concentration of cyanide in feed solution and temperature of environment, were significant. Also, there were effects due to interaction of several factors that affected the removal process. A model was obtained to predict the removal of cyanide from the solutions under different operating conditions. Optimum condition of operation for maximum removal of cyanide was obtained using the predictor model. The assumptions of normality of residuals and equality of variance in statistical analysis of data from factorial experiments were found in compliance.

4.2 Total Dissolved Solids

Industrial process solutions have a wide range of total dissolved solids present in them. Knowledge of the effect of total dissolved solids present in the acceptor solution would be helpful in selecting the area of application of this technology and the process solutions that could be effectively used as acceptor. The effect of total dissolved solids was investigated at optimum conditions obtained from the statistical analysis of data from factorial experiments. Fig. 12 shows the variation of removal of cyanide with changes in total dissolved solids in the acceptor solution. The total dissolved solids in the acceptor solution were varied by addition of reagent grade sodium chloride salt in the alkaline solution at pH 12. The results shown are based on the amount of sodium chloride salt added in the alkaline solution. The values of total dissolved solids do not take into

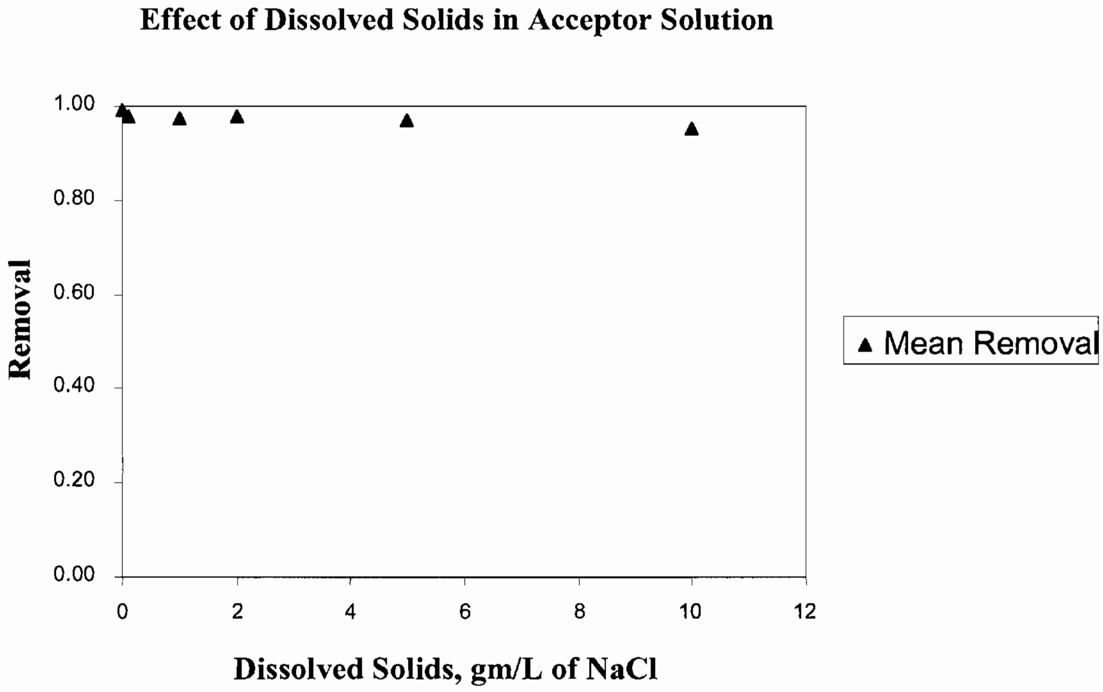


Fig. 12. Effect of Dissolved Solids on Removal of Cyanide

account the dissolved solids resulting from addition of sodium hydroxide to adjust the pH to 12 and the dissolved solids present in deionized water. From Fig. 12, it can be concluded that there is very little effect of dissolved solids in the acceptor solution on removal of cyanide from aqueous solution. There is a small drop in removal efficiency from 0.993 to 0.954 upon addition of 10 gm of sodium chloride salt in one liter of acceptor solution.

4.3 Cyanide Concentration in Acceptor Solution

The concentration of cyanide in the feed and the acceptor solutions affect the concentration of hydrogen cyanide in them. Therefore, it is important and interesting to investigate the performance of the membrane module at different concentrations of cyanide in the feed and acceptor solutions. Fig. 13 shows the removal of cyanide as the cyanide concentration in the acceptor solution changes. From Fig. 13, it becomes apparent that there is some effect of cyanide concentration in acceptor solution on removal efficiency. The removal of cyanide drops from 0.993 to 0.894, about 10 %, when the cyanide concentration in the acceptor solution increases from zero to 500 parts per million CN^- ion. The removal of cyanide then stabilizes and does not decrease further upon increase in cyanide concentration up to 5000 parts per million CN^- ions in the acceptor solution. From these results, it can be inferred that if the acceptor solution is recirculated, the removal efficiency shall decrease slightly as the cyanide concentration in the acceptor solution builds up. It can also be seen that there is a very small decrease in removal efficiency even when the cyanide concentration increased from zero to 100 parts

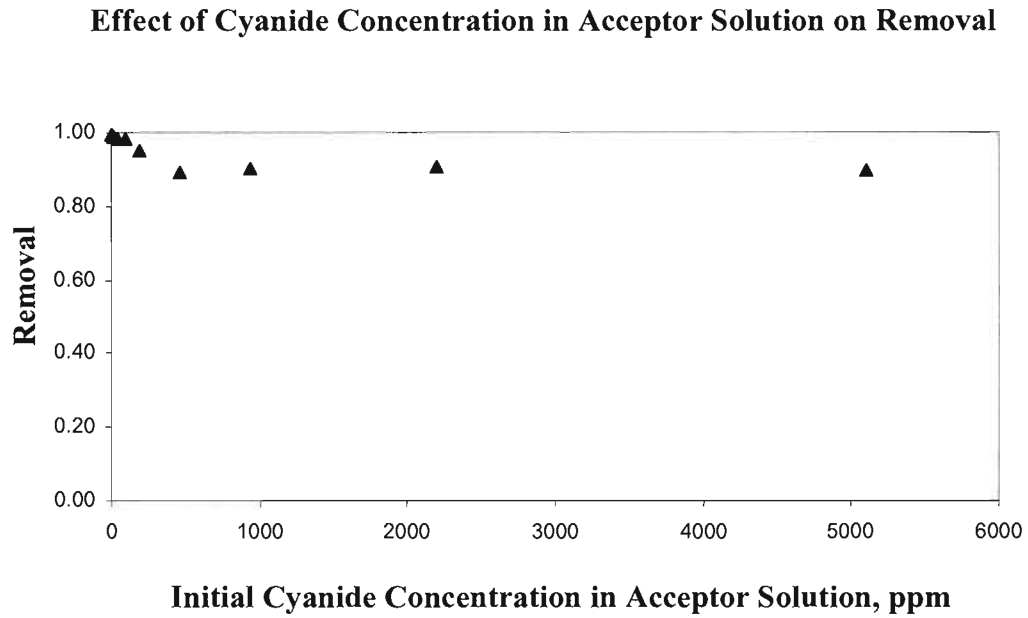


Fig. 13. Effect of Cyanide Concentration in Acceptor Solution on Removal of Cyanide

per million CN^- ions in acceptor solution, implying that the acceptor solution could be recirculated up to the point when the cyanide concentration in the acceptor solution has reached 100 parts per million, without losing much on the cyanide removal efficiency. This finding could be useful in reuse of cyanide solution for leaching application in the industry. Cyanide recovered from process solutions into acceptor solution can be reused for leaching or other applications.

4.4 Lime vs. Sodium Hydroxide

Lime is widely used in industries, especially in mining and metallurgical processing, where it is required to control the pH of the process solutions. Lime is preferred over sodium hydroxide and other reagents due to its lower cost, and easier availability and storage. Fig. 14 compares the removal of cyanide from aqueous solution when sodium hydroxide and calcium hydroxide are used to raise the pH of the acceptor solution. From the results shown in Fig. 14, it can be concluded that sodium hydroxide is a better chemical to raise the pH of the acceptor solution than calcium hydroxide, as the removal of cyanide was greater when sodium hydroxide was used in the acceptor solution, in both co-current and countercurrent flow modes of the feed and the acceptor solutions. From the industrial application point of view, calcium hydroxide can be used in the acceptor solution when the flow mode of solutions is countercurrent, without much loss in removal efficiency. Change in removal of cyanide is observed when two different bases are used to raise the pH of acceptor solution, probably due to differences in alkalinity and base dissociation constant. Another reason for difference in cyanide removal could be the difference in reaction kinetics of hydrogen cyanide with the two chemicals. The use of

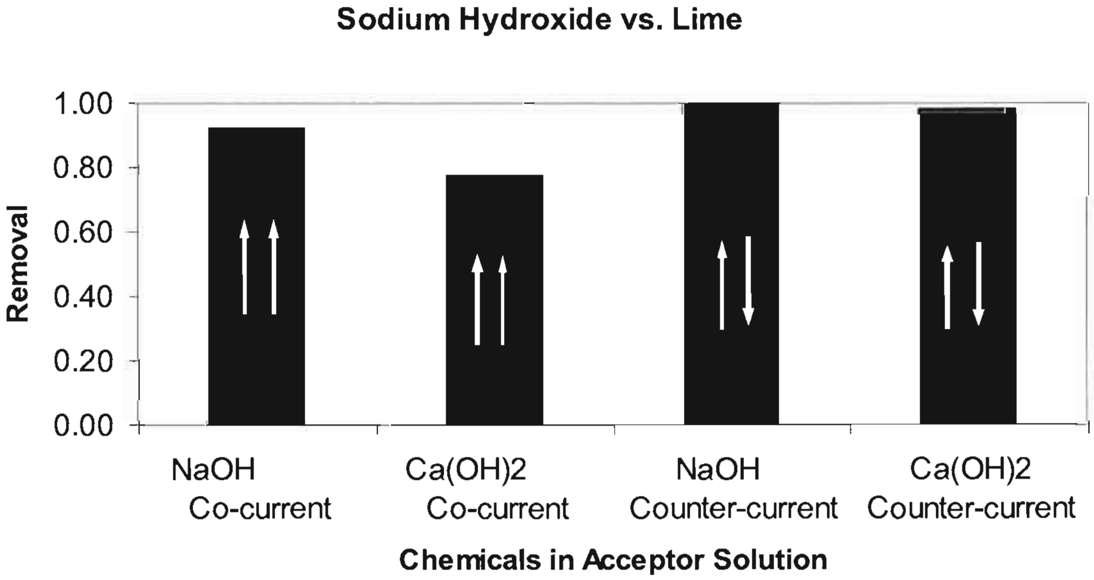


Fig. 14. Comparison of Removal of Cyanide with Sodium Hydroxide and Calcium Hydroxide in the Acceptor Solution

calcium hydroxide will require a pretreatment of acceptor solution to prevent the clogging of membrane pores from the resulting suspended solids.

4.5 Modes of Flow for Feed and Acceptor Solutions

Experiments were conducted to investigate the effect of flow direction for the feed and the acceptor solutions. The results of experiments conducted at optimum operating conditions obtained from the statistical analysis of factorial experiments are displayed graphically in Fig. 14. From the figure, it can be seen that improvement in removal of cyanide was achieved when the mode of flow of feed and acceptor solutions was changed from co-current to countercurrent. The difference in removal of cyanide was prominent when calcium hydroxide was used for the acceptor solution. The higher removal in countercurrent flow could be explained by stating that the feed solution encountered the fresh unloaded acceptor solution as it proceeded along the length of the membrane. On the other hand, in the case of co-current mode, the feed solution encounters the solution that is already loaded with hydrogen cyanide as it proceeds in the membrane fibers. Hence the absorption of hydrogen cyanide in the acceptor solution is lower in co-current mode than in countercurrent mode. From these results, it can be concluded that countercurrent flow of feed and acceptor solution is a better mode of operation for removal of cyanide using hollow fiber membranes as it increased the removal efficiency.

4.6 pH of Feed Solution

The composition of cyanide in solution varies with pH of the solution. At low pH, most of the cyanide is present in the form of hydrogen cyanide, whereas at high pH, cyanide is mostly present as cyanide anion, CN^-. The effect of pH of the feed solution was studied by determining the removal efficiency by the membrane module at different pH of feed solutions in the counter current mode. Fig. 15 shows the removal of cyanide obtained at different pH values for the feed solution. It appears that the removal of cyanide from the feed solution was higher at lower pH and that the removal decreased with an increase in the pH of the feed solution. The removal of cyanide did not vary much between the pH values of 3 to 6, gradually decreased when the pH was 7 and was drastically reduced at pH 9. The higher removal at lower pH could be attributed to the presence of most of the cyanide in solution as hydrogen cyanide. Since at higher pH most of the cyanide in solution is in the form of cyanide anion, small amounts of hydrogen cyanide are formed so that diffusion through the membrane and collection to the acceptor solution is reduced. The insight obtained from the study of the effect of feed solution pH on cyanide removal could be useful in selecting the proper pH of the feed solution for the desired level of removal and for determining the number of stages of treatment required at a certain pH value to reach the target discharge values for cyanide concentration.

4.7 Difference in Temperatures of Feed and Acceptor Solutions

Temperature of operation is an important factor that affects the removal of cyanide from process solutions. Fig. 16 shows the effect of difference in temperatures of feed and acceptor solutions. The feed and acceptor solutions were kept at different temperatures, with differences varying from zero to 25 °C, to observe the changes in removal efficiency. The difference in temperature of the two solutions was obtained by keeping the feed solution at 30 °C and varying the temperature of acceptor solution from 5 °C to

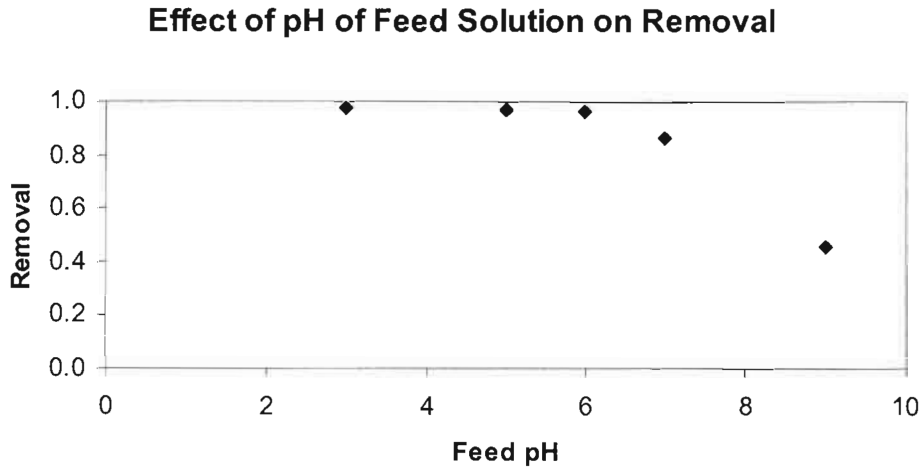


Fig. 15. Removal of Cyanide from the Feed Solution as Function of Feed Solution pH.

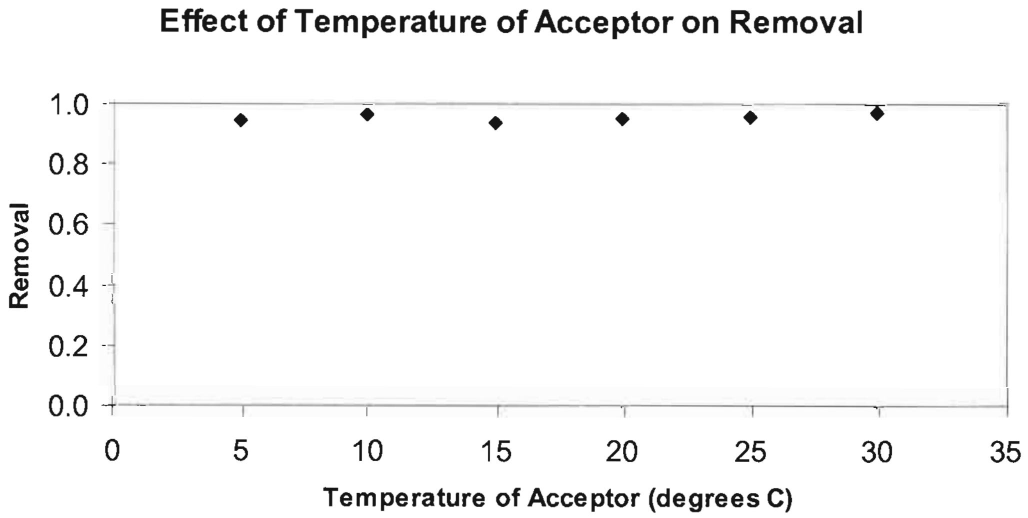


Fig. 16. Removal of Cyanide at Different Temperatures of Acceptor Solution

30 °C. The flow of the two solutions was kept in a countercurrent mode, with feed solution flowing in the lumen side and acceptor solution flowing in the shell side of the membrane.

From Fig. 16, it can be seen that the difference in temperatures of the feed and the acceptor solutions did not have any significant impact on removal efficiency. The removal efficiency appears to improve slightly when the temperature of the feed and the acceptor solutions are equivalent. At equal temperatures of the feed and the acceptor solutions, the vapor pressure due to water might be equal on the two sides of the membrane. This would facilitate the transport of only hydrogen cyanide across the membrane due to the difference in vapor pressure of hydrogen cyanide caused by different concentrations of hydrogen cyanide in the feed and the acceptor solutions. At different temperatures of the two solutions, the water vapor pressure difference on two sides would drive water vapors to migrate, hindering the transport of hydrogen cyanide, resulting into lower removal efficiency for cyanide. Therefore, for maximum removal of cyanide from the feed solution, the temperature of the feed and the acceptor solutions must be higher and equal.

4.8 Mass Transfer Coefficients

The removal of cyanide using membranes is dependent on the mass transfer coefficient of the system. The overall mass transfer coefficient was calculated using Equation (22). The overall mass transfer coefficient, K, is comprised of three components: feed side mass transfer coefficient, k_f, membrane mass transfer coefficient,

k_m and acceptor side mass transfer coefficient, k_a. Equation (25) relates the overall mass transfer coefficient with its three components.

$$\ln\frac{C_d}{C_f} = -K\frac{A}{Q} \tag{22}$$

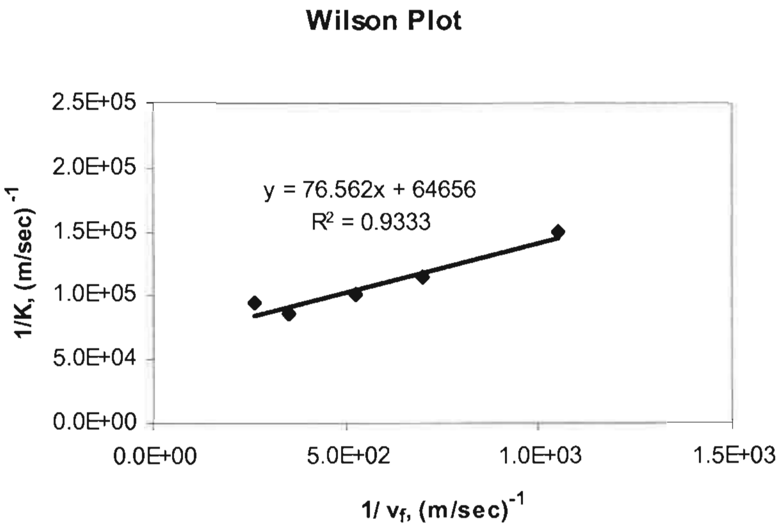
$$\frac{1}{K} = \frac{1}{k_f} + \frac{1}{k_m} + \frac{1}{k_a} \tag{25}$$

With known values of concentration of the feed solution, concentration of discharge solution, flow rate of the feed solution and active area of the membrane, the overall mass transfer coefficient was calculated for different flow rates. The flow velocities of the feed and the acceptor solutions were obtained from Equations (23) and (24), and plots of 1/K and 1/v , where v can be either v_f or v_a, were plotted as per the Wilson Plot method.

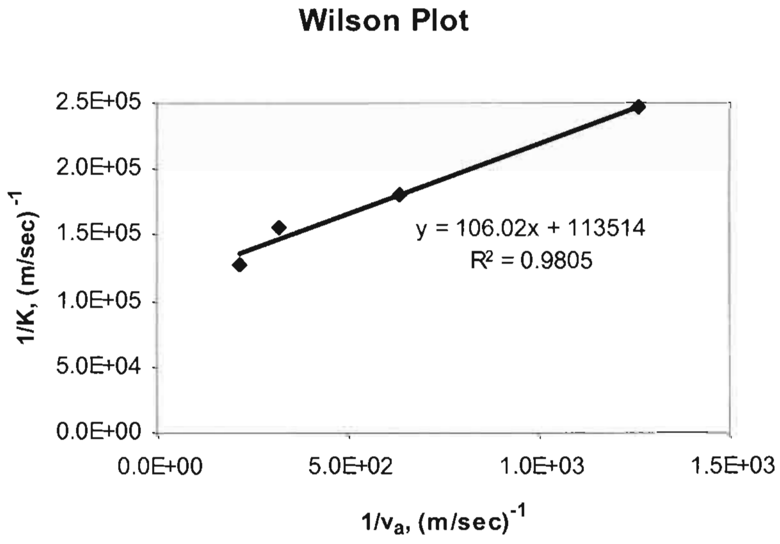
$$v_s = \frac{Q_s L}{V} \tag{23}$$

$$v_t = \frac{Q_t}{n\pi r_i^2} \tag{24}$$

The Wilson plots for feed solution at pH values 3 and 6 and acceptor solution at a pH value 12 using MiniModule 1x 5.5 are displayed in Fig. 17 and Fig.18, respectively.



(a)

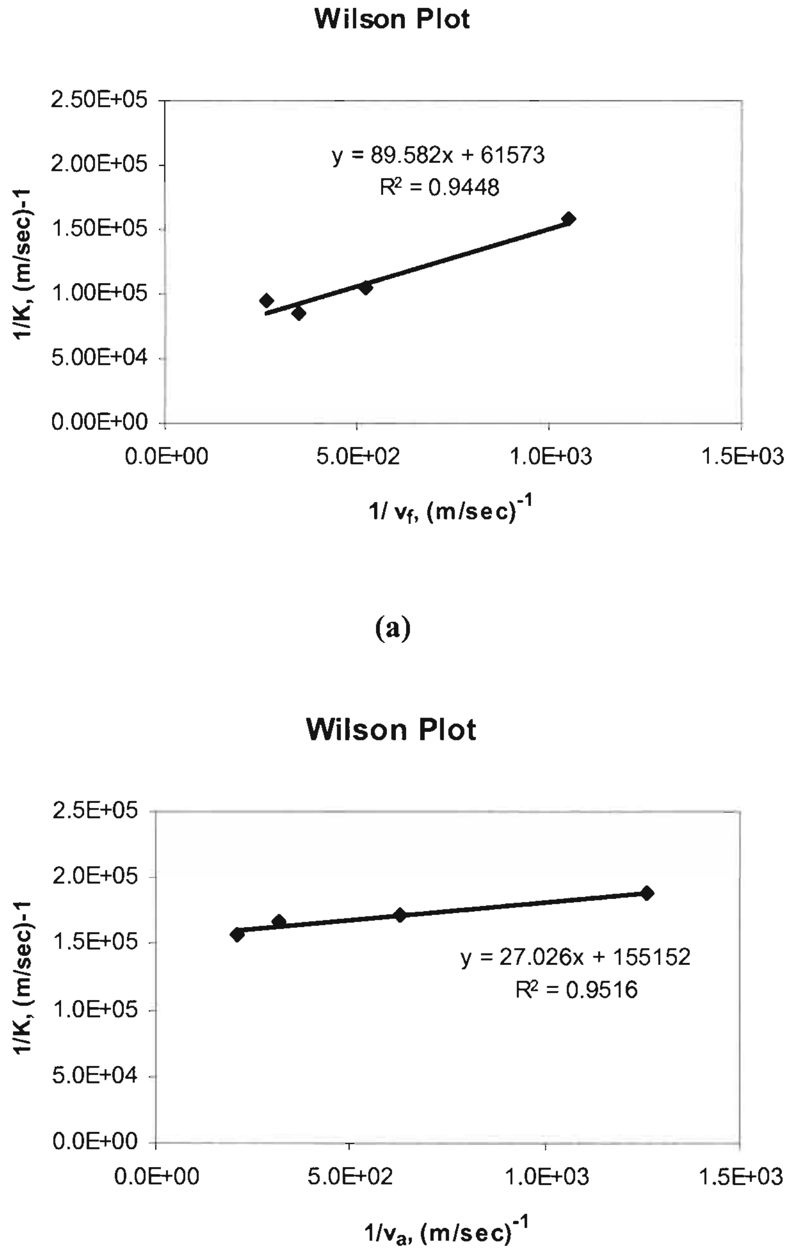


(b)

Fig. 17. Overall Mass Transfer Coefficients for Hydrogen Cyanide at pH of the Feed Solution Equal to 3, Using MiniModule 1 x 5.5.

(a). Variation of Overall Mass Transfer Coefficient with the Feed Solution Velocity.

(b). Variation of Overall Mass Transfer Coefficient with the Acceptor Solution Velocity.



(a)

(b)

Fig. 18. Overall Mass Transfer Coefficients for Hydrogen Cyanide at pH of the Feed Solution Equal to 6, Using MiniModule 1 x 5.5.

(a). Variation of Overall Mass Transfer Coefficient with the Feed Solution Velocity.

(b). Variation of Overall Mass Transfer Coefficient with the Acceptor Solution Velocity

The intercept, I_f, of the straight line plot, from the feed solution flow, provides information on the membrane and the acceptor side mass transfer coefficients.

$$\mathbf{I_f = \frac{1}{k_m} + \frac{1}{k_a}} \tag{26}$$

Similarly, the intercept, I_a, of the straight line plot, from the acceptor solution flow, provides information on the membrane and the feed side mass transfer coefficients.

$$\mathbf{I_a = \frac{1}{k_f} + \frac{1}{k_m}} \tag{27}$$

The overall mass transfer coefficient was calculated with the feed and the acceptor flows at optimum operating condition using Equation (22). The individual components of overall mass transfer coefficient were calculated using the overall mass transfer coefficient value at optimum condition from Equation (22), Equation (25), Equation (26) and Equation (27). The straight line plot of 1/K against 1/v shows that the overall mass transfer coefficient is related to the fluid flow velocities (v_f or v_a), on either side of the membrane. The feed solution flows through the tube side, whereas the acceptor solution flows through the shell side of the MiniModule 1 x 5.5. The values of overall mass transfer coefficient and its components for hydrogen cyanide at pH values 3 and 6, using MiniModule 1 x 5.5, are presented in Table 7.

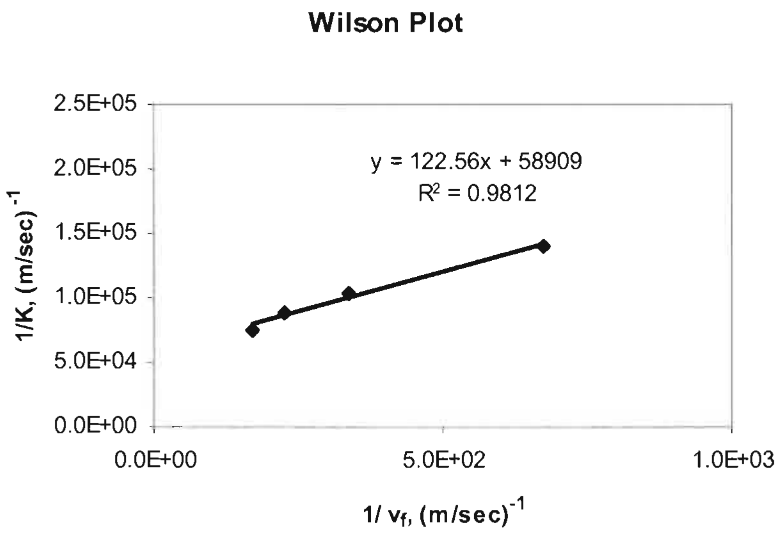
Similarly, the Wilson plots for the feed and the acceptor solutions at the pH values 3

Table 7. Overall Mass Transfer Coefficient and Its Components at pH Values 3 and 6, for Hydrogen Cyanide Using Liqui-Cel MiniModule 1 x 5.5.

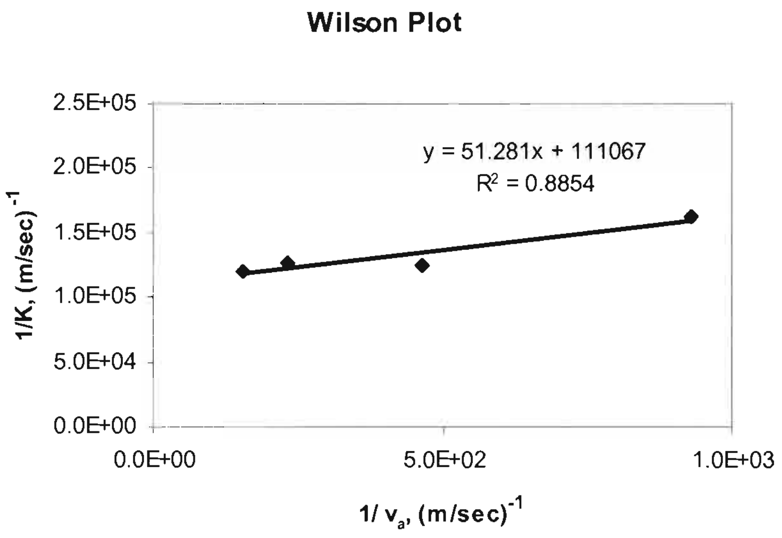
pH	1/K $(m/sec)^{-1}$	I_f $(m/sec)^{-1}$	I_a $(m/sec)^{-1}$	k_f (m/sec)	k_m (m/sec)	k_a (m/sec)	K (m/sec)
3	1.49×10^{5}	6.46×10^{5}	1.13×10^{5}	1.18×10^{-5}	3.45×10^{-5}	2.80×10^{-5}	6.70×10^{-6}
6	1.58×10^{5}	6.16×10^{5}	1.55×10^{5}	1.04×10^{-5}	1.70×10^{-5}	3.81×10^{-4}	6.34×10^{-6}

and 6 using Extra-Flow 2.5 x 8 module are displayed in Fig. 19 and Fig. 20, respectively. The optimum condition for operation of Extra-Flow module was considered similar to that for MiniModule, except that the magnitude of the flow rate of the feed and the acceptor solution varied. The individual components of overall mass transfer coefficient for hydrogen cyanide using the Extra-Flow module were calculated using the overall mass transfer coefficient value at optimum condition from Equation (22), Equation (25), Equation (26) and Equation (27). In this case, as the flow of the feed solution was along the shell side and the flow of acceptor solution was on the tube side, Equation (23) was used to determine the velocity of feed solution, and Equation (24) was used to determine the velocity of acceptor solution. The mass transfer coefficients obtained for the feed side, the membrane and the shell side, in this case, are presented in Table 8.

Comparing the results displayed in Table 7 and 8, it can be observed that the overall mass transfer coefficient, the feed side mass transfer coefficient and the membrane mass transfer coefficient were higher at lower pH (pH value equal to 3), for both the MiniModule and the Extra-Flow module. The acceptor side mass transfer coefficient was higher at higher pH value for both the membrane modules. Also, the overall mass transfer



(a)

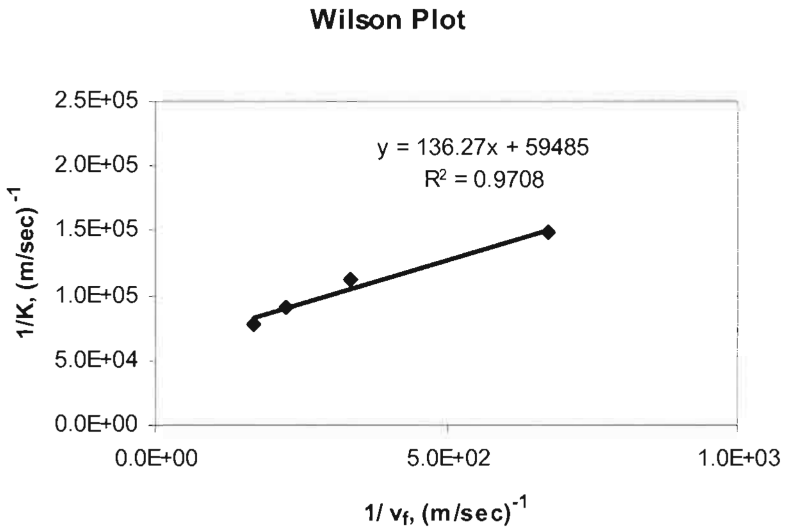


(b)

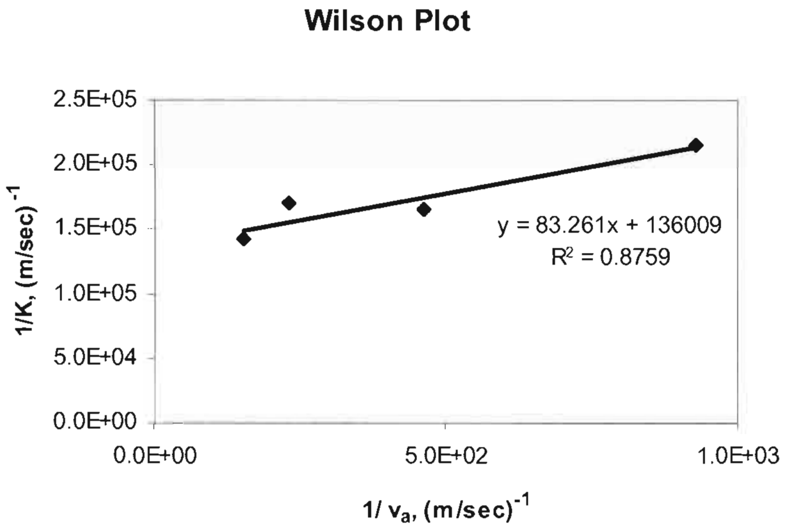
Fig. 19. Overall Mass Transfer Coefficients for Hydrogen Cyanide at pH of the Feed Solution Equal to 3, Using Extra-Flow 2.5 x 8 Module.

(a). Variation of Overall Mass Transfer Coefficient with the Feed Solution Velocity.

(b). Variation of Overall Mass Transfer Coefficient with the Acceptor Solution Velocity



(a)



(b)

Fig. 20. Overall Mass Transfer Coefficients for Hydrogen Cyanide at pH of the Feed Solution Equal to 6, Using Extra-Flow 2.5 x 8 Module.

(a). Variation of Overall Mass Transfer Coefficient with the Feed Solution Velocity.

(b). Variation of Overall Mass Transfer Coefficient with the Acceptor Solution Velocity

Table 8. Overall Mass Transfer Coefficient and Its Components at pH Values 3 and 6, for Hydrogen Cyanide Using Liqui-Cel Extra-Flow 2.5 x 8 Module.

pH	1/K (m/sec)$^{-1}$	I_f (m/sec)$^{-1}$	I_a (m/sec)$^{-1}$	k_f (m/sec)	k_m (m/sec)	k_a (m/sec)	K (m/sec)
3	1.21×10^5	0.59×10^5	1.11×10^5	1.62×10^{-5}	2.03×10^{-5}	1.03×10^{-4}	8.28×10^{-6}
6	1.42×10^5	0.59×10^5	1.36×10^5	1.22×10^{-5}	1.86×10^{-5}	1.74×10^{-4}	7.05×10^{-6}

coefficients and its components have higher values for Extra-Flow module when compared to the values obtained for MiniModule, except in the case of pH value equal to 6. The increase in mass transfer coefficient values may be attributed to the differences in the designs of the two modules. The MiniModule follows the pure parallel flow pattern, in which the feed solution flows in the tube side, and the acceptor solution flows along the shell side, in a countercurrent mode. On the other hand, in case of Extra-Flow module, the feed solution, emanating from the central perforated tube, flows along the shell side in a way across the hollow fiber membranes, into which the acceptor solution flows, resulting into a cross flow pattern. As observed by previous researchers, the cross flow pattern of the flow of the solutions results in the higher mass transfer coefficient. Thus, the Extra-Flow module incorporates the countercurrent mode of flow in a cross flow pattern, which leads to the increase in mass transfer coefficient values even at the higher flux of the feed solution than in the case of MiniModule.

The values of mass transfer coefficients obtained from the experiments are of the similar order as obtained by other researcher in similar application of these membranes. Wickramasinghe et al. [65] carried out experiments to remove cyanide from waste water solution in laboratory scale and pilot scale operations, usng 10 % NaOH solution as an alkaline solution to accept cyanide, at 16 to 20 ^{o}C, with flows of 180 milliliters per minute for both the feed and the acceptor solutions, using self-prepared modules from similar membranes having different pore size and thickness. The values obtained from the experiments and those obtained by Wickramasinghe et al. [65] are compared in Table 9. The slight difference in the values of mass transfer coefficients obtained could be attributed to the difference in operating conditions, membrane properties and acceptor solution concentration. Also, the acceptor side mass transfer coefficient was not calculated by Wickramasinghe et al. [65].

4.9 Performance of Membrane Modules Using Actual Process Solutions

The results obtained from the experiments conducted to study the removal of cyanide from aqueous solutions using Hollow Fiber Membranes show that the technology was effective in removing and recovering cyanide from the solutions prepared in the laboratory under optimum conditions of operation. The performance of the modules might change with the actual process solutions in the industries, due to changes in

Table 9. Comparison of the Experimental Mass Transfer Coefficients Values Obtained from This Research and by Other Researcher.

Module	**pH**	**1/K** $(m/sec)^{-1}$	**I_f** $(m/sec)^{-1}$	**I_a** $(m/sec)^{-1}$	**k_f** (m/sec)	**k_m** (m/sec)	**k_a** (m/sec)	**K** (m/sec)
1 x 5.5	**3**	1.49×10^5	0.65×10^5	1.13×10^5	1.18×10^{-5}	3.45×10^{-5}	2.80×10^{-5}	0.67×10^{-5}
1 x 5.5	**6**	1.57×10^5	0.62×10^5	1.55×10^5	1.04×10^{-5}	1.70×10^{-5}	3.81×10^{-4}	0.63×10^{-5}
2.5 x 8	**3**	1.21×10^5	0.59×10^5	1.11×10^5	1.62×10^{-5}	2.03×10^{-5}	1.03×10^{-4}	0.83×10^{-5}
2.5 x 8	**6**	1.42×10^5	0.59×10^5	1.36×10^5	1.22×10^{-5}	1.86×10^{-5}	1.74×10^{-4}	0.71×10^{-5}
Literature (Wickramasinghe et al, 2004)					2.31×10^{-5}	3.53×10^{-5}	-	1.11×10^{-5}

solution chemistry. The performance of membrane modules in removal of cyanide could be tested and verified by performing experiments using actual process solution samples. Various solutions having different solution composition could be tested under optimum conditions obtained to compare the results with those obtained from experiments conducted with synthetic solution prepared at the laboratory.

The performance of hollow fiber membrane modules for removal of cyanide from aqueous solutions was tested using actual process solution provided by Newmont Mining Corporation. Fig. 21 shows a simple flow sheet explaining the different steps involved in gold cyanidation and the process solutions present in the plant. The removal of cyanide from solutions was studied using both the MiniModule 1 x 5.5 and Extra-Flow 2.5 x 8 module. Two different solutions with different cyanide concentrations and chemical composition were tested. The Reverse Osmosis (RO) Permeate, a solution obtained as a product from Reverse Osmosis water treatment plant at Newmont's Minera Yanacocha operation in Peru, had cyanide concentration of about 8 parts per million when received. The total cyanide concentration present in the solution was 8.69 parts per million of cyanide anion. The total dissolved solids in the solution was 89 parts per million, with most of the metal ions present in concentrations less than 0.05 parts per million, except calcium, sodium, and potassium, which were present in concentrations ranging from 2.05 to 26 milligrams per liter. The flow rate of the Reverse Osmosis Permeate solution in the actual plant operations is 240 cubic meters per hour.

Another solution called the Barren solution, a cyanidation plant solution from which gold is stripped, had a cyanide concentration of about 24 parts per million in a sample received from the plant. The Barren solution at the plant had a total cyanide

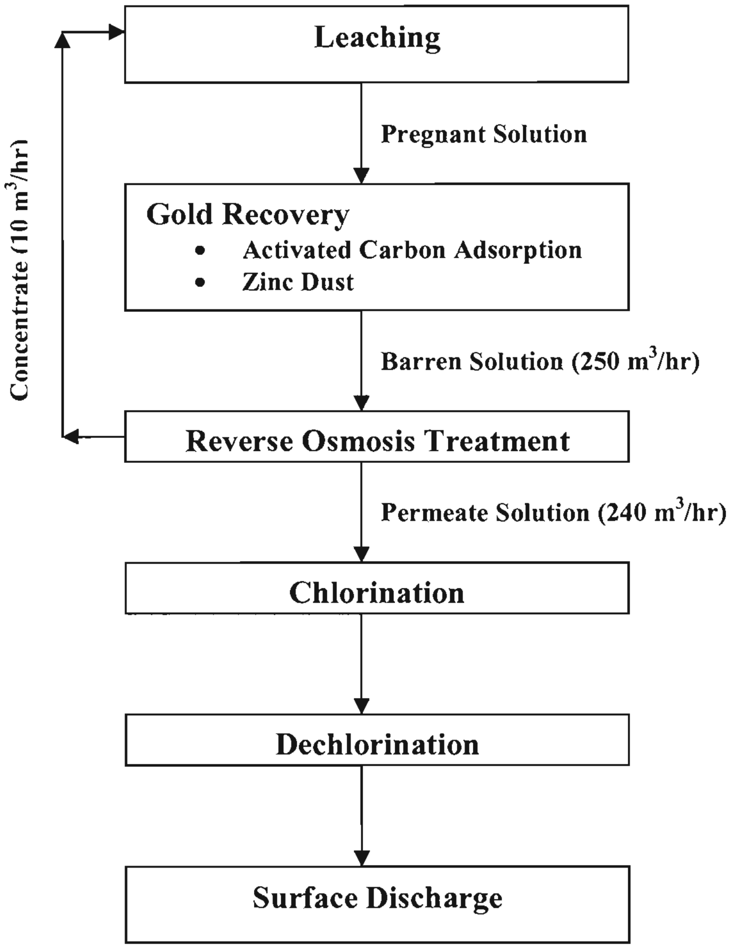


Fig. 21. Different Steps and Solutions Present in the Gold Cyanidation Plant

concentration of 78.9 parts per million of cyanide anion, with a Free cyanide concentration of 44.2 parts per million and Weak Acid Dissociable (WAD) cyanide concentration 31.3 parts per million of cyanide anion.. The total dissolved solids present in the solution was 2269 parts per million with high concentrations of metals such as calcium, copper, potassium, sodium, arsenic, selenium, molybdenum and antimony ranging from 0.12 to 376 milligrams per liter. The Barren solution is fed to the Reverse Osmosis Plant at a flow rate of 250 cubic meters per hour, to separate heavy metals and other contaminants from the gold stripped solution. Details about the chemical composition of the Reverse Osmosis Permeate solution and the Barren solution are presented in Appendix E.

The removal of cyanide using hollow fiber membrane technology was tested using the two solutions to observe the performance of membrane modules with actual process solutions at two different feed pH levels: pH equal to 3 and pH equal to 6. The pH of the solutions as received was about pH 10 to prevent cyanide from degrading naturally. For experiments, the pH of these solutions was adjusted to 3 and 6 using concentrated hydrochloric acid. Three liters of each solution was taken out of the five gallon bucket and the pH adjusted to the required level for the experiments with Extra-Flow membrane module. Five hundred milliliters of the solutions were used for experiments with MiniModule. Table 10 and Table 11 present the results for cyanide removal obtained using actual process solutions, and Table 12 compares the overall mass transfer coefficients for hydrogen cyanide obtained using the synthetic solution, the Reverse Osmosis Permeate solution and the Barren solution. The overall mass transfer coefficients for hydrogen cyanide obtained from the experiments are of similar order,

Table 10. Removal of Cyanide from Actual Process Solutions Using MiniModule 1 x 5.5.

Exp.	Feed	pH_f	Q_f	Q_a	Feed	Discharge	Removal	K	v
			ml/min	ml/min	ppm	ppm		m/sec	m/sec
1	Permeate	3	20	60	7.00	0.276	0.961	5.98×10^{-6}	9.54×10^{-4}
3	Permeate	6	20	60	7.75	0.584	0.925	4.79×10^{-6}	9.54×10^{-4}
5	Barren	3	20	60	22.70	2.100	0.907	4.41×10^{-6}	9.54×10^{-4}
7	Barren	6	20	60	24.00	5.970	0.751	2.58×10^{-6}	9.54×10^{-4}

Table 11. Removal of Cyanide from Actual Process Solutions Using Extra-Flow 2.5 x 8 Module.

Exp.	Feed	pH_f	Q_f	Q_a	Feed	Discharge	Removal	K	v
			ml/min	ml/min	ppm	ppm		m/sec	m/sec
2	Permeate	3	200	600	6.99	0.508	0.927	6.24×10^{-6}	1.48×10^{-3}
4	Permeate	6	200	600	6.96	0.692	0.901	5.50×10^{-6}	1.48×10^{-3}
6	Barren	3	200	600	22.80	1.510	0.934	6.46×10^{-6}	1.48×10^{-3}
8	Barren	6	200	600	23.90	7.980	0.666	2.61×10^{-6}	1.48×10^{-3}

Table 12. Comparison of Overall Mass Transfer Coefficients Obtained Using Synthetic, Reverse Osmosis Permeate and Barren Solutions.

			K (m/sec)		
Sl. No.	Module	pH_f	Synthetic	RO Permeate	Barren
1	1 x 5.5	3	6.70×10^{-6}	5.98×10^{-6}	4.41×10^{-6}
2	2.5 x 8	3	7.14×10^{-6}	6.24×10^{-6}	6.46×10^{-6}
3	1 x 5.5	6	6.34×10^{-6}	4.79×10^{-6}	2.58×10^{-6}
4	2.5 x 8	6	5.16×10^{-6}	5.50×10^{-6}	2.61×10^{-6}

though it was highest for synthetic solution and lowest for the barren solution. The mass transfer coefficients obtained for the synthetic solution and the Reverse Osmosis Permeate solution are close to each other because these solutions are almost free of other contaminants. The synthetic solution was prepared from laboratory deionized water and sodium cyanide, whereas the Reverse Osmosis Permeate solution is obtained as a product from the Reverse Osmosis that is one of the tightest filtration techniques, ideally allowing only water to pass through the Reverse Osmosis membrane. Both of these solutions contained cyanide as the primary contaminant in them. On the other hand, the barren solution might consist of a variety of chemical salts and complexes. The Barren solution is the resulting solution after gold is stripped from the loaded solution. This solution, generally, is high in total dissolved solids and cyanide concentration. Cyanide being present in the form of variety of complexes in the Barren solution, the dissociation of these complexes under low pH conditions might be difficult or slow. The presence of metal cyanide complexes in the Barren solution, especially at higher pH 6, might have resulted in the lower the overall mass transfer coefficient of hydrogen cyanide.

Another reason for lower overall mass transfer coefficient of hydrogen cyanide in the case of the Barren solution could be the residence time of the solution in the hollow fiber membranes, which was insufficient for the cyanide present in higher concentration in the solution to diffuse through the membrane.

Aging of the membranes could be another reason for differences in overall mass transfer coefficients obtained for different solutions. As the microporous hollow fiber membranes are continuously used, the water present in the solution vaporizes and condenses in the pores, gradually deteriorating the hydrophobic properties of the membrane. When the membrane pores are filled with water, they no longer allow the transport of gaseous hydrogen cyanide freely, and also cause the alkaline acceptor solution or the acidic feed solution to get transported on the other side of the membrane. If the pressure on the acceptor side is higher, the alkaline solution will leak into the acidified feed solution, raising its pH and, hence, lowering the hydrogen cyanide concentration in the feed solution, and finally lowering the removal of cyanide. This phenomenon might be useful in explaining our observation of higher pH of the discharge solution, which was termed as membrane failure.

Although there were differences in the removal of cyanide and the overall mass transfer coefficients for hydrogen cyanide using the three different solutions, the membrane modules were able to remove greater than 90 % of cyanide when the feed solution pH was adjusted to 3. Except for the Barren solution, the membrane modules were able to remove more than 90 % of cyanide even when the pH of the feed solution was equal to 6. Therefore, it can be considered that the hollow fiber membrane technology was successful in removing and recovering cyanide from the actual process solutions.

CHAPTER 5

ENGINEERING CONSIDERATIONS FOR SCALE-UP

In industry, since the production of metals is carried out in large quantities, huge volumes of process solutions are generated and used. The flow rates of solutions are much higher than the flow used in laboratory experiments to investigate the use of hollow fiber membrane technology in the removal and recovery of cyanide. In order to treat the huge volume of solutions, very large modules with high membrane surface area are required to handle high flow rates. For the successful implementation of this technology at larger scale, the issues associated with the scale up of the membrane modules must be investigated to avoid surprises. Engineering details must be considered in detail to transform the technology from the laboratory scale to the full size industrial scale. The issues associated with scale-up and industrial application of this technology are identified and discussed in this chapter. Several factors were identified that could be important in the design of membrane modules and the process flow sheet for successful implementation of this technology. They are the following:

1. Process Solutions
2. Flow Rate of the Solutions
3. Membrane Surface Area
4. Mode of Flow for Feed and Acceptor Solutions

5. Module Design and Geometry
6. Circuit Design for Multiple Membrane Modules

All these factors might be critical in planning the industrial application of hollow fiber membrane technology. The understanding of the effect of these factors will help in determining the type, the size and the number of membrane modules required to treat a specific process solution with known cyanide concentration, pH and flow rate, for cyanide removal.

5.1 Process Solutions

A variety of process solutions is present in any cyanidation plant. Each solution has its own physical and chemical characteristics. In order to choose an appropriate solution for application of hollow fiber membrane technology, it is necessary to find out the characteristics that favor the removal of cyanide. From the results of laboratory experiments, it is clear that the cyanide removal is best when the solution has a lower concentration of cyanide, the pH of the solution is low, and the solution temperature is high. The pH of the feed solution is an important factor to determine the number of stages required to reach a desired cyanide concentration level for the discharge solution. Also, from the results of actual process solutions, it was seen that cyanide removal was better for the Reverse Osmosis Permeate solution than for the Barren solution that had high dissolved solids and other cyanide complexes, suggesting that a cleaner solution was better for maximum cyanide removal using hollow fiber membranes. The removal of cyanide present in the form of strong complexes that can not be dissociated by the addition of acid in the solution has not been investigated. With our understanding of the removal process, strong cyanide complexes that do not dissociate at low pH would not be able to form hydrogen cyanide, and hence, its transport through the membrane would not occur. In addition, the solution must be free from suspended solids as the pores of membranes might clog with solid particles present in the feed solution. Therefore, the pretreatment of the feed stream for the removal of suspended solids is a must for successful operation this technology. These points must be kept in mind while selecting the feed solution from which cyanide is to be removed.

When selecting the acceptor solution, the pH, cyanide concentration in the solution, temperature and the dissolved solids present in the solution must be considered. From our experiments, it was observed that the cyanide removal was maximum when the pH and the temperature of the acceptor solution were high and the total dissolved solids and the cyanide concentration in the solution were low. The removal of cyanide decreased slightly when the cyanide concentration in the acceptor solution rose to 500 parts per million. Upon further increase in cyanide concentration, the removal was not affected much. With increase in dissolved solid contents in the solution, the removal of cyanide gradually decreased. Also, sodium hydroxide in the acceptor solution yielded better cyanide removal than lime. These observations suggested that for better cyanide removal, the acceptor solution will have lower cyanide concentration, lower total dissolved solids, and sodium hydroxide instead of lime, present in it. As in the case of selecting the feed solution, the pretreatment of the acceptor stream for the removal of suspended solids is necessary to prevent the pores of membranes from clogging.

5.2 Flow Rate of the Solutions

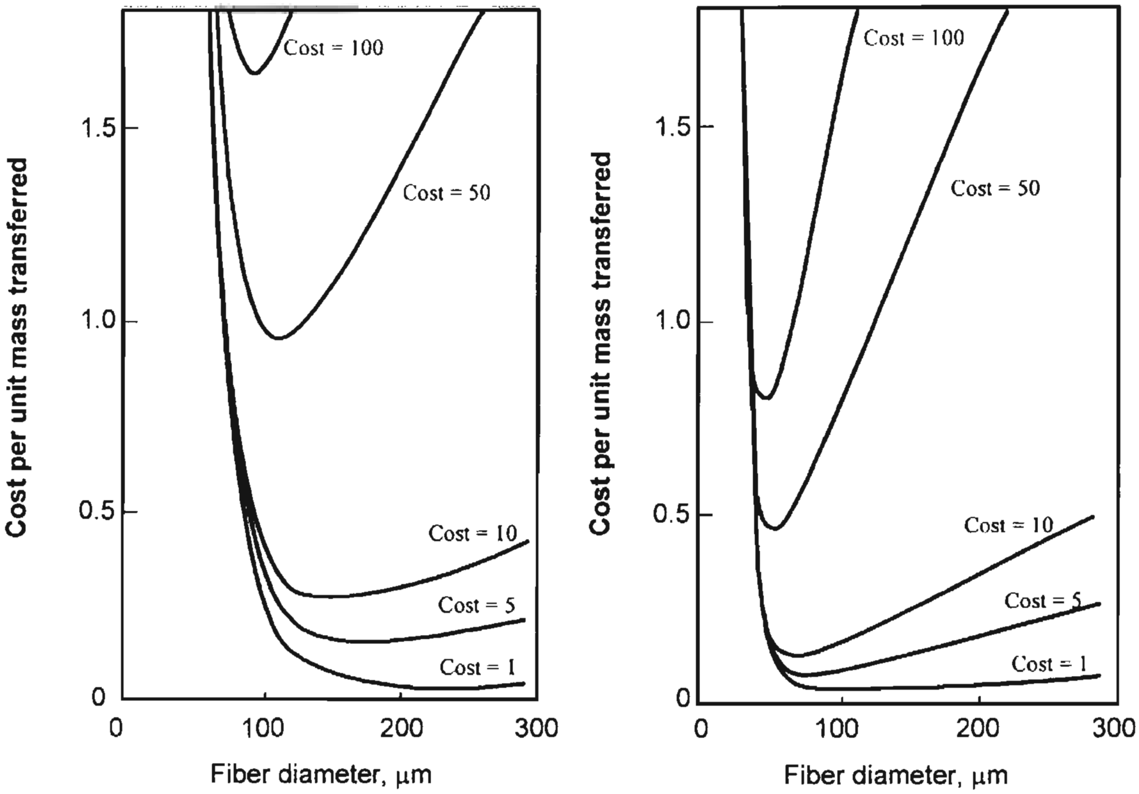
The flow rates of the feed and the acceptor solution determine the residence time of the solutions in a membrane module. The flow rate of feed solution determines the flux through the membrane module calculated as flow rate per unit area of the membrane, which is the industry practice to determine the size of the membrane modules required for a specific flow. The higher the flux, the greater the load on the membranes and the lower the residence time of the solution in the membrane module, resulting into lower removal. The flow rate of feed solution determines the size and the number of membrane modules required to treat the volume of solution generated. Also, the flow rate of the acceptor solution is useful in determining the volume of the acceptor side of the membrane. In addition, from the results of the experiments, it was found that the removal of cyanide was improved when the flow rate of the acceptor solution was high. This might be attributed to the ready availability of fresh unloaded acceptor solution for reaction with diffused hydrogen cyanide on the acceptor side.

5.3 Membrane Surface Area

The microporous hollow fiber membranes consist of numerous pores that allow the diffusion of hydrogen cyanide through them. The mass of hydrogen cyanide diffusing through the pores of the membranes per unit time will increase if the number of pores in the membranes increases. For certain porosity of the membrane material, the number of pores in a membrane will increase with increase in membrane area. Therefore, for increase in the removal of cyanide, the available membrane surface area should be high. If the membrane surface area is higher for a fixed flux of the feed solution through the membrane module, the flow rate of the feed solution the membrane can handle without compromising on the discharge concentration will be higher. Therefore, fewer membranes will be required to handle the total volume of the feed solution.

The surface area of membranes could be increased by increasing the inner and outer diameter and/or the length of the membrane. The total surface area of the membranes in any membrane module could be increased by increasing the number of hollow fiber membranes in the module. As investigated by Wickramasinghe et al. [61], there exists an optimum for the diameter of the hollow fiber membrane for the minimum cost per unit mass transfer. For a fixed length of membrane, with increase in the membrane diameter, the pumping cost will decrease but the membrane cost will increase. Also, with increase in the length, the optimum diameter will increase for a fixed cost per unit mass transfer, as the pumping cost will increase due to larger lengths of modules, suggesting higher membrane diameters to check the increase in pumping cost. Fig. 22 and Fig. 23 present the variation of cost per unit mass transferred with fiber diameter, for fixed membrane length and fixed membrane cost, respectively, obtained from oxygen and bromoform stripping.

The membrane surface area for a module can be increased by increasing the number of the hollow fibers in it. For fixed module geometry, increasing the number of hollow fibers will lead to the decrease in flow in each membrane and, hence, the velocity of the fluid flowing inside the fiber will decrease. The shell side volume will also decrease with increase in the number of fibers.

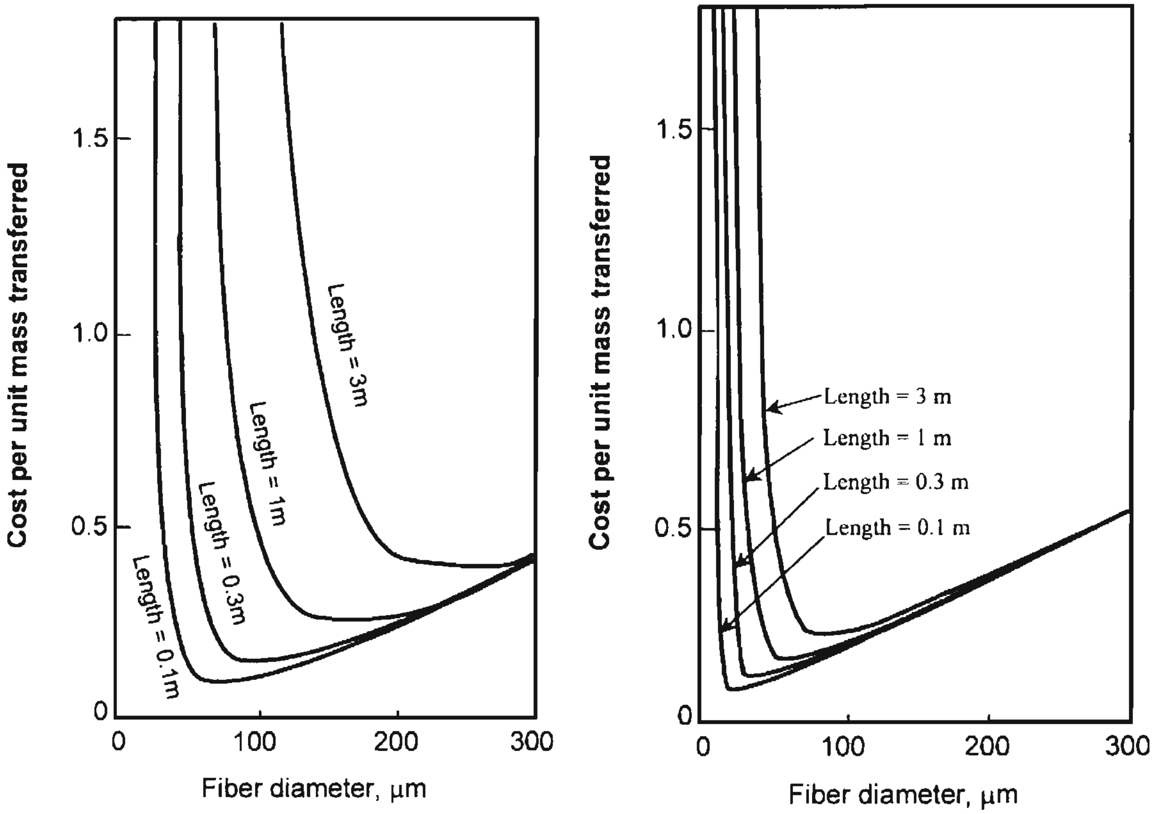


(a) **(b)**

Fig. 22. Cost Per Unit Mass Transferred for Oxygen and Bromoform Stripping at Fixed Membrane Module Length [5].

(a). Cost Per Unit Mass Transferred ($/(mol/minute)) for Oxygen Stripping from Water into Nitrogen Using a Module 1 m in Length. The Parameter is Membrane Cost in $/m^2 year.

(b). Cost Per Unit Mass Transferred ($/(mol/minute)) for Bromoform Stripping. Again the Module is 1 m in Length, and the Parameter is Membrane Cost in $/m^2. year.



(a)

(b)

Fig. 22. Cost Per Unit Mass Transferred for Oxygen and Bromoform Stripping at Fixed Membrane Module Cost [5].

(a). Cost Per Unit Mass Transferred (\$/(mol/minute)) for Oxygen Stripping. This Figure Shows the Effect of Module Length for a Fixed Membrane Cost of \$10/m^2 year.

(b). Cost Per Unit Mass Transferred (\$/(mol/minute)) for Bromoform Stripping. This Figure Shows the Effect of Module Length for a Fixed Membrane Cost of \$10/m^2 year

5.4 Mode of Flow for Feed and Acceptor Solutions

The feed and the acceptor solution can flow in the membrane module with different types of flow patterns depending on the direction of flow of the solutions. The two types of flow patterns are the parallel flow and the cross flow. When the flow of feed solution is parallel to the flow of acceptor solution, the flow pattern is called Parallel flow pattern. When the flow of the solutions is perpendicular to each other, the flow pattern is called Cross flow pattern. In the Parallel flow pattern, two modes are possible: the co-current and the countercurrent modes of flow. In the co-current mode of flow, the two solutions flow parallel to each other and in the same direction, whereas in the countercurrent flow, the two solutions flow parallel to each other but in opposite directions. Wang and Cussler [49] found that the parallel flow countercurrent mode of flow must be preferred when the membrane or the tube side resistance controls the transport process, whereas cross flow pattern must be used when the shell side resistance is significant. They also found that the flow normal rather than parallel to the fibers led to higher mass transfer coefficient but, at the same time, decreased the efficiency. The efficiency could be increased by introducing baffles that provide the elements of both the countercurrent parallel flow and the cross flow.

In the experiments conducted to compare the performance of the MiniModule 1 x 5.5 and the Extra-Flow 2.5 x 8modules for the removal and recovery of cyanide, it was observed that the overall mass transfer coefficient for hydrogen cyanide was better in the case of the Extra-Flow 2.5 x 8 module than the MiniModule 1 x 5.5, even with higher feed flux in case of the Extra-Flow 2.5 x 8 module. These results confirmed that the Extra-Flow module, which had a central baffle, provided better mass transfer coefficient and efficiency of removal than the MiniModule 1 x 5.5 , which had no baffles. In the case of the Extra-Flow 2.5 x 8 module, the feed solution moved along the shell side while the acceptor solution passed through the tube side, which was opposite to that in case of the MiniModule 1 x 5.5.

The results of experiments to compare the removal of cyanide obtained in the co-current and countercurrent mode show that the countercurrent mode of flow yielded higher removal than in the co-current mode. In the countercurrent mode, the relative velocity of the two solutions is higher than in co-current mode. Also, the feed solution faces the less loaded acceptor solution as it moves along, resulting into higher removal.

5.5 Module Design and Geometry

The design and geometry of the membrane modules depend on the length and the diameter of the membranes, the number of hollow fiber membranes, the shell side volume, the knowledge of the solutions flowing inside the module, the volume of solution to be treated per unit time and the flow rate of solutions through the module. The length of the module is a key design parameter as it is directly related to the number of modules required. Longer modules offer higher efficiency but at the cost of pressure drop. For an optimum diameter of hollow fiber membranes, the length and the number of hollow fibers in a module can be obtained from the total surface area of membranes required for successful removal of cyanide at a given flux. As discussed previously, the cross flow pattern with baffles, as in case of the Extra-Flow module, is a better design for higher overall mass transfer coefficient. The feed solution flowing in the shell side of the module provides higher membrane surface area for interaction due to a larger outer diameter. The total volume of the solution to be treated per unit time provides help in calculating the total membrane surface area required, whereas the flow rates of the feed and the acceptor solutions are used to calculate the length and the number of the hollow fiber membranes and the shell side volume in a module. The available surface area of the membranes for the shell side flow of the feed solution, A_s, is given by Equation (30). On the other hand, the available surface area of the membranes for the tube side flow of the feed solution, A_t, is given by Equation (31).

$$\mathbf{A_s = 2\pi r_o L_s n} \tag{30}$$

$$\mathbf{A_t = 2\pi r_i L n} \tag{31}$$

where

r_o = The outer radii of the hollow fiber membranes

r_i = The inner radii of the hollow fiber membranes

L_s = The length of the shell side

L = The length of the hollow fiber membranes

n = The number of hollow fiber membranes in a module

For the industrial applications, the objective of the design exercise is to minimize the cost per amount of mass transferred, which may not necessarily coincide with the maximum solute transferred per unit volume.

5.6 Circuit Design for Multiple Membrane Modules

Industrial process solutions are generated in huge volumes and a single membrane module shall be insufficient in treating the solution successfully. Therefore, multiple membrane modules might be required to handle huge volumes of process solutions. Also, a single stage of membrane separation might not be sufficient to reach the desired level of cyanide concentration in the discharge solution. Multiple membrane modules will be required to adequately treat the huge volumes of process solutions in series and parallel combination. A circuit design for multiple membrane modules in use is required to be prepared to determine the total number of modules required and the appropriate placement of these modules in series and parallel connections.

The pH of the feed solution is an important parameter that determines the number of stages required for the removal of cyanide to the desired concentration in the discharge solution. Fig. 15 shows the effect of the pH of the feed solution on the removal of cyanide. For the target concentration of the discharge solution as 0.2 parts per million, which is the current Drinking Water Standard for cyanide in water as established by USEPA, the number of stages of the membrane treatment required for the feed solution with 10 parts per million of cyanide is shown in Fig. 24, at different pH values. The number of stages of membrane treatment required was calculated using Equation (32).

$$\mathbf{C_{d_n} = C_f(1 - R)^n} \tag{32}$$

Equation (32) can be rearranged and written as Equation (33):

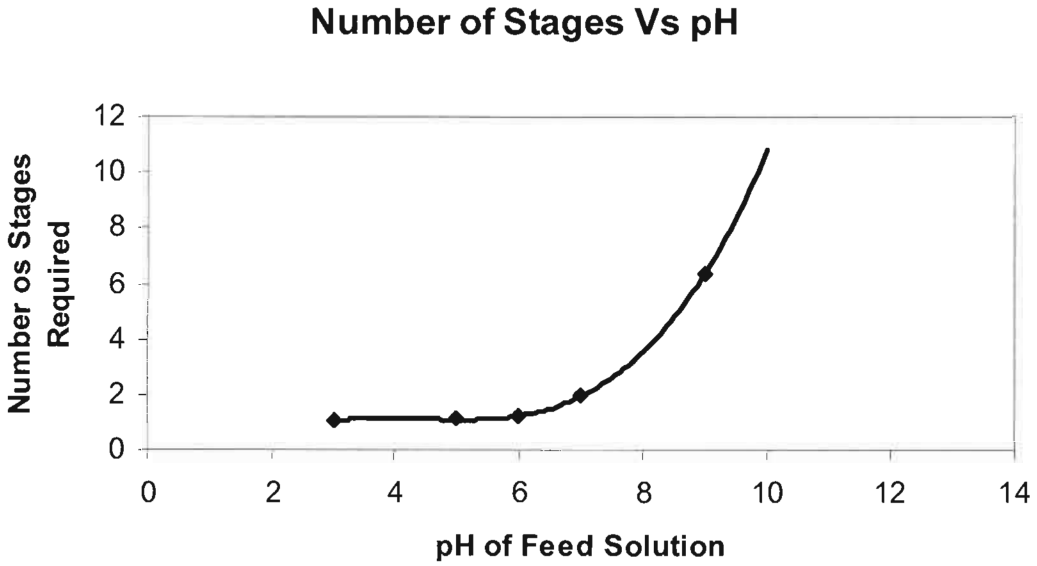


Fig. 24. Number of Stages of Membrane Treatment Required for the Feed Solution at 10 ppm of Cyanide, to Reach the Discharge Concentration of 0.2 ppm of Cyanide, at Various pH Levels of the Feed Solution.

$$\mathbf{n} = \frac{\mathbf{Ln}(\frac{\mathbf{C}_{\mathbf{d\,n}}}{\mathbf{C}_{\mathbf{f}}})}{\mathbf{Ln(1-R)}} \tag{33}$$

where

n = The number of stages of membrane treatment.

$C_{d\,n}$ = The concentration of cyanide in the Discharge Solution after n stages.

C_f = The concentration of cyanide in the Feed Solution.

R = The fraction of cyanide removed in a single stage.

From Figure 24, it can be seen that as the pH of the feed solution increases, the number of stages required to reach the target discharge concentration of 0.2 parts per million of cyanide increases exponentially. At very high pH of the feed solution, when the all the cyanide is present in the solution is in the form of cyanide anion, CN^-, infinite stages will be required, as no hydrogen cyanide is present in the feed solution that could transport across the membrane. Similarly, at very low pH of the feed solution, all the cyanide present in the solution will be in the form of hydrogen cyanide, and a single stage of membrane treatment would be enough to allow the removal of cyanide from the feed solution. The exponential nature of the graph, running asymptotically as it approaches pH 9, confirms our hypothesis that the removal of cyanide in hollow fiber membrane technology occurs mainly due to the transportation of hydrogen cyanide from the feed solution side to the acceptor solution side.

The number of stages required for the treatment of feed solution provides the number of membrane modules required to be placed in series connection. The total volume of feed solution to be treated per unit time can be used to calculate the number of membrane modules required to be placed in parallel connection for a fixed membrane module size. Equation (34) is used to calculate the number of membrane modules required to be placed in parallel connection.

$$\mathbf{n_p = \frac{Q_p}{Q_f}} \tag{34}$$

where

n_p = The number of membrane modules in parallel connection

Q_p = Flow rate of the process solution to be treated

Q_f = Optimum Flow Rate of the feed solution for a single membrane module

Since the membrane modules cannot be in fractions, the next higher integer is used as the number of membrane module required to be placed in series and parallel connection. The product of number of membrane modules in series and number of membrane modules in parallel connection provides the total number of membrane modules required to treat the entire volume of process solution.

In order to avoid a large number of membrane modules required, a membrane module of appropriate length could be used to carry out a single stage treatment of process solution. The appropriate length can be calculated depending on the membrane surface area required for single stage treatment of the feed solution. As discussed previously, the membrane surface area of the module can be changed by increasing the length of the hollow fiber membranes, the inner and outer diameters of the hollow fibers and the number of hollow fiber membranes in a module. In order to avoid the increase in the number of membrane modules to be placed in series due to rounding off of the fractional part of the calculated number of modules in series, the length of the membrane modules can be adjusted accordingly.

An example of calculations for the length and the number of modules required for the treatment of process solutions in a mine is discussed further. The flow rate of Reverse Osmosis Permeate Solution and the Barren Solution at Minera Yanacocha Mine operated by Newmont Mining Corporation, are 240 cubic meters per hour and 250 cubic meters per hour (obtained from verbal communication with Mr. Charles Bucknam of Newmont Mining Corporation). The removal of cyanide from these solutions using the MiniModule 1 x 5.5 and the Extra-Flow 2.5 x 8 modules have been studied previously, while comparing the performance of the membrane modules for the removal of cyanide from actual process solutions. Based on the results of the experiments, further calculations were conducted to arrive at the number of modules required to treat the entire flow of the Reverse Osmosis Permeate Solution and the Barren Solution, for both the membrane modules, separately. Table 13 and Table 14 provide details about the number of stages of membrane treatment required, the appropriate length of the membrane modules if a single stage treatment was preferred, and the total number of the membrane modules required to handle the entire flow of process solutions, for the feed solution at pH value equal to 3 and pH value equal to 6, using MiniModule 1 x 5.5 and Extra-Flow 2.5 x 8 module. The calculations are based on the assumptions that the optimum flow rates for the feed and the acceptor solutions through each module were 20 milliliters per minute and 60 milliliters per minute, respectively, for the MiniModule 1 x 5.5 and 200 milliliters per minute and 600 milliliters per minute, respectively, for the Extra-Flow2.5 x 8 module; the

Table 13. Calculation of the Number of Stages Required to Treat Actual Process Solutions for Given Flow Rates, Using MiniModule 1 x 5.5.

	pH_f	3		6	
	Process Solution	**RO Permeate**	**Barren**	**RO Permeate**	**Barren**
	Removal	0.96	0.91	0.92	0.75
	Flows (m^3/hr)	240	250	240	250
Multiple Stage Operation	**n**	1.21	1.64	1.51	2.81
	Area (m^2)	0.18	0.18	0.18	0.18
	Length (inches)	5.5	5.5	5.5	5.5
	n_p	200000	208333.3	200000	208333.3
	N	400000	416667	400000	625000
Single Stage Operation	**Area (m^2)**	0.22	0.30	0.27	0.51
	Length (inches)	6.7	9.0	8.3	15.5
	N	200000	208334	200000	208334

Table 14. Calculation of the Number of Stages Required to Treat Actual Process Solutions for Given Flow Rates, Using Extra-Flow 2.5 x 8 Module.

	pH_f	3		6	
	Process Solution	**RO Permeate**	**Barren**	**RO Permeate**	**Barren**
	Removal	0.927	0.934	0.901	0.666
	Flows (m^3/hr)	240	250	240	250
Multiple Stage Operation	**n**	1.49	1.44	1.69	3.57
	Area (m^2)	1.4	1.4	1.4	1.4
	Length (inches)	8	8	8	8
	n_p	20000	20833.3	20000	20833.3
	N	40000	41667	40000	83334
Single Stage Operation	**Area (m^2)**	2.09	2.02	2.37	4.99
	Length (inches)	11.9	11.5	13.56	28.53
	N	20000	20834	20000	20834

temperature of the two solutions was maintained at 30 °C, and the mode of flow was countercurrent. The pH of the acceptor solution was equal to 12 in both the cases. The total number of membrane modules required is denoted in Table 13 and Table 14 by N.

Similar calculations were projected for the largest membrane module, the Extra-Flow 14 x 28, supplied by Liqui-Cel®, which provided us with the MiniModule and the Extra-Flow 2.5 x 8 modules. The calculations assumed that the removal efficiency did not vary with the membrane module and the optimum flow rates of the feed and the acceptor solutions, in the case of the Extra-Flow 14 x 28, could be calculated based upon the same flux through the Extra-Flow 2.5 x 8. Table 15 provides the flux values for the three modules discussed and Table 16 provides the estimates of the number of stages required to treat actual process solutions for given flow rates, using the Extra-Flow 14 x 28 module, with calculated optimum flow rate for feed solution for the module. The total number of membrane modules required is denoted by N in the Table 16.

The optimum flow rate of the feed and the acceptor solutions was calculated as 31.43 liters per minute and 94.29 liters per minute, respectively. From Table 16, it can be seen that a reasonable number of industrial membrane modules are required for the treatment

Table 15. Flux of the Feed Solution for Different Membrane Modules

Modules	**MiniModule 1x5.5**	**ExtraFlow 2.5x8**	**ExtraFlow 14x28**
Optimum Flow Rates			
Feed Solution (ml/min)	20	200	31429
Acceptor Solution (ml/min)	60	600	94286
Membrane Surface Area (m^2)	0.18	1.4	220
Feed Flux (ml/(m^2.min))	111.11	142.86	142.86

Table 16. Calculation of the Number of Stages Required to Treat the Actual Process Solutions for Given Flow Rates Using Extra-Flow 14 x 28 Module.

	$\mathrm{pH_f}$	**3**		**6**	
	Process Solution	**RO Permeate**	**Barren**	**RO Permeate**	**Barren**
	Removal	0.927	0.934	0.901	0.666
	Flows (m^3/hr)	240	250	240	250
Multiple Stage Operation	**n**	1.49	1.44	1.69	3.57
	Area (m^2)	220	220	220	220
	Length (inches)	28	28	28	28
	n_p	127.3	132.6	127.3	132.6
	N	256	266	256	532
Single Stage Operation	**Area (m^2)**	328.27	317.04	372.84	784.59
	Length (inches)	41.8	40.4	47.5	99.9
	N	128	133	128	133

of the Reverse Osmosis Permeate Solution and the Barren Solution. The number of membrane modules required for a single stage treatment of the Reverse Osmosis Permeate Solution and the Barren Solution come out to be 128 and 133, respectively, with increased length of the membrane modules. Further, the economic analysis of the application of this technology in industry would help in ascertaining the economic viability.

5.7 Economic Analysis

The economic viability of the technology is important for its industrial application. The cost of removal and recovery of cyanide from process solutions depends on the fixed cost and the operating cost. The fixed cost includes the cost of membrane modules, infrastructure cost, such as pumps and pipelines and the cost of land and building required to install the membrane units. The operating cost includes the cost of energy required to pump the process solutions, cost of reagents added and the maintenance cost.

The fixed cost remains unchanged for a plant of fixed capacity, whereas the operating cost changes with a change in the cost of energy and reagents, and spare parts for maintenance. Therefore, proper estimate of the fixed and operating costs involved in any application is necessary before implementation.

The operating cost of the treatment plant for cyanide removal using hollow fiber membranes was estimated by calculating the pumping cost and the required reagent cost per unit volume of the solution. Equation (35) relates the energy required to pump the solution of specific gravity, $\boldsymbol{\rho}$, at a flow rate, Q, with a head, H, for time, t. The efficiency of the pumping system is denoted by $\boldsymbol{\eta}$.

$$\mathbf{E = \rho g H Q t / \eta} \tag{35}$$

The total operating cost for the treatment plant, including the pumping cost and the reagent cost for the Reverse Osmosis Permeate and the Barren solutions, was calculated as \$ 0.01 per cubic meter of treated process solutions These calculations assumed the pumping system efficiency of 50 %, head for pumping as 2 m, cost of electricity as \$ 0.11 per kilowatt hour, and the cost of hydrochloric acid as \$ 72 per short ton of hydrogen chloride on 100 % basis. Table 17 provides details about the calculation of the total operating cost including the pumping and the acid cost per cubic meter of solution for removal of cyanide using hollow fiber membrane technology.

Table 18 shows the fixed cost and the investments required for removal of cyanide from process solutions using hollow fiber membranes, taking into account the investment due to the membrane modules only. The calculations for estimation of fixed cost assumed

Table 17. Pumping and Reagent Costs involved in Cyanide Removal Using Hollow Fiber Membrane Technology

Application	pH	Efficiency, n	Head	Energy	Pumping Cost	Volume of Acid	Cost of Reagent	Total Cost
			(m)	(KWH)	($/m^3)	(ml/m^3)	($/m^3)	($/m^3)
RO Permeate	3	0.5	2	2.61	0.0012	320	0.008	0.01
Barren	3	0.5	2	2.72	0.0012	400	0.010	0.01
RO Permeate	6	0.5	2	2.61	0.0012	200	0.005	0.01
Barren	6	0.5	2	2.72	0.0012	260	0.006	0.01

Table 18. Investments and Savings from Hollow Fiber Membrane Technology for Cyanide Removal

Application	pH	C_f	Removal	Flow	Number of Modules	Cyanide Recovery Savings	Investment	Chlorine Savings	Total Savings
		(ppm)		(m^3/hr)		($/hr)	($)	($/hr)	($/m^3)
RO Permeate	3	8	0.927	240	256	7.54	3609600	14.4	0.09
Barren	3	24	0.934	250	266	23.58	3750600	15	0.15
RO Permeate	6	8	0.901	240	256	7.51	3609600	14.4	0.09
Barren	6	24	0.666	250	665	23.59	9376500	15	0.15

that the industrial scale Extra-Flow 14 x 28 module costs $ 14,100 per module, and the number of modules required to treat the entire flow of the Reverse Osmosis Permeate and the Barren solutions were calculated using the cyanide concentration in the given solutions as feed cyanide concentration and the desired discharge concentration as 0.2 parts per million of free cyanide. From Table 18, it can be seen that the total savings in the form of elimination of cyanide detoxification using chlorine, and the recovery of cyanide from the process, is $ 0.09 per cubic meter for the Reverse Osmosis Permeate solution at pH 3 and pH 6 and $ 0.15 and $ 0.12 per cubic meter for the Barren solution at pH 3 and pH 6, respectively.

It is expected that the total savings shall increase with an increase in cyanide concentration in the feed solution, assuming that the removal of cyanide from the process solutions does not change with an increase in cyanide concentration. The higher the cyanide in the feed solution, the larger will be the savings by elimination of cyanide detoxification and the recovery of the cyanide, as more of the cyanide could be recovered from the feed solution. Also, from the results of the factorially designed experiments, the cyanide removal did not change much when the concentration of cyanide in the feed solution was changed from 10 parts per million to 1000 parts per million, suggesting that there was no significant effect of cyanide concentration on cyanide removal under optimum conditions of the factors studied. Table 19 shows the calculations of total savings that could be achieved by using the hollow fiber membrane technology for removal and recovery of cyanide from the process solutions, under assumption that the cyanide removal does not change with change in cyanide concentration in the feed solution from 10 parts per million of free cyanide to 1000 parts

Table 19. Projected Total Cost Savings at Different Cyanide Concentrations in the Reverse Osmosis Permeate and the Barren Solutions.

Application	pH	C_f	Flow	Number of Modules	Cyanide Recovery Savings	Investment	Chlorine Savings	Total Savings
		(ppm)	(m^3/hr)		($/hr)	($)	($/hr)	($/$m^3$)
RO Permeate	3	8	240	256	7.54	3609600	14.4	0.09
		10	240	256	9.29	3609600	14.4	0.10
		100	240	384	94.56	5414400	14.4	0.45
		1000	240	512	947.34	7219200	14.4	4.01
Barren	3	24	250	266	23.58	3750600	15	0.15
		10	250	266	9.67	3750600	15	0.10
		100	250	399	98.50	5625900	15	0.45
		1000	250	532	986.81	7501200	15	4.01
RO Permeate	6	8	240	256	7.51	3609600	14.4	0.09
		10	240	256	9.29	3609600	14.4	0.10
		100	240	384	94.56	5414400	14.4	0.45
		1000	240	512	947.34	7219200	14.4	4.01
Barren	6	24	250	665	23.59	9376500	15	0.15
		10	250	532	9.67	7501200	15	0.10
		100	250	798	98.50	11251800	15	0.45
		1000	250	1064	986.81	15002400	15	4.01

per million of free cyanide, for the Reverse Osmosis Permeate solution and the Barren solution. From Table 19, it can be seen that the total cost savings increase from $0.10 per cubic meters at 10 parts per million of free cyanide to $ 4.01 per cubic meter at 1000 parts per million of free cyanide for both the solutions. The calculations take into account, the cost of sodium cyanide is $ 0.93 per pound and the cost of chlorine treatment is $ 0.06 per cubic meter of these solutions. The cost information was obtained from Newmont Mining Corporation by electronic communication. These calculations are preliminary estimates of the operating costs and the investment required for the industrial scale application of the hollow fiber membrane technology for cyanide removal and recovery from the process solutions. A detailed investigation of different items required for the plant set up and the costs associated with them would provide a better insight into the economics of the process and, hence, decide the economic viability of the technology for such application in the gold industry.

CHAPTER 6

CONCLUSION

Application of Hollow Fiber Membrane technology for the removal and recovery of cyanide from the process solutions was investigated. Different membrane technologies were discussed. The objective of the research was to evaluate the use of hollow fiber membrane technology for removal of cyanide from process solutions and to investigate and identify the different factors that affect the removal process to determine the optimum operating conditions. The research included the comparison of performance of the membrane modules with synthetic and actual process solutions and a discussion on the engineering aspects for the scale up of the technology.

The different factors expected to affect the removal of cyanide from aqueous solutions were identified and their effect studied using statistical analysis of the results obtained from the factorially designed experiments with six factors at two levels and with two replicates. The study yielded that all the identified factors, namely pH of the feed solution, pH of the acceptor solution, temperature of operation, concentration of cyanide in the feed solution and the flow rates of the feed and the acceptor solutions, were significant in the removal of cyanide. Presence of dissolved solids in the acceptor solution did not have a significant impact on the removal of cyanide from the synthetic feed solution. The removal of cyanide decreased slightly, from 99.3 % to 91.6 % when the concentration of cyanide in the acceptor solution increased from zero to 500 parts per million of cyanide in the solution. Upon further increase in the cyanide concentration, the cyanide removal did not vary much and remained constant.

Use of lime in place of sodium hydroxide in the acceptor was investigated and the results showed that the removal of cyanide was better when sodium hydroxide solution was used as the acceptor solution, when the mode of flow for the feed and the acceptor solutions was co-current. In a co-current mode of flow of the two solutions, the removal of cyanide was 92 % with sodium hydroxide and 77.4 % with calcium hydroxide as acceptors in the solution. Comparable results were obtained when the mode of flow of the two solutions was changed to counter-current, where the removal of cyanide was 99.1 % with sodium hydroxide and 98.3 % with calcium hydroxide as acceptors in the solution, suggesting that lime could also be used as the acceptor in solution to minimize cost as it is easily available and is less expensive than sodium hydroxide.

The effect of mode of flow of the feed and the acceptor solution was also investigated. Two different membrane modules of different capacities, MiniModule 1 x 5.5 (0.18 square meter membrane surface area, and at the feed solution flow rate of 20 milliliters per minute) and Extra-Flow 2.5 x 8 (1.4 square meter membrane surface area and at the feed solution flow rate of 200 milliliters per minute), were used to study the effect of mode of flow these solutions. MiniModules offered a pure parallel flow pattern, in which co-current and countercurrent modes were investigated, whereas the Extra-Flow module offered elements of both the crossflow pattern and the counter current modes. The countercurrent mode of flow showed higher removal when compared to the co-current mode of flow of the feed and the acceptor solutions. The highest overall mass transfer coefficient was obtained when the Extra-Flow 2.5 x 8 module was used, as it provided the elements of both the cross flow pattern and the countercurrent mode. Results are summarized in Table 17.

Effects of pH of the feed solution and the temperature difference on the two sides of the membranes were investigated. It was found that the pH of the feed solution was an important parameter useful in determining the number of stages of membrane treatment required to reach a desired level of cyanide concentration in the discharge solution. The removal of cyanide was 97.5 % at pH value 3, which was reduced to 45.9 % at pH value 9. The number of stages required varied exponentially with the pH of the feed solution. The removal of cyanide was slightly improved when the temperature of both the feed and the acceptor solutions were equal and high.

The overall mass transfer coefficient and the individual mass transfer coefficients for the feed side, the membrane and the acceptor side were calculated for the transport of hydrogen cyanide using the Wilson Plot method for both the MiniModule and the Extra-Flow membrane modules. Higher mass transfer coefficients were obtained for the Extra-Flow module with both the synthetic process solution and the actual process solutions, namely, the Reverse Osmosis Permeate Solution and the Barren Solution, from Minera Yanacocha Mine operated by Newmont Mining Corporation. The calculated mass transfer coefficient values for the synthetic process solution, when compared to the values reported in the literature, were found to be of similar order and close, validating the values obtained from experiments during this research. Results are summarized in Table 20. The difference in the values obtained for the actual process solutions, when

Table 20. Comparison of the Experimental Mass Transfer Coefficients Values Obtained for Synthetic, Reverse Osmosis Permeate and Barren Solutions, from This Research and by Other Researcher

Module	pH_f	1/K (m/sec)$^{-1}$	I_f (m/sec)$^{-1}$	I_a (m/sec)$^{-1}$	k_f (m/sec)	k_m (m/sec)	k_a (m/sec)	K (m/sec)
Synthetic Solution								
1 x 5.5	**3**	149171.2	64656	113514	1.18 x 10^{-5}	3.45 x 10^{-5}	2.80 x 10^{-5}	0.67 x 10^{-5}
1 x 5.5	**6**	157780	61573	155152	1.04 x 10^{-5}	1.70 x 10^{-5}	3.81 x 10^{-4}	0.63 x 10^{-5}
2.5 x 8	**3**	120741.7	58909	111067	1.62 x 10^{-5}	2.03 x 10^{-5}	1.03 x 10^{-4}	0.83x 10^{-5}
2.5 x 8	**6**	141764.6	59485	136009	1.22 x 10^{-5}	1.86 x 10^{-5}	1.74 x 10^{-4}	0.71 x 10^{-5}
Literature (Wickramasinghe et al, 2004)					2.31 x 10^{-5}	3.53 x 10^{-5}	-	1.11 x 10^{-5}
1 x 5.5	**3**	Reverse Osmosis Permeate Solution						0.60 x 10^{-5}
1 x 5.5	**6**	Reverse Osmosis Permeate Solution						0.48 x 10^{-5}
2.5 x 8	**3**	Reverse Osmosis Permeate Solution						0.62x 10^{-5}
2.5 x 8	**6**	Reverse Osmosis Permeate Solution						0.55 x 10^{-5}
1 x 5.5	**3**	Barren Solution						0.44 x 10^{-5}
1 x 5.5	**6**	Barren Solution						0.26 x 10^{-5}
2.5 x 8	**3**	Barren Solution						0.65 x 10^{-5}
2.5 x 8	**6**	Barren Solution						0.26 x 10^{-5}

compared with those for synthetic solution, was explained as the effect due to the presence of other cyanide complexes, which might require more time and lower pH to dissociate, and dissolved chemicals in the actual process solutions.

Engineering considerations for the scale up of the membrane modules for successful application of this technology by industry were discussed. Several factors were identified that could be important in the design of membrane modules and the process flow sheet for successful implementation of this technology, namely, the chemical and physical properties of process solutions to be considered, the flow rates of the solutions, the membrane surface area, the mode of flow for the feed and the acceptor solutions, the module design and geometry and the circuit design for multiple membrane modules. The number of membrane modules required to reach the target discharge concentration of 0.2 parts per million of free cyanide as per the Drinking Water Standard for cyanide in drinking water, established by USEPA, was calculated at different pH values of the feed solution for different process solutions with actual flow rates used in the plant operations. A reasonable number of industrial membrane modules for the treatment of the Reverse Osmosis Permeate Solution and the Barren Solution suggested the technology has potential for application in gold cyanidation plants. Table 21 provides details about the number of stages of the Extra-Flow 14 x 28 Industrial modules required to the treat the process solutions with typical flow rates.

The estimated savings from the elimination of cyanide detoxification and the recovery of cyanide is $ 0.09 per cubic meter at pH value 3 and 6 and cyanide concentration of 8 parts per million free cyanide in the Reverse Osmosis Permeate solution. In the case of the Barren solution, the estimated savings are $ 0.15 per cubic meter at pH value 3 and

Table 21. Number of Extra-Flow 14 x 28 Industrial Modules Required to Treat the Plant Solutions

pH_f	3		6	
Process Solution	**RO Permeate**	**Barren**	**RO Permeate**	**Barren**
Removal	0.927	0.934	0.901	0.666
Flows (m^3/hr)	240	250	240	250
n	1.49	1.44	1.69	3.57
Area (m^2)	220	220	220	220
Length (inches)	28	28	28	28
n_p	127.3	132.6	127.3	132.6
N	256	266	256	532

$ 0.12 per cubic meter at pH value 6 and cyanide concentration of 24 parts per million free cyanide. From Table 22, it can be seen that the savings from treatment technology could be as high as $ 4.01 per cubic meter of the solution when the cyanide concentration in the two solutions is at 1000 parts per million of free cyanide, assuming that the removal and recovery of cyanide remain the same even at very high concentration. The estimated combined pumping and reagent consumption cost for the two solutions is $ 0.01 per cubic meter based on the pH and the flow rate of the solutions, which is much lower than $ 0.07, the cost for chlorination of cyanide containing solutions at Minera Yancocha operation of Newmont Mining Corporation in Peru. Although, these calculations are preliminary estimates of the operating costs and the investment required for the industrial scale application of the hollow fiber membrane technology for cyanide removal and recovery from process solutions, a detailed investigation of different items required for the plant set up and the costs associated with them would provide a better insight into the economics of the process.

Table 22. Estimated Costs and Savings Involved in Cyanide Removal Using Hollow Fiber Membrane Technology

Application	Cyanide Concentration	Flow	Pumping and Reagent Costs	Savings
	(ppm CN^-)	(m^3/hr)	($\$/m^3$)	($\$/m^3$)
RO Permeate	10	240	0.01	0.10
	1000	240	0.01	4.01
Barren	10	250	0.01	0.10
	1000	250	0.01	4.01

The technology has several advantages and disadvantages. Cyanide is removed from the aqueous solution without the addition of a large quantity of chemicals. The only chemical that is required to be added is the acid, to reduce the pH of the feed solution so that hydrogen cyanide is generated. The feed and the acceptor solutions are separated by a membrane which prevents their contact at the same time allowing the transport of hydrogen cyanide. Therefore, contamination of the treated solution with the acceptor solution is prevented. The process of treatment of contaminated solution is continuous rather than in batches. Since the membrane is a low pressure membrane, pumping costs would be much lower when compared to the reverse osmosis and nanofiltration techniques. The cyanide removed from the feed solution is recovered in the acceptor solution, which could be reused for heap leaching operations, saving the cost of destruction and reducing the addition of the make-up cyanide.

The acceptor solution can be an alkaline solution of sodium hydroxide or calcium hydroxide, as desired, though the performance with sodium hydroxide is better, as deduced from the results of this research. The modular design of these membranes provides flexibility of designing a treatment system for easy replacement and maintenance. The design could be easily prepared and modified for larger scale operation by simple adding the number of modules to handle the larger flow.

The hollow fiber membrane technology is only suitable for free and weak acid dissosciable cyanide species present in the solution. This is one of the major disadvantages as cyanide in the solutions in gold cyanidation plants is also present in the form of strong complexes. Removal of these strong metal cyanide complexes will need an extra treatment step, which would result in higher cost for cyanide removal. Another disadvantage of this technology is the pretreatment requirements for the feed and the acceptor solutions. The size of the pores in the hollow fiber membranes is 0.03 micrometers. The solutions have to be prefiltered to remove the suspended particles larger than 0.03 micrometers, so that these particles do not clog the pores of the membranes. If the pores are clogged, the hydrogen cyanide gas would not be transported across the membrane, resulting in a reduction in cyanide removal efficiency.

The membrane module is efficient in the removal of gaseous species when the pores in the membranes are not wetted. Upon continuous use, the pores in the membrane are gradually wetted because of condensation of water vapor, turning the pores from the "nonwetted" to the "wetted" state. The wetting of pores results in the transport of solution from one side of the membrane to the other side and the two solutions remain no longer separated. This drastically reduces the efficiency for the removal of cyanide as the pH values for the solutions on the two sides no longer remain optimum. This was observed twice during the experiments when the removal efficiency of the membrane dipped down and the membrane was considered damaged and not suitable for use in this research program. Therefore, for good removal efficiency, the membrane must be operated in a nonwetted mode.

For a better insight into the separation by hollow fiber membrane modules, future research work is required. The membranes investigated in this research were made of polypropylene. Other materials, such as perflouroalkoxy (PFA), polyvinylideneflouride (PVDF) and similar hydrophobic materials, might have different mass transfer coefficient values for the same application. The mass transfer coefficient may vary with the pore size and porosity of the membranes, which has not been investigated in this research. Industrial wastewater and process solutions have a large amount of dissolved solids and microorganisms that might foul the membranes. Good operating procedures and cleaning practices would enhance the life of these membranes, and this has to be investigated in future for successful application of hollow fiber membrane technology in gold cyanidation plants. Also, the performance of the multiple membrane modules in series and parallel combinations must be investigated to see the advantages of modular membranes over a single large membrane module. The application of this technology could be used in separation of other volatile species from solutions, such as removal of ammonia from wastewater, separation of alcohol from the mixture of alcohol and water, extraction of flavors from fruit juices and flower and plant extracts and many other similar applications.

With a set of its own advantages and disadvantages, the hollow fiber membrane technology is a unique process to separate volatile components from aqueous solutions. The technology shows good potential for its application in various industries, including mining and mineral processing, food and beverage, and wastewater treatment. Under this research work, the removal and the recovery of cyanide from the process solutions using the hollow fiber membrane technology was successfully accomplished, with over 90 % removal of cyanide from the synthetic and the actual process solutions.

APPENDIX A

REMOVAL AND RECOVERY OF CYANIDE FROM SYNTHETIC SOLUTIONS IN FACTORIALLY DESIGNED EXPERIMENTS

Table 23. Factors and Their Levels

Factors		Levels		Units
		-1	**1**	
pH Feed	**pH_f**	3	9.5	
Temperature	**T**	5	35	Degrees C
Flow Feed	**Q_f**	20	80	ml/min
Concentration	**C**	10	1000	PPM
Flow Acceptor	**Q_a**	10	60	ml/min
pH Base	**pH_a**	9.5	12	

Table 24. Removal and Recovery of Cyanide from Synthetic Solutions at Different Levels of Factors Identified to Have Effect

Exp	**pH_f**	**T**	**Q_f**	**C**	**Q_a**	**pH_a**	**Replicate 1**		**Replicate 2**	
							Removal	Recovery	Removal	Recovery
1	-1	-1	-1	-1	-1	-1	0.14	0.13	0.18	0.11
2	-1	-1	-1	-1	-1	1	0.51	0.22	0.38	0.34
3	-1	-1	-1	-1	1	-1	0.35	0.47	0.25	0.58
4	-1	-1	-1	-1	1	1	0.71	0.99	0.68	1.21
5	-1	-1	-1	1	-1	-1	0.25	0.13	0.19	0.16
6	-1	-1	-1	1	-1	1	0.15	0.10	0.13	0.11
7	-1	-1	-1	1	1	-1	0.35	0.29	0.29	0.46
8	-1	-1	-1	1	1	1	0.52	0.49	0.47	0.70
9	-1	-1	1	-1	-1	-1	0.15	0.06	0.06	0.06
10	-1	-1	1	-1	-1	1	0.10	0.10	0.18	0.11
11	-1	-1	1	-1	1	-1	0.16	0.24	0.20	0.21
12	-1	-1	1	-1	1	1	0.30	0.28	0.35	0.28
13	-1	-1	1	1	-1	-1	0.16	0.04	0.12	0.03
14	-1	-1	1	1	-1	1	0.19	0.04	0.18	0.04
15	-1	-1	1	1	1	-1	0.15	0.16	0.14	0.17
16	-1	-1	1	1	1	1	0.17	0.22	0.13	0.22
17	-1	1	-1	-1	-1	-1	0.27	0.15	0.22	0.15
18	-1	1	-1	-1	-1	1	0.88	1.04	0.94	0.58
19	-1	1	-1	-1	1	-1	0.72	0.74	0.58	0.49
20	-1	1	-1	-1	1	1	0.94	1.11	0.91	1.08
21	-1	1	-1	1	-1	-1	0.38	0.11	0.24	0.13
22	-1	1	-1	1	-1	1	0.31	0.20	0.33	0.27
23	-1	1	-1	1	1	-1	0.43	0.48	0.35	0.49
24	-1	1	-1	1	1	1	0.94	1.00	0.97	0.94
25	-1	1	1	-1	-1	-1	0.07	0.04	0.04	0.06
26	-1	1	1	-1	-1	1	0.84	0.43	0.86	0.44
27	-1	1	1	-1	1	-1	0.25	0.14	0.23	0.19
28	-1	1	1	-1	1	1	0.80	0.94	0.80	0.89

Table 24. continued

29	-1	1	1	1	-1	-1	0.05	0.06	0.07	0.06
30	-1	1	1	1	-1	1	0.10	0.09	0.14	0.11
31	-1	1	1	1	1	-1	0.48	0.17	0.49	0.23
32	-1	1	1	1	1	1	0.36	0.40	0.38	0.37
33	1	-1	-1	-1	-1	-1	0.03	0.08	0.06	0.08
34	1	-1	-1	-1	-1	1	0.62	0.20	0.91	0.28
35	1	-1	-1	-1	1	-1	0.27	0.14	0.50	0.12
36	1	-1	-1	-1	1	1	0.86	0.87	0.88	0.65
37	1	-1	-1	1	-1	-1	0.02	0.03	0.04	0.04
38	1	-1	-1	1	-1	1	0.08	0.07	0.10	0.08
39	1	-1	-1	1	1	-1	0.10	0.28	0.25	0.16
40	1	-1	-1	1	1	1	0.20	0.38	0.31	0.35
41	1	-1	1	-1	-1	-1	0.09	0.04	0.08	0.03
42	1	-1	1	-1	-1	1	0.34	0.10	0.42	0.17
43	1	-1	1	-1	1	-1	0.22	0.37	0.15	0.23
44	1	-1	1	-1	1	1	0.62	0.78	0.56	0.70
45	1	-1	1	1	-1	-1	0.08	0.02	0.03	0.02
46	1	-1	1	1	-1	1	0.01	0.02	0.06	0.02
47	1	-1	1	1	1	-1	0.07	0.15	0.08	0.12
48	1	-1	1	1	1	1	0.10	0.12	0.12	0.12
49	1	1	-1	-1	-1	-1	0.16	0.12	0.14	0.13
50	1	1	-1	-1	-1	1	0.73	0.40	0.70	0.53
51	1	1	-1	-1	1	-1	0.32	0.37	0.31	0.38
52	1	1	-1	-1	1	1	0.65	0.80	0.71	0.61
53	1	1	-1	1	-1	-1	0.02	0.11	0.09	0.06
54	1	1	-1	1	-1	1	0.11	0.16	0.14	0.14
55	1	1	-1	1	1	-1	0.06	0.18	0.13	0.16
56	1	1	-1	1	1	1	0.10	0.27	0.13	0.27
57	1	1	1	-1	-1	-1	0.06	0.03	0.03	0.04
58	1	1	1	-1	-1	1	0.46	0.35	0.39	0.39
59	1	1	1	-1	1	-1	0.16	0.13	0.14	0.15
60	1	1	1	-1	1	1	0.41	0.49	0.39	0.46
61	1	1	1	1	-1	-1	0.04	0.01	0.03	0.02
62	1	1	1	1	-1	1	0.05	0.06	0.04	0.04
63	1	1	1	1	1	-1	0.16	0.06	0.02	0.07
64	1	1	1	1	1	1	0.15	0.18	0.06	0.18

APPENDIX B

HALF NORMAL AND NORMAL PROBABILITY PLOTS OF EFFECTS

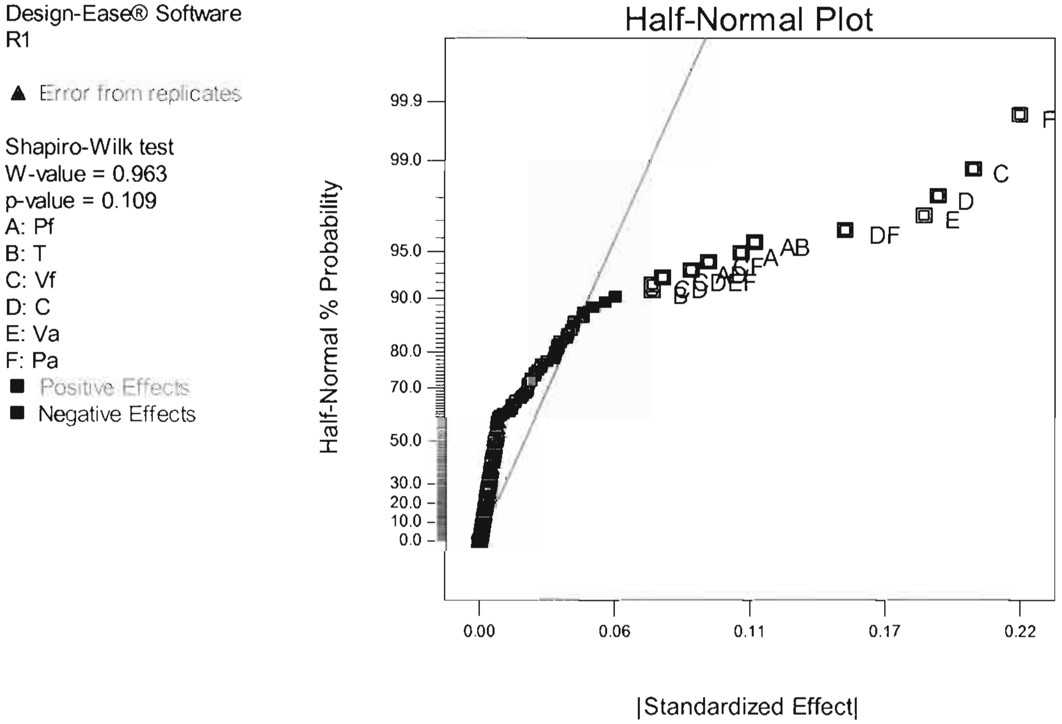


Fig. 25. Half Normal Probability Plot of Effects

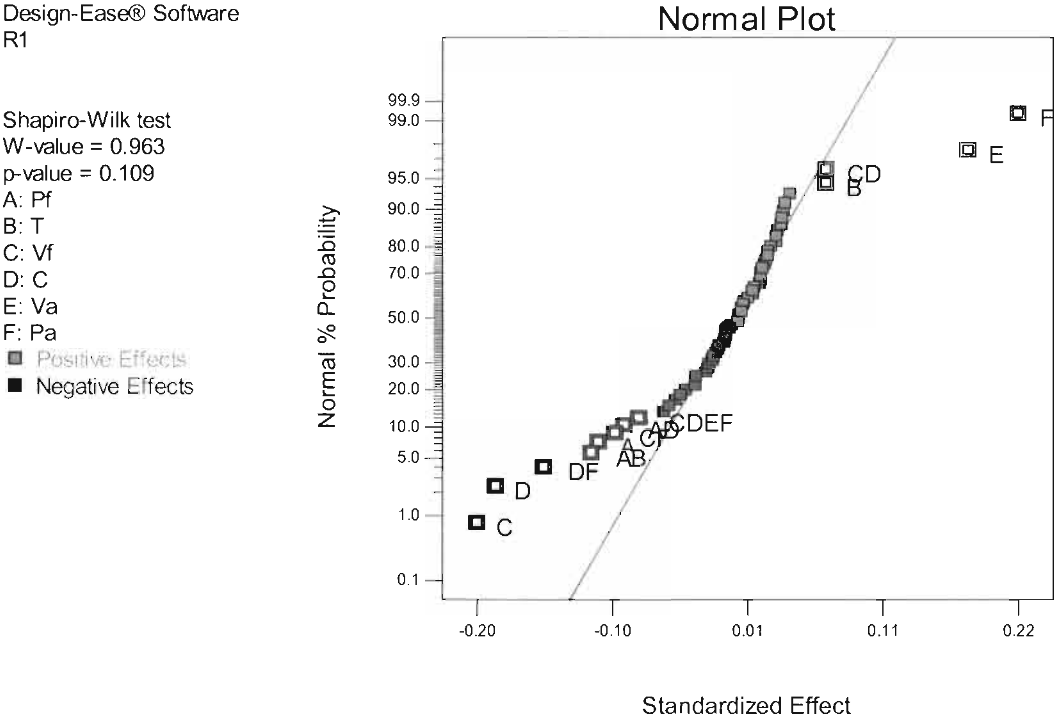


Fig. 26. Normal Probability Plot of Effects

APPENDIX C

NORMAL PROBABILITY PLOT OF RESIDUALS

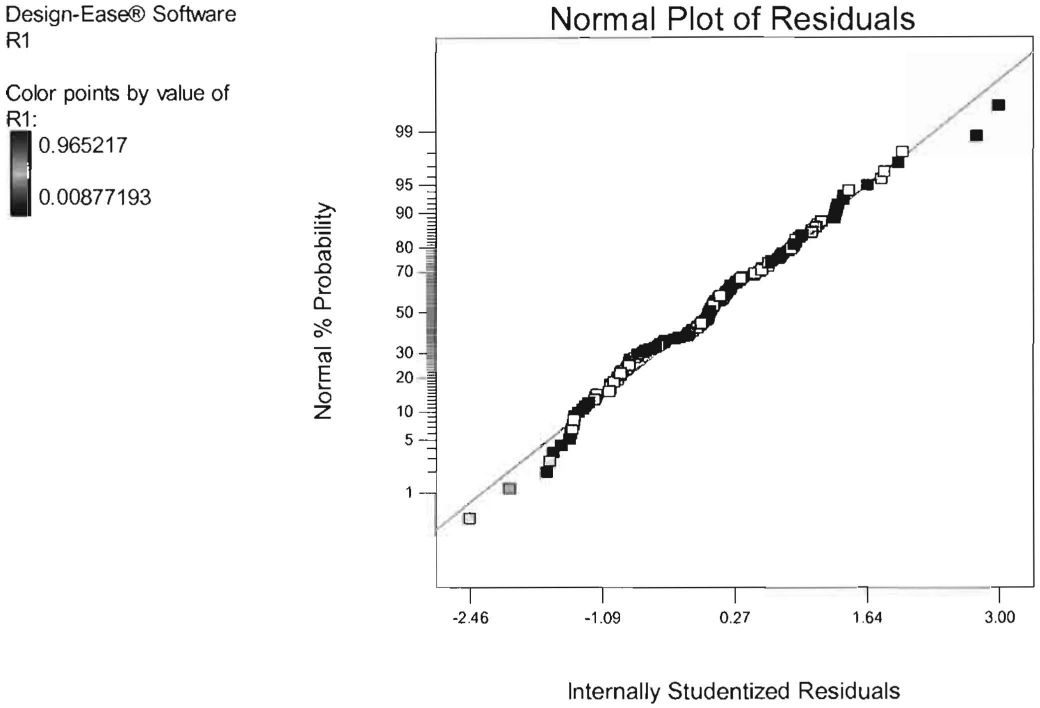


Fig. 27. Normal Probability Plot of Residuals

APPENDIX D

RESIDUALS AND RESPONSE SURFACES

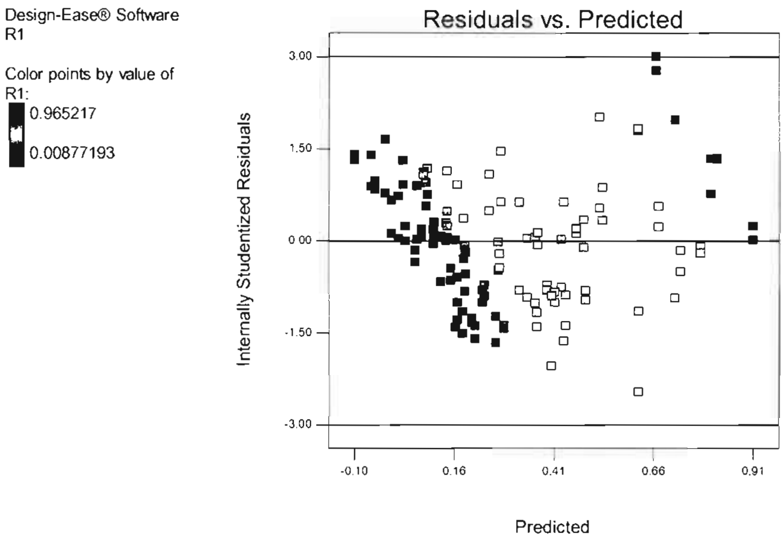


Fig. 28. A Plot of Residuals against Predicted Response, Cyanide Removal

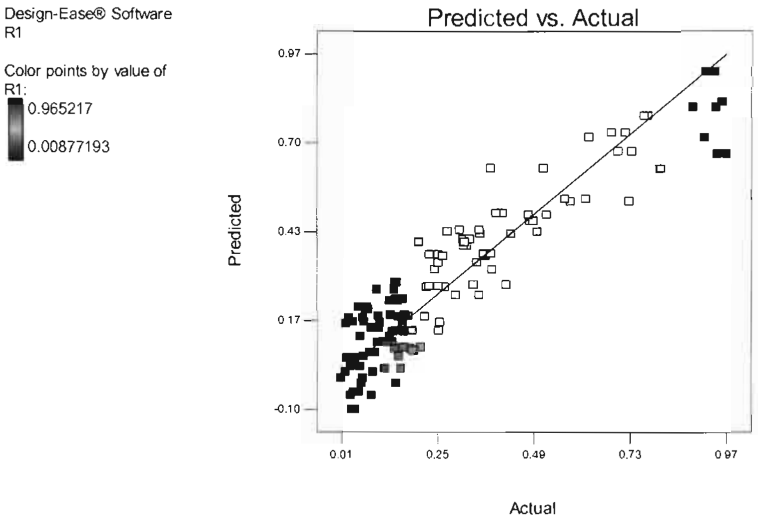


Fig. 29. A Plot of Predicted Cyanide Removal against Actual Cyanide Removal

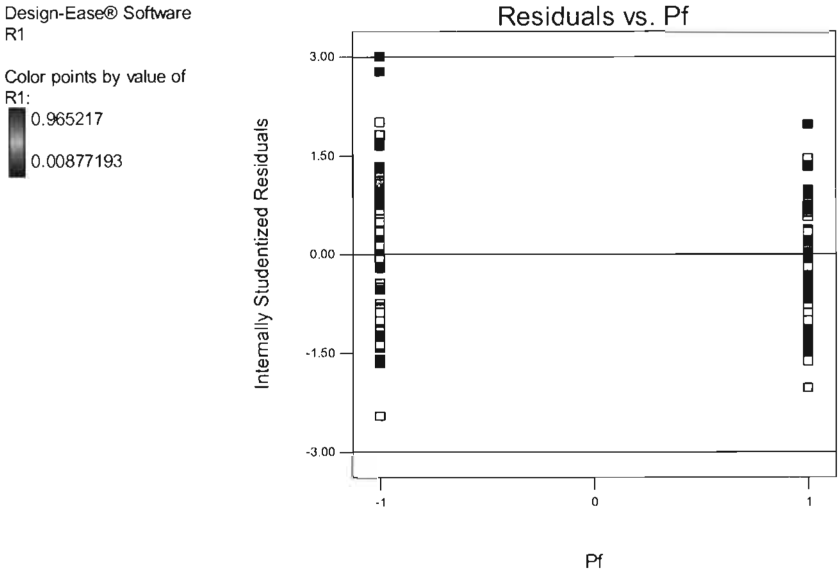


Fig. 30. A Plot of Residual against pH of the Feed Solution, pH_f

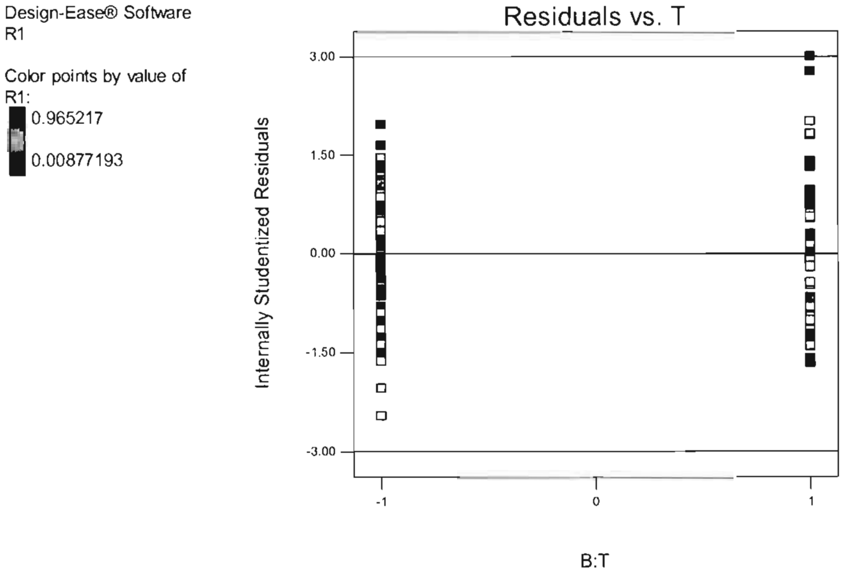


Fig. 31. A Plot of Residual against Temperature of Operation, T

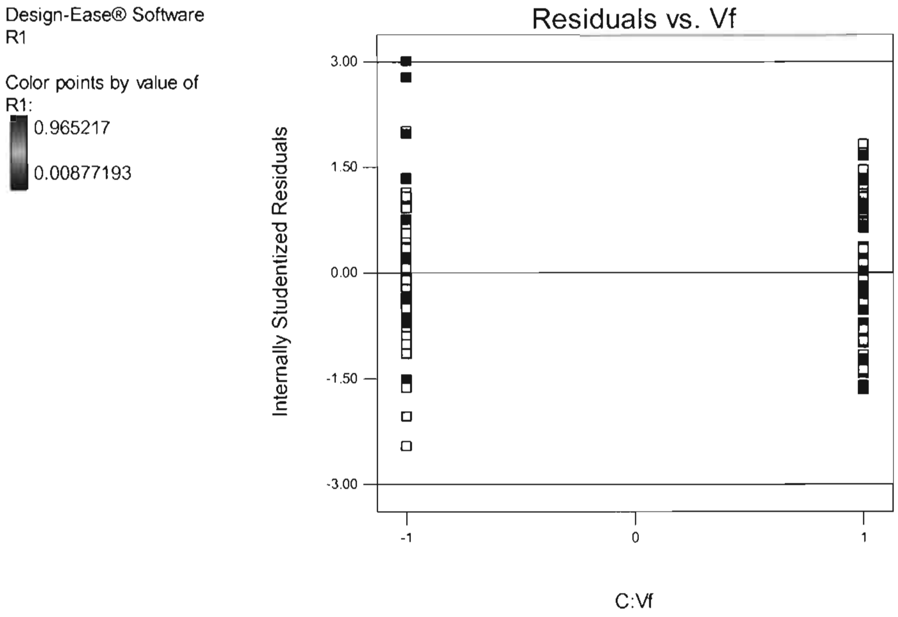


Fig. 32. A Plot of Residual against Flow Rate of the Feed Solution, Q_f

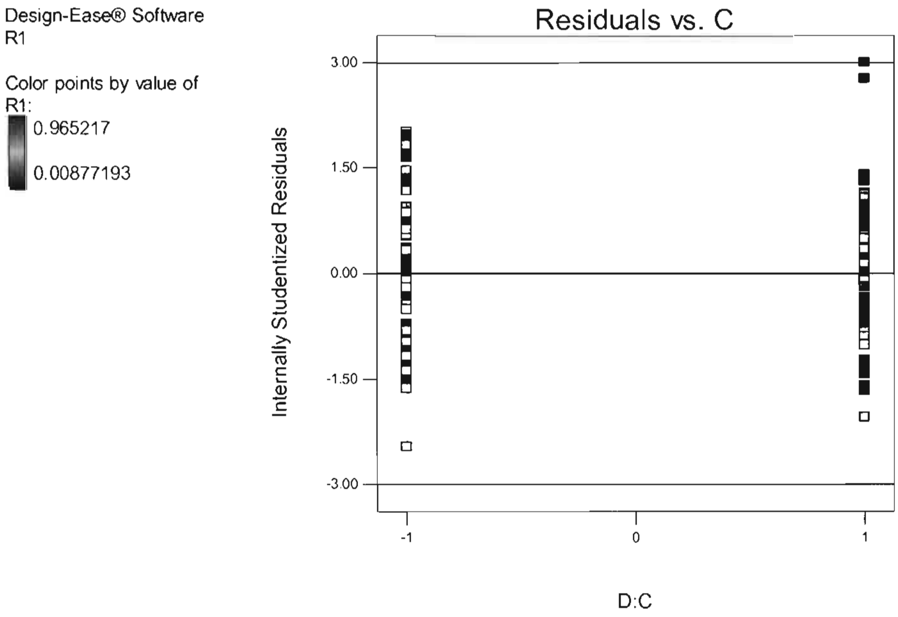


Fig. 33. A Plot of Residual against Concentration of Cyanide in the Feed Solution, C

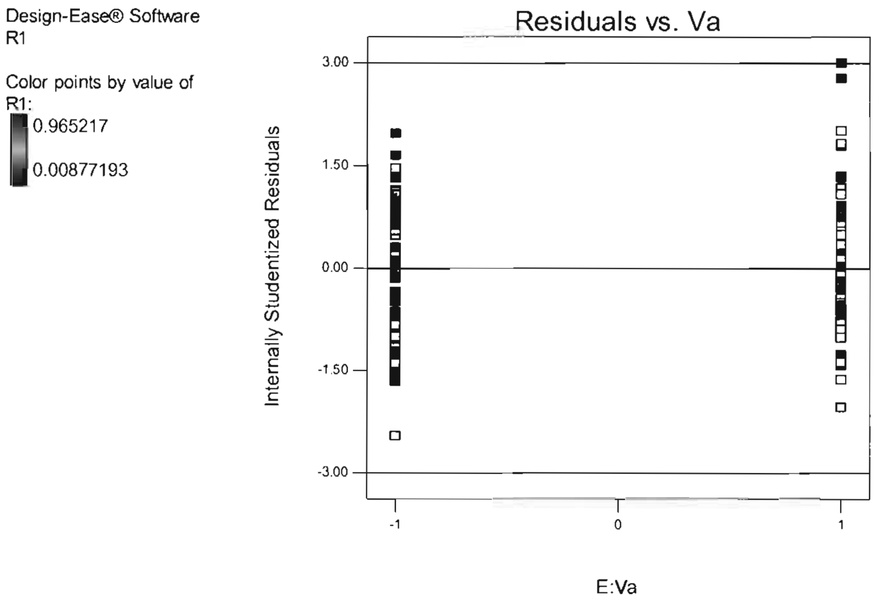


Fig. 34. A Plot of Residual against Flow Rate of the Acceptor Solution, Q_a

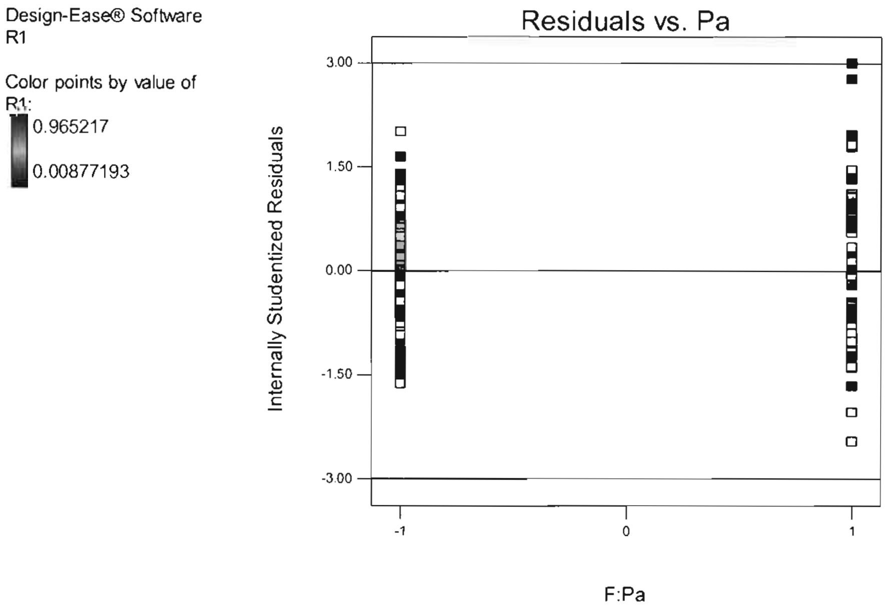


Fig. 35. A Plot of Residual against pH of the Acceptor Solution, pH_a

The Response Surfaces Incorporating Different Factors Investigated

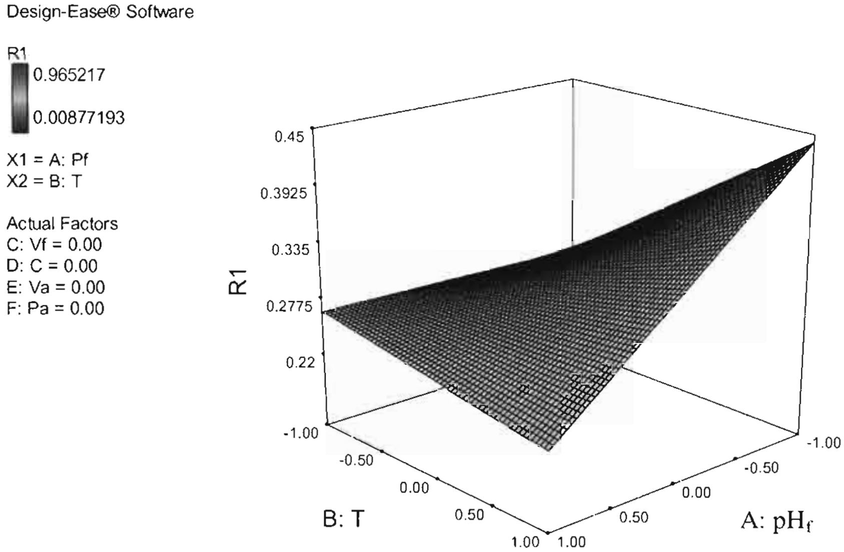


Fig. 36. The Response Surfaces Incorporating Temperature of Operation, T and pH of the Feed Solution, pH_f

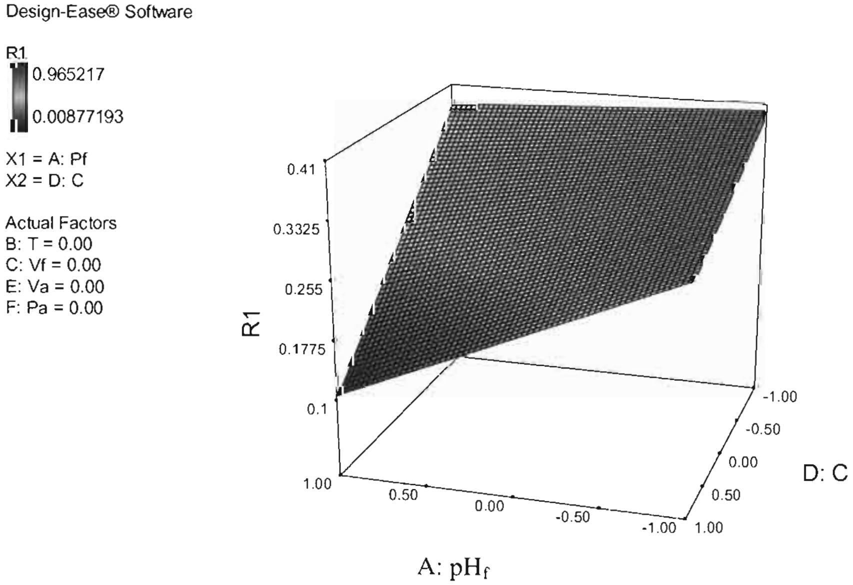


Fig. 37. The Response Surfaces Incorporating pH of the Feed Solution, pH_f and the Concentration of Cyanide in the Feed Solution, C

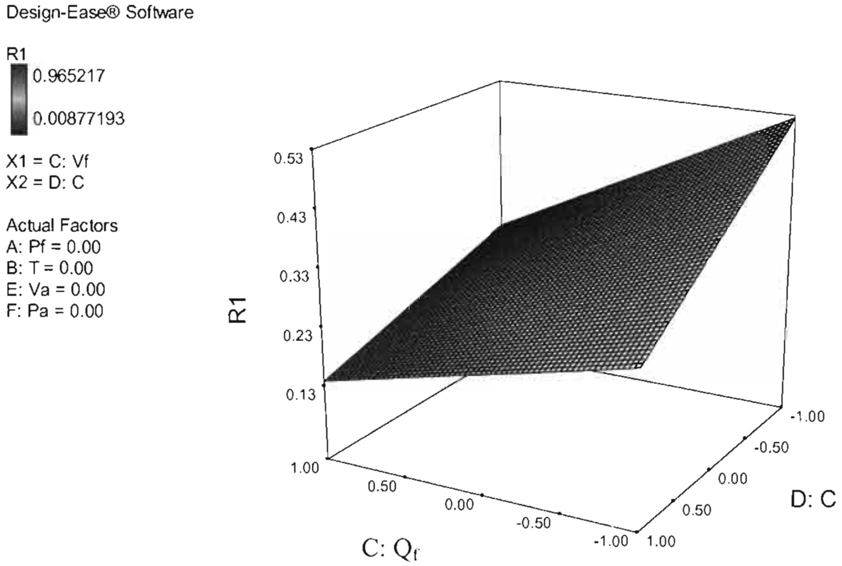


Fig. 38. The Response Surfaces Incorporating Flow Rate of the Feed Solution, Q_f and Concentration of Cyanide in the Feed Solution, C

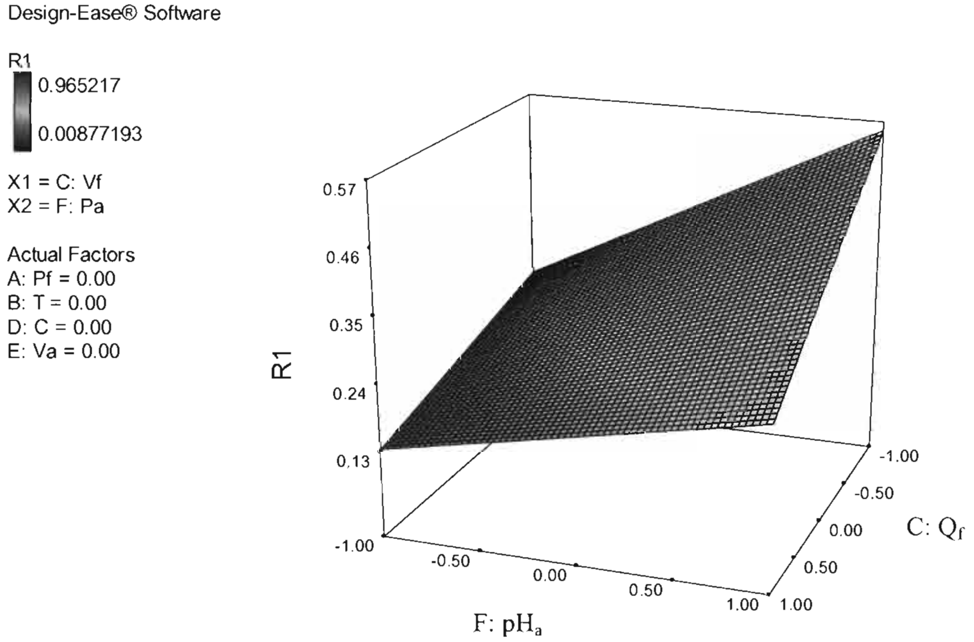


Fig. 39. The Response Surfaces Incorporating pH of the Acceptor Solution, pH_a and Flow Rate of the Feed Solution, Q_f

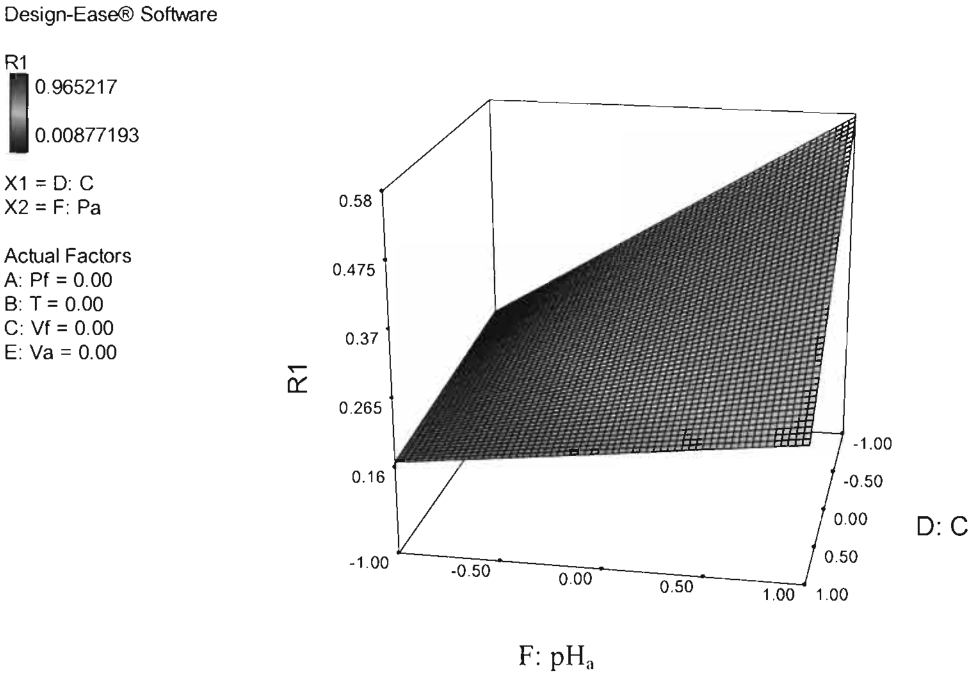


Fig. 40. The Response Surfaces Incorporating pH of the Acceptor Solution, pH_a and Concentration of Cyanide in the Feed Solution, C

APPENDIX E

CHEMICAL ANALYSIS OF THE REVERSE OSMOSIS PERMEATE SOLUTION AND THE BARREN SOLUTION

Table 25. Properties and Chemical Composition of the Reverse Osmosis (RO) Permeate and the Barren Solutions

Properties and Elements	**Units**	**Barren Solution**	**RO Permeate**
Alkalinity	mg/l of CaCO3	249	127
pH	-	10.4	10.6
Total Dissolved Solids (TDS)	ppm	2269	89
Chloride, Cl	mg/l	81.9	1.43
Flouride, F	mg/l	0.18	0.05
Nitrogen as Nitirite, NO_2^- -N	mg/l	4.46	0.24
Nitrogen as Nitirate, NO_3^- -N	mg/l	<0.05	2.96
Nitrogen as Ammonia, NH_3 -N	mg/l	30.9	23.7
Phosphate, PO_4^{3-} -P	mg/l	<0.10	<0.10
Phosphorous, P	mg/l	0.51	<0.05
Sulfate, SO_4^{2-}	mg/l	1162.3	4.4
Sulfur, S	mg/l	874	<0.05
Cyanide, OCN	mg/l	5.56	0.39
Thiocyanate, SCN	mg/l	13.93	1.03
Free Cyanide, CN-FREE	mg/l	44.2	8.65
Total Cyanide, CN-TOT	mg/l	78.9	8.69
Weak Acid Dissociable Cyanide, CN-WAD	mg/l	75.5	8.1
Mercury, Hg	µg/L	16.9	<0.1
Gold, Au	mg/l	0.045	0.008
Silver, Ag	mg/l	0.056	0.006
Aluminum, Al	mg/l	0.231	0.148
Barium, Ba	mg/l	0.035	<0.020
Calcium, Ca	mg/l	376	2.05
Cobalt, Co	mg/l	0.227	<0.050
Chromium, Cr	mg/l	<0.050	<0.050
Copper, Cu	mg/l	11.5	0.054
Iron, Fe	mg/l	0.131	<0.050
Potassium, K	mg/l	43.4	3.09
Magnesium, Mg	mg/l	1.05	<0.050
Manganese, Mn	mg/l	<0.010	<0.010
Sodium, Na	mg/l	310	26.2
Nickel, Ni	mg/l	0.083	<0.050
Tin, Sn	mg/l	<0.050	<0.050
Strontium, Sr	mg/l	0.714	<0.050
Titanium, Ti	mg/l	<0.050	<0.050
Vanadium, V	mg/l	<0.050	<0.050
Zinc, Zn	mg/l	9.1	<0.050
Arsenic, As	µg/L	388	1.9
Boron, B	µg/L	34.4	7.4

Table 25. continued

Beryllium, Be	µg/L	<0.1	<0.1
Cadmium, Cd	µg/L	<0.10	<0.10
Lithium, Li	µg/L	<0.1	<0.1
Molybdenum, Mo	µg/L	734	2.8
Lead, Pb	µg/L	<0.1	<0.1
Antimony, Sb	µg/L	16.3	0.4
Selenium, Se	µg/L	120	3
Tellurium, Te	µg/L	<0.1	<0.1
Thallium, Tl	µg/L	<0.1	<0.1

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