Pretreatment and Encapsulation of Ion Exchange Resins in Polyethylene

M. Ali, R.M. Doty, and P.D. Kalb

October 1994

Work Conducted by the
Environmental & Waste Technology Center
Dept. of Advanced Technology
Brookhaven National Laboratory
Upton, NY 11973

Work Conducted Under a Cooperative Research and
Development Agreement (CRADA) between
Vectra Technologies, Columbia, SC and
United States Department of Energy
CRADA No. BNL-C-93-02
Contract No. DE-AC02-76CH00016

MASTER

UNLIMITED RELEASE

THIS PAGE IS BLANK

ABSTRACT

Ion exchange resins were successfully encapsulated in low-density polyethylene (LDPE) using the single screw encapsulation process. The ion exchange resins were thermally pretreated in an oven to decrease swelling properties. The waste forms obtained, showed minor dimensional and weight changes during a 90-day water immersion test conducted. The thermal pretreatment of the resin and the mechanical properties of the LDPE were considered factors in keeping the final waste forms from complete structural failure due to swelling. The data obtained for the changes in volume and weight during the 90-day water immersion were used to make recommendations on maximum and conservative waste loadings. For thermally pretreated cation, anion, and mixed bed (2:1), the maximum waste loading (wt %) for encapsulation in LDPE, using the extrusion process, is 70 wt %. The conservative waste loadings, for which the changes in weight and volume were stable, are: 50 wt % for pretreated cation ion exchange resin and 60 wt % for pretreated anion and mixed bed ion exchange resin.

THIS PAGE IS BLANK

TABLE OF CONTENTS

	<u>Page</u>
Abstract	iii
List of Figures	vi
List of Tables	vii
1.0 Introduction	1
2.0 Properties of Ion Exchange Resin Beads	2
3.0 Properties of Low-Density Polyethylene	4
4.0 Pretreatment of Ion Exchange Resins	6
4.1 Pretreatment Methods	6
4.1.1 Pyrolysis	6
4.1.2 Incineration	7
4.1.3 Quick-freezing	7
5.0 Preparation of Simulated Ion Exchange Resin Waste	9
5.1 As-received Ion Exchange Resin	9
5.2 Loading	9
5.3 Resin De-Watering	11
5.4 Pretreatment for Polyethylene Encapsulation Process	12
6.0 Extrusion Processing	17
7.0 Water Immersion Testing	20
8.0 Conclusion	30
References	31
Appendix I	33
Appendix II	46

LIST OF FIGURES

	<u>Page</u>
Figure 5.1 Cation resin bead (IRN-77), 1a, dried in oven @ 100°C for 18 hours	13
Figure 5.2 Cation resin bead (IRN-77), 1a, dried in oven @ 118°C for 18 hours and rehydrated	13
Figure 5.3 Cation resin bead (IRN-77), 6b, heated in oven @ 300°C for 1 hour	13
Figure 5.4 Cation resin bead (IRN-77), 6b, heated in oven @ 300°C for 1 hour and rehydrated	13
Figure 5.5 Anion resin bead (IRN-78), 6c, heated in oven @ 300°C for 1 hour	14
Figure 5.6 Anion resin bead (IRN-78), 6c, heated in oven @ 300°C for 1 hour and rehydrated	14
Figure 6.1 The single-screw extruder processing unit (Davis-Standard (Model # DS15H) extruder and Merrick (Model # 3000) loss-in-weight feeders	18
Figure 7.1 Sample contained in cup of deionized water for the 90-day water immersion test	23
Figure 7.2 Average (Samples A and B) % Change in Weight, vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water	24
Figure 7.3 Average (Samples A and B) % Change in Weight, vs. Time (Days) for Pretreated Anion (IRN-78) ion Exchange Resin Immersed in Deionized Water	25
Figure 7.4 Average (Samples A and B) % Change in Weight, vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water	26
Figure 7.5 Average (Samples A and B) % Change in Volume, vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water	27
Figure 7.6 Average (Samples A and B) % Change in Volume, vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water	28

LIST OF FIGURES (Continued)

	<u>Page</u>
Figure 7.7 Average (Samples A and B) % Change in Volume, vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water	29
Figure A.1 Volume (cu.cm) of Sample A, measured using a caliper, vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water	34
Figure A.2 Volume (cu.cm) of Sample B, measured using a Caliper, vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water	35
Figure A.3 Weight (grams) of Sample A vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water	36
Figure A.4 Weight (grams) of Sample B vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water	37
Figure A.5 Volume (cu.cm) of Sample A, measured using a caliper, vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water	38
Figure A.6 Volume (cu.cm) of Sample B, measured using a Caliper, vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water	39
Figure A.7 Weight (grams) of Sample A vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water	40
Figure A.8 Weight (grams) of Sample B vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water	41
Figure A.9 Volume (cu.cm) of Sample A, measured using a Caliper, vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water	42
Figure A.10 Volume (cu.cm) of Sample B, measured using Caliper, vs.. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water	43
Figure A.11 Weight (grams) of Sample A vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water	44
Figure A.12 Weight (grams) of Sample B vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water	45

LIST OF TABLES

	<u>Page</u>
Table 5.1 Density (p), moisture content (wt%), and pH for as-received, 100% loaded, and 60% loaded IRN-77, IRN-78, and Mixed Bed resin beads	10
Table 5.2 The number of grams of NaCl and milliliters (ml) of deionized water required for a saturated solution to load the resins 100% and 60%	10
Table 5.3 Density (p), moisture content (wt %), and pH for 100% and 60% loaded damp IRN-77, IRN-78, and Mixed Bed resin beads	10
Table 5.4a Changes in diameter for cation (IRN-77) ion exchange resin beads loaded to 60% with Na ⁺ and thermally degraded in the oven	16
Table 5.4b Changes in diameter for anion (IRN-78) ion exchange resin beads loaded to 60% with Cl ⁻ and thermally degraded in the oven	16
Table 6.1 Specifications of Davis-Standard (Model # DS15H) Single Screw Extruder	19
Table 6.2 The zone temperatures, melt temperature, melt pressure, current draw, screw speed, and vacuum pressure monitored during processing	19
Table 7.1 Maximum and Conservative waste loadings obtained, using 90-day water immersion test, for thermally pretreated ion exchange in LDPE	23
Table A.1 Volume Measurements Using a Caliper for Cation (IRN-77), Sample A, Ion Exchange Resin	47
Table A.2 Volume Measurements Using a Caliper (IRN-77), Sample B, Ion Exchange Resin	48
Table A.3 Weight Measurements for Cation (IRN-77), Sample A, Ion Exchange Resin	49
Table A.4 Weight Measurements for Cation (IRN-77), Sample B, Ion Exchange Resin	49
Table A.5 Volume Measurements Using a Caliper for Anion (IRN-78), Sample A, Ion Exchange Resin	50
Table A.6 Volume Measurements Using a Caliper for Anion (IRN-78), Sample B, Ion Exchange Resin	51

LIST OF TABLES (Continued)

	<u>Page</u>
Table A.7 Weight Measurements for Anion (IRN-78), Sample A, Ion Exchange Resin	52
Table A.8 Weight Measurements for Anion (IRN-78), Sample B, Ion Exchange Resin	52
Table A.9 Volume Measurements Using a Caliper for Mixed Bed (2:1 ratio), Sample A, Ion Exchange Resin	53
Table A.10 Volume Measurements Using a Caliper for Mixed Bed (2:1 ratio), Sample B, Ion Exchange Resin	54
Table A.11 Weight Measurements for Mixed Bed (2:1 ratio), Sample A, Ion Exchange Resin	55
Table A.12 Weight Measurements for Mixed Bed (2:1 ratio), Sample B, Ion Exchange Resin	55

1.0 INTRODUCTION

Ion exchange resin columns, with either individual cation or anion resins or a homogeneous mixture of both resin types (mixed bed), are used in nuclear plants to treat radioactive streams. These streams include primary coolant, turbine condensate, water in the spent fuel storage pools, and liquid radwaste resulting from different plant operations. In the treatment of these radioactive streams, the ion exchange resins interchange ions from its solid phase with radioactive ionic species and particulate matter. As a result the resins concentrate radioactive species. The activities for ion exchange resin can typically be 0.1-10 microcurie/cc for resin used in waste processing and may exceed 500 microcurie/cc in primary coolant purification [1].

Spent ion exchange resins can be regenerated by introducing a flow of solution which will displace the exchanged ions and replace them with fresh counter ions. However, ion exchange resin columns have to be replaced in nuclear facilities if either of the following criteria is satisfied [2]: (1) depletion of exchange capacity (breakthrough) or (2) significant personnel dose as a consequence of the contained radioactivity. At nuclear facilities, the possible dose hazards to workers from the handling and exposure to the high activity spent ion exchange resin, rather than the exhaustion of ion exchange service life as a chemical exchanger, is usually the reason for replacement of ion exchange columns [2].

The disposal of spent ion exchange resin requires that the migration of radionuclides be minimized. Encapsulation, using cement, bitumen, and polyethylene, has been previously shown [3] to restrict the physical washing from burial sites and reduce the surface area for contact by ground water and therefore reduce the potential for exchange of radionuclides on the resin with naturally occurring minerals in the ground water. Waste forms of ion exchange resin beads encapsulated in cement and bitumen, however, were characterized by excessive swelling and cracking due to expansion, from absorption of water, of the ion exchange resin beads.

Therefore, in this project loaded ion exchange resin were first thermally pretreated, to reduce the hygroscopic properties of the ion exchange beads, and then encapsulated in low-density polyethylene, using an extruder. A 90-day water immersion test was conducted to determine the swelling of the waste form and, also, to determine if any catastrophic failure of the waste form will occur.

2.0 PROPERTIES OF ION EXCHANGE RESIN BEADS

The most used ion exchange resin beads in the nuclear industry are the synthetic organic resin beads. The gel structure (matrix) of these resin beads is composed of an irregular, macromolecular, 3-dimensional network of hydrocarbon chains (linear polystyrene chains cross-linked with divinylbenzene) [4]. The matrix carries ionic groups, such as SO_3^- (anion resin) and NH_3^+ (cation resin), which provide the exchange capability.

The non-uniform mesh width (heteroporosity) is determined by the degree of cross-linking. The random network is flexible and expands, or "swells", by taking up solvents. The swelling ability of the resin bead is determined by the mesh width and thus the degree of cross-linking. Highly cross-linked resin beads have a reduced ability to swell since the networks are rigid [4].

Gregor's Model [5,6,7] is a practical way of looking at the swelling phenomena of the resin beads. In Gregor's Model, ion exchange resin are modeled as strong electrolytes with a matrix analogous to coiled springs. These coiled springs are under pressure when water absorption, by osmosis, swells the matrix. This swelling is finite and reaches an equilibrium when the tension of the coiled spring balances the osmotic pressure. At the equilibrium state the difference in the osmotic pressure (Π) and the spring force (Σ) is termed the swelling pressure

$$P = \Pi - \Sigma \quad (1)$$

The encapsulated resin beads will exert this swelling pressure on the encapsulating material.

The osmotic pressure, Π , can be defined as [7]

$$\Pi = vRT\phi m \quad (2)$$

where v is the number of ions into which the electrolyte dissociates, R (J/mol K) the gas constant, T (K) the absolute temperature, ϕ the osmotic coefficient, and m (mol/m³), the molarity. The spring force (Σ) can be obtained by [7]

$$\Sigma = \alpha^n K \quad (3)$$

where α is the water content, n is an empirical constant, and K (Pa) is the elastic constant of the bead. Using (2) and (3), (1) becomes

$$P = \nu RT \phi m - \alpha^n K \quad (4)$$

The experimental results of Matsuda et. al. [7] confirmed that Gregor's model, and thus (4), is valid for determining the swelling pressure, P . Matsuda et. al. [7] measured the swelling pressure to change over a range of 0-60 MPa for cation exchange resin with different properties and this agreed closely with the values calculated from (4).

3.0 PROPERTIES OF LOW DENSITY POLYETHYLENE

Polyethylene is an organic polymer material of crystalline-amorphous structure, formed through the polymerization of ethylene gas at high and low pressure processes [8]. Several types of polymers (low density, linear low-density, and high density), each with its own characteristics, are formed. Low density polyethylene (LDPE), made by polymerizing ethylene gas at high pressure, was selected because of its relative ease of processibility due to lower processing pressures and temperatures and better material flow. These characteristics of polyethylene will enhance homogeneity and stability of the final waste form.

Pertinent physical and mechanical properties of LDPE are given in Table 3.1. LDPE is characterized with superior mechanical properties, such as compressive and tensile strength, which can allow for high waste loadings. LDPE is resistant to most acids, bases, and organics, as normally found in waste streams. LDPE has excellent resistance to water or moisture which is helpful in decreasing the absorption of water by the encapsulated ion exchange resin beads. LDPE waste forms will retain their physical and mechanical properties under normal temperature conditions but exhibit a loss in mechanical properties at temperatures above their glass transition temperature (T_g).

Portland cement and bitumen are other materials which have been used to immobilize spent ion exchange resin beads. In comparison with polyethylene, Portland cement has excellent compressive strength but has very weak tensile strength. Portland cement is not well-suited for immobilization of ion exchange resin beads because the hygroscopic properties of the resin beads can affect the hydration process in cement and thus make the final waste form unstable. In addition, expansion of resin beads in the presence of moisture exceeds cement's tensile strength, leading to severe waste form cracking. Ion exchange resin waste loading in cement is limited to ≤ 13 wt% to eliminate cracking [2].

Table 3.1: Physical and Mechanical Properties of Low Density Polyethylene (LDPE).

Tensile Strength (psi)	600-2300
Elongation (%)	90-800
Compressive Strength (lb/in²)	No Break
Impact Strength	0.20-0.36
Hardness, Rockwell	M124-128
Specific Gravity	0.917-0.932
Water Absorption, 24hr	< 0.01

4.0 PRETREATMENT OF ION EXCHANGE RESINS

Pretreatment of spent ion exchange resin beads is done to reduce the waste volume to be encapsulated and to decrease the swelling properties of the beads. The reduction in waste volume is accomplished, using relatively simple processes, that eliminates interstitial liquids (i.e., water) or decreases the interstitial spaces. The effect of heat has been shown to decrease the hygroscopic properties of the ion exchange resin beads, as well [4]. Therefore, thermal pretreatment processes are used to decrease the swelling properties of the beads in the presence of moisture and thus make the final encapsulated waste package more stable.

4.1 Pretreatment Methods

Drying, compaction, vibration, and application of high confining pressure are examples of pretreatment methods which decrease the volume of the spent ion exchange resin [3]. Drying at 70°C has been shown to reduce the volume by 56% [3]. Volume reduction by compaction or vibration is relatively less effective (volume reduction of 7.8% for compaction and 7.1% for vibration) because of the uniform particle size, elastic properties, and particle cohesion properties of the resin beads [3]. Application of high pressure (e.g., 258 MPa for one minute) has been demonstrated to decrease the volume by 40% [3].

The simple processes to decrease the volume of spent resin beads have no effect on swelling properties. However, ion exchange resin will lose some of their ability to swell if exposed to high temperatures. The exposure to high temperature alters the molecular composition of the ion exchange resin bead by decomposing the functional groups into gaseous forms. Therefore, thermal processes, such as pyrolysis and incineration, not only reduce volume but also significantly reduce the swelling properties of the ion exchange resin beads.

4.1.1 Pyrolysis

Pyrolysis, destruction of complex molecules by the use of heat in an inert environment, has been shown to decrease the hygroscopic properties of ion exchange resin beads [7]. The ion exchange resin matrix is decomposed at temperatures between 300-500 °C. The volume of the ion exchange resin residue after pyrolysis is about nine times less than the original contaminated waste [3].

The effects of pyrolysis are different for cation and anion resin beads, even though the base

polymer, styrene-divinylbenzene, is the same. The results of Matsuda et. al. [7] experiments on pyrolysis of ion exchange resin show that anion resin decompose in two stages, between 200-400 °C, and the decomposition ratio was 90 wt% for above 400 °C. The cation decomposed in one stage, between 200-300 °C, and the decomposition ratio was 50 wt% even at 600 °C. The hygroscopic properties (g H₂O / g residue) of cation reduced from 0.7 at 200 °C to 0.05 at 300 °C. Matsuda et. al. attributed the differences between the cation and anion resins pyrolysis to the different functional groups, sulfonic acid and quaternary ammonium, respectively. Through experiments, Matsuda et. al. [9], discovered that the low decomposition of the cation during pyrolysis occurs due to the conversion of the sulfonic acids to sulfonyl and sulfur bridges between the base polymer. The formation of these bridges make the base polymer thermally stable and cause the weight loss of cation beads to be relatively less than anion beads during pyrolysis.

4.1.2 Incineration

Incineration can also be used to reduce the volume and decompose low level ion exchange resin beads. The two types of incinerators developed for commercial use are the fluidized-bed incinerator and an air-suspension burning device [10]. With incineration, an average volume reduction factor of 40% can be achieved [11]. The resins are difficult to combust, since tars and char form, therefore other materials, such as wood and coal, are added. The resins are incinerated, at temperatures around 1000 °C, in slurry form and the residual ash, a charcoal-like material, is immobilized.

Incineration of ion exchange resin can lead to excessively high radiation dose rates due to the concentration of activity in the ash product [12]. Complicated off-gas systems which incorporate treatment, filtration, sampling, and discharge equipment for the combustion products are required. These factors make the siting and permitting of an incinerator facility difficult and significantly increase processing cost.

4.1.3 Quick-freezing

Freezing also changes the structure of the ion exchange resins beads [13]. Yim et. al. quick-froze ion exchange resin beads, which contained 40-60 wt% moisture, using liquid nitrogen and solid carbon dioxide, and discovered that the freezing expansion pressure, estimated to be 100 MPa, destroys the structure of the bead. The resin beads did not recover

their original structure after thawing.

Yim et. al. [13] tested the quick-freezing pretreatment for grinding of resin beads. They discovered that the grindability of cation resin beads increase by the quick-freeze pretreatment. Anion resins, which have a lower cross-linking than cation, can be ground easily without pretreatment. Therefore, the effects of quick-freezing, on anion resin beads, were not as significant as for cation resin beads. The particle size distribution for both types of resin, after grinding, was more uniform.

5.0 PREPARATION OF SIMULATED ION EXCHANGE RESIN WASTE

5.1 As-received Ion Exchange Resin

Nuclear grade Amberlite ion exchange resins (Rohm and Haas Co.), typical of those used in the nuclear industry, were used. These are "gel" type synthetic ion exchange resins with elastic structures formed by crosslinking linear polystyrene with 8% divinylbenzene by weight. The cation form, IRN-77, is a strongly acidic resin and has sulfonic acid functionality. A minimum of 95% of its exchange sites are in the hydrogen form. Anion resin, IRN-78, is a strongly basic quaternary ammonium functionality resin, containing a minimum 80% of its exchange sites in the hydroxide form with a maximum of 5% in chloride form and a maximum of 15% in the carbonate form. Mixed bed resin was formed by combining two parts cation ion exchange resin and one part anion ion exchange resin by dry weight.

The density, water content, and the pH of the as-received resins were determined and are shown in Table 5.1. The density was calculated by measuring the weight using a standard laboratory scale and volume using a pycnometer. The water content of the resins was calculated according to ASTM Standard Test Method D2187-77, "Physical and Chemical Properties of Ion Exchange Resins," [14]. In this procedure, the mass loss of resins, due to drying in a gravity convection oven at 110 °C for 18 ± 2 hours, is used to calculate the water moisture in the following manner:

$$\text{wt\% water} = \frac{\text{wt. of wet resin} - \text{wt. of dry resin}}{\text{wt. of wet resin}} \times 100 \quad (5)$$

The pH was measured using a standard laboratory pH meter.

5.2 Loading

"Cold" (non-radioactive) cation and anion resins were batch loaded, to 60% and 100% of their sorption capacity (the number of ionogenic groups contained in the specific amount of resin material), in a solution of sodium chloride (NaCl) and deionized water to provide Na^+ and Cl^- ions. The 60% loading is used to represent the activity level at which the ion exchange

Table 5.1 : Density (ρ), moisture content (wt %), and pH for as-received, 100% loaded, and 60% loaded IRN-77, IRN-78, and Mixed Bed resin beads.

	As-received			100% Loaded			60% Loaded		
	$\rho^{(a)}$ (g/cm ³)	wt % ^(a)	pH	$\rho^{(a)}$ (g/cm ³)	wt% ^(a)	pH	$\rho^{(a)}$ (g/cm ³)	wt % ^(a)	pH
IRN -77	0.72	46.9	4.0	0.76	64.7	5.65	0.76	66.7	3.7
IRN -78	0.82	35.2	10.2	0.86	65.9	10.3	0.81	72.4	12.4
Mix. Bed	0.77	56.1	6.25	0.78	62.7	4.1	0.75	63.7	N/A

(a) Average of 3 replicates

Table 5.2 : The number of grams of NaCl and milliliters (ml) of deionized water required for a saturated solution to load the resins 100% and 60%.

	100% Loading		60% Loading	
	g of NaCl	ml of H ₂ O	g of NaCl	ml of H ₂ O
IRN-77	766	2175	153.21	430
IRN-78	214.4	700 ^(a)	85.91	341 ^(a)

(a) 100 ml extra added for Na solubility

resins are typically replaced in nuclear power plants. The sorption capacity of the dry cation and anion resins were obtained from the manufacturer to be 4.7 meq/g and 3.5 meq/g, respectively. The number of grams (g) of NaCl required for 100% and 60% loading were determined based on the equivalent quantity of dry resin (see Table 5.2).

The saturated solutions of NaCl were prepared using 100 ml of deionized water for every 35.7 grams of NaCl (see Table 5.2). The resins were soaked in the saturated NaCl and deionized water solution for 18 hours, at 23 °C, with occasional stirring. The resins were then drained, using a polyethylene sieve, and rinsed five times with deionized water.

5.3 Resin De-Watering

Resin de-watering was accomplished by a pressurized column technique to obtain a product similar to commercial de-watering processes. Salt loading solutions and rinse water were drained from the loaded IRN-77, IRN-78, and mixed bed resin slurry by using a column (3 3/8" ID x 18") through which argon (Ar) gas was forced through the top. The liquid from the resin slurry flowed through a glass fiber filter at the bottom of the column. The remaining liquid, held between the interstitial spaces of the resin beads by capillary forces, was removed by forcing Ar gas, at 2 psi, for 10 min. (or until no moisture was observed). The resin prepared in this manner is termed "damp resin".

The density and moisture content of the 100% and 60% loaded damp IRN-77, IRN-78, and mixed bed resin beads were measured. The methods of measurement were the same as for the as-received resin. The results are tabulated in Table 5.3.

Table 5.3 : Density (ρ), moisture content (wt %), and pH for 100% loaded and 60% loaded damp IRN-77, IRN-78, and Mixed Bed resin beads.

	100 % Loaded			60 % Loaded		
	$\rho^{(a)}$ (g/cm ³)	wt % ^(a)	pH	$\rho^{(a)}$ (g/cm ³)	wt % ^(a)	pH
IRN-77	0.69	48.3	4.0	0.69	51.7	3.7
IRN-78	0.81	48.6	9.95	0.81	61.2	12.4
Mixed Bed	0.74	49.7	8.2	0.73	53.4	N/A

(a) Average of 3 replicates

5.4 Pretreatment for Polyethylene Encapsulation Process

Previous development work conducted at Brookhaven National Laboratory (BNL) indicated that significantly higher ion exchange resin waste loadings could be achieved by polyethylene encapsulation than compared with conventional hydraulic cement processes (30 wt% vs. 13 wt%, respectively), without suffering degradation under water immersion testing. For this project, ion exchange resins were pretreated in an attempt to further improve waste loading potential for polyethylene encapsulated ion exchange resins.

A thermal pretreatment method using a conventional convection oven was used. The purpose of this pretreatment method, similar to other pretreatment methods described in Section 4, was to reduce waste volume and swelling properties of the ion exchange resin beads. The volume of the damp resin beads was reduced by evaporation of the remaining interstitial water. As in pyrolysis, the resin beads were thermally degraded by the decomposition of the functional groups into gaseous forms, effectively reducing the resin bead swelling and rendering the final encapsulated waste form more stable. This section describes the method for determining pretreatment parameters. Temperatures and residence time in the oven were varied to determine the point at which all the interstitial water will evaporate and the swelling properties of the individual beads will decrease. The beads were then removed from the oven and diameters of the individual beads were measured from magnified (magnification 200x) pictures, see Figures 5.1-5.6, of the thermally degraded ion exchange resin beads. The thermally degraded beads were rehydrated with de-ionized water and measurements of the diameters were taken again to determine the effect of the temperature and time on the hygroscopic nature of the beads. Results of various time and temperatures are described below and are shown in Table 5.4a and 5.4b:

Temperature: 110 °C and Time: 18 hours

Both the dried anion and cation resin beads swelled when hydrated with deionized water. The swelling occurred even though the cation resin bead was cracked in various places.

Temperature: 200 °C and Time: 2 hours

The result of this increase in temperature and decrease in time had no effect on the swelling of the cation but the swelling of the anion decreased significantly.

Figure 5.1: Cation resin bead (IRN-77), 1a, dried in oven @ 110 °C for 18 hour .

Figure 5.2: Cation resin bead (IRN-77), 1a, dried in oven @ 118 °C for 18 hours and rehydrated.

13

Figure 5.3: Cation resin bead (IRN-77), 6b, heated in oven @ 300 °C for 1 hour.

Figure 5.4: Cation resin bead (IRN-77), 6b, heated in oven @ 300 °C for 1 hour and rehydrated.

Figure 5.5: Anion resin bead (IRN-78), 6c, heated in oven @ 300 °C for 1 hour.

Figure 5.6: Anion resin bead (IRN-78), 6c, heated in oven @ 300 °C for 1 hour and rehydrated.

Temperature: 250 °C and Time: 1 hour

The increase in temperature caused the anion to lose its swelling capacity completely but the cation swelling capacity was not affected.

Temperature: 250 °C and Time: 18 hours

The increase in time did not decrease the swelling capacity of the cation but instead caused part of the cation resin bead to break off due to an increase in internal pressure from hydration. The anion was observed to have lost its capacity to hydrate at this temperature and time.

Temperature: 400 °C and Time: 0.5 hours

The high temperature was chosen to determine if the resin beads will be catastrophically destroyed and result in a decrease in swelling properties. After 0.5 hours the resin beads were found to be deformed and charred black. The swelling properties of the cation decreased significantly and the swelling properties of the anion resin bead disappeared.

Temperature: 300 °C and Time: 1 hour

The temperature was decreased to avoid breaking apart of the beads, and thus increasing the exposed surface area. The temperature was decreased to avoid the catastrophic break up of the resin beads. At 300 °C both resin beads showed an excellent decrease in the swelling properties. Therefore this was the temperature and time at which the both resin beads were placed in the oven to be pretreated for the encapsulation process.

The temperature chosen for pretreatment is within the temperature range, 300-500 °C, recommended by Matsuda et. al. [7] for pretreatment by pyrolysis. Also, the difference in swelling properties of anion and cation resins may possibly be due to their different functional groups, as was observed by Matsuda et. al. [9].

Table 5.4a: Changes in diameter for cation (IRN-77) ion exchange resin beads loaded to 60% with Na⁺ and thermally degraded in the oven.

Bead #	Temp. (°C)	Time (Hours)	Diam. Hydra. Bead (mm)	Diam. Dried Bead (mm)	Diff. in Diam. (mm)	% Inc. in Diam.
1	110	18	.321	.238	.084	35.3
2	200	2	.338	.250	.088	35
3	250	1	.318	.243	.075	31
4	250	18	.338	.238	.100	42.2
5a	400	0.5	.293	.269	.024	8.9
5b	400	0.5	.258	.230	.028	12.1
6a	300	1	.229	.222	.006	2.8
6b	300	1	.218	.211	.008	3.6
6c	300	1	.230	.222	.008	3.4

Table 5.4b: Changes in diameter for anion (IRN-78) ion exchange resin beads loaded to 60% with Cl⁻ and thermally degraded in the oven.

Bead #	Temp. (°C)	Time (Hours)	Diam. Hydra. Bead (mm)	Diam. Dried Bead (mm)	Diff. in Diam. (mm)	% Inc. in Diam.
1a	110	18	.254	.222	.032	14.3
1b	110	18	.286	.254	.032	12.5
2	200	2	.262	.258	.004	1.48
3	250	1	.211	.211	0	0
4	250	18	.211	.211	0	0
5	400	0.5	.163	.163	0	0
6a	300	1	.204	.204	0	0
6b	300	1	.216	.211	.005	2.4
6c	300	1	.197	.197	0	0

6.0 EXTRUSION PROCESSING

The pretreated ion exchange resin beads were encapsulated in low-density polyethylene (LDPE) using the extrusion process. The solidification of the pretreated ion exchange resin beads in LDPE occurs, by heating, mixing, and extrusion, in one operation. The single-screw extruder used, Davis-Standard Model # DS15H, consisted of the following main components (see Figure 1 and Table 6.1 for specifications): 1) Loss-in-weight feeders, 2) A single rotating auger-like screw, 3) A heated cylinder in which the screw rotates, and 4) An output die assembly to shape the final product.

The pretreated ion exchange resin beads and LDPE pellets are fed separately into the extruder by two Merrick, Model # 3000, loss-in-weight feeders. The feeders are controlled by microprocessors that monitor the instantaneous weight loss as material is delivered. The actual mass feed rate is compared with the pre-set rate and adjustments in delivery speed are made automatically to keep the feed rate within about 1% of the set rate. The two individual controllers are regulated, in turn, by a master controller which monitors and adjusts the delivery of each feeder so that the resin bead/LDPE pellet ratio is maintained. The setting for the feeders were varied to maintain recipes of 10-70 wt% pretreated ion exchange resin beads and 90-30 wt% LDPE.

The mixture of pretreated ion exchange resin beads and LDPE is conveyed through a heated cylinder by the motion of the rotating auger-like screw. The mixture is melted due to the frictional heat generated by the screw and by 5 electric resistance band heaters placed on the cylinder. External cooling fans are used to remove excessive heat from the cylinder. The screw rotation also assists in the mixing of the materials to a homogeneous state. A vent stack and vacuum system is used to vent the cylinder of any moisture or volatiles present in the mixture. Zone temperatures, melt temperature, melt pressure, current draw, screw speed, and vacuum pressure were monitored during processing (See Table 6.2).

The molten mixture of ion exchange resin beads and LDPE is forced through an output die into a copper mold. The samples, 2.54 cm diameter x 2.54 cm height, are removed from the molds when they are cooled and solidified.

Figure 6.1: The single-screw extruder processing unit (Davis-Standard (Model # DS15H) extruder and Merrick (Model # 3000) loss-in-weight feeders.

Table 6.1: Specifications of Davis-Standard (Model # DS15H) Single Screw Extruder

Diameter of Screw	1-1/2"
L/D	30:1
Barrel	Alloy Steel
Barrel Cooling Zones	5 Air-cooled
Vent Stack and Vacuum System	Yes
Gearbox	24 HP @ 125 rpm
Motor (DC)	10 HP, 1750 rpm

Table 6.2: The zone temperatures, melt temperature, melt pressure, current draw, screw speed, and vacuum pressure monitored during processing

Zone 1 Temp. (°F)	240
Zone 2 Temp. (°F)	240
Zone 3 Temp. (°F)	280
Zone 4 Temp. (°F)	280
Zone 5 Temp. (°F)	300
Melt Temp. (°F)	300
Current Draw (amps)	3.5
Screw Speed (rpm)	20.0
Vacuum Pressure (in. of Hg)	17

7.0 WATER IMMERSION TESTING

7.1 Procedure

The samples of ion exchange resin encapsulated in LDPE were immersed in deionized water for 90 days. The volume of deionized water was chosen to be 10 times the surface area of the samples, as recommended by the Nuclear Regulatory Commission in the Branch Technical Position on Waste Form [15]. The samples and deionized water were contained in cups which were clearly marked with the type of sample. The samples were suspended by nylon string and completely immersed in water to prevent the samples from hitting the bottom or touching the sides (see Figure 7.1). The volume of the samples was calculated from measurements of the diameter and height, made with a digital caliper.

7.2 Results

The LDPE encapsulated anion (IRN-77), cation (IRN-78), and mixed bed (2 cation:1anion ratio) ion exchange resin waste forms maintained their integrity for the 90-day water immersion test. At waste loadings up to 70 wt%, the waste forms remained free-standing monolithic solids, with no gross failure in structural integrity, and no surface cracks were observed. These waste loadings, are far superior than those reported using hydraulic cement, (13 wt%) or LDPE (50 wt%), in which no thermal pretreatment of the ion exchange resin was conducted. [2,8] However, dimensional and weight changes did occur, due to the water absorption by the waste forms, during the 90-day water immersion testing. For some waste forms, volume increases were still being recorded at the end of the 90-day water immersion test. Other waste forms showed less overall volume increases and appeared to reach an equilibrium in relation to weight and volume changes. These changes in volume and weight were used to determine conservative formulation recommendations (ion exchange resin-to-LDPE ratio) for which catastrophic failure of the integrity of the waste form, under saturated conditions, is less likely.

Figure 7.1: Sample contained in cup of deionized water for the 90-day water immersion test.

Figures A.1 and A.2 (see Appendix I) show the change in volume of cation (IRN-77) ion exchange resin during the 90-day water immersion test. The volume does not increase significantly for waste loadings ≤ 50 wt% because the tensile strength of the LDPE retards the swelling (see Section 2.0). Figures A.3 and A.4 show that the increase in weight of cation ion exchange resin waste forms due to water absorption is also most apparent for waste loadings above 50 wt%.

The increase in volume for anion (IRN-78) ion exchange resin samples over the 90-day water immersion test are shown in Figures A.5 and A.6. The anion ion exchange resin encapsulated in LDPE have lower swelling properties than cation and show no increase in volume for waste loadings above 60 wt%. Even samples with the maximum waste loading (70 wt%) swelled very little. The changes in weight over time for the anion ion exchange waste forms (Figures A.7 and A.8), follow the trend of the changes in its volume. Insignificant weight increases were measured for waste loadings ≤ 60 wt%.

The trend in swelling and weight increases for encapsulated mixed bed (2:1 ratio) ion exchange resin waste forms over time (Figures A.9 - A.12) is similar to the anion ion exchange resin waste forms. No apparent increases in swelling or weight are observed for ≤ 60 wt% and very small increases were observed for the 70 wt% anion ion exchange waste forms.

The results of this 90-day water immersion test can be used to determine conservative formulations for which the pretreated ion exchange resin encapsulated in LDPE are stable under saturated disposal conditions. The average (samples A & B) percent change in volume and weight over time (Figures 7.2 - 7.7) provides the basis for determining maximum and conservative waste loadings shown in Table 7.1. The maximum waste loading is considered to be the waste loading at which no catastrophic destruction occurred. Using the pretreatment and encapsulation process described, the maximum waste loading for the cation, anion, and mixed bed ion exchange resin is 70 wt %. Cation, anion, and mixed bed ion exchange resin waste forms with waste loadings below their respective conservative recommended waste loadings, remained stable with regard to changes in weight or volume over time.

Table 7.1: Maximum and Conservative waste loadings obtained, using 90-day water immersion test, for thermally pretreated ion exchange resin in LDPE

Resin Type	Maximum Waste Loading (wt %)	Conservative Waste Loading (wt %)
Cation (IRN-77)	70	50
Anion (IRN-78)	70	60
Mixed Bed (2 cation : 1 anion ratio)	70	60

Figure 7.2 : Average (Samples A and B) % Change In Weight, vs. Time (Days)
for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed In Deionized Water

Figure 7.3 : Average (Samples A and B) % Change in Weight, vs. Time (Days)
for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water

Figure 7.4 : Average (Samples A and B) % Change In Weight, vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed In Deionized Water

Figure 7.5 : Average (Samples A and B) % Change in Volume, vs. Time (Days) for Pretreated Catlon (IRN-77) Ion Exchange Resin Immersed in Deionized Water

Figure 7.6 : Average (Samples A and B) % Change in Volume, vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water

Figure 7.7 : Average (Samples A and B) % Change in Volume, vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water

8.0 CONCLUSION

The combination of thermal pretreatment and LDPE extrusion has been successfully demonstrated for the encapsulation of ion exchange resin. The waste forms produced did experience changes in dimension and weight, but no structural destruction of the waste form, as observed with cement [2] and LDPE encapsulation process without pretreatment [5], occurred. The following conclusions may be drawn as a result of this investigation:

- Thermal pretreatment (@ 300 °C for 1 hour in conventional oven) reduced the swelling properties of anion and cation ion exchange resin.
- Thermal pretreatment decreases the swelling properties of anion resin more than cation resin.
- The maximum waste loadings (wt %) recommended for encapsulation of cation, anion, and mixed bed (2:1 ratio) ion exchange resin is 70 wt%.
- The conservative waste loadings (wt%) recommended for encapsulation of cation ion exchange resin is 50 wt% and for anion and mixed bed ion exchange resins is 60 wt%.

Future research and development efforts are required to obtain more detailed information on performance of LDPE encapsulated ion exchange resin waste forms, following thermal pretreatment.

REFERENCES

- [1] McCoy, S.B., "Advances in the Disposal of Radioactive Ion Exchange Resins", *Proceedings of Waste Management '83*, Vol. 1, p.327-329.
- [2] Neilson, R.M. and Colombo, P., Solidification of Ion Exchange Resin Wastes, BNL-51615, Brookhaven National Laboratory, Upton, NY, August 1982.
- [3] International Atomic Energy Agency (IAEA), Treatment of Spent Ion-Exchange Resins for Storage and Disposal, Technical Reports Series No.254, IAEA, Vienna (1985).
- [4] Kunin, R., Ion Exchange Resins, Robert E. Krieger Publishing Co., Huntington, NY, 1972.
- [5] Helfferich, F., Ion Exchange, McGraw-Hill, New York, NY, 1972.
- [6] Gregor, H. P., "A General Thermodynamic Theory of Ion Exchange Processes", *Am. Chem. Soc.*, 70, 1293 (1948).
- [7] Matsuda, M., Nishi, T., Chino, K., and Kikuchi, M., "Solidification of Spent Ion Exchange Resin Using New Cementitious Material, (I) Swelling Pressure of Ion Exchange Resins", *J. of Nucl. Sci. and Tech.*, Vol. 29, No. 9, p.883-889, Nov. 1992.
- [8] Kalb, P. D., and Colombo, P., Polyethylene Solidification of Low-Level Wastes, Topical Report, BNL-51867, Brookhaven National Laboratory (BNL), Upton, NY, Oct. 1984.
- [9] Matsuda, N., Nishi, T., and Kikuchi, M., "Solidification of Spent Ion Exchange Resin Using New Cementitious Material, (II), Improvement of Resin Content by Fiber Reinforced Cement", *J. of Nucl. Sci. and Tech.*, Vol. 29, No.11, p.1093-1099, Nov. 1992.
- [10] Moghissi, A. A., Godbee, H. W., and Hobart, S. A., Radioactive Waste Technology, American Society of Mechanical Engineers, New York, NY, 1992.
- [11] Barnhart, V., and Gussman, H., "Incineration of Low-Level Radioactive Waste and Ion Exchange Resins", *Proceedings of Waste Management '84*, Vol.2, p.227-230.

REFERENCES (continued)

- [12] Farinoso, F., Deltete, C., and Wilson, R., "Spent Resin Incineration: Should Radioactivity Preclude it?", Proceedings of Waste Management '84, Vol.2, p.219-222.
- [13] Yim, S. P., Kim, J., Park, H. H., Suh, I. S., "The Effect of Quick Freeze Pretreatment on Grinding of Spent Organic Ion Exchange Resins", Proceedings of Waste Management '91, Vol. 2, p.295-298.
- [14] ASTM, Standard Method of Test for Physical and Chemical Properties of Ion Exchange Resins, D2187-77, American Society for Testing and Materials, Philadelphia, PA, 1975.
- [15] USNRC, "Technical Position on Waste Form", US Nuclear Regulatory Commission, Low-Level Waste Licensing Branch, Washington, DC, May 1983.

APPENDIX I

Plots of Changes in Volume and Weight for Ion
Exchange Waste Forms Immersed in Water.

Figure A.1 : Volume (cu. cm) of Sample A, measured using a caliper, vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water

Figure A.2: Volume (cu. cm) of Sample B, measured using a Caliper, vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed in Deionized Water

Figure A.3: Weight (grams) of Sample A vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed In Deionized Water

Figure A.4: Weight (grams) of Sample B vs. Time (Days) for Pretreated Cation (IRN-77) Ion Exchange Resin Immersed In Deionized Water

Figure A.5 : Volume (cu. cm) of Sample A, measured using a caliper, vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water

Figure A.6: Volume (cu. cm) of Sample B, measured using a Caliper, vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water

Figure A.7: Weight (grams) of Sample A vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed In Deionized Water

Figure A.8: Weight (grams) of Sample B vs. Time (Days) for Pretreated Anion (IRN-78) Ion Exchange Resin Immersed in Deionized Water

Figure A.9 : Volume (cu. cm) of Sample A, measured using a Caliper, vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water

Figure A.10: Volume (cu. cm) of Sample B, measured using a Caliper, vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water

Figure A.11: Weight (grams) of Sample A vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed In Deionized Water

Figure A.12: Weight (grams) of Sample B vs. Time (Days) for Pretreated Mixed Bed (2:1 ratio) Ion Exchange Resin Immersed in Deionized Water

APPENDIX II

**Data Collected for Changes in Volume and
Weight of Ion Exchange Resin Waste Forms.**

Table A.1: Volume Measurements Using a Caliper for Cation (IRN-77), Sample A, Ion Exchange Resin

Time (Days)	Vol. 10 wt% (cm ³)	Vol. 20 wt% (cm ³)	Vol. 30 wt% (cm ³)	Vol. 40 wt% (cm ³)	Vol. 50 wt% (cm ³)	Vol. 60 wt% (cm ³)	Vol. 70 wt% (cm ³)
0	13.847	13.379	13.98	13.078	13.747	13.84	14.337
0.04	14.075	13.216	14.174	13.132	13.962	13.784	14.505
0.21	14.181	13.137	14.182	13.082	13.958	13.758	14.653
1	13.958	13.316	14.274	13.154	13.949	13.833	14.717
2	14.005	13.329	14.315	13.062	14.018	13.69	14.667
3	14.047	13.462	14.227	13.148	14.148	13.868	14.914
4	14.058	13.402	14.204	13.096	14.106	13.842	14.928
11	14.302	13.367	14.21	13.078	14.019	13.627	15.353
18	14.849	13.481	14.199	13.102	14.014	13.789	16.486
25	15.293	13.591	14.296	13.163	14.046	13.772	17.193
32	16.302	13.476	13.87	13.152	14.128	13.794	17.343
39	17.016	13.548	14.21	13.132	14.34	13.917	17.776
46	17.163	13.723	14.244	13.225	14.167	13.822	18.541
60	17.824	13.865	14.255	13.231	14.451	13.896	18.861
70	18.07	13.774	14.242	13.34	14.458	13.875	19.163
80	18.198	13.8	14.301	13.319	14.556	13.856	19.27
90	18.401	13.814	14.368	13.357	14.604	13.95	19.377

Table A.2: Volume Measurements Using a Caliper for Cation (IRN-77), Sample B, Ion Exchange Resin

Time (Days)	Vol. 10 wt% (cm ³)	Vol. 20 wt% (cm ³)	Vol. 30 wt% (cm ³)	Vol. 40 wt% (cm ³)	Vol. 50 wt% (cm ³)	Vol. 60 wt% (cm ³)	Vol. 70 wt% (cm ³)
0	13.14	13.677	13.274	13.431	12.789	13.224	14.126
0.04	13.61	13.87	13.148	13.708	13.081	13.324	14.259
0.21	13.411	13.537	13.167	13.943	13.083	13.577	14.36
1	13.126	14.016	13.26	14.024	12.963	13.712	14.265
2	13.555	13.868	13.138	14.194	12.968	13.586	14.363
3	13.409	13.505	13.265	14.072	12.991	13.592	14.674
4	13.905	13.875	13.252	13.812	12.887	13.656	14.79
11	13.486	13.829	13.224	13.959	13.007	13.856	14.948
18	13.504	13.893	13.377	13.962	13.134	14.599	15.646
25	13.485	13.187	13.45	13.993	13.062	15.279	16.42
32	13.337	13.435	13.298	14.121	13.366	16.399	17.04
39	13.517	13.808	13.348	14.406	13.441	16.97	17.67
46	13.466	13.804	13.4	14.372	13.408	17.415	18.42
60	13.539	13.876	13.534	14.973	13.585	17.946	18.812
70	13.589	13.929	13.563	15.069	13.589	18.425	19.2
80	13.537	13.959	13.54	15.274	13.579	18.634	19.335
90	13.61	14.237	13.575	15.522	13.615	18.844	19.529

Table A.3: Weight Measurements for Cation (IRN-77), Sample A, Ion Exchange Resin

Time (Days)	Wt. 10 wt% (gm)	Wt. 20 wt% (gm)	Wt. 30 wt% (gm)	Wt. 40 wt% (gm)	Wt. 50 wt% (gm)	Wt. 60 wt% (gm)	Wt. 70 wt% (gm)
0	12.05	12.58	12.43	14.15	12.71	14.74	15.49
0.04	12.05	12.6	12.42	14.15	12.73	14.77	15.52
0.21	12.06	12.56	12.43	14.17	12.77	14.8	15.58
1	12.11	12.61	12.48	14.17	12.71	14.81	15.61
2	12.08	12.58	12.48	14.19	12.71	14.8	15.63
3	12.1	12.55	12.47	14.19	12.77	14.88	15.73
4	12.03	12.58	12.43	14.21	12.74	14.92	15.78
11	12.05	12.59	12.44	14.24	12.74	15.18	16.23
18	12.05	12.6	12.46	14.26	12.74	15.69	16.98
25	12.07	12.6	12.47	14.28	12.75	15.8	17.58
32	12.07	12.58	12.47	14.31	12.76	16.72	18.24
39	12.07	12.6	12.48	14.34	12.77	17.4	18.83
46	12.08	12.6	12.47	14.36	12.76	18.02	19.43
60	12.08	12.6	12.48	14.39	12.78	18.68	19.74
70	12.09	12.62	12.5	14.44	12.79	19.07	20.06
80	12.09	12.62	12.51	14.47	12.79	19.25	20.24
90	12.09	12.62	12.51	14.5	12.79	19.38	20.35

Table A.4: Weight Measurements for Cation (IRN-77), Sample B, Ion Exchange Resin

Time (Days)	Wt. 10 wt% (gm)	Wt. 20 wt% (gm)	Wt. 30 wt% (gm)	Wt. 40 wt% (gm)	Wt. 50 wt% (gm)	Wt. 60 wt% (gm)	Wt. 70 wt% (gm)
0	12.1	12.16	12.96	14.31	12.17	14.35	15.27
0.04	12.09	12.13	12.94	14.32	12.18	14.39	15.29
0.21	12.08	12.12	12.92	14.29	12.21	14.45	15.32
1	12.16	12.2	12.96	14.38	12.19	14.44	15.36
2	12.11	12.14	12.96	14.4	12.17	14.55	15.36
3	12.09	12.19	13	14.35	12.17	14.51	15.42
4	12.11	12.16	12.98	14.39	12.18	14.55	15.45
11	12.09	12.17	12.99	14.45	12.19	14.87	15.72
18	12.11	12.18	13.01	14.51	12.2	15.45	16.27
25	12.12	12.18	13.02	14.56	12.21	16.13	16.83
32	12.14	12.17	13.03	14.63	12.21	16.74	17.54
39	12.12	12.19	13.04	14.69	12.22	17.38	18.21
46	12.14	12.19	13.06	14.77	12.23	17.98	19.07
60	12.13	12.2	13.06	14.87	12.24	18.66	19.56
70	12.14	12.19	13.08	14.99	12.24	19.13	20
80	12.15	12.19	13.09	15.08	12.25	19.38	20.2
90	12.15	12.21	13.11	15.23	12.25	19.59	20.38

Table A.5: Volume Measurements Using a Caliper for Anion (IRN-78), Sample A, Ion Exchange Resin

Time (Days)	Vol. 10 wt% (cm ³)	Vol. 20 wt% (cm ³)	Vol. 30 wt% (cm ³)	Vol. 40 wt% (cm ³)	Vol. 50 wt% (cm ³)	Vol. 60 wt% (cm ³)	Vol. 70 wt% (cm ³)
0	13.433	13.469	13.537	12.942	12.795	13.175	14.076
0.04	13.81	13.75	13.75	13.227	12.936	13.192	14.158
0.21	13.712	13.681	13.764	13.302	12.943	13.336	14.109
1	13.627	13.639	13.698	13.214	12.97	13.371	14.269
2	13.575	13.737	13.503	13.452	13.021	13.355	14.353
3	13.793	13.746	13.853	13.453	12.988	13.35	14.416
4	13.765	13.651	13.708	13.354	13.09	13.369	14.326
11	13.755	13.6	13.858	13.361	12.986	13.359	14.549
18	13.818	13.637	13.884	13.297	13.004	13.352	15.274
25	13.658	13.876	13.239	13.339	13.08	13.383	14.969
32	13.695	13.86	13.266	13.67	13.365	13.444	15.748
39	13.842	14.041	13.569	13.653	13.31	13.43	15.981
46	13.962	14.039	13.556	13.644	13.23	13.319	16.005
60	14.044	14.113	14.141	13.728	13.257	13.464	16.076
70	14.051	14.127	14.089	13.725	13.35	13.536	16.067
80	13.998	14.167	14.077	13.733	13.291	13.547	16.071
90	13.967	14.134	14.097	13.725	13.387	13.552	16.108

Table A.6: Volume Measurements Using a Caliper for Anion (IRN-78), Sample B, Ion Exchange Resin

Time (Days)	Vol. 10 wt% (cm ³)	Vol. 20 wt% (cm ³)	Vol. 30 wt% (cm ³)	Vol. 40 wt% (cm ³)	Vol. 50 wt% (cm ³)	Vol. 60 wt% (cm ³)	Vol. 70 wt% (cm ³)
0	13.509	13.48	13.239	12.703	13.066	13.039	13.606
0.04	13.697	13.663	13.685	13.019	13.199	13.172	13.53
0.21	13.591	13.624	13.607	13.039	13.306	13.229	14.087
1	13.527	13.763	13.657	13.035	13.24	13.151	13.963
2	13.638	13.688	13.664	13.134	13.187	13.284	14.057
3	13.505	13.628	13.602	13.11	13.229	13.257	14.09
4	13.58	13.732	13.613	13.035	13.296	13.339	14.105
11	13.637	13.697	13.825	13.062	13.283	13.334	14.297
18	13.797	12.949	13.817	13.086	13.372	13.588	14.346
25	13.769	13.764	14.001	13.255	13.343	13.503	14.312
32	13.746	13.481	13.876	13.119	13.47	13.507	14.581
39	13.713	13.764	14	13.24	13.443	13.722	14.6
46	13.74	13.763	13.886	13.158	13.339	13.657	14.55
60	13.87	13.87	14.053	13.23	13.44	13.74	14.571
70	13.82	13.842	14.082	13.264	13.448	13.769	14.549
80	13.821	13.814	14.03	13.277	13.443	13.764	14.569
90	13.779	13.83	14.041	13.29	13.466	13.792	14.574

Table A.7: Weight Measurements for Anion (IRN-78), Sample A, Ion Exchange Resin

Time (Days)	Wt. 10 wt% (gm)	Wt. 20 wt% (gm)	Wt. 30 wt% (gm)	Wt. 40 wt% (gm)	Wt. 50 wt% (gm)	Wt. 60 wt% (gm)	Wt. 70 wt% (gm)
0	12.26	12.59	12.26	12.23	12.3	12.61	12.9
0.04	12.26	12.58	12.23	12.24	12.3	12.63	12.95
0.21	12.26	12.58	12.26	12.25	12.35	12.65	12.98
1	12.27	12.64	12.28	12.26	12.3	12.63	13.03
2	12.3	12.58	12.25	12.25	12.31	12.65	13
3	12.21	12.59	12.28	12.3	12.35	12.63	13.03
4	12.28	12.58	12.27	12.27	12.32	12.64	13.06
11	12.26	12.59	12.27	12.3	12.34	12.67	13.3
18	12.27	12.59	12.27	12.33	12.35	12.68	13.67
25	12.28	12.6	12.28	12.35	12.35	12.66	13.99
32	12.28	12.6	12.28	12.32	12.35	12.69	14.18
39	12.28	12.62	12.28	12.34	12.37	12.72	14.29
46	12.29	12.62	12.29	12.37	12.39	12.73	14.46
60	12.27	12.62	12.28	12.41	12.38	12.74	14.56
70	12.29	12.61	12.29	12.39	12.38	12.74	14.56
80	12.29	12.61	12.3	12.34	12.4	12.76	14.59
90	12.29	12.62	12.29	12.35	12.4	12.77	14.58

Table A.8: Weight Measurements for Anion (IRN-78), Sample B, Ion Exchange Resin

Time (Days)	Wt. 10 wt% (gm)	Wt. 20 wt% (gm)	Wt. 30 wt% (gm)	Wt. 40 wt% (gm)	Wt. 50 wt% (gm)	Wt. 60 wt% (gm)	Wt. 70 wt% (gm)
0	12.23	12.19	12.59	12.06	12.24	12.53	12.82
0.04	12.21	12.17	12.56	12.02	12.23	12.54	12.83
0.21	12.25	12.18	12.53	12.04	12.28	12.54	12.85
1	12.28	12.22	12.61	12.05	12.23	12.55	12.85
2	12.24	12.2	12.55	12.07	12.25	12.57	12.83
3	12.24	12.18	12.61	12.1	12.27	12.57	12.83
4	12.25	12.2	12.59	12.05	12.26	12.53	12.86
11	12.24	12.21	12.6	12.06	12.29	12.57	12.9
18	12.25	12.22	12.61	12.06	12.31	12.61	12.92
25	12.25	12.24	12.61	12.11	12.3	12.59	12.94
32	12.25	12.19	12.62	12.09	12.29	12.6	12.95
39	12.25	12.22	12.62	12.08	12.32	12.63	12.98
46	12.26	12.23	12.62	12.08	12.33	12.63	13.03
60	12.26	12.24	12.62	12.09	12.34	12.65	13.03
70	12.25	12.24	12.63	12.1	12.35	12.66	13.04
80	12.26	12.24	12.63	12.09	12.37	12.66	13.07
90	12.27	12.24	12.62	12.09	12.38	12.68	13.07

Table A.9: Volume Measurements Using a Caliper for Mixed Bed (2:1 ratio), Sample A, Ion Exchange Resin

Time (Days)	Vol. 10 wt% (cm ³)	Vol. 20 wt% (cm ³)	Vol. 30 wt% (cm ³)	Vol. 40 wt% (cm ³)	Vol. 50 wt% (cm ³)	Vol. 60 wt% (cm ³)	Vol. 70 wt% (cm ³)
0	12.922	12.272	12.378	12.98	12.683	12.951	13.138
0.04	13.035	12.411	12.649	13.028	12.901	12.979	13.443
0.21	12.99	12.585	12.732	13.091	12.762	13.089	13.323
1	13.002	12.455	12.62	13.044	12.865	12.947	13.402
2	13.03	12.336	12.605	13.212	12.924	13.139	13.361
3	13.027	12.604	12.682	13.134	12.952	13.1	13.341
4	12.86	12.628	12.677	13.087	12.977	13.132	13.31
11	12.825	12.602	12.722	13.072	12.818	13.206	13.406
18	12.901	12.722	12.781	13.067	12.975	13.34	13.58
25	12.919	12.742	12.759	13.047	12.941	13.368	13.606
32	13.101	12.555	12.805	13.109	13.285	13.392	13.855
39	13.254	12.779	12.778	13.122	13.211	13.484	14.051
46	13.288	12.757	12.855	12.936	13.295	13.559	14.257
60	13.446	12.75	12.874	12.999	13.292	13.744	14.317
70	13.355	12.797	12.966	13.05	13.399	13.778	14.52
80	13.349	12.833	12.978	13.035	13.42	13.797	14.572
90	13.26	12.928	12.967	13.101	13.406	13.918	14.758

Table A.10: Volume Measurements Using a Caliper for Mixed Bed(2:1 ratio), Sample B, Ion Exchange Resin

Time (Days)	Vol. 10 wt% (cm ³)	Vol. 20 wt% (cm ³)	Vol. 30 wt% (cm ³)	Vol. 40 wt% (cm ³)	Vol. 50 wt% (cm ³)	Vol. 60 wt% (cm ³)	Vol. 70 wt% (cm ³)
0	12.49	13.062	12.616	12.82	13.147	12.813	13.014
0.04	12.892	13.305	12.911	12.835	13.29	12.966	12.889
0.21	12.806	13.148	12.745	12.833	13.35	13.101	12.931
1	12.688	13.002	13.009	12.805	13.337	13.096	12.88
2	12.814	13.355	12.801	12.938	13.403	13.106	12.939
3	12.794	13.092	12.869	12.955	13.257	13.095	12.926
4	12.897	13.193	12.928	12.882	13.188	13.136	12.855
11	12.763	13.131	13.049	12.788	13.207	13.054	13.168
18	12.808	13.166	13.057	12.854	13.378	13.204	13.297
25	12.783	13.225	13.032	12.754	13.321	13.206	13.635
32	12.851	13.1	13.068	12.999	13.507	13.406	13.704
39	12.829	13.366	13.13	12.986	13.436	13.451	14.219
46	12.953	13.384	13.048	13.115	13.383	13.451	14.524
60	12.974	13.363	13.108	13.245	13.54	13.61	14.551
70	12.989	13.362	13.157	13.228	13.537	13.617	14.81
80	13.013	13.282	13.143	13.295	13.508	13.666	14.993
90	12.952	13.37	13.166	13.302	13.555	13.735	15.304