MLM-2908

Development of Low-Level Liquid-Waste-Treatment Systems: October 1981-March 1982

Melvin K. Williams and C. Mark Colvin

May 28, 1982

MOUND FACILITY
Miamisburg, Ohio 45342

operated by
MONSANTO RESEARCH CORPORATION
a subsidiary of Monsanto Company

for the
U. S. DEPARTMENT OF ENERGY
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Foreword

Under the sponsorship of the DOE Division of Waste Management, Production and Reprocessing, and the direction of the Idaho Operations Office which is responsible for the management of Low Level Waste Programs, Mound is responsible for the development and demonstration of separation methods for removing radionuclides from intermediate-level and low-level liquid processing wastes.

This report is submitted by W. T. Cave, Director, Nuclear Operations, and B. R. Kokenge, Manager, Nuclear Technology, from contributions prepared by members of the Nuclear Waste Technology Section, R. R. Jaeger, Manager, and the Liquid Volume Reduction Technology Group, W. H. Bond, Leader.

To provide an easier understanding of the relationship of the work described herein to the entire project, a work breakdown structure and FY-1982 milestone chart are provided.

Previous reports on this project are listed below:

April-September 1979	MLM-2684
October 1979-March 1980	MLM-2735
April-September 1980	MLM-2795
October 1980-March 1981	MLM-2869
April-September 1981	MLM-2899

Contents

Abstract

A plant design for a reverse osmosis (RO) membrane unit was completed. The design includes a conceptual diagram, specifications for a RO unit producing 40 gal/min of permeated product, a list of radioisotopes tested on RO units and the rejections achieved, a discussion of the principle of RO, a discussion of the upper limits of cation and anion concentrations (there are no lower limits), a discussion of membrane configurations and porosities, a discussion of factors affecting membranes, a section on calculating the membrane area needed for a particular application, and capital and operating cost calculations.

The three factors found to affect the adsorption of cobalt on ion exchange resins were investigated in an interaction effects design experiment. These factors are solution pH, and sulfite and ammonium concentrations. The effects of these factors were investigated with both anionic and cationic resins. Greater than 99% of the cobalt can usually be removed from solutions at a pH between 3 and 6.

A design for an ion-exchange pilot plant was completed. The design includes a schematic diagram; flow, resin, and column specifications; impurity limits; and operating and capital costs. A short theoretical discussion and process description are also included. The design retains flexibility so that application to a specific stream can be determined.

Introduction

This report is organized to conform to the Work Breakdown Structure (WBS) for the Ultrafiltration and Adsorbents program. A copy of the WBS is shown in Figure 1. Figure 2 is the FY-1982 Milestone Chart for the program.

3.1.2.3 Membrane Plant Design

C. Mark Colvin

Introduction

Reverse osmosis (RO) is an effective tool in the volume reduction of low level radioactive waste solutions with low to medium levels of dissolved solids [1-6]. Table 1 lists some typical rejections of radionuclides using reverse osmosis membranes. There are, at present, several nuclear facilities using reverse osmosis technology to obtain volume reduction of low-level radioactive waste streams from, for instance, floor drains and laundry wastes [6-8]. Table 2 lists some of these facilities, the type of waste treated, and the volume reductions obtained.

Reverse osmosis and osmotic pressure

The term "Reverse Osmosis" was originally derived because the water transport in reverse osmosis is the opposite of the water transport in normal osmosis. In other words, in normal osmosis water flows from a less concentrated solution through a semipermeable membrane to a more concentrated solution (Figures 3 and 4), whereas in reverse osmosis, water is forced to flow from a more concentrated solution to a less concentrated solution through a semipermeable membrane.

There is a potential energy difference between any two solutions of differing concentrations separated by a semipermeable membrane. The potential energy between the two solutions separated by a membrane is termed osmotic pressure. The osmotic pressure must be overcome in order to produce a less concentrated solution from a more concentrated solution. Thus a limiting factor in reverse osmosis is the potential energy inherent in a particular solution. Highly ionized solutions, such as those containing sodium chloride, have a high osmotic pressure (approximately 1 psi per 100 ppm NaCl concentration). Many other solutions with ionic impurities such as $NiSO_4$, H_2CrO_4, $Cd(NO_3)_2$, have relatively low osmotic pressures [16,22,23].

Sea water has about 3.5%, or 35,000 ppm, NaCl with an inherent osmotic pressure of 350 psi. Since pumps, membranes, and other reverse osmosis equipment are best operated below 600 psig, the purification of water higher in NaCl concentration than sea water tends to be uneconomical [23].

Many chemicals with concentrations as high as 10-15% by weight are amenable to RO processing because their osmotic pressure at a given concentration is not as high as the osmotic pressure of NaCl. Tables 3 and 4 show the rejection of different materials using a SEPA-97 membrane (manufactured by Osmonics, Inc.) at 400 psig operating pressure. The tables also give the approximate maximum economical con- concentration for the particular ion listed.

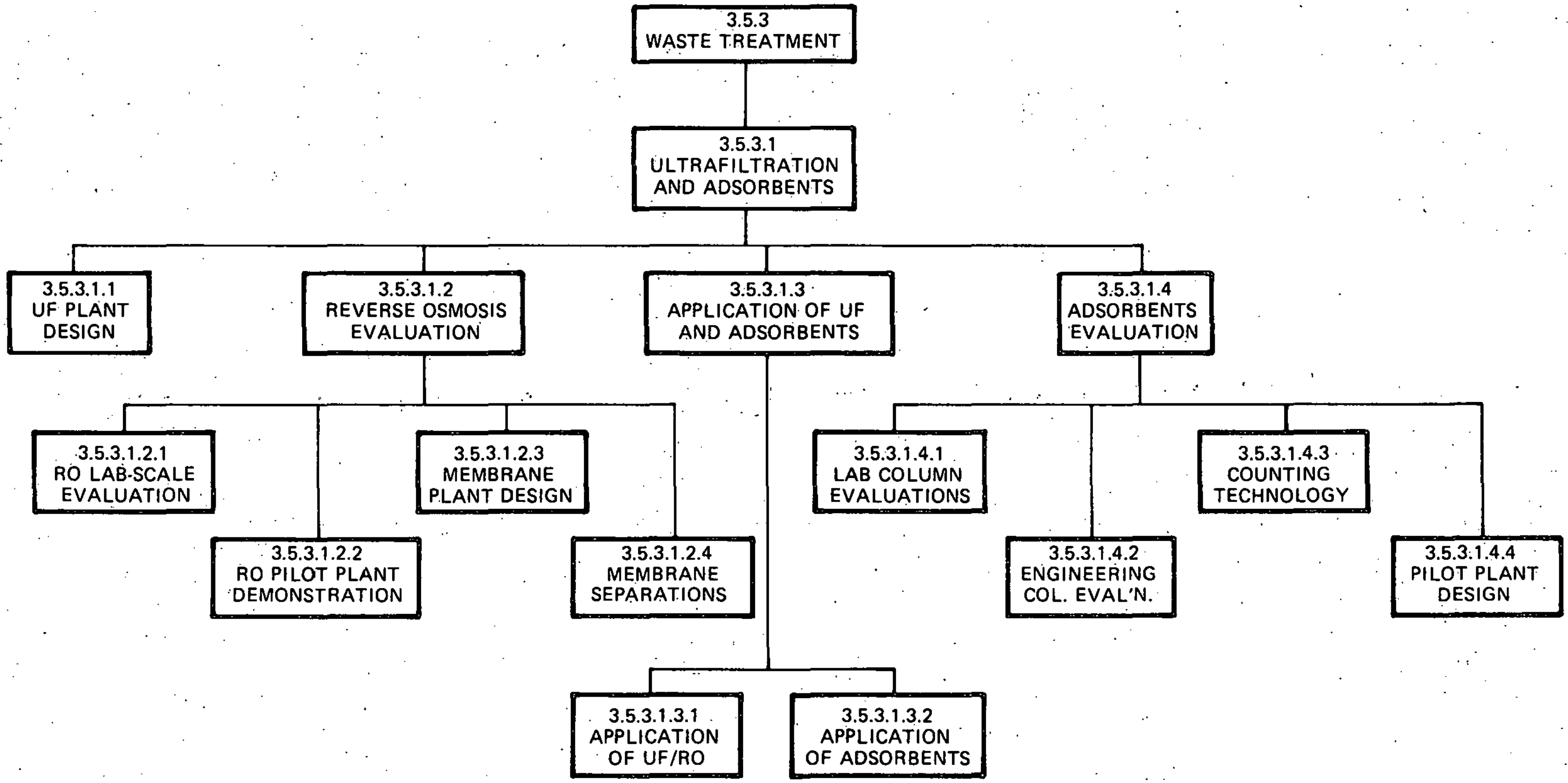

FIGURE 1 - Work breakdown structure.

Milestone Schedule																	
Milestone No.	Milestone		FY-1982											FY-1982			
		O	N	D	J	F	M	A	M	J	J	A	S	1Q	2Q	3Q	4Q
1	Complete Membrane Plant Design																
2	Complete Engineering Column Evaluations																
3	Complete Adsorbent Pilot Plant Design																

FIGURE 2 - FY-1982 Milestone Chart

The mechanism of reverse osmosis

There are two fundamental mechanisms of rejection at work in the reverse osmosis process, one being the mechanism of salt rejection. Salt rejection occurs because of the repulsion of the salt ions from the surface of the membrane and the adsorption of water to the membrane surface. Because of the physical and chemical properties of the cellulose acetate membrane, a pure water layer about two molecules thick (∿10 Å thick) develops at the surface of the membrane. Salts are repelled from the surface of the membrane, with the higher valence ions being repelled to a greater distance. If ions of two different valences of a salt, e.g., Ca^{+2} and $2Cl^{-1}$, are in solution, the Ca^{+2} tends to hold the Cl^{-1} with it, and both ions are repelled from the membrane as if both had a valence of two. The highest valence ion of a salt is usually the dictating species in predicting membrane rejection performance [22,23]. The mechanism of salt rejection with a cellulose acetate reverse osmosis membrane is illustrated in Figure 5. The second mechanism is that of organic rejection in which the dissolved organics are rejected by a screening or sieving mechanism. The rejection of any given organic molecule is a function of membrane pore size, size of the molecule, and the geometry of the molecule. Ions complexed with organics of large molecular weight will usually be rejected at approximately the same rate as are the organics they are complexed with [15,23].

Membrane module configurations

There are three basic types of membrane module configurations: tubular, spiral wound, and hollow fiber. Membranes in the form of a tube are inserted into tubular casings so that the membranes line the casings. The tubular casings, which have porous walls, serve both as the pressure vessel and as the support for the membranes. Solvent permeates the membranes and then seeps through the porous walls of the casings. Spiral-wound reverse osmosis modules are made with planar membranes. They are

Table 1 - TYPICAL REJECTIONS OF RADIONUCLIDES USING REVERSE OSMOSIS

Element	Chemical Form	Membrane Rejection (%)	Type of Evaluation	References
Americium	Am^{+3}	98.9	Laboratory	1
Barium	Ba^{+2}	92.5	Laboratory	9,10,
Bromine	Br^{-1}	95.0	Laboratory	11,12
Cadmium	Cd^{+2}	98.0	Laboratory	9,11,12,13
Cerium	Ce^{+3}	99.92	Liquid Radwaste	3,14
Cesium	Cs^{+1}	97.1	Laboratory	2
Chromium	CrO_4^{-2}	98.5	Industrial	9,11,12,13
Cobalt	Co^{+2}	97.7	Laboratory	5
Copper	Cu^{+2}	98.6	Industrial	9,13,15
Iodine	I^{-1}	92.9	Laboratory	5
Iron	Fe^{+3}	98.0	Laboratory	9,10,16
Lanthanum	La^{+3}	98.0	Laboratory	10
Lead	Pb^{+2}	98.5	Industrial	10,15
Manganese	Mn^{+2}	+99.9	Liquid Radwaste	3,11,16
Molybdenum	MoO_4^{-2}	97.6	Liquid Radwaste	3
Neptunium	Np^{+5}	99.0	Laboratory	1
Nickel	Ni^{+2}	99.2	Industrial	11,13,17
Niobium	Nb^{+3}	99.9	Liquid Radwaste	3
Phosphorous	PO_4^{-3}	99.5	Industrial	11,17
Plutonium	Pu^{+4}	99.0	Laboratory	1
Radium	Ra^{+2}	99.0	Well Water	18
Ruthenium	Ru^{+2}	99.9	Liquid Radwaste	9,10
Silver	Ag^{+1}	96.0	Laboratory	9,11
Sodium	Na^{+1}	96.5	Laboratory	11
Strontium	Sr^{+2}	99.0	Potable Source	10,11,15
Thorium	Th^{+4}	+99.9	Mining Waste Water	14,17
Uranium	U^{+6}	99.1	Laboratory	1
Zironium	Zr^{+4}	99.8	Laboratory	3

Table 2 - TYPICAL APPLICATIONS OF ULTRAFILTRATION AND REVERSE OSMOSIS PROCESSES

Plant (Name & Location)	Unit Size	Membrane Type and Configuration	Total Solids Level (mg/L)	Source of Waste	Volume Reduction	Reference
Tsuruga Station Japan Atomic Power Comp.	UF Pilot Plant UF Full Scale	Noncelluosic Tubular Membranes	10-15	Equipment Drains	75-150	7
Soviet Test Cells Russia	RO Laboratory Test Cells	Cellulose-Acetate Plant-Frame Membrane	500-700	Industrial Radwaste	400	6
Point Beach Nuclear Plant Wisconsin - USA	RO Pilot Plant	Polyamide Hollow Fiber Membranes	90	Radwaste	2-10	7
H. B. Robsin Plant S. Carolina - USA	RO Pilot Plant	Cellulose-Acetate Outside-in ceramic tubes	7.1	Radwaste	2	7
Mound Laboratory Ohio - USA	UF Full Scale	Noncellulose tubular membranes	30-70	Fuel Reprocessing Radwaste	200	8
Rocky Flats Plant Colorado - USA	RO pilot plant & Full Scale	Cellulose Acetate Spiral Wound Membranes	221	Caustic Radioactive Water	100-200	19
Westinghouse Elec. Corp. Pennsylvania - USA	RO Laboratory Scale	Cellulose Acetate Tubular Membranes	-	Steam Generator Blow Down	10	20
Brunswick Steam Elec. Plant N. Carolina - USA	RO Full Scale	Cellulose Acetate Spiral Wound Membrane	5450-7400	Floor Drains	3-5	7
Hitachi Research Lab Ibaraki - Japan	RO Pilot Plant	Cellulose Acetate Tubular Membrane	10-20	Laundry	1000	21
R. E. Ginna Station New York, USA	RO Full Scale	Cellulose Acetate Tubular Membrane	2200-6100	Floor Drain and Laundry	400	7
Chalk River Nuclear Lab Ontario - Canada	RO Pilot Plant	Cellulose Acetate Tubular Membrane	100-3000	Hot Shower and Laundry	150-200	7

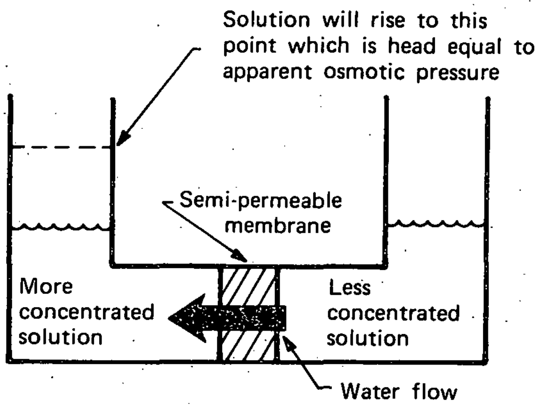

FIGURE 3 - Osmosis taken from Osmonics literature.

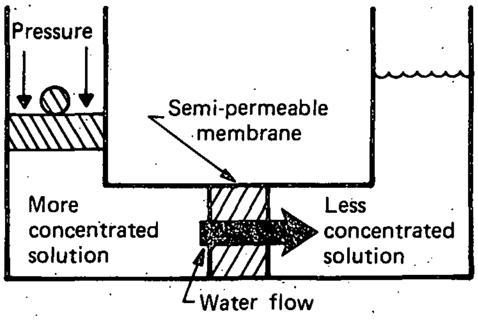

FIGURE 4 - Reverse osmosis taken from Osmonics literature.

fabricated by sandwiching a porous supporting material between the planar reverse-osmosis membranes; sealing the edges of the membranes to each other and to a central tube; and then wrapping membranes, porous support, and a mesh feed-side spacer into a spiral around the central tube. The spiral of membranes, spacer, and porous support is slipped into a cylindrical casing capable of withstanding high pressures. The pressurized feed solution is fed into the casing so that it flows through the mesh feed-side spacers and along the surfaces of the membranes. Part of the solvent permeates the membrane and flows through the porous support material into the central tube, from which it is collected.

In hollow-fiber reverse-osmosis units, the membranes are spun into hollow fibers. These are almost as fine as a human hair (100 to 200 μm) but are hollow, with walls about 25 μm thick. Cylinders this small need no supporting structure to withstand large pressures without collapsing. A bundle of long fibers is arranged in a U-shape, and the open ends of the U-shaped bundle are potted in plastic. The bundle with its potted ends is arranged in a cylindrical pressure shell. Feed solution is introduced into the middle of the fibers through a porous tube at one end of the cylinder, and the concentrated product leaves from an effluent tube at the same end. The permeate transfers through the fibers and flows through each fiber to the potted end, where it leaves the cylinder [24].

Some of the preceding types of membrane module configurations are more suitable for certain applications than are others. The features of the various types are compared in Table 5.

Table 3 - TYPICAL MEMBRANE CATION REJECTIONS/PASSAGES (97% SODIUM CHLORIDE REJECTION MEMBRANE)[a]

Cation Name	Symbol	Rejection (%)	Passage Average (%)	Maximum Concentration (%)
Sodium	Na^{+}	94-96	5	5-10
Calcium	Ca^{+2}	96-98	3	b
Magnesium	Mg^{-2}	96-98	3	b
Potassium	K^{+}	94-96	5	5-10
Iron	Fe^{+2}	98-99	2	b
Manganese	Mn^{+2}	98-99	2	b
Aluminum	Al^{+3}	99 +	1	10-20
Ammonium	NH_4^{+1}	88-95	8	3-8
Copper	Cu^{+2}	98-99	1	10-20
Nickel	Ni^{+2}	98-99	1	10-20
Zinc	Zn^{+2}	98-99	1	10-20
Strontium	Sr^{+2}	96-99	3	-
Hardness	Ca and Mg	96-98	3	b
Cadmium	Cd^{-2}	95-98	3	10-20
Silver	Ag^{+1}	94-96	5	b
Mercury	Hg^{+2}	96-98	3	-

[a] Taken from Osmonics literature [11]

[b] Must watch for precipitation, other ion controls maximum concentration

Membrane porosity

Reverse osmosis membranes are classified by NaCl rejection. There are several types of reverse osmosis membranes with different NaCl rejections. Table 6 lists some general specifications for five types of spiral-wound membranes manufactured by Osmonics Inc. Membranes with NaCl rejection of 0, 50, and 97 (manufactured by Osmonics Inc.) were tested at Mound for rejection of the folowing isotopes: ^{239}Pu, ^{233}U, ^{241}Am, ^{237}Np, ^{137}Cs, ^{125}I, and ^{60}Co [1,2,5].

The 0 membrane, it should be pointed out, is an ultrafiltration membrane, not a reverse osmosis membrane. A reverse osmosis membrane is capable of rejection, or selective retention, of ionic impurities. The ionic impurities are repelled by the membrane and restricted from passing through the membrane pore. The size of the ionic impurity is normally smaller than the membrane pore. Reverse osmosis has become generally accepted as the removal of ionic impurities from water by means of a membrane. The rejection, or selective retention, of nonionic impurities such

Table 4 - TYPICAL MEMBRANE ANION REJECTIONS/PASSAGES (97% SODIUM CHLORIDE REJECTION MEMBRANE)[a]

Anion Name	Symbol	Rejection (%)	Passage Average (%)	Maximum Concentration (%)
Chloride	Cl^{-1}	94-95	5	5-8
Bicarbonate	HCO_3^{-1}	95-96	4	5-10
Sulfate	SO_4^{-2}	99+	1	5-15
Nitrate	NO_3^{-1}[b]	85-95	10	3-6
Fluoride	F^{-1}	94-96	5	5-8
Silicate	SiO_2^{-2}[b]	80-95	10	-
Phosphate	PO_4^{-3}	99+	1	10-20
Bromide	Br^{-1}	94-96	5	5-8
Borate	$B_4O_7^{-2}$[b]	35-70[b]	-	-
Chromate	CrO_4^{-2}[b]	90-98	6	8-12
Cyanide	CN^{-1}[b]	90-95	6	8-12
Sulfite	SO_3^{-2}	98-99	1	5-15
Thiosulfate	$S_2O_3^{-2}$	99+	1	10-20
Ferrocyanide	$Fe(CN)_6^{-3}$	99+	1	10-20

[a] Taken from Osmonics literature [11].

[b] Extremely dependent on pH; tends to be an exception to the rule

as organics and emulsified materials has become known as ultrafiltration (UF). Membranes that remove impurities based on size are classified as ultrafiltration membranes. In general, a UF membrane has become commonly accepted as a membrane that does not reject ionic materials. The O membrane, because ionic rejection was attempted at operating pressures associated with reverse osmosis, will be referred to as an RO membrane. The fact that the O membrane is fabricated of polysulfone, which is tolerant to solutions ranging in pH from 0.5 to 12.5 and is resistant to temperatures in excess of 180°F, makes this a potentially useful membrane. The maximum suggested operating pressure is 200 psig. The manufacturer's suggested operating pressure is 100 psig, although polysulfone membranes tend to compact at pressures above 50 psig. The O membrane has an average pore size of 15 Å and a molecular weight cutoff of 1000 for organics. The O membrane is not effective in salt separation that is dependent on ionization.

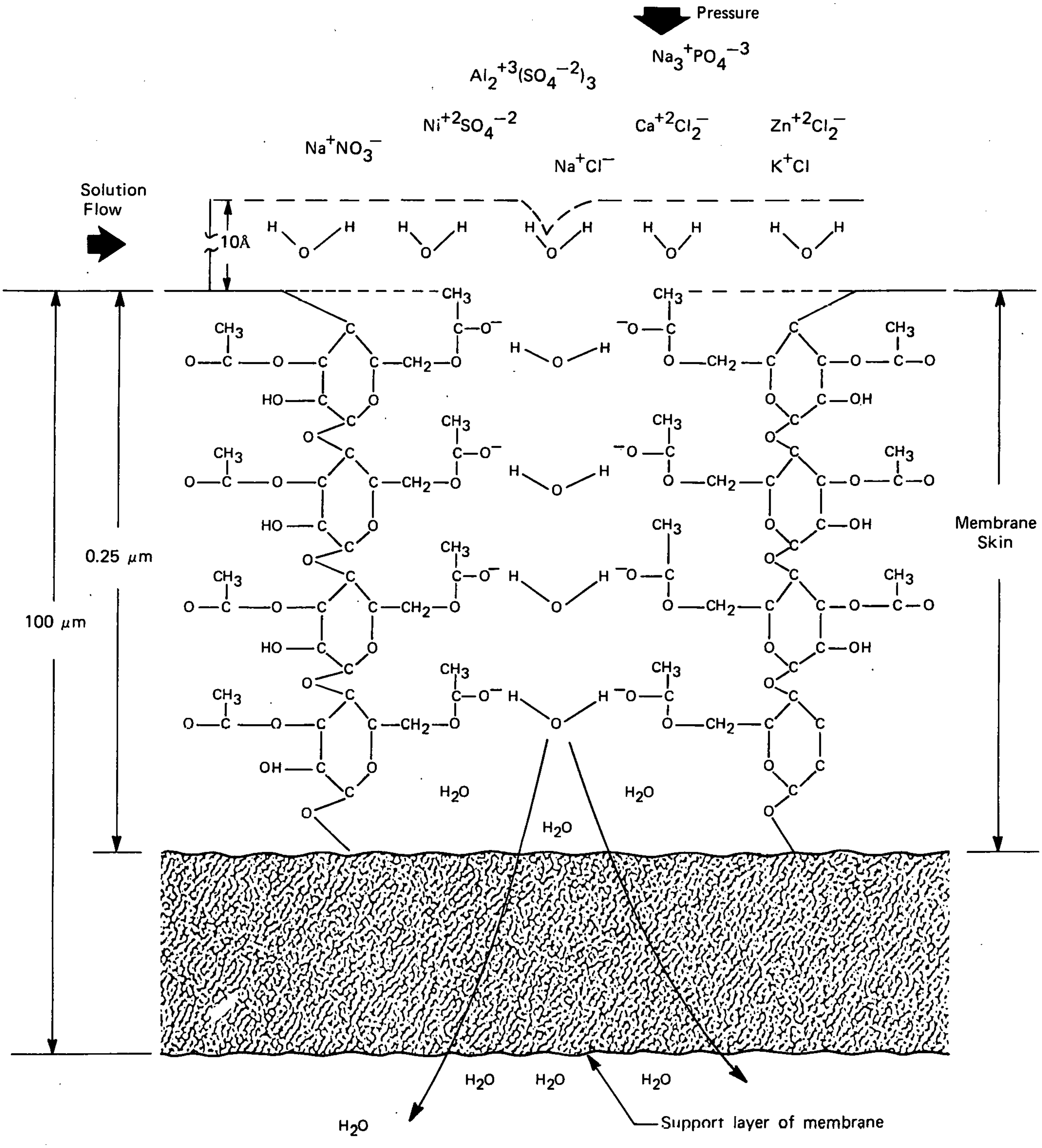

FIGURE 5 - Conception of salt rejection with a "97%" rejection membrane cellulose acetate.

Table 5 - FEATURES OF DIFFERENT MEMBRANE CONFIGURATIONS

Commercially Available Configuration	Advantages	Disadvantages
Tubular	1. Easily cleaned chemically or mechanically if membranes become fouled 2. Can process dirty feeds with minimal pretreatment	1. High holdup per unit membrane area 2. Relatively expensive 3. Requires moderately large floor space per square foot of membrane surface
Spiral Wound	1. Low in cost 2. Compact, low floor space per square foot of membrane surface 3. Low holdup per unit membrane area	1. Susceptible to particle plugging 2. Badly fouled membranes difficult to clean.
Hollow-Fiber	1. Compact 2. Inexpensive	1. Very susceptible to particle plugging 2. Badly fouled membrane modules nearly impossible to clean

Table 6 - GENERAL SPECIFICATION FOR RO/UF MEMBRANE MODULES

	PERMEATION RATES (gal/hr)				
	200 psi		400 psi		
	"0"	"50"	"89"	"92"	"97"
OSMO-52	9.4	4.7	5.0	4.2	2.8
OSMO-112	21	10.8	10.8	9.0	6.0
OSMO-192	31	15.8	15.8	13.1	8.8
OSMO-334	78	35	35	28	19
OSMO-554	134	60	60	48	33
NaCl% Rejection	0-10	40-70	85-90	90-94	94-98
Organic Cut-Off Molecular Weight	1000	600	400	300	200

NOTES

1. Permeation rates assume 1000 ppm NaCl feed, 77°F at 10% recovery. 0 and 50 modules at 200 psig; 89, 92, and 97 modules at 400 psig.
2. Permeation rates are proportional to pressure.
3. Suggested operating temperature is 32-85°F. Temperatures over 85°F will reduce membrane life.

In the 0 membrane studies performed at Mound, there was a great deal of variation in the results, but this was expected because of the low salt rejection of the membrane and dependence on particle size for rejection (Table 7).

Both the 50 and 97 membranes are constructed of cellulose acetate and should be used only in the pH range from 3 to 6. The cellulose acetate membranes vary in maximum operating pressure yet, unlike the polysulfone membrane, the cellulose acetate membranes resist compaction at high pressure. The maximum suggested long-term operating pressure is 300 psig, and the recommended operating pressure is 200 psig for the 50 membrane. The 50 membrane has a molecular weight cutoff of 600 for organics and an average pore size of 11 Å. For the 97 membrane, the maximum suggested operating pressure is 800 psig, and the suggested operating pressure for low compaction is 400 psig. The 97 membrane has a molecular weight cutoff of 200 for organics and an average pore size of 5 Å.

The 50 membrane performed better than anticipated with the actinides and about as expected with the fission products. The 50 membrane demonstrated better than 95% rejections with actinides which are of higher valence and larger size than the fission products which averaged around 50% rejection (Table 7).

The 97 membrane demonstrated the best performance of the membranes tested. The 97 membrane had high rejections with all the isotopes tested (Table 7).

Both the 50 and 97 membranes demonstrated excellent potential for the volume reduction of actinide-contaminated waste streams, but the 97 membrane should be used for fission products.

Table 7 - RESULTS OF RO MEMBRANE TESTS

Isotope	0-Membrane Rejection (%)	50-Membrane Rejection (%)	97-Membrane Rejection (%)
^{239}Pu	64.0 ± 35.8	99.4 ± 0.7	98.9 ± 1.5
^{237}Np	35.5 ± 29.5	96.8 ± 1.7	99.0 ± 1.0
^{241}Am	21.8 ± 28.3	98.6 ± 1.2	98.9 ± 0.1
^{233}U	14.3 ± 1.4	98.8 ± 0.1	99.1 ± 0.2
^{137}Cs	1.1 ± 2.5	42.2 ± 1.5	97.1 ± 0.2
^{125}I	2.9 ± 0.6	49.8 ± 1.9	92.9 ± 0.3
^{60}Co	4.9 ± 4.7	95.4 ± 0.1	97.5 ± 0.9

Factors affecting the membrane

There are five main factors that affect the useful life of a reverse osmosis membrane: pressure, chemical change, bacteria, temperature, and surface coating or plugging.

Since the reverse osmosis membrane is a plastic material somewhat resembling a sponge, pressure tends to deform or compact the membrane. As with all plastics, there is a continuous yield of the membrane above a certain operating pressure. The continuous yielding of the membrane structure causes the substructure of the compacted film to become less and less porous. The permeation rate decreases as the membrane is compacted, but the salt rejection does not change substantially [23].

Compaction of spiral-wound RO membranes is an irreversible process, which is dependent on pressure and temperature and is most pronounced at pressures above 500 psig. At 400 to 500 psig and 77°F, a 10% decrease in initial permeation rate can be expected per year. At pressures of 150 to 300 psig, there appears to be little if any compaction at temperatures below 80°F. Pressures in excess of 500 psig have a high compaction rate showing decreases in permeation rates from 20 to 50% per year. Currently, 600 psig is the maximum pressure used for practical RO processing; however, in some specialized industrial processing where there are high osmotic pressures, pressures of 800 psig are warranted. Seawater desalting requires a pressure of 600-800 psig, with some experts advocating 1500 psig. At 1500 psig, membrane life is very short and may be reduced to 50% of initial capacity in less than six months, depending on temperature. Membrane compaction is significant but can be allowed for in the initial system design. Since compaction occurs continuously and is predictable, most manufacturers will design for the loss of permeation rate during the first year.

The least understood limitation in reverse osmosis is the effect of chemicals on the membrane. In general, cellulose acetate membranes should be used with solutions with a pH between 2 and 8. For the longest life of the membrane, the pH should be between 2.5 and 7. In solutions with pH greater than 7 and those with pH less than 2.5, the acetate radicals in the membrane are hydrolyzed from the cellulose acetate, and the membrane becomes a straight cellulose membrane [25]. Since cellulose membranes do not reject salt, the salt rejection of the reverse osmosis system decreases as the membrane is chemically changed. Hydrolysis rates are dependent on pH and temperature. The hydrolysis rates are dependent on the particular compound that imparts the pH to the solution. For example, a sodium phosphate or sodium carbonate induced alkaline pH does not affect the membrane in the same way as a sodium hydroxide induced pH [23,25,27].

In waste water applications, bacteria are an important factor in the RO system and must be controlled. Generally, bacteria will not harm the RO membrane, although a large growth of bacteria can impair flow through the channels between the membranes. Reduction of channel flow reduces turbulence and causes loss in efficiency of the system. There are a few strains of bacteria that can digest the microporous top layer of the membrane and reduce the ability of the membrane to reject salt. Chlorination of the feed stream is a simple and successful way to control biological growth in a system.

Reverse osmosis systems are designed to operate on solutions at ambient temperatures. Temperatures above 100°F are generally avoided because of problems in the membrane support structures, seals, and the accelerated membrane compaction rates. Operating at ambient temperatures also reduces the cost of a system substantially because corrosion rates are decreased.

The fifth limitation to membrane life is surface coating. Of the limitations discussed, surface coating, or precipitation, is the only one that is reversible. Some paraffin compounds and nonsoluble proteins have been found to coat the membrane and mask the pores. Other oils that are emulsified have been easily concentrated with the RO membrane modules. When materials coat the membrane, the membrane must be cleaned periodically with detergent or an enzyme cleaner in order to restore the permeation rate. Various cleaning compounds can be used, although caustic cleaners cannot be used because they will hydrolyze the membrane.

Salts that are at or near their saturation point become supersaturated over the membrane and precipitate onto the membrane. Most precipitated salts will not harm the membrane except that they mask the pores and plug the channels, thus reducing the permeation rate. Precipitated salts can ususally be removed from an RO system by flushing with an acid solution at a pH of approximately 2.5. One common salt, calcium carbonate, carries a pH of over 10 with it as it precipitates. Calcium carbonate quickly hydrolyzes the membrane material whenever it is deposited, causing salt rejection to decrease.

Reverse osmosis equipment must be used with care when preceded by clarifiers or other processes which use precipitation as a method of waste treatment. If sodium hydroxide is used to cause precipitation, then the clarifier effluent must have the pH lowered to redissolve the precipitated salts still in the solution. Clarifiers using lime will usually have an effluent that is saturated in calcium sulfate. Calcium sulfate solubility is not dependent on pH, and even at a low pH, it can precipitate during concentration. Generally, reverse osmosis should be applied while the solutes are still highly soluble.

Membrane radiation stability

The exposure of a polymeric membrane material to a radioactive environment for an extended time period has raised questions regarding potential membrane degradation. This degradation may be manifested by changes in membrane physical and mechanical properties (tensile strength, elongation, elasticity, solution viscosity, stiffness, and hardness), or in performance characteristics (permeability and rejection) [26]. Because of this degradation potential, many experiments have been performed to assess membrane radiation stability [7].

In Russia, cellulose acetate RO membrane material was exposed to radiation at different levels up to 8 Mrad. Membrane flux and rejection values were used as indications of radiation damage during the study. The results of the study strongly indicated that the surface life of the membrane did not impose any restrictions upon the process during the treatment of low-level liquid radioactive wastes [6].

Evirongenics Systems Company has exposed cellulose acetate membranes up to 1 x 10^5 rad. The results did not indicate any significant change in membrane flux, rejection, and tensile properties. Also, cellulose acetate could be subjected to a continuous dose rate of 3.0 rads/hr for 3 yr [7].

Definition of terminology

- FEED is the untreated waste solution that is introduced to the RO system under pressure. For this discussion, let the solute concentration = C_f.
- PERMEATE is the solution (usually purified water) that passes through the membrane. The solute concentration = C_p.
- CONCENTRATE (BLOW-BY) is the solution that exits from the system and that has not passed through the membrane. It is enriched in a particular rejected material. The solute concentration = C_c.
- RECOVERY is the ratio of permeation rate to feed rate:

$$\text{Recovery} = \frac{\text{Permeation Rate}}{\text{Feed Rate}} = \frac{(PR)}{(FR)} \tag{1}$$

- CONCENTRATE CONCENTRATION is the concentration of the concentrate stream, or blow-by, as it exits the RO unit. It is related to feed concentration and recovery as follows:

$$C_c = \frac{C_f}{(1 - \text{Recovery})} \tag{2}$$

NOTE: This formula is based on the mass balance $(FR)C_f = (CR)C_c + (PR)C_p$ and assumes that $C_p = 0$. This is an oversimplification that assumes a "perfect" membrane. It works satisfactorily when the solute rejection is 95% or greater but severely distorts the true system when solute rejections are less than 85%.

- AVERAGE CONCENTRATION is the generalized mixture of feed and concentrate to which the membrane is exposed. It is defined as the feed concentration plus the concentrate concentration divided by two:

$$C\ \text{avg.} = (C_f + C_c)/2 \tag{3}$$

NOTE: Again this is an oversimplification and has the same restrictions as the above. It will tend to give a higher C avg. than what will actually occur and is therefore a conservative estimate.

For a given input feed rate (FR), the permeation rate (PR) obtained from an RO unit is a function of a number of interrelated factors. Among these are:

- The membrane area
- The type of membrane used
- The apparent osmotic pressure, ΔP, of the solution. (ΔP is a function of average concentration and kind of solute).

- The operating pressure
- The temperature of the solution
- The condition of the membrane

Table 8 lists some example osmotic pressures.

Estimation of costs

When a solution that has a high osmotic pressure is considered, the effect of apparent osmotic pressure, ΔP, cannot be neglected as insignificant, and the basic equation of reverse osmosis becomes important. This equation is:

$$Peff = Pop - \Delta P \quad (4)$$

where Pop = The operating pressure applied against the membrane

P = Apparent osmotic pressure

Peff = Effective pressure available to force permeation through the membrane.

When an application is being considered, the Peff must be found in order to estimate the PR that can be expected from a module. The PRact is the actual permeation rate for a particular system. PRsp is the specified permeation rate when the effect of ΔP is negligible. For estimating:

$$PRact = \frac{Peff}{Psp} PRsp \quad (5)$$

where the Psp is the pressure at which the PRsp is given. For the 97% membrane, the PRsp is given as Psp = 400 psig.

The calculations for a waste stream containing 500 ppm total dissolved solids

Table 8 - EXAMPLES OF OSMOTIC PRESSURES

Salts	Concentration (%)	Osmotic Pressure (psi)
Sodium Chloride, NaCl	0.5	55
	1.0	125
	3.5	410
Sodium Sulfate, Na_2SO_4	2	110
	5	304
	10	568
Calcium Chloride, $CaCl_2$	1	90
	3.5	308
Copper Sulfate, $CuSO_4$	2	57
	5	115
	10	231

NOTE:
1. Percent concentration times 10,000 is equivalent to ppm or mg/L.
2. One oz/gal is equivalent to 750 mg/L.
3. Linear interpolation can be used to estimate intermediate concentrations.

(TDS) with a recovery of 90% using an OSMO 97 membrane are as follows:

$$C_c = \frac{C_f}{1\text{-recovery}} \qquad (6)$$

where Recovery = 90% = 0.90
C_f = 500 ppm

$$\text{Thus } C_c = \frac{500}{1 - 0.90} = \frac{500}{0.1} = 5000$$

$$\text{Cavg} = \frac{C_f + C_c}{2} \qquad (7)$$

where C_f = 500 ppm
C_c = 5000 ppm

$$\text{Thus Cavg} = \frac{500 + 5000}{2} = \frac{5500}{2} = 2750 \text{ ppm}$$

The osmotic pressure varies with different salt solutions (Table 8). Because a NaCl solution has the highest osmotic pressure (approximately 1 psi per 100 ppm TDS), it is best to assume that the TDS is composed entirely of NaCl when estimating, in order to be sure not to underestimate. Therefore, the estimated apparent osmotic pressure for the Cavg calculated in Equation 7 (2750 ppm TDS) is approximately 28 psi.

$$\text{Peff} = \text{Pop} - \Delta P \qquad (8)$$

where Pop = 400 psi
ΔP = 28 psi
Thus Peff = 400 psi - 28 psi
Peff = 372 psi

Then, in order to estimate the permeation rate for an OSMO - 774-97 module, the following equation is used

$$\text{PRact} = \frac{\text{Peff}}{\text{Psp}} \text{PRsp} \qquad (9)$$

where PRsp = 0.55 gal/min
Psp = 400 psig
Peff = 372 psig

Thus

$$\text{PRact} = \frac{372}{400} (0.55) = 0.51 \text{ gal/min per 774-97 module}$$

The following equations are used to determine the number of 774-97 modules needed for an RO plant to handle an input feed rate of 40 gal/min with a recovery rate of 90%.

Feed Rate (Recovery) = permeation rate (10)
Where Feed rate = 40 gal/min
Recovery = 90%
40 gal/min (90) = 36 gal/min permeation
Feed rate - Permeation rate = Concentration rate
40 gal/min - 36 gal/min = 4 gal/min concentration rate

PR plant ÷ PR module = modules (11)
36 gal/min ÷ 0.51 gal/min = 71 modules

The area of the membrane in the 774-97 module is 77 ft^2. Therefore, in a membrane plant with 71 modules, there would be 5,467 ft^2 of membrane. The capital cost of a membrane plant can be estimated by multiplying the total membrane area by $11.00/$\text{ft}^2$ [27]. Therefore, the estimated capital cost of a membrane plant capable of handling a feed rate of 40 gal/min with 500 ppm TDS and operating at 90% recovery, would be approximately $60,137.

Table 9 lists some typical capital costs of reverse osmosis systems operating at 90% recovery. Figure 6 is a graphical representation of the capital cost as a function of the permeation rate. The operating costs range from about $0.75 to $2.00 per 1000 gal of water, with 10% going for electricity, 75% for membrane

Table 9 - REVERSE OSMOSIS SYSTEMS WITH 97 MEMBRANE AT 90% RECOVERY[a]

Membrane area (ft^2)	2940	4200	5880	7140	8820	10,800
Permeation rate						
(gal/min)	20	30	40	50	60	70
(gal/day)[b]	9,600	14,400	19,200	24,000	28,000	33,600
Net Capital Cost[c]	$44,600	$50,800	$63,660	$69,290	$78,000	$86,500
Approximate Size (ft)	18Lx6Hx2W	21Lx6Hx3W	21Lx6Hx4W	21Lx6Hx5W	21Lx6Hx5W	21Lx6Hx6W

[a] Data from D. Musser, Osmonics, Inc., Hopkins, Minn.

[b] Gallons per day are based on an 8-hr day.

[c] Add 10% for waste streams with chloride concentrations above 6000 ppm, as 304 stainless steel must be replaced with 316; add 50% for two-stage system for 99% recovery.

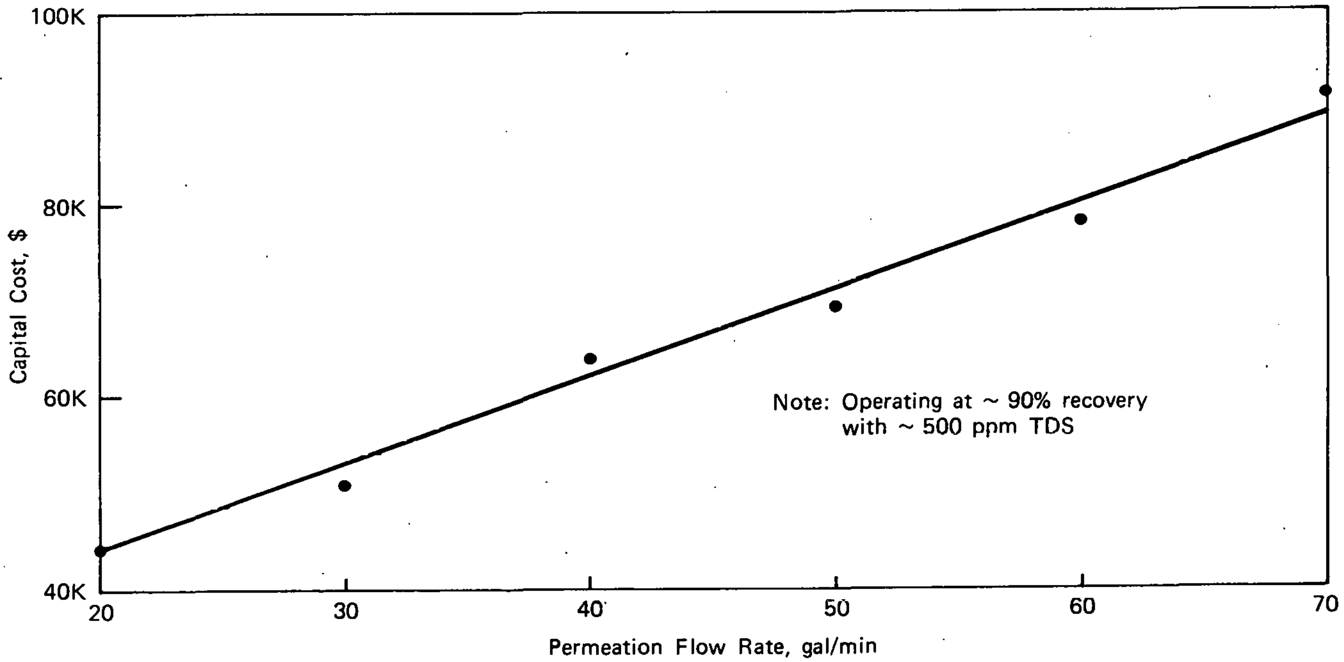

FIGURE 6 - Approximate capital cost as a function of permeation flow rate for reverse osmosis.

replacement, 5% for chemicals, and 10% for maintenance*.

The operating cost of reverse osmosis remains constant up to a feed water concentration of about 2000 ppm TDS and increases only slightly above 2000 ppm [11]. The operating cost per 1000 gal decreases as unit permeation flow rates increase. The capital cost of a membrane system is increased by 10% if chlorine levels in the feed stream are greater than 6000 ppm, because the 304 stainless steel in the RO unit must be replaced by 316 stainless steel.

To obtain a recovery of greater than 95% with solutions high in salts, a two-stage system is necessary. This would increase the capital cost by 50%. Recovery can be converted to volume reduction as follows:

Recovery (%)	Volume Reduction
67	3X
90	10X
97	30X
98	50X
99	100X

The primary purpose of incorporating reverse osmosis as a means of decontaminating radioactive streams is to produce a purified stream concurrent with reducing the volume of radioactively contaminated water. This approach assumes necessary volume reductions of 10 to 400, or water recoveries in excess of 90%. This level of water recovery is possible only if the primary constituents within the stream do not cause scaling, the inherent osmotic pressure does not become excessive, and proper design restrictions are met.

Reverse osmosis plant design

A reverse osmosis system designed for continuous operation and producing 40 gal/min incorporates 5775 ft^2 of 97 cellulose acetate membrane operated at 400 psig (Figure 7). This system is rated for feed water with a constant inlet pressure between 30-60 psig at 77°F. Chemical feed equipment to maintain the feed solution pH at 6.0 ±0.5 is included. The purpose of the chemical feed equipment is to provide optimum life of the membrane and to reduce the possibility of precipitation of calcium and magnesium salts. Pure water recovery of the feed water can be set at 90% to 95%. Feed water must be below 85°F and a maximum continuous water temperature below 80°F is suggested. If higher temperatures are used, it should be realized that the permeation rate will increase, but the economic life of the membrane modules will decrease due to membrane compaction. Controls are supplied to keep the high pressure pump from running dry, to protect against low flow in the system, and to protect against high temperature in the system.

SUMMARY OF EQUIPMENT

Prefilters: Stainless steel housing with 25 μm cartridges (not necessary if UF is used for pretreatment).

Chemical feed pump: Precision chemical feed pump for sulfuric acid feed. Pump operated off electrical signal from pH monitor to maintain pH = 6.0. Feed water pressure must be constant and below 60 psig. A bactericide can also be added to the feed solution and a residual of 0.2 ppm chlorine is suggested if water may be contaminated.

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*Data from L. Combs, Osmonics, Inc., Hopkins, Minn.

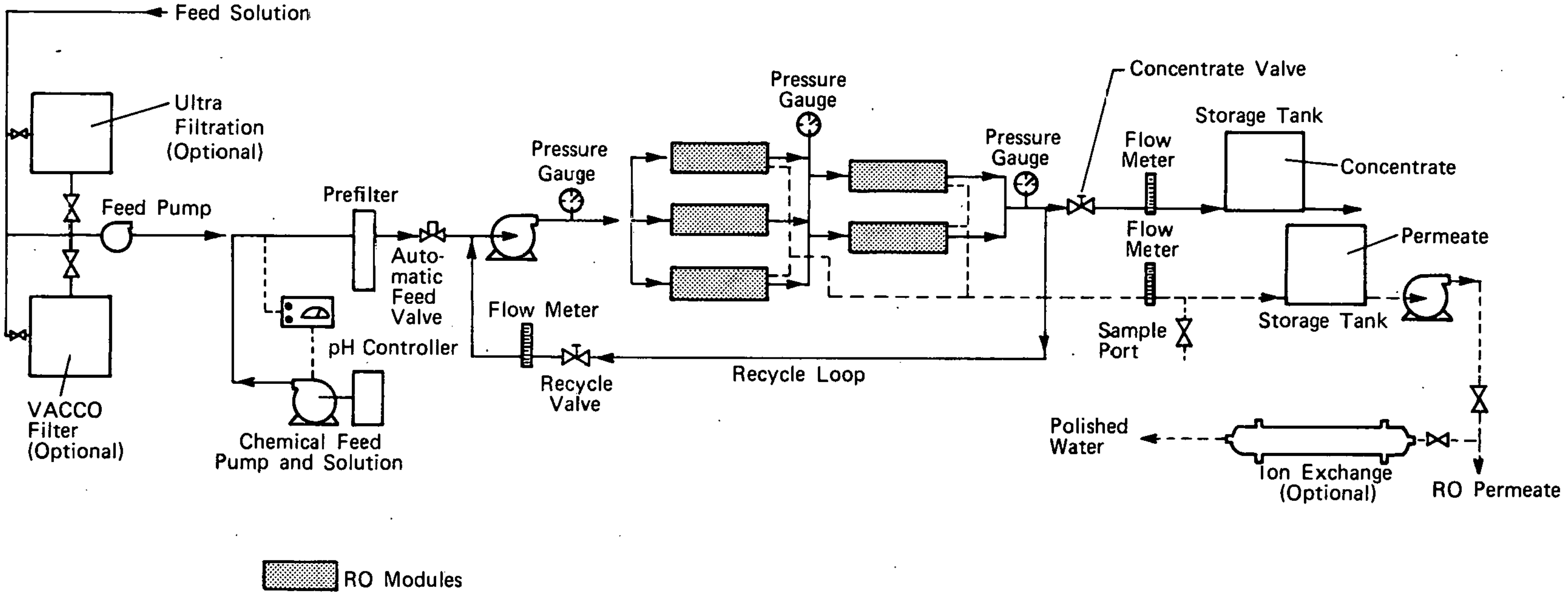


FIGURE 7 - Reverse osmosis system.

pH Controllet-Recorder: Continuous controlling and indicating of the chemical feed pump with alarm to shut down system if pH goes too high.

High Pressure Pump: Centrifugal pump with stainless steel casting and stainless steel impellers.

Motors: 40 Hp, 460 volt A.C., three phase 60 Hz, 3600 rpm, O.D.P.

Pipe Sizes: Inlet: 2 in. Flange
Permeated product or pure water: 2 in. Flange
Concentrate or blow-by: 1-1/4 in. Flange

Pressure Vessels: 15
Number: All stainless steel type 304 for extended life and lightweight. Rated over 2500 psi burst.

Membrane Module: 5 OSMO - 774 - 97 modules per vessel

Inter-Vessel Piping: 304 S.S. Tubing; 316 S.S. Tubing fittings

Instrumentation:
Permeated Product Conductivity Monitor: Continuous monitor and temperature compensated cell with adjustable alarm set point.
Flow Meters: Rotometer type for measurement of permeated product flow rate and concentrate flow rate. Readouts are panel mounted. Recycle rotometer is mounted in-line.
Pressure Gauges: Two panel-mounted 4-1/2 in. gauges indicate initial and final pressures through module banks. Each module bank has an independent pressure gauge on manifolds. Permeate has an in-line pressure gauge.
Thermometer: Thermometer to read temperature of solution in modules is mounted in-line. Stainless steel wetted components.
Temperature Control Switch: With stainless steel well. Adjustable set point. All stainless steel wetted components.
pH Controller: See previous discussion.
Size: 21 ft long, 4 ft wide, 6 ft high.
Approximate Weight: 3300 lb.

AVAILABLE OPTIONS

1. Additional electrical indicators and switches to show which alarm shut down the unit. Six indicator lights are for the five basic alarm conditions plus one alarm that can be wired to indicate such conditions as high permeation pressure, high or low conductivity, low pH. Indicators tell which alarm caused unit to shut down.

2. Permeation high pressure switch to shut down unit if permeation pressure exceeds 100 psi.

3. Permeation pressure relief valve to exhaust pressure from permeated product should a valve be closed while unit is in operation.

4. Heat Exchanger for removal of pumping energy in high recovery systems. Brass and bronze construction of heat exchanger. Uses cold water at 65°F or lower to cool feed.

3.1.4.2 Engineering Column Evaluation

Melvin K. Williams

Introduction

The cobalt-60 main effects design experiment [5] resulted in the choice of three variables for inclusion in the cobalt-60 interaction design. Those three variables were: hydroxide ion concentration [OH^-] in terms of pH, sulfite ion concentration [$SO_3^=$] in parts per million, and ammonium ion concentration [NH_4^+] in parts per million. The determined hydroxide ion concentration limits were: low limit, pH=3; midpoint, pH=6.5; and high limit, pH=10. The limits for sulfite and ammonium ions were: low limit, 1 ppm; midpoint, 50 ppm; and high limit, 100 ppm. (Table 10)

The cobalt-60 interaction design was a three-factor interaction design. This design was used to determine the magnitude of the effects of the three variables and the magnitudes of the interactions of the three variables with respect to the removal of cobalt-60 from an aqueous solution by

Table 10 - VARIABLE LIMITS, CHEMICAL LEVELS, AND CONSTANTS

		Concentration				
Ion	Level	(ppm)	(mg/L)	(g/L)	(MW)	(M)
NH_4^+	+	100	100	0.100	18	5.56×10^{-3}
	0	50	50	0.050	18	2.78×10^{-3}
	-	1	1	0.001	18	5.56×10^{-5}
$SO_3^=$	+	100	100	0.100	80.06	1.25×10^{-3}
	0	50	50	0.050	80.06	6.25×10^{-4}
	-	1	1	0.001	80.06	1.25×10^{-5}

Chemical	Level	(M)	(MW)	(g/L)	(g/15L)	10 ml spike (g/L)
NH_4Cl	+	5.56×10^{-3}	53.5	2.97×10^{-1}	4.46	446.0
	0	2.78×10^{-3}	53.5	1.49×10^{-1}	2.23	223.0
	-	5.56×10^{-5}	53.5	2.97×10^{-3}	4.46×10^{-2}	4.46
Na_2SO_3	+	1.25×10^{-3}	126.0	1.58×10^{-1}	2.36	236
	0	6.25×10^{-4}	126.0	7.88×10^{-2}	1.18	118
	-	1.25×10^{-5}	126.0	1.58×10^{-3}	2.36×10^{-2}	2.36

CONSTANTS:

[Co^{60}] = 10,000 counts/min/ml
Flow rate = 400 ml/min
Resins = Sodium form AG50WX8, MSC-1, HCR-2W-H

OH^- will be adjusted with a pH meter. The variable levels for OH^- are:

+ pH = 10.0
0 pH = 6.5
- pH = 3.0

a cation exchange resin. Three separate resins were tested with this experimental design. The resins tested (MSC-1, HCR-2W-H and AG50WX8) were all strong acid cation exchange resins. The interaction design consisted of nine solution compositions which represented the corners and the centerpoint of a cube formed by the variables on three-dimensional cartesian axes (See Figure 8).

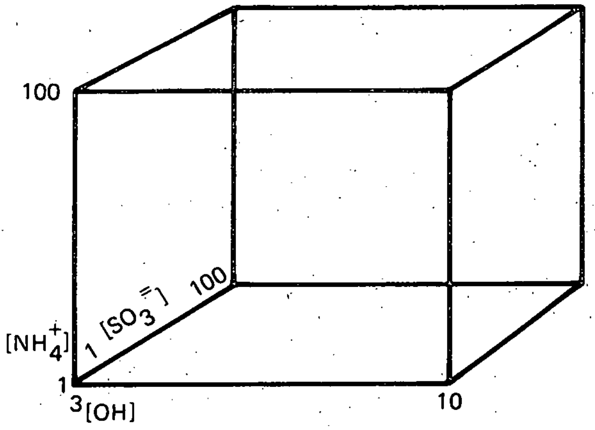


FIGURE 8 - Cubic space formed by the three variables of the cobalt-60 interaction design.

The experimental design (Figure 9) determined the solution composition for each run according to the convention of plus being the high variable limit, minus being the lower limit, and zero being the midpoint. For statistical determination of the variance, the centerpoint was replicated three times with two replicates on each of the eight corners.

Once analyzed and formed into a prediction equation, the data should give a good representation of how those three variables interact to produce an effect at any position inside or on the surface of the cube. Areas outside the cube cannot be predicted. Quite often the equation produced by this simple design will accurately describe the effects caused by the variables. Sometimes, however, a more complex model is needed.

The aqueous chemistry of cobalt (II) and cobalt (III) compounds is complex. Cobalt has an outer electron shell which has availability for three electrons in the 3d shell ($[Ar]3d^7 4s^2$) [27]. Cobalt (III) has an ($[Ar]3d^6$) electron configuration. This arrangement is very convenient for octahedral complex formation because six hybrid orbitals (d^2sp^3) are available for coordination (See Figure 10).

This is a diamagnetic arrangement since all 3d electrons are paired. Most coordination compounds of cobalt (III) have this configuration [27]. A few cobalt (III) compounds are reported to be paramagnetic [27]. Their orbital arrangement would be as in Figure 11.

These cobalt (III) compounds are not generally present in aqueous solution. Normally cobalt (III) compounds in aqueous solution will be octahedrally coordinated with some ligand or ligands.

Cobalt (III) ions in aqueous solution will not exist without stabilization from coordination [28,29] (See Figure 12).

Trial	Run #	Y	X_1 $[OH^-]$	X_2 $[NH_4^+]$	X_3 $[SO_3^=]$	X_1X_2	X_1X_3	X_2X_3	Y's	$\bar{Y}$	$(Y-\bar{Y})$	$(Y-\bar{Y})^2$	S^2	df r-1	Y_{PRED}	$\tau = Y_{PRED} - Y_{Ob}$
CP	1		o	o	o	o	o	o								
CP	10		o	o	o	o	o	o								
CP	19		o	o	o	o	o	o								
1	5 16		-	-	-	+	+	+								
2	6 14		+	-	-	-	-	+								
3	7 11		-	+	-	-	+	-								
4	4 17		+	+	-	+	-	-								
5	8 13		-	-	+	+	-	-								
6	3 15		+	-	+	-	+	-								
7	2 18		-	+	+	-	-	+								
8	9 12		+	+	+	+	+	+								

$\Sigma X\bar{Y} =$

$\Sigma X\bar{Y}/(T/2) =$

$\frac{2\Sigma X\bar{Y}/T}{2} = b =$

FIGURE 9 - Cobalt-60 interaction design.

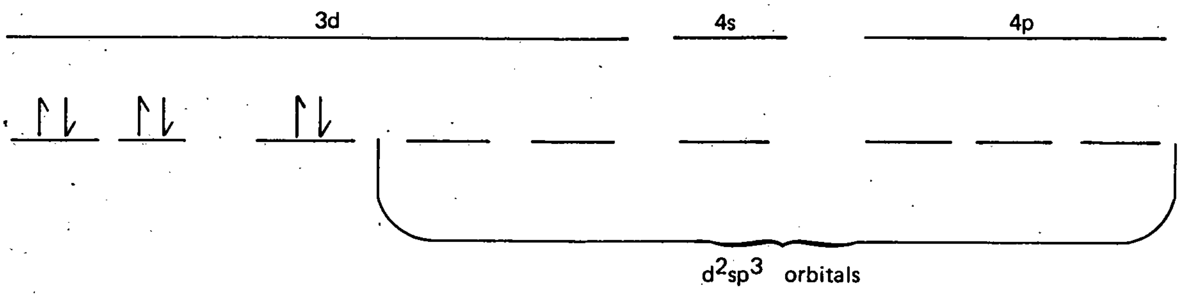


FIGURE 10 - Valence bond theory of bonding in cobalt (III).

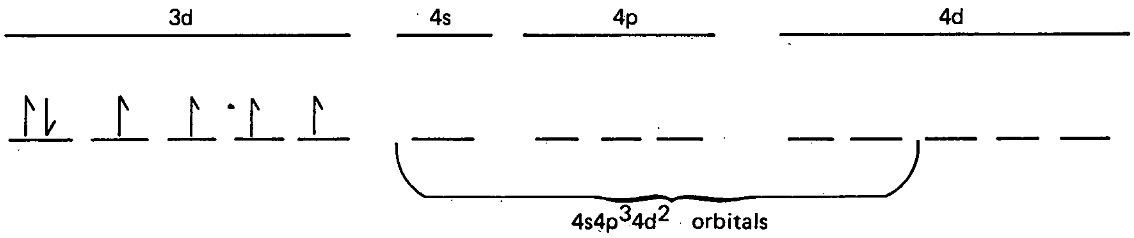


FIGURE 11 - Orbital arrangment of paramagnetic cobalt (III) compounds.

EQUATION	**POTENTIAL (E°)**
$Co^{++} \rightleftharpoons Co^{+++} + e^-$	−1.82
$[Co(NH_3)_6]^{++} \rightleftharpoons [Co(NH_3)_6]^{+++} + e^-$	−0.1
$[Co(CN)_6]^{++} \rightleftharpoons [Co(CN)_6]^{+++} + e^-$	+0.83

FIGURE 12 - Stabilization of cobalt (III) through coordination.

Procedure

The procedure for preparing the feed solutions for the ion exchange runs was to first determine from the experimental design what the levels of the three variables should be. For instance, run number four from the experimental design (Figure 9) gives the levels + for $[OH^-]$, + for $[NH_4^+]$, and - for $[SO_3^=]$. From Table 10 it can be seen that this corresponds to pH=10, 100 ppm NH_4^+, and 1 ppm $SO_3^=$. Stock solutions of NH_4Cl and Na_2SO_3 had been made so that 10 ml of the stock solution in 15 liters of reverse osmosis treated water would give the proper level of NH_4^+ and $SO_3^=$. After the ammonium and sulfite were added, the solution was probed with a calibrated pH electrode and adjusted while being mixed to the proper pH with either sodium hydroxide or hydrochloric acid. In this case (run 4), the pH was increased to 10.00 ± 0.02. After a stable reading was reached, the solution was spiked from a cobalt-60 stock solution which was calculated to give 10,000 counts/min/ml. The solution was then mixed and sampled and was ready to be run as a feed solution through the ion exchange resins.

The procedure for preparing the ion exchange resins for each run was to generate, or regenerate, the resin by running a 1.0 M sodium chloride solution through the resin until the resin was in sodium form. Regenerations were ended when the regenerant reached background level so that all previously exchanged cobalt-60 was removed from the resin and replaced by sodium. The resin was then washed with at least 10 bed volumes of reverse osmosis treated water. If any gas had been generated in the resin bed, the resin was backwashed to remove the gas pockets to prevent streaming during the run. After the resin was regenerated, washed, and backwashed, the feed solution was run through the resin at a flow rate of 400 ml/min. During the run, three samples of the effluent were taken from each column. These samples were prepared for scintillation counting on a Packard 460CD scintillation counter and counted along with a blank or background sample and the feed sample from the run. The background was subtracted from the other samples, the effluent samples were averaged, and the percent of cobalt removed was calculated. This value was the "Y" value placed on the experimental design.

Results

In general, all three cation exchange resins tested showed >99% removal of cobalt on the pH=3 runs and the centerpoint where the pH was 6.5. The pH=10 runs, however, varied from 92% cobalt removed to 9% cobalt removed. These results were expected. From Figure 13 it can be seen that in the pH range of 3 to 7 almost none of the ammonium ion present has been reacted to ammonia. And because of the large differences in the stability of cobalt (II) complexes and cobalt (III) complexes, and the inverse difference in the stability of cobalt (II) simple salts and cobalt (III) simple salts, at pH 3 and 6.5 all or >99% of the cobalt present will be in the form of cobalt (II) dipositive ions. These are easily removed by ion exchange. At pH=10, however, of 100 ppm NH_4^+ put into the solution, only about 15% will be in that form, and 85% will be in the form of NH_3. With NH_3 present, the formation of cobalt (III) complexes is favored over cobalt (II) simple salts. The large difference between the amounts of cobalt-60 removed by the various pH 10 runs

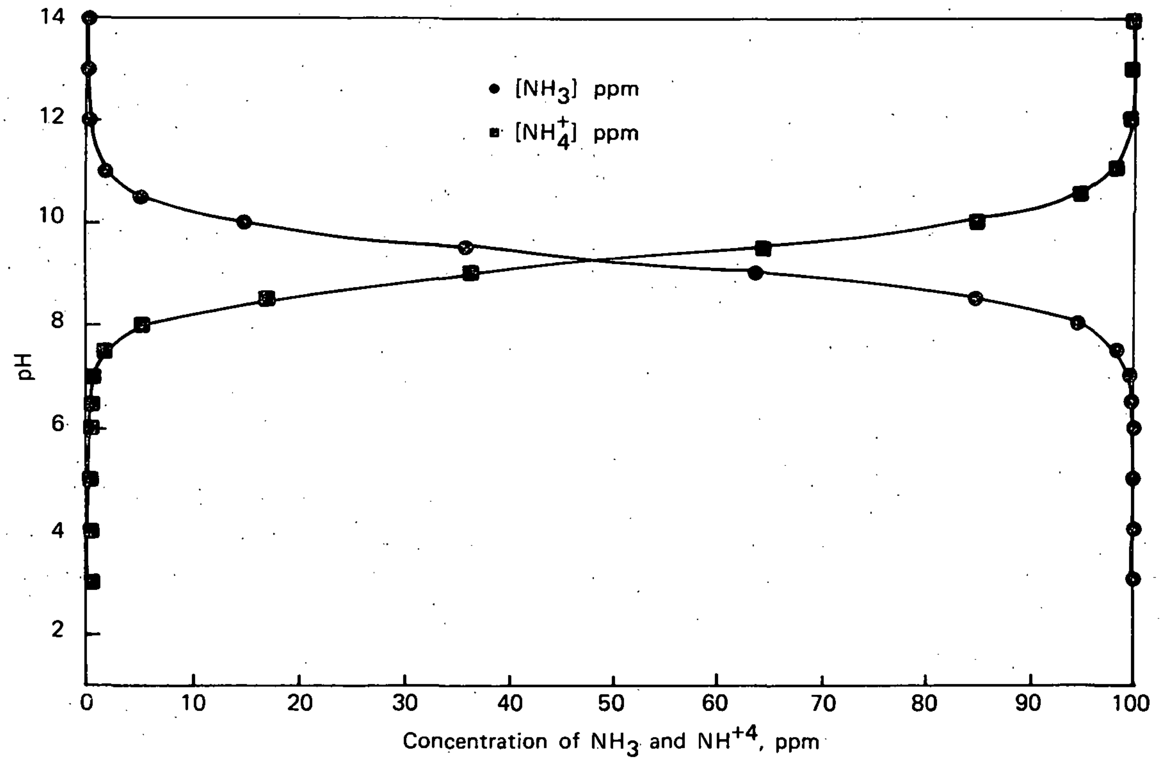


FIGURE 13 - Concentration of NH_4^+ as a function of pH in the reaction $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$, calculated using $K = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.6885X10^{-10}$ starting with 100 ppm NH_4^+ and 0 ppm NH_3.

stems from the amounts of NH_4^+ and $SO_3^=$ placed originally in those runs. Four combinations of ammonium and sulfite were run at pH=10 on each of the resins. Each combination was run twice.

The pH=10 runs, their levels of ammonium and sulfite, and the results ($\overline{y}$) are listed in Table 11. As can be seen from Table 11, when both $[NH_4^+]$ and $[SO_3^=]$ were at the 1 ppm level, about 90% of the cobalt-60 was removed. This means that about 10% of the cobalt-60 present was in the form of cobalt (III) complexes which were either negative or neutral. When 1 ppm NH_4^+ and 100 ppm $SO_3^=$ were present, about 63% of the cobalt-60 was removed. This is roughly 30% less cobalt-60 removed than when the $SO_3^=$ concentration was only 1 ppm. This result probably means that when the concentrations of NH_4^+ and $SO_3^=$ were both 1 ppm, about 40% of the cobalt was in the form of cobalt (III) complexes, but only about 10% were

Table 11 - pH=10 RUNS

Resin	Run No.	(ppm)	(ppm)	$\overline{y}$ % Co_{60} Removed
AG50WX8	6/14	1	1	89.6
	3/15	1	100	63.9
	4/17	100	1	47.6
	9/12	100	100	20.7
MSC-1	6/14	1	1	90.0
	3/15	1	100	63.1
	4/17	100	1	44.9
	9/12	100	100	20.5
HCR-2W-H	6/14	1	1	91.5
	3/15	1	100	61.9
	4/17	100	1	41.5
	9/12	100	100	13.1

negative or neutral. The others were complexes such as $[Co(NH_3)_6]^{+3}$, $[Co(NH_3)_5H_2O]^{+3}$, $[Co(NH_3)_4(H_2O)_2]^{+3}$, $[Co(NH_3)_5SO_3]^{+1}$, $[Co(NH_3)_5OH]^{+2}$, $[Co(NH_3)_4(H_2O)(OH)]^{+2}$, and $[Co(NH_3)_4(H_2O)SO_3]^{+1}$. With the additional $SO_3^=$ present in runs 3 and 15, most of the cobalt (III) present was probably in neutral or negative form, such as $[Co(NH_3)_4(SO_3)_2]^-$ and $[Co(NH_3)_4(SO_3)(OH)]^o$. One might think that 1 ppm NH_4^+ is a very small amount, when up to six NH_3 molecultes can complex with one cobalt atom. However, at 10,000 counts/min/ml the concentration of cobalt-60 is approximately 0.000004 ppm. Therefore, chemically, 1 ppm NH_4^+ is a large excess. Again in Table 11, runs 4/17, the concentration of NH_4^+ is 100 ppm, and the concentration of $SO_3^=$ is 1 ppm. This combination averaged roughly 45% cobalt-60 removed. This is a further decrease from runs 3/15. In this case, about 55% of the cobalt was in the form of neutral or negative cobalt (III) complexes. From the much lower results on runs 9/12, it is believed that roughly 80% of the cobalt in runs 4/17 was in the form of coablt (III) complexes; however, about 25% were positively charged. In runs 9/12, roughly 20% of the cobalt-60 was removed, so roughly 80% of the cobalt was in the form of cobalt (III) neutral or negative complexes. It is believed that most of the cobalt would eventually go to cobalt (III) in these solutions with NH_3 present, but either more time or more molecular oxygen would be needed for the oxidation to occur [30].

The experimental design, results, and analyses for the resins AG50WX8, MSC-1, and HCR2W-H are shown in Figures 14,15, and 16 respectively. All three resins behaved basically the same with only slight differences in the actual values of the variable coefficients. The strongest single factor was the effect of hydroxide ion concentration, ammonium concentration was the next strongest, then sulfite concentration. Two interactions were found. Of the two interactions, the hydroxide ion concentration-ammonium ion concentration interaction was the stronger, and the hydroxide ion concentration-sulfite ion concentration interaction was the weaker. The ammonium ion concentration-sulfite ion concentration interaction was less than the response variation. The three-factor interaction, $x_1x_2x_3$, was also less than the response variation. In the order of decreasing effect, the variables can be listed as follows: $[OH]>[NH_4^+] = [OH^-][NH_4^+]>[SO_3^+] = [OH^-][SO_3^=]$.

The first generation prediction equations are listed in Table 12. As the table indicates, these equations do not predict well at the centerpoint. At pH=6.5, the centerpoint (See Figure 13), only a fraction of a percent (0.18%) of the NH_4^+ present is in the form of NH_3. Since so little NH_3 is present, almost all the cobalt will be removed as cobalt (II) ions. This nonlinearity of response eliminates a linear equation as a good model. Since the first model was not adequate to describe the response over the entire cubic region described by the variables, more data were necessary. Three more points were selected, to be done with one replicate each, necessitating performing six more runs. The points chosen were from the centerpoint to the center of the ammonium ion concentration-sulfite ion concentration plane. These points held the ammonium ion and sulfite ion concentrations constant and increased the hydroxide ion concentration from pH=6.5 at the centerpoint to pH=10 on the face of the $[NH_4^+][SO_3^=]$ plane (See Figure 17).

Trial	Run #	Y	X_1 $[OH^-]$	X_2 $[NH_4^+]$	X_3 $[SO_3^=]$	X_1X_2	X_1X_3	X_2X_3	Y's	$\overline{Y}$	$(Y-\overline{Y})$	$(Y-\overline{Y})^2$	S^2 $\frac{ss}{df}$	df r-1	Y_{PRED}	$\tau = Y_{PRED} - Y_{Ob}$	$X_1X_2X_3$
CP	1		o	o	o	o	o	o	99.7		0.2	0.04					
CP	10		o	o	o	o	o	o	99.6	99.5	0.1	0.01	0.07	2			
CP	19		o	o	o	o	o	o	99.2		-0.3	0.09					
1	5 16		-	-	-	+	+	+	99.8 99.5	99.7	0.10 -0.20	0.01 0.04	0.05	1			-
2	6 14		+	-	-	-	-	+	88.1 91.0	89.6	-1.50 1.40	2.25 1.96	4.21	1			+
3	7 11		-	+	-	-	+	-	99.8 99.9	99.9	-0.1 0.0	0.01 0.0	0.01	1			+
4	4 17		+	+	-	+	-	-	40.9 54.2	47.6	-6.70 6.60	44.89 43.56	88.45	1			-
5	8 13		-	-	+	+	-	-	99.8 99.7	99.8	0.0 -0.1	0.0 0.01	0.01	1			+
6	3 15		+	-	+	-	+	-	59.5 68.2	63.9	-4.40 4.30	19.36 18.49	37.85	1			-
7	2 18		-	+	+	-	-	+	99.7 99.7	99.7	0.0 0.0	0.0 0.0	0.0	1			-
8	9 12		+	+	+	+	+	+	25.7 15.6	20.7	5.0 -5.1	25.0 26.01	51.0	1			+
$\Sigma X\overline{Y} =$			-177.3	-85.1	-52.7	-85.3	-52.5	-1.5									-0.90
$\Sigma X\overline{Y}/(T/2) =$			- 44.3	-21.3	-13.2	-21.3	-13.1	-0.38									-0.23
$\frac{2\Sigma X\overline{Y}/T}{2} = b =$			-22.2	-10.6	-6.6	-10.7	-6.6	-0.19									-0.11

b_o = Avg $\overline{y}$ corners

$b_o = 77.61$

$\Sigma df=10$

$\Sigma S^2 x df=181.7$

$S_p^2 = \frac{181.7}{10} = 18.2$

$S_p = 4.26$, 10 df $t = 2.23$

$$Y = b_o + b_1x_1, + b_2x_2 + b_3x_3 + b_{1,2}x_1x_2 + b_{1,3}x_1x_3 + b_{2,3}x_2x_3 + b_{1,2,3}x_1x_2x_3$$

$$Y = 77.6-22.2x_1-10.6x_2-6.6x_3-10.7x_1x_2-6.6x_1x_3$$

Physical Units $x_1 = \frac{X_1-6.5}{3.5}$; $x_2 = \frac{X_2-50.5}{49.5}$; $x_3 = \frac{X_3-50.5}{49.5}$

b conf lim $= \pm t\, S_p\sqrt{\frac{1}{T_r}}$

bcL $= \pm 2.37$

$\overline{Y}$cL $= \pm 6.72$

Model Pit = 21.9 ± 6.43

FIGURE 14 - Experimental design, results, and analysis for AG50WX8.

Trial	Run #	Y	X_1 $[OH^-]$	X_2 $[NH_4^+]$	X_3 $[SO_3^=]$	X_1X_2	X_1X_3	X_2X_3	Y's	$\overline{Y}$	$(Y-\overline{Y})$	$(Y-\overline{Y})^2$	s^2	df r-1	Y_{PRED}	$\tau = Y_{PRED} - Y_{Ob}$	$X_1X_2X_3$
CP	1		o	o	o	o	o	o	95.7		-2.5	6.25					
CP	10		o	o	o	o	o	o	99.6	98.2	1.4	1.96	4.61	2			
CP	19		o	o	o	o	o	o	99.2		1.0	1.0					
1	5 16		-	-	-	+	+	+	99.5 99.1	99.3	0.2 -0.2	0.04 0.04	0.03	1			-
2	6 14		+	-	-	-	-	+	90.0 90.0	90.0	0 0	0 0	0.00	1			+
3	7 11		-	+	-	-	+	-	99.8 99.9	99.9	-0.05 0.05	0.003 0.003	0.006	1			+
4	4 17		+	+	-	+	-	-	35.6 54.2	44.9	-9.3 9.3	86.5 86.5	172.98	1			-
5	8 13		-	-	+	+	-	-	99.8 99.6	99.7	0.10 -0.10	0.01 0.01	0.02	1			+
6	3 15		+	-	+	-	+	-	68.9 57.2	63.1	5.8 -5.9	33.64 34.81	68.45	1			-
7	2 18		-	+	+	-	-	+	98.9 99.6	99.3	-0.40 0.30	0.16 0.09	0.25	1			-
8	9 12		+	+	+	+	+	+	28.7 12.2	20.5	8.2 -8.3	67.24 68.89	136.13	1			+
$\Sigma X\overline{Y}$ =			-179.7	-87.5	-51.5	-87.90	-51.10	1.5	b_o = 77.09								3.50
$\Sigma X\overline{Y}/(T/2)$ =			- 44.93	-21.88	-12.88	-21.98	-12.78	0.38									0.88
$\frac{2\Sigma X\overline{Y}/T}{2}$ = b =			- 22.5	-10.9	- 6.4	-11.0	-6.4	0.19									0.44

$Y = 77.09-22.5x_1-10.9x_2-6.4x_3-11.0x_1x_2-6.4x_1x_3$

$\Sigma df=10$

$\Sigma S^2 x df = 387.1$

$S_p^2 = 38.71$

$S_p = 6.22$ $t = 2.23$

bcL = ± 3.47

$\overline{Y}cL$ = ± 9.81

Model fit = -21.1 ± 9.39

FIGURE 15 - Experimental design, results, and analysis for MSC-1.

Trial	Run #	Y	X_1 $[OH^-]$	X_2 $[NH_4^+]$	X_3 $[SO_3^=]$	X_1X_2	X_1X_3	X_2X_3	Y's	$\bar{Y}$	$(Y-\bar{Y})$	$(Y-\bar{Y})^2$	S^2	df r-1	Y_{PRED}	$\tau = Y_{PRED} - Y_{Ob}$	$X_1X_2X_3$
CP	1		o	o	o	o	o	o	99.8		0.30	0.09					
CP	10		o	o	o	o	o	o	99.3	99.5	-0.20	0.04	0.09	2			
CP	19		o	o	o	o	o	o	99.3		-0.20	0.04					
1	5 16		-	-	-	+	+	+	99.6 99.7	99.7	-0.10 0.0	0.01 0.0	0.01	1			-
2	6 14		+	-	-	-	-	+	90.9 92.0	91.5	-0.6 0.5	0.36 0.25	0.61	1			+
3	7 11		-	+	-	-	+	-	99.8 99.9	99.9	0.1 0.0	0.01 0.0	0.01	1			+
4	4 17		+	+	-	+	-	-	38.8 44.1	41.5	-2.7 2.6	7.29 6.76	14.05	1			-
5	8 13		-	-	+	+	-	-	99.8 99.6	99.7	0.1 0.1	0.01 0.01	0.02	1			+
6	3 15		+	-	+	-	+	-	68.6 55.1	61.9	6.7 -6.8	44.89 46.24	91.13	1			-
7	2 18		-	+	+	-	-	+	99.6 99.5	99.6	0.0 0.1	0.0 0.01	0.01	1			-
8	9 12		+	+	+	+	+	+	17.1 9.0	13.1	4.0 -4.1	16.00 16.81	32.81	1			+
$\Sigma X\bar{Y}$ =			-190.9	-98.7	-58.3	-98.9	-57.7	0.9	b_o = 75.9								1.50
$\Sigma X\bar{Y}/(T/2)$ =			-47.7	-24.7	-14.5	-24.7	-14.4	0.23									0.38
$\frac{2\Sigma X\bar{Y}/T}{2}$ = b =			-23.9	-12.3	-7.3	-12.4	-7.2	0.11									0.19

$\Sigma df = 10$

$\Sigma S^2 x df = 138.83$

$S_p^2 = 13.88$

$S_p = 3.73$ t = 2.23

bcL = ± 2.08

$\bar{Y}$cL = ± 5.88

$$Y = 75.9 - 23.9x_1 - 12.3x_2 - 7.3x_3 - 12.4x_1x_2 - 7.2x_1x_3$$

FIGURE 16 - Experimental design, results, and analysis for HCR2WH.

Table 12 - FIRST GENERATION PREDICTION EQUATIONS

Resin	Equation	Center point Predicted	Center point Actual
AG50WX8	$y = 103.16-1.29X_1+0.18X_2+0.13X_3-0.06X_1X_2-0.04X_1X_3$	77.78%	99.5%
MSC-1	$y = 103.70-1.38X_1+0.17X_2+0.13X_3-0.06X_1X_2-0.04X_1X_3$	77.23%	98.2%
HCR-2W-H	$y = 106.39-1.27X_1+0.21X_2+0.11X_3-0.07X_1X_2-0.94X_1X_3$	78.39%	99.5%

Table 13 - RESULTS OF EXTRA EXPERIMENTS

	Point 1		Point 2		Point 3	
	Y's	$\bar{Y}$	Y's	$\bar{Y}$	Y's	$\bar{Y}$
Resin	(% ^{60}Co Removed)	(% ^{60}Co Removed)	(% ^{60}Co Removed)	(% ^{60}Co Removed)	(% ^{60}Co Removed)	(% ^{60}Co Removed)
AG50WX8	94.3 91.1	92.7	33.1 36.8	35.0	8.9 24.7	16.8
MSC-1	93.4 90.2	91.8	31.0 33.0	32.0	6.6 22.1	14.4
HCR-2W-H	94.1 91.0	92.6	32.5 35.3	33.9	8.8 23.9	16.4

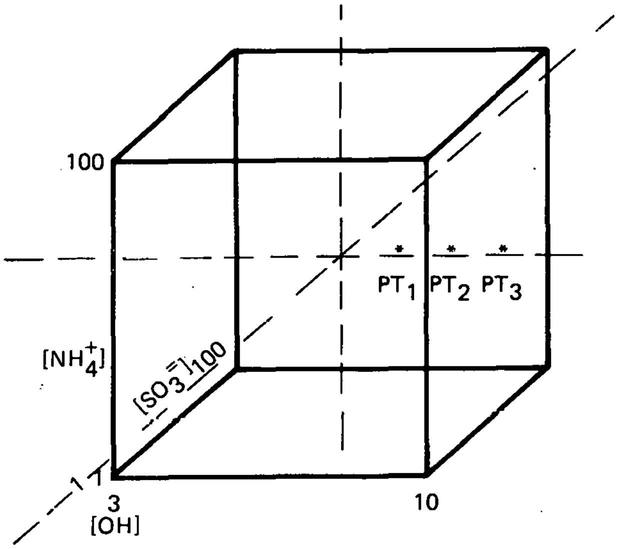


FIGURE 17 - Extra points chosen for cobalt-60 interaction design.

These points, written as three dimensional cartesian coordinates of the form ([OH$^-$], [NH$_4^+$], [SO$_3^=$], are:

Point 1	(7.67, 50, 50)
Point 2	(8.83, 50, 50)
Point 3	(10.00, 50, 50)

These results of these experiments are given in Table 13.

All points of the interaction design and the three extra points were entered in a computer program to obtain prediction equations of the form $Y=b+C_1X_1+C_2X_2+C_3X_3+C_4X_1^2+C_5X_1X_2+C_6X_2^2+C_7X_1X_3+C_8X_2X_3+C_9X_3^2$. These equations, presented in Table 14, are fairly good predictors of the percentage of cobalt removed at the center point and the corners of the cubic space

Table 14 - SECOND GENERATION PREDICTION EQUATIONS

Resin	Equation	Center Point	
		Predicted	Actual
AG50WX8	$y=-56.67+69.03X_1-1.71X_2-5.42X_1^2-0.06X_1X_2+0.02X_2^2-0.04X_1X_3$	95.0%	99.5%
MSC-1	$y=-59.13+70.24X_1-1.79X_2-5.51X_1^2-0.06X_1X_2+0.02X_2^2-0.04X_1X_3$	92.6%	98.2%
HCR-2W-H	$y=-54.37+68.07X_1-1.57X_2-5.33X_1^2-0.07X_1X_2+0.02X_2^2-0.04X_1X_3$	98.6%	99.5%

defined by the variable limits. However, they are not an accurate model of the actual chemical process going on in the solutions. Contour plots from the prediction equation for MSC-1 (Figures 18 and 19) for the $[OH^-]-[NH_4^+]$ plane at the low and high levels of $SO_3^=$ show that the prediction equation gives a saddlepoint contour. It can be easily seen that this model, although a good predictor for the center point and corners, is not a good model elsewhere. For instance, at pH=3 and 50 ppm NH_4^+, 40% to 57% cobalt removed is predicted. Because of the lack of NH_3 for complexing the cobalt (II) to cobalt (III) and because of the lack of $SO_3^=$ at pH=3 (See Figure 20), the cobalt present in solution would almost certainly be in the form of cobalt (II) ions and would be at least 99% removed from the solution by MSC-1. Since this is clearly a poor model, an attempt was made to fit the data to a quadratic with a natural logrithmic term. Each of several modifications of this mathematical form resulted in similar saddlepoint models which were also poor models. In order to produce a good model, more data points would be necessary. Because the areas where cobalt-60 may be effectively removed from solution and the areas where cation exchange does not work well have already been determined, further refinement was considered to be unnecessary.

In general if the pH of the solution is kept acidic, 99% of the cobalt can be expected to be removed from the solution by cation exchange resins. If the solution is basic and cannot be made acidic and free ammonia is present, cation and anion exchange resins must be used and will not remove the neutral complexes that are present. A larger portion of the complexes can be made negative by adding negative ligands such as $SO_3^=$. Other negative ions are known to form negative complexes with cobalt (III). Some of the more common ones that would be of importance in aqueous solution would be $CrO_4^=$, $SO_4^=$, NO_2^-, NO_3^-, CN^-, and OH^-.

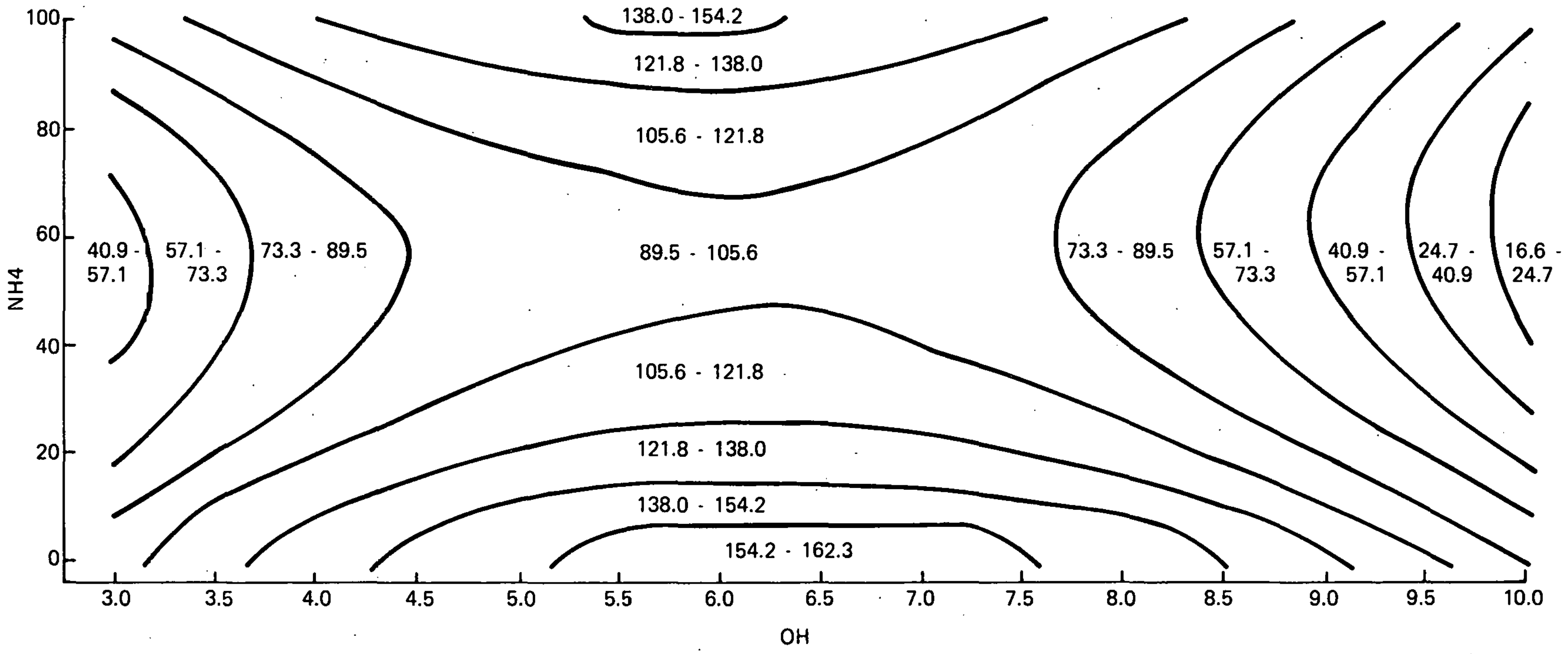


FIGURE 18 - Contour plot from the prediction equation for MSC-1 for the $[OH^-]$-$[NH_4^+]$ plane at the low level of $SO_3^=$.

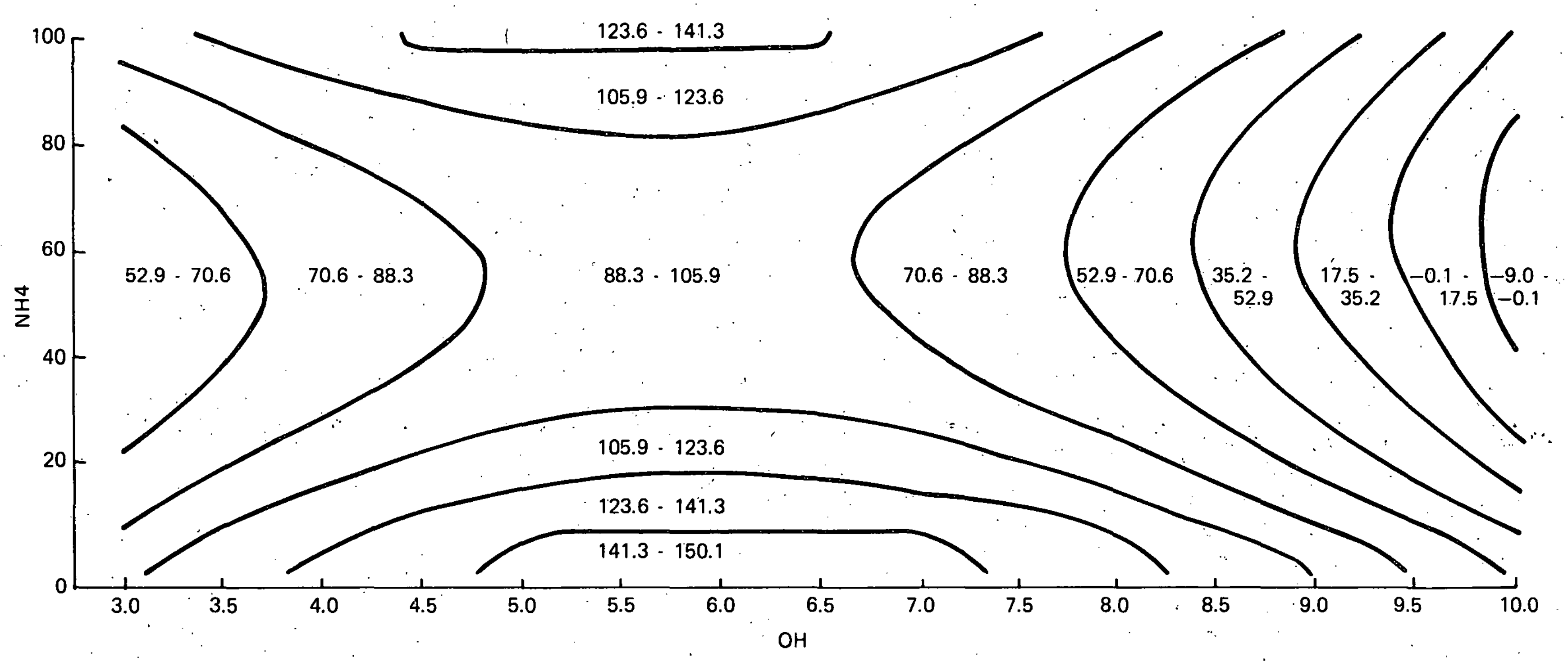


FIGURE 19 - Contour plot from the prediction equation for MSC-1 for the $[OH^-]$-$[NH_4^+]$ plane at the high level of $SO_3^=$.

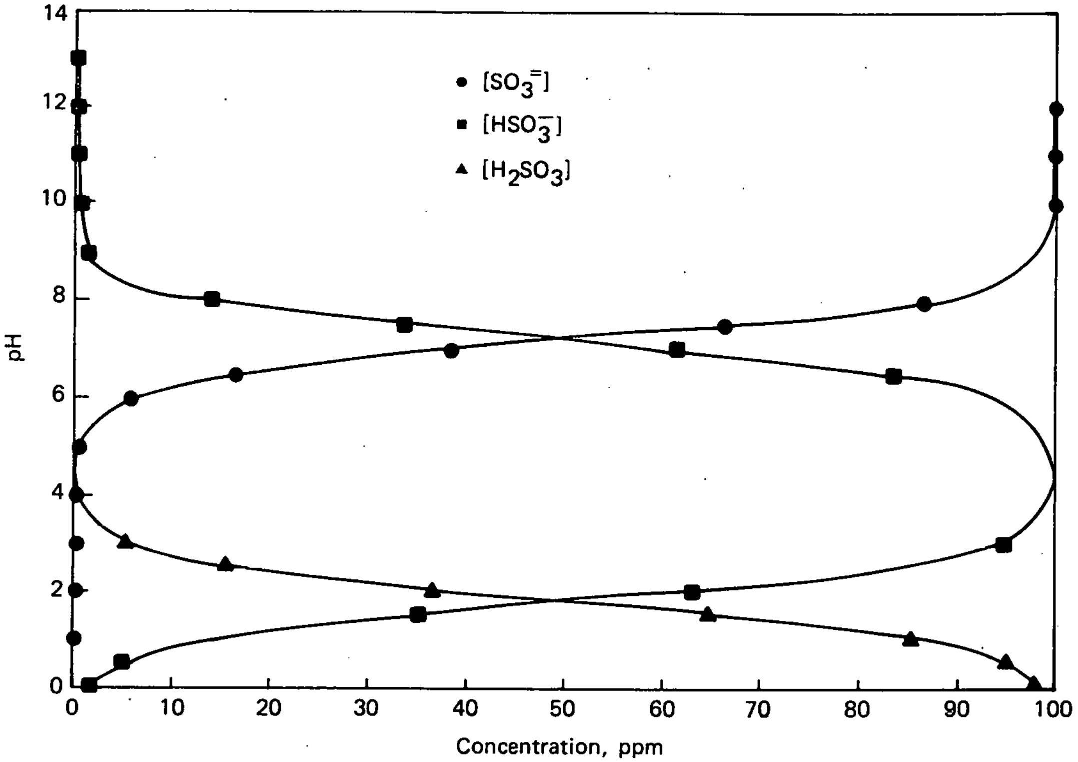


FIGURE 20 - Concentrations of $SO_3^=$, HSO_3^- and H_2SO_3 in aqueous solution as a function of pH (calculted).

Discussion

From the results of the cation exchange resin interaction design with cobalt-60, it can be seen that at pH 10 in the presence of free ammonia (NH_3), the cobalt (II) ion is oxidized to cobalt (III) [30]. The simple cobalt (III) ion is unstable in water and would be reduced to cobalt (II) except for the ammonia present. The ammonia coordinates with the cobalt (III) and forms complexes that are stable in water [28,29]. These complexes can be either positive, negative, or neutral. The positive complexes will be removed by a cation exchange resin just as any other positive ion would be. The neutral and negative complexes, however, would remain in the solution and pass through the resin. To further elucidate the complexation process, a complete cobalt interaction design experiment, with exactly the same solution parameters as used in the cation exchange resin experiment, was run on an anion exchange resin. Because the anion exchange resin would remove the negative complexes and let the positive complexes pass through, the anion exchange results should be an inverse of the cation results, except where neutral complexes are formed. In this manner, an approximation can be made of the amount of positive, negative, and neutral complexes formed in each solution.

The anion exchange interaction design and parameters are the same as for the cation exchange experiment (See Table 10 and Figure 9). The anion resin used was MSA-1, a strong base anion exchanger in chloride form. The anion exchange interaction design was run several weeks after the cation experiment using solutions made up at the time of the cation experiment, so any complexes that would form would have had ample time for formation. As in the cation experiment at pH 3 to 7, nearly all the cobalt was in the form of cobalt (II) ions and where most were absorbed in the cation experiment, in this case most passed through the anion resin. Therefore, once again the runs of interest in terms of cobalt (III) complex formation are the pH=10 runs (Table 15).

The complete anion exchange design and results are presented in Figure 21. The results of the pH=10 runs in Table 15 are consistent with cobalt (III) complex chemistry.

In Runs 6 and 14, the solution composition is 1 ppm NH_4^+ and 1 ppm $SO_3^=$ at pH=10 with $4.0X10^{-6}$ ppm cobalt-60. Since the pH is 10, from Figure 13 it can be discerned that about 0.85 ppm is NH_3 and 0.15 ppm is NH_4^+. Cobalt (III) complexes prefere NH_3 to $SO_3^=$ for complex formation, but will form complexes with both. In this case, probably very few neutral complexes are formed, but likely some are formed. About 10 to 36% of the complexes formed are negative. Since more of the cobalt was in the form of negative complexes in the anion exchange experiment than in the cation experiment, the additional time the solution was in existance did cause the formation of more cobalt (III) complexes. In runs 3 and 15, the composition is 1 ppm NH_4^+, 100 ppm $SO_3^=$ at pH 10, and $4.0X10^{-6}$ ppm cobalt-60. Here, once again, the low concentration of NH_3 as compared to the $SO_3^=$ concentration eliminates most of the neutral cobalt complexes. Between 37 and 50% of the complexes from these solutions are negative, depending on how much time they are given for formation. In Runs 4, 17, 9, and 12, where the NH_3 concentration is 85 ppm, a large portion of neutral complexes is formed (See Table 15).

From Figure 12 it can be seen that the cobalt (III) ion in water will spontaneously be reacted to cobalt (II) [29], whereas when it is octahedrally coordinated with ammonia or cyanide, it is much more stable. Also, if instability or dissociation constants are consulted, it can be seen readily that the cobalt (II) ammonium complex is much less stable in water than the cobalt (III) ammonium complex.

The dissociation constant or instability constant for the cobalt (II) ammonium complex [31] is $1X10^{-5}$. The instability constant for the cobalt (III) ammonium complex [31] is $1X10^{-34}$. In aqueous solutions, cobalt (II) will almost always

Table 15 - EXPERIMENTS IN WHICH pH=10

Run. No.	$[NH_4^+]$ (ppm)	$[SO_3^=]$ (ppm)	Cation (Avg. % R)	Anion (Avg. % R)	Neutral (Prob. %)
6/14	1	1	90.4	35.9	<1
3/15	1	100	63.0	50.3	<1
4/17	100	1	44.7	15.6	39.7
9/12	100	100	18.1	26.2	55.7

Trial	Run #	Y	X_1 $[OH^-]$	X_2 $[NH_4^+]$	X_3 $[SO_3^=]$	X_1X_2	X_1X_3	X_2X_3	Y's	$\bar{Y}$	$(Y-\bar{Y})$	$(Y-\bar{Y})^2$	S^2	df r-1	Y_{PRED}	τ Y_{PRED} $-Y_{Ob}$	$X_1X_2X_3$
CP	1		o	o	o	o	o	o	0.00								
CP	10		o	o	o	o	o	o	2.30	0.77				2			
CP	19		o	o	o	o	o	o	0.00								
1	5 16		-	-	-	+	+	+	0.00 1.54	0.77				1			-
2	6 14		+	-	-	-	-	+	26.51 45.21	35.9				1			+
3	7 11		-	+	-	-	+	-	1.31 1.95	1.63				1			+
4	4 17		+	+	-	+	-	-	14.01 17.21	15.61				1			-
5	8 13		-	-	+	+	-	-	0.57 0.00	0.03				1			+
6	3 15		+	-	+	-	+	-	42.10 58.56	50.30				1			-
7	2 18		-	+	+	-	-	+	0.00 0.02	0.01				1			-
8	9 12		+	+	+	+	+	+	22.31 30.16	26.20				1			+
$\Sigma X\bar{Y} =$			125.57	-43.55	22.63	-45.23	27.38	-4.69		AVG Com							-2.93
$\Sigma XY/(T/2) =$			31.39	-10.89	5.66	-11.31	6.85	-1.17		$b_o = 16.31$							-0.73
$\frac{2\Sigma\ x\ \ y/T}{2} = b =$			15.70	- 5.44	2.83	-5.65	3.42	-0.59									-0.37

FIGURE 21 - MSA-1 anion experimental design results.

be found in a noncomplexed ionic form. Cobalt (III) will almost always be complexed since, ionic form, it would react to form cobalt (II) and is only stabilized in aqueous solutions when complexed [27,28,29].

For clarity it must be understood that the complexes discussed in this paper are all inorganic complexes. It was decided at the onset of the cobalt experiment that, if organics were included, the scope of the experiments would be too vast to complete in the required time. Therefore, organics are considered to be absent from the solutions being treated for ion exchange. In the ion exchange pilot plant design (this publication), a pretreatment is described for removing organics.

The factors used in the cobalt-60 interaction design were $[OH^-]$, $[SO_3^=]$, and $[NH_4^+]$. The reactions that might occur and reasons that led to their inclusion in the design will now be discussed for each factor.

Hydroxide ion concentration was used as a factor because it was proven to have a consistent effect in the cobalt main effects design [5]. Also ammonia, which is a major component of a vast majority of aqueous cobalt III complexes, will not form from ammonium ion at acid pH's (See Figure 13). Some reactions the hydroxide ion may undergo are:

$$Co^o + 2OH^- \rightleftharpoons Co(OH)_2 + 2e^-$$
$$Co(OH)_2 + OH^- \rightleftharpoons Co(OH)_3 + e^-$$
$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

Hydroxide may also be included in cobalt complexes such as [21,28] $[Co(NH_3)_5OH]^{+2}$, $[Co(NH_3)_4(OH)_2]^{+1}$, $[CO_2(OH)_3(NH_3)_6]^{+3}$, $[Co_2(OH)_2(NH_3)_4]^{+4}$, $[Co(OH)_4]^{-2}$, and $[Co(OH)_6]^{-4}$.

The cobalt (II) complexes $[Co(OH)_4]^{-2}$ and $[Co(OH)_6]^{-4}$ are not expected to be found in aqueous solution. Sulfite ion concentration was included as a factor because it is believed to be a part of the large factor interaction in runs 9 and 10 of the cobalt main effects design [5]. Also, sulfite, because of its double negative charge, can sometimes, when complexed with cobalt, cause the complex to be neutral or negative. Sulfite forms complexes with cobalt such as $[Co(NH_3)_4(SO_3)_2]^{-1}$, $[Co(NH_3)_4(SO_3)(OH)]^o$, $[Co(NH_3)_3(SO_3)_3]^{-3}$, $[Co(NH_3)_5(SO_3)]^{+1}$, $[Co(SO_3)_3]^{-3}$, and $[Co(SO_3)_2(NH_3)_2]^{-1}$.

Ammonium ion concentration was included as a factor because so many inorganic cobalt complexes contain ammonia [27,29].

Ammonium ion reacts with hydroxide ion to form ammonia (See Figure 13).

The reaction is $NH_4^+ + OH^- = NH_3 + H_2O$. Cobalt (II), which is normally a dipositive ion in aqueous solution [29], will, in the presence of NH_3 and OH^-, be to some extent converted to cobalt (III) which is complexed with ammonia or hydroxide, or both [29]. This statement is substantiated by the results of this experiment. Also from the standard electrode potential [32], V° for the electrode couple $Co^{+2} = CO^{+3} + e^-$, $V° = -1.808$ J/C; if $\Delta G°$, the standard free energy, is calculated from the equation $V° = \Delta G°/nF$ [32], where n is the number of electrons and F is the Faraday constant, we find ΔG° = -174.45 kJ/mole. Since this ΔG° is negative, the reaction should proceed spontaneously. The rate of the reaction is not a consideration in these calcualations, however, and the large, negative ΔG° proves only that such a reaction is favorable [33].

Summary

An interaction experimental design for removal of cobalt-60 from aqueous solution by three cation exchangers was performed and analyzed. Cobalt (III) inorganic complex formation was discussed, and a comparison was made between an interaction design using an anion exchanger and the interaction design using cation exchangers. The cation exchangers used were AG50W-X8, MSC-1, and HCR-2W-H. The anion exchanger used was MSA-1. The variables for both experimental designs were $[OH^-]$, $[NH_4^+]$, and $[SO_3^=]$.

3.1.4.4 Ion Exchange/Adsorbent Pilot Plant

Melvin K. Williams

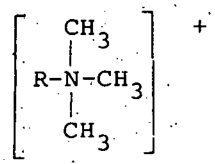
Introduction

A decontamination of greater than 99% of the actinides and fission products contained in radioactive waste water can be obtained using ion exchange resins. A system for achieving this result is described in this paper. This ion exchange pilot plant design is the culmination of 5 yr of study of the decontamination of radioactive waste streams by ion exchange resins and other adsorbents at MRC-Mound.

In order to maintain maximum flexibility of treatments, this pilot plant design is a conceptual design with specific flows, resins, and column specifications, but with many optional features and no rigid equipment specifications. This flexibility allows the system to be amenable to almost any radioactive waste stream. Very specific designs can be constructed from this conceptual design for the treatment of any specific waste stream.

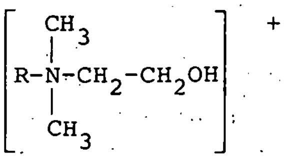
Ion exchange may be used to remove any charged specie existing in aqueous solution. There are three basic theories of ion exchange which try to explain why ion exchange works and describe the mechanism involved [34]. They are the crystal lattice theory, the double layer theory, and the Donnan membrane theory. The crystal lattice theory is probably the best description of a synthetic organic exchanger although aspects of the other theories apply. The crystal lattice theory is the better description of how a synthetic organic exchanger works because it explains how the polar medium of an aqueous solution encourages the exchange of ions [34], and it assumes a fixed number of exchage sites [34] that must be satisfied regardless of change in pH or concentration. The most common synthetic organic ion exchangers are divinylbenzene crosslinked polystyrene polymers which have ionizable groups attached to the benzene rings [35]. For cation resins these ionizable groups are acidic groups such as $R\text{-}SO_3H$, $R\text{-}CO_2H$, or

$R-PO_3H_2$. In anion resins these ionizable groups are basic groups such as [36]



$$\left[\begin{array}{c} CH_3 \\ | \\ R-N-CH_3 \\ | \\ CH_3 \end{array}\right]^+$$

or

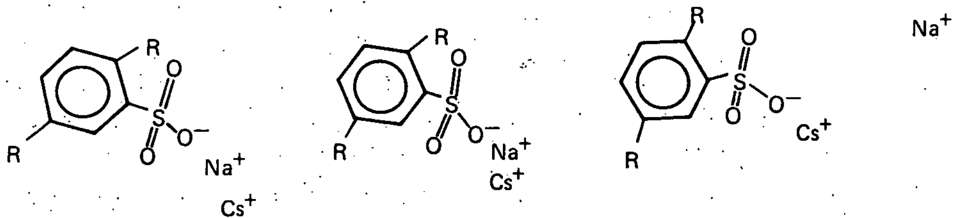


$$\left[\begin{array}{l} \;\;\;\;CH_3 \\ \;\;\;\;| \\ R-N-CH_2-CH_2OH \\ \;\;\;\;| \\ \;\;\;\;CH_3 \end{array}\right]^+$$

When these charged crosslinked polymers are placed in a polar solvent such as water, the ionic bond becomes weakened somewhat, so that the cation or anion may be exchanged for a different cation or anion. For instance, if a strong acid cation exchanger has a sodium ion associated with it and a cesium ion comes in to close proximity, the sodium ion may be released into the solution, and the cesium ion may remain at the exchange site. The exchange in this case is very probable since cesium is more electropositive than sodium and will, therefore, be more strongly attracted to the negative site (See Figure 22).

Process Description

This system is designed to process waste water on a batch basis at a flow rate of 40 gal/min (24 hr/day). This is approximately 20,000 gal/8 hr. This process description is in reference to the pilot plant flow chart, Figure 23. Incoming waste water is pumped into any of four 20,000-gal influent tanks. When one tank is nearly full and ready for processing, a sample is removed and analyzed for radioactivity, total dissolved solids, suspended solids, total organic carbon, iron content, and pH. If the waste solution is low enough in radioactivity that treatment is unnecessary, it is pumped to one of the four 20,000-gal effluent holding tanks where it is analyzed for radioactivity again and released in the effluent, or recycled, if for some reason it is found to be radioactive. If the influent tank sample is high enough in radioactivity that treatment is necessary, then the rest of the analyses must meet the limits for chemical and impurity limits (from Table 16) before the waste solution can be processed by ion exchange. These limits can be met by some combination of the pretreatment systems shown in Figure 23. These pretreatment systems, Vacco filter system, ultrafiltration, and reverse osmosis, are also effective systems for the removal of radioactivity from waste water [1,5,8,37]. If pretreatment with all three systems is necessary, it is possible that no further treatment would be required.



Cesium Approaches Exchange Sites

Cesium Replaces Sodium At Exchange Site

Sodium Moves Away From Exchange Site

FIGURE 22 - Cation exchange.

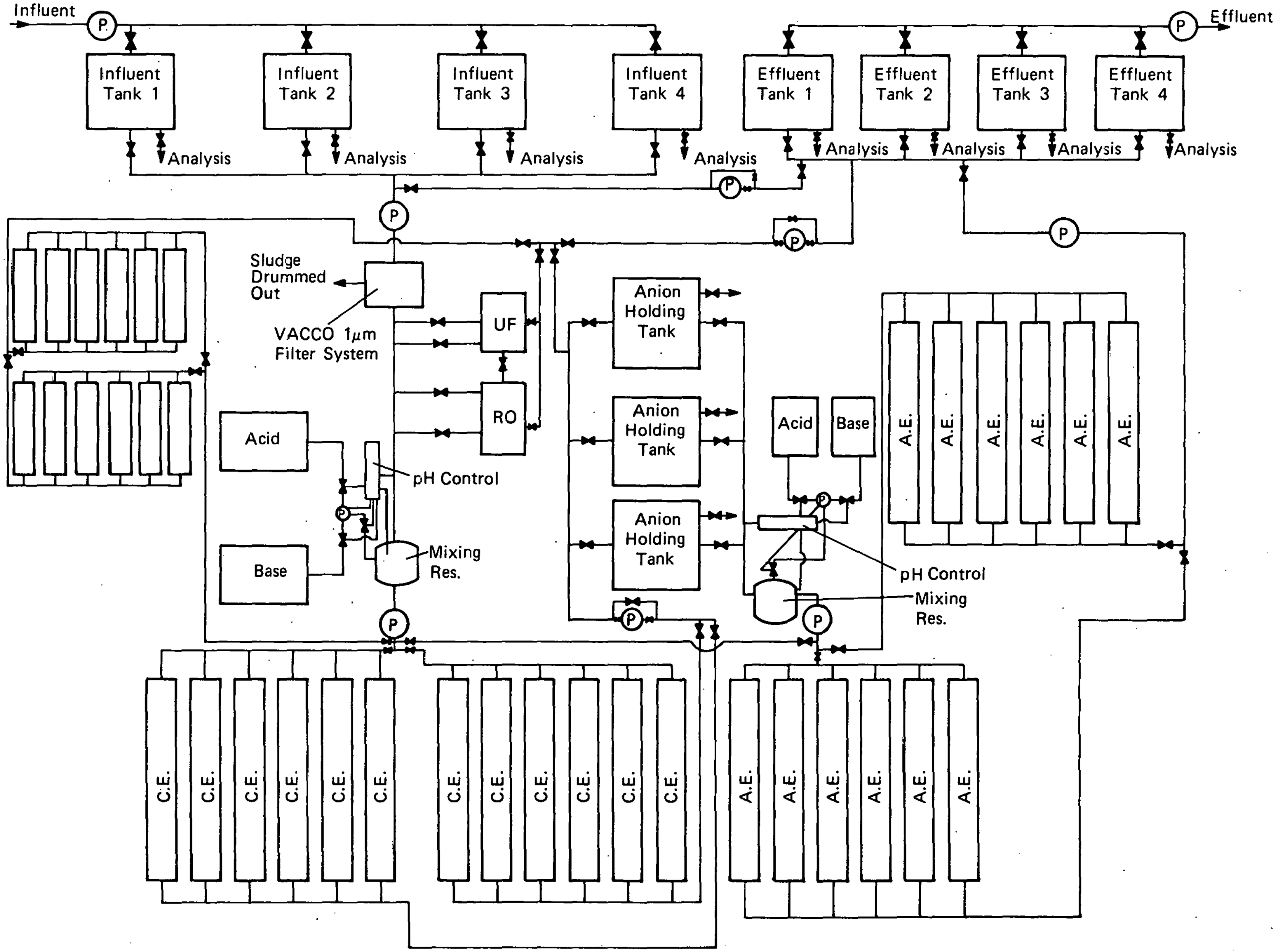


FIGURE 23 - Pilot plant flow chart.

Table 16 - WASTE STREAM CHEMICAL AND IMPURITY LIMITS

Analysis	Lower Limit	Upper Limit
Total Dissolved Solids	None	1000 ppm
Suspended Solids Particle Size	None	0.1 μm Diameter
Total Organic Carbon	None	0.01 mg/L
Iron	None	1 ppm
pH	2	11

In such a case, the pretreated waste water would be pumped to an effluent tank, analyzed, and released. Tanks and pumps associated with the pretreatment systems are not included in the system flow chart. If after pretreatment, or if pretreatment is not necessary, the radioactivity of the waste water is still too high to be released, the waste water will then be processed by ion exchange. The first step in this process is to adjust the pH to the proper range according to the recommended pH given in Table 17. If only cesium is present [1,2], then the waste water is pumped through the cation exchange columns to an effluent tank where it is analyzed and either released or recycled. If only iodine is present [5], the waste water is pumped through the anion exchange columns to an effluent tank. If only cobalt is present [38], it will be pumped through the cation exchange columns to the anion holding tanks and sampled. At pH 3 to 6, no further processing should be necessary, but if it is necessary, the solution will then be pumped through the anion exchange columns to an effluent tank. If any of the actinides are present, processing through both cation and anion exchangers is necessary [37,42-44]. Auxiliary columns are also present and could be used with bonechar for actinides, since bonechar has proven to be particularly efficient at removing most actinides [37,45-49]. This system is designed for maximum flexibility in treating a wide variety of radioactive waste streams. If the waste stream is not greatly variable, the system need not be as flexible and could be tailored to suit only that stream. For instance, if the waste stream were free of particulate material, low in dissolved solids, and entirely contaminated with cesium-137, no pretreatment would be necessary and no anion exchangers would be necessary.

There are several basic rules for selectivity in ion exchangers [1]. In general the exchanger prefers the larger, more highly charged ions over the smaller, lower charged ions. For instance Al^{+++} would be perferred over Ca++ or Na+. These rules are listed in Reference 1.

Table 17 - ION EXCHANGE/ADSORBENT TREATMENT SPECIFICATION

Radioactive Specie	Recommended Cation Resin	Recommended Anion Resin	Other Resins		Other Adsorbents	Recommended pH Range
			Cation	Anion		
^{238}Pu	MSC-1	IRA938	200,AG50WX8	MSA-1	Bonechar	5 to 8
^{233}U	MSC-1	IRA938	200,AG50WX8	MSA-1	Bonechar	5 to 8
^{237}Np	MSC-1	IRA938	200,AG50WX8	MSA-1	Bonechar	5 to 8
^{241}Am	MSC-1	IRA938	200,AG50WX8	MSA-1	Bonechar	5 to 8
^{137}Cs	MSC-1	None	200,AG50WX8 HCR2W-H	None	Duracil, White Sand	5 to 8
^{60}Co	MSC-1	IRA938	HCR2W-H,200 AG50WX8	MSA-1,SAR IRA430		3 to 6
^{131}I	None	IRA938	None	SAR,MSA-1 IRA430		6 to 8

Because of the importance of charge in ion exchange, it is extremely important to known the charge of the ion one wishes to remove from solution. Many elements exhibit multiple valence states, so each element of interest will now be briefly examined to determine what charges may have to be considered in an ion exchange pilot plant of this type. The elements of interest are: the actinides; plutonium (Pu), neptunium (Np), americium (Am), and uranium (U); and the fission products; cesium (Cs), cobalt (Co), and iodine (I). The actinides may be discussed as a group since their chemistry, although somewhat different, is similar in aqueous solution. For uranium, neptunium, plutonium, and americium, the common valence states listed are +3, +4, +5, and +6 although the most stable oxidation state in solution [38] is different for each one. They are +6 for uranium, +5 for neptunium, +4 for plutonium, and +3 for americium. Other valence states have been reported [38-40] but they are unimportant in aqueous solution. The most common species in aqueous solution for the higher oxidation states of uranium, neptunium, plutonium, and americium are the oxygeneated cations MO_2^{+} and MO_2^{++} and the oxoanions $(MO_6)^{-4}$, $(MO_6)^{-5}$, and $(MO_4)^{-6}$ [38]. Because of this wide variety of oxidation states for these actinides and the common formation of negative oxoanions, both anion and cation exchangers would be needed unless an exact characterization of the solution were performed. For instance, if the solution were analyzed and found to contain plutonium and uranium in the forms of $(PuO_6)^{-4}$ and $(UO_6)^{-4}$ only, then no cation resin would be necessary. Anion resins alone would remove those negative ions easily.

The fission products, iodine and cesium, will normally exist as I^- and Cs^+ in aqueous solutions. Although iodine does exhibit other oxidation states, some of which are positive [5], these compounds are not commonly found in low level radioactive waste water. The treatment for cesium is simply a cation exchanger [1,2] and the treatment for iodine is simply an anion exchanger.

Cobalt is a different problem. Cobalt has only two major oxidation states in aqueous solution, +2 and +3. Cobalt (II) simple compounds can normally be found in aqueous solutions, whereas cobalt (III) simple compounds are unstable in aqueous solution [34]. However, cobalt (III) forms many complexes that are stable in aqueous solution [5,27,41]. The cobalt (II) simple compounds are no problem for ion exchange because the cobalt is always Co^{+2} and can be easily removed by cation exchangers. The cobalt (III) presents quite diverse problems because cobalt (III) complexes with many other compounds and ions [27,41]. The problem for ion exchange is that many of these complexes are negative or neutral. The positive and negative species can be removed by passing the solution through a cation exchanger and then an anion exchanger, but the neutral species cannot be removed by ion exchange.

In reference to the waste stream chemical and impurity limits (Table 16), the upper limit given on these is an extreme case where ion exchange will still work but will probably not be economical. The 1000-ppm limit for total dissolved solids is really high for ion exchange. At the flow rates given, if the waste stream contained 1000 ppm Total Dissolved Solids (T.D.S.), as much as 15 resin changes per day would be necessary. This would become expensive very quickly since the resins are not being regenerated but disposed of in some other way. We feel the best way to dispose of the resins would be by incineration since this would greatly reduce the volume that would have to be buried. The suspended solids should be as close to zero as possible since they could clog the ion exchange columns. The total organic carbon should be as close to zero as possible also, because organics could complex with almost any of the radioactive species and possibly neutralize their charge. Of course, if the species have no charge, ion exchange will not work. Iron concentration also should be as low as possible since iron oxidizes easily inside the resin particles to Fe(III) which will render the resin nearly useless by reducing its surface area significantly. The pH is the least restrictive of these limitations and will not really affect the resin adversely between pH 2 and 11. The pH used should be the range recommended in Table 17.

Plant specifications

To obtain the flow rate of 40 gal/min, a bed volume of 15 gal of 16 to 40 mesh resin would be used in six columns. This is a flow rate of 0.44 bed volumes per minute or approximately 20,000 gal/8 hr. The pressure produced in the column at this flow should be very low. A high pressure would indicate some blockage of the flow through the column. The column should have a length-to-diameter ratio of at least 5.0. Several possible column dimensions are given in Table 18. Rather than fabricate such a column, a commericially available column which satisfies the 15-gal bed volume (30-gal total volume) and the L/D ratio of at least 5.0 would be used. The material should be stainless steel either lined or unlined. The resin specifications are given in Table 19. Tanks are considered to be part of the building in which the system exists. All lines and pumps would be specified according to the flows, pressures, and uses.

Table 18 - COLUMN DIMENSIONS

Length (ft)	Diameter (in.)	L/D (in./in.)	Volume (gal)
5.5	12	5.5	32.31
6.0	11	6.55	29.62
6.0	11.5	6.26	32.37
7.0	10.5	8.00	31.49
7.5	10.0	9.00	30.60
8.5	9.5	10.74	31.30

Table 19 - ION EXCHANGE RESIN SPECIFICATION

			Capacity				
Resin	Type	Form	Wet Vol. Min.	Wet Vol. Min.	Manufacturer	Size Mesh	Cost ($)
MSC-1	Strong Acid	Na	1.7 meq/ml	4.5 meq/g	Dow Chemical Dowex	16-40	100/ft^3
IRA938	Strong Base	Cl	0.5 meq/ml	-	Rohm & Haas Amberlite	16-40	336.25/ft^3
200	Strong Acid	Na	1.7 meq/ml	-	Rohm & Haas Amberlite	16-40	78.40/ft^3
AG50WX8 DOWX50WX8	Strong Acid	Na	1.7 meq/ml	-	Bio-Rad Dow Chemical	16-40	∿44.00/L 75/ft^3
HCR2S-H	Strong Acid	Na	2.0 meq/ml	4.4 meq/ml	Dow Chemical Dowex	16-40	85/ft^3
MSA-1	Strong Base	Cl	1.0 meq/ml	4.0 meq/g	Dow Chemical Dowex	16-40	204/ft^3
SAR	Strong Base	Cl	1.4 meq/ml	3.5 meq/g	Dow Chemical Dowex	16-40	193/ft^3
IRA430	Strong Base	Cl	1.1 meq/ml	-	Rohm & Haas Amberlite	16-40	

As stated earlier, this system is designed for maximum flexibility and therefore, all possible fabrication combinations could not be presented.

Operating costs

Operating costs are based on the worst possible combination of conditions to obtain the highest estimate. The actual cost, if such a system were in operation, should be considerably less. The resin costs are based on treating a 1000-ppm total dissolved solids waste stream with both anion and cation resins. The resins used for the cost estimate are MSA-1 at \$204/ft^3 and MSC-1 at \$100/ft^3. At 40 gal/min, if all of the capacity of the resin is taken up by ions which are part of the 1000-ppm total dissolved solids, the resins would have to be changed 10 times each 8 hr. Since more than half of the total dissolved solids in almost any waste solution would be sodium, a more reasonable upper limit would be five resin changes per 8 hr. Therefore, the range possible for resin changes is estimated at between 0.33 and 5 resin changes per 8 hr day. It is quite possible that less than 0.33 resin changes per day would be needed on some waste streams, but highly unlikely that more than five resin changes per day would ever be necessary. This represents a range of from $2424/day to $36,480/day needed for resins. The $2424/day figure is estimated on a 20-ppm TDS stream.

The cost of chemical and radiological analyses is estimated at $500/week if a full-time chemist is available to perform the analyses. The manpower necessary is one chemist and two operators for an 8 hr/day, 4 day/week operation. The chemists's salary is estimated at from $24,000 to $30,000/yr, and each operator is estimated at from $17,000 to $25,000/yr. Of course, salaries vary by geographic area so the actual salaries could be more or less than these ranges.

The cost of chemicals is expected to be no more than $2000/month. Electrical costs are estimated at $1200 to $1500/month. Drums for drumming the waste resins and transportaion and burial for each drum is estimated at $100 per drum. The number of drums needed is based on burial of the resins instead of incineration of the resin and burial of the ash. The amount of resin that can be put in a drum for burial depends on the amount of external radiation generated, but a reasonable range would be from 15 gal to 45 gal of resin per drum. The total cost of operation is compiled in Table 20.

These estimates also include the total salaries of the chemist and operators, whereas some cost estimates include only the actual time they work on the system. Also, cheaper rates could be obtained for the resins by buying in quantity.

The lower level for drums is based on 45 gal of resin/drum and a 20-ppm TDS stream all year. The upper level is based on 15 gal of resin/per drum and 1000-ppm TDS stream all year. These costs are based on using the resins once and disposing. If the resins are eluted and regenerated, the chemical cost/per year would be approximately doubled, but the resin costs and drum costs could be reduced by a factor of 100. The new costs would be:

	UPPER	LOWER
Total	$260,358.00	$151,716.00
	$0.0652/gal	$0.0380/gal

Capital costs

Since this is a conceptual design for an ion exchange pilot plant and the design is intended to have a large amount of flexibility, the capital costs could vary greatly depending on the equipment chosen to be included. The equipment chosen would of course depend on the waste stream being treated. From 12 to 36 ion exchange columns could be included. From 4 to 11 pumps of varying sizes could be included. And from 0 to 3 pretreatment systems could be included. All of these varying configurations would have different numbers of valves and different amounts of piping. Three capital cost analyses by I. R. Higgins [50]

Table 20 - ANNUAL OPERATING COST BASED ON AN 8 HR/DAY, 208 WORK DAY/YEAR OPERATION

	Upper	Lower
Resin	$7,587,840.00	$504,192.00
Analysis	26,000.00	26,000.00
1 Chemist	30,000.00	24,000.00
2 Operators	50,000.00	34,000.00
Chemicals	24,000.00	24,000.00
Electric	18,000.00	14,400.00
Drums	1,248,000.00	27,500.00
Total	$8,983,840.00	$654,092.00
Total gal/year = 3,993,600	$2.25/gal	$0.16/gal

of an ion exchange plant with 12 times the flow of this pilot plant give capital costs of 5.5¢/1000 gal to 6.76¢/1000 gal. These costs estimates are old (1963) and would be expected to be much higher at 1982 prices. If fabricated, columns for this pilot plant would be between $1000 to $3000 each, and pumps will vary, according to size, from $4000 to $300. Commercial ion exchange units currently available at 40 gal/min range from about $7,000 to $25,000* depending on what regulations and codes must be met. If a specific waste stream were described, a specific pilot plant and a specific cost could be given.

Summary

A 40 gal/min ion exchange-adsorbents pilot plant for the removal of the actinides plutonium, neptunium, americium, and uranium and the fission products cesium, iodine, and cobalt was described. Column and resin specifications are given,and impurity limits for the solution to be treated are listed. Operating costs are calculated, and capital costs are given.

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