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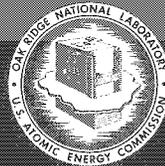
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HTGR FUEL DEVELOPMENT: USE OF UO_3 TO
LOAD CATION EXCHANGE RESIN FOR
MICROSPHERE PREPARATION

P. A. Haas



OAK RIDGE NATIONAL LABORATORY

OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

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RESIN FOR MICROSPHERE PREPARATION

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ABSTRACT

Coated particles made from ion exchange resins offer an attractive alternative to "fissile" particles specified for advanced HTGR's. The concept of reacting cation exchange resins in the hydrogen form with UO_3 , using dilute uranyl salt solutions as a transfer medium, has important advantages for preparation of HTGR fuel particles from ion exchange resins. Dowex 50W-X8 (with nuclear sulfuric acid exchange groups attached to a styrene-divinylbenzene polymer lattice) satisfies the product requirements better than do other strong acid resins, but the sulfuric acid exchange group leaves sulfur in the carbonized particle. Weakly acidic cation exchange resins with carboxylic acid exchange groups leave only carbon and oxygen after carbonization and thus give particles more comparable with the UC_2 or UO_2 commonly used for HTGR fuels. Amberlite IRC-72 was identified as having a better combination of properties than any other weak acid resin tested. The procedure of reacting UO_3 with cation exchange resins in the hydrogen form using uranyl nitrate as the transfer solution allows efficient and well controlled loading of either strong or weak acid resins without formation of dilute uranium solution. The final solution concentration can be selected and controlled by mixing the desired amounts of UO_3 , resin, and solution without any need to monitor flow rates or concentrations. Mixing of UO_3 with the resin is the only procedure which has demonstrated practical, stoichiometric loadings of a weak acid resin with uranium. Satisfactory mixing of resins, UO_3 , and uranyl nitrate solution was demonstrated in agitated baffled vessels, in a screen-bottom basket of the resin-in-pulp type of contactor, and in a fluidized resin bed with a separate mixer for the addition of UO_3 .

1. INTRODUCTION

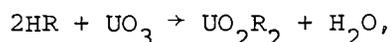
The high-temperature gas-cooled reactors (HTGR's) use fissile particles which are small spheres of carbide or oxide fuel encased in pyrolytic carbon coatings. This type of reactor is typified by the Fort St. Vrain (FSV) Reactor, which is being constructed by Gulf General Atomic. The size and composition of the fissile particles differ for successive FSV cores and for later full-scale reactors.^{1,2} Recycle cores require the remote fabrication of the spherical particles from recycle ^{235}U and ^{233}U .

Coated particles made from ion exchange resins offer an attractive alternative to "fissile" particles currently specified for advanced HTGR's.³ One reference fissile particle consists of 100- μ -diameter, fully dense UC_2 kernels coated with a 100- μ -thick buffer coating (density $1.2 \pm 0.2 \text{ g/cm}^3$) and a composite outer coating consisting of 20 μ of pyrolytic carbon, 30 μ of SiC, and 30 μ of pyrolytic carbon. The density of the pyrolytic carbon in the outer coating is $1.75 \pm 0.05 \text{ g/cm}^3$. If we consider everything within the outer coating, the metal density is 1.57 g U/cm^3 and the porosity is 38%. One alternative fuel particle consists of a void-diluted kernel with a diameter of $300 \pm 10 \mu$, 38% porosity, and a uranium density of 1.58 g/cm^3 . To make this kernel, an ion exchange resin is contacted with uranyl nitrate until a uniform concentration of uranium is achieved throughout the sphere. The resin microspheres are then filtered and dried. After drying, the particles are carbonized by heating in helium or argon in a fluidized bed.

The two most promising types of ion exchange resins for preparing fuel particles are cation exchange resins, in which the exchange groups are either nuclear sulfonic acids (strong acid resins) or carboxylic acids (weak acid resins). Anion exchange resins are less suitable, as the uranium must be complexed by an excess of a complexing anion and the uranium capacity per unit amount of anion resin is too small. The strong acid resins are easy to load with uranium, but the carbonized particle contains a large residue of sulfur, probably primarily as a mixed carbide-sulfide (USC). The removal of sulfur and excess carbon can be promoted

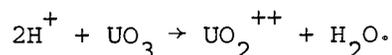
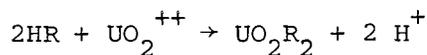
by high-temperature treatments with steam or H_2 to approach UC compositions. The carboxylic acid cation resins have a higher theoretical exchange capacity on both volumetric and weight bases, and contain U-C-O (no sulfur) after carbonization. This represents much less of a composition change from accepted particle compositions than the U-S-C composition and is therefore more acceptable for use in HTGR fuel elements.

A procedure with important advantages for loading ion exchange resins with uranium is to react the cation exchange resin in the hydrogen form with UO_3 using a small amount of a uranyl salt solution as a transfer medium. The overall reaction is:



where HR represents the resin.

This overall reaction is the sum of:



UO_3 powder readily dissolves in uranyl nitrate solutions to give acid-deficient uranyl nitrate solutions with U/NO_3^- mole ratios up to 0.65 at high U concentrations. The simplest method of loading resins, using this concept, is to agitate the resin and the UO_3 in the uranyl salt solution until all the UO_3 is dissolved.

The objective of the investigations reported here was to develop and scale-up the concept of loading the cation exchange resins, using UO_3 as the uranium feed. Aspects of particular importance when the investigations were started were:

1. More efficient and better controlled loading of strong acid resins without formation of large volumes of dilute uranium solutions.
2. Loading of weak acid resins to a high percentage of their theoretical capacity.
3. Determination of conditions to give the maximum practical loading of uranium.

4. Equipment scale-up studies to demonstrate equipment which would be practical for full-scale, remote loading of ^{235}U or ^{233}U .

Investigations in which the ion exchange resin is contacted with uranyl nitrate solution only (no UO_3) are not reported here.

2. PRODUCT REQUIREMENTS

The loaded ion exchange resin must be suitable for processing to give a particle usable for the final applications. For all the studies reported here, the final application is the fissile particle for HTGR (High Temperature Gas-Cooled Reactor) fuels of the Gulf General Atomic type. Some of the requirements for this particle would not be valid for other applications.

The fuel particles prepared from ion exchange resins have much lower U densities than the UC or UO_2 fissile particle kernels selected for Fort St. Vrain HTGR fuel elements. Pollock, Scott and Leitnaker³ have proposed that the low-density kernel prepared from ion exchange resins can provide the void volume to accommodate fuel swelling and gas release. Thus, the resin-derived particle with a thin buffer layer to protect the outer coating from fission recoil damage is an attractive alternate to the conventional fissile particles. The initial irradiations of carbonized resin particles show acceptable performance.⁴

Preliminary material specifications for fissile fuel carbonized ion exchange resins were prepared by the Metals and Ceramics Division at ORNL. These specifications impose certain requirements on the properties of the unloaded resins and on the allowable effects of the loading, drying, and carbonization operations. Important requirements as a result of these specifications are listed individually.

2.1 Uranium Concentrations

High, reproducible, and uniform loadings of uranium on the ion exchange resin are essential to achieving the required concentrations of uranium per unit volume after carbonization; also, the amounts of

ion exchange resin required decrease as the uranium loadings increase. Acceptable amounts of uranium were loaded on strong acid resins, using conventional loading procedures with uranyl nitrate, but the conventional procedures did not give the desired loadings of weak acid resins. Even for the strong acid resins, procedures to increase U loadings are desirable to give flexibility to meet varying requirements. In summary, the loading specifications for this study would involve:

- a. Reproducibility of a specified loading.
- b. Uniformity from particle to particle.
- c. The maximum U concentrations practical, with 1.8 meq U per ml of resin (H^+ form) as the minimum value of interest. This minimum was the values already demonstrated by conventional loading procedures.

2.2 Sphericity

Greater than 99% of the particles shall have a major-to-minor axis ratio equal to or less than 1.2. Fragments of spheres can be shape separated after loading or carbonization, but we would prefer that the unloaded resin meet the sphericity criteria in order to minimize recycle of waste material. The formation of cracks during loading is very undesirable.

2.3 Microstructure

Greater than 99% of the particles shall be crack-free and exhibit no internal voids in excess of 0.1 μm diameter.

2.4 Diameter

At least 99% of the particles shall have diameters greater than 90% of the mean value. At least 99% of the particles shall have diameters less than 110% of the mean value. As with sphericity, we would prefer that the unloaded resin meet the criteria in order to minimize recycle of waste.

2.5 Impurities

The iron content shall not exceed 100 ppm as determined by test specification MET-CER-TS-14. All other impurities shall not exceed a 2200-m/sec absorption cross-section boron equivalent of 10 ppm. The relevant elements to be determined and test methods shall be in accordance with ASTM standard for uranium or ASTM provisional standard for plutonium.

3. EXPERIMENTAL PROCEDURES AND RESULTS

All investigations were batch-type operations using measured amounts of ion exchange resin, UO_3 , uranyl nitrate solution, and nitric acid with agitation. Tests with up to 200 ml of ion exchange resin were usually made in standard glass beakers of 250- to 600-ml volume using a combination magnetic stirrer-hot plate. Larger quantities of resin (up to 2000 ml) were tested using motor-driven paddle or propeller agitators in glass beakers of 1-, 2-, or 4-liter volume modified to provide three or four vertical baffles for mixing. Other contactors considered for scale-up are described with the scale-up study results. The resin samples were dried overnight by drawing laboratory air through the resin on a coarse-porosity fritted-glass filter or a screen. Solution pH values were determined using a standard laboratory pH meter with an all-purpose electrode calibrated with pH = 2.0 buffer.

3.1 Results for Strong Acid Resins

The promising initial results for this method of particle preparation were obtained with Dowex 50W-X8 ion exchange resin,³ and this resin remains the reference standard for strong acid resins. It is a strongly acidic cation exchange resin with nuclear sulfonic acid exchange groups attached to a styrene-divinylbenzene polymer lattice. The Dowex 50W-X8 resin is superior to all other strong acid resin samples examined in one or more of the following respects: amount of cracking, amount of voids, amount of nonspherical particles, and/or capacity per unit volume. The differences are small for the best of the other resin samples.

The use of UO_3 provides an efficient, reproducible, and well controlled loading of the strong acid resins.

Example 1: The following were combined in a 250-ml beaker and warmed to 70°C with stirring:

8 meq uranyl nitrate
77 meq UO_3 (based on 2 eq/mole)
39.5 cc Dowex 50W-X8 resin
 H_2O to give 70 cc total volume

Within 15 minutes after mixing, the solution was clear, free of UO_3 slurry, and had a pH = 2.2. This shows complete loading of a strong acid resin in 15 minutes, leaving only uranium solution which could be used to load the next batch using UO_3 only without any recovery treatments or additional uranyl nitrate.

Example 2: The following were combined in a four-liter baffled beaker and warmed to 46°C with stirring:

150 meq uranyl nitrate
3920 meq UO_3 (based on 2 eq/mole)
1960 cc Dowex 50W-X8 resin
 H_2O to give about 2.8-liter total volume

After one hour, the solution was clear, free of UO_3 slurry, and had a pH = 1.7.

This procedure with agitation promotes rapid and uniform loading of the resin. There is no need to monitor flow rates or concentrations; the selected amounts of UO_3 , resin, and solutions are mixed to give the final concentrations desired at equilibrium. Uniform partial loadings are possible if desired, while fixed-bed loadings can only approximate uniformity by continuing solution flow until the exit concentration approaches the inlet concentration (that is, the resin is in equilibrium with the feed). The fixed-bed flowsheets in use at the start of this investigation required three to eight hours loading time and as high as 600% excess uranium. These flowsheets for fixed-bed loadings have since been improved by using multiple beds

and lower U concentrations, thus providing efficient loading of stoichiometric amounts of uranium on fixed beds of strong acid resins.

In general, loading of uranium on the strong acid acids is relatively easy and simple. Loading conditions and results are tabulated in the Appendix for Dowex 50W-X8 (Table A-1) and several strong acid resins (Table A-2). The larger samples were for carbonization, heat treating, and coating development and did not represent any studies of loading variables. Some effects of loading variables are tabulated (Table 1), and analyses after drying and carbonization are listed (Table 2). By using UO_3 to maintain acid-deficient conditions during loading, Dowex 50W-X8 resin can be loaded to more than the stoichiometric amount of UO_2^{++} . This result is discussed in Section 3.3 on maximizing uranium loadings.

3.2 Results for Weak Acid Resins

As a part of this investigation, Amberlite IRC-72 was identified as having a better combination of properties than any other weak acid resin tested. Loading conditions and results are tabulated in the Appendix for a number of weak acid resins (Table A-3). Some effects of loading variables are tabulated (Table 3), and analyses after drying and carbonization are listed with those for strong acid resins (Table 2). Many of the weak acid resins, such as Amberlite IRC-50 and Duolite CS-101, are irregular in shape with few perfect spheres and, therefore, cannot satisfy the sphericity specifications. Other resins which were nearly all spheres before loading showed excessive cracking before the loadings of uranium reached the desired values. Amberlite IRC-84 and Duolite CC-3 showed this excessive cracking and also loaded very slowly--requiring over 48 hours at 80°C. Relite-CC loaded slowly and had 90% as much capacity as Amberlite IRC-72. While exactly identical conditions were not tested, the Relite-CC appears somewhat inferior to the Amberlite IRC-72, but better than any other weak acid resin tested. The examples will be limited to use of Amberlite IRC-72 (H^+ form).

Table 1. Effects of Resin and Loading Variables for Strong Acid Resins

Resin	Variable	% Increase in Non-Spherical Particles	Other Remarks
Dowex 50W-X8	Before loading	—	Standard for strong acid resins
	Drying before loading ^a	None	No effect on loading
	Loading to 2.05 meq/ml U	None	Requires less than one hour
	Loading to 2.28 meq/ml U	1	Required seven hours
	Loading to 2.45 meq/ml U	2	Required 29 hours
	30/35 mesh versus 20/50 mesh	-1	No effect on loading
	Low or high NO ₃ ⁻ concentration in solution	None	Affects rate of UO ₃ dissolution
Amberlite IRC-120	Different manufacturer	2	Same loading behavior as Std.
	Drying before loading ^a	—	No effect on loading
Duolite C-25	Different manufacturer	5	Less capacity than standard

^aDried in flowing room air at room temperature.

Table 2. Analyses of Loaded and Carbonized Resin Samples

Resin	U Loading (meq/ml)	Dried ^b Resin (wt % U)	Carbonized Resin (usually 1000°C) ^a					Surface Area (m ² /g)	Hg Density at 15,000 psi (g/cc)
			wt % U	wt % C	wt % H	S or O (wt %)			
Dowex 50W-X8	2.0	28.4							
	2.02	32.2							
	2.03	32.2							
	2.04	31.0							
	2.04	31.0							
	2.04	32.2							
	2.28	34.0							
	2.45	34.1							
Amberlite IR-120	1.88	29.7	49.1	32.3	0.28	10.3-S	0.59	2.96	
Amberlite IRC-72	3.1 ^c	—	76.5 ^c	17.0		2.12-O ₂		5.94	
	3.1	43.8							
	3.2	—	67.4	17.6					
	3.3	42.8							
	3.3	43.3							
	3.2	44.4							
	3.4	45.4							
Amberlite IRC-50	2.6	36.1							
	3.2	37.0	67.9	17.7	0.54	—	17.4	4.80	
Amberlite IRC-84	<0.6	3.0							
	1.1	17.1	46.5	44.0	0.3	—	—	—	
	1.6	—	52.3	37.7	—	—	—	2.85	
	1.9	26.0							
	1.9	26.6							
	2.1	27.7	60.7	26.3	—	—	—	3.61	
Relite CC	2.6	31.7							

^aPersonal communication with C. Pollock *et al.*, ORNL, 1971.

^bDried in flowing room air at room temperature.

^cLoaded with 93% ²³⁵U, heat-treated at 1600°C, and characterized for irradiation specimens.

Table 3. Effects of Resin and Loading Variables for Weak Acid Resins

Resin	Variable	% Increase in Non-Spherical Particles	Other Remarks
Amberlite IRC-72	Before loading	—	Standard for weak acid resins
	Loading to 3.1 meq/ml	None	Requires less than two hours
	Loading to 3.4 meq/ml	None	Required 28 hours
	Drying before loading ^a UO ₃ was 93% ²³⁵ U	None	Loaded slowly to 2.4 meq/ml No effects
Relite CC	Different manufacturer	2	Contains more particles larger than 1200 microns; 50% of >1200-micron particles cracked
Amberlite IRC-50	Different resin	>90	Very few spheres as received; easy to load with U
	Drying before loading ^a Higher than 3 N NO ₃ ⁻ ; pH <2	— None	Loaded slowly, incompletely Incomplete loading of U
Amberlite IRC-84	Different resin	None	Loading of U very slow, incomplete
	Loading to 1.0 meq/ml	None	Required ~24 hr at pH >2.6
	Loading to 1.6 meq/ml	None	About 2% of spheres show cracks Required ~48 hr at pH >2.8
	Loading to >1.8 meq/ml	2 to 70	All spheres show cracks Required >48 hr at pH >2.9
	High NO ₃ ⁻ concentration with pH <2	None	Loadings less than 0.6 meq/ml
Duolite GC-3	Different manufacturer	—	One test showed same loading behavior and cracking as Amberlite IRC-84
Duolite CS-101	Different manufacturer	>80	Same appearance as Amberlite IRC-50

^aDried in flowing room air at room temperature.

Example 3: The following were combined in a 600-ml baffled beaker and warmed to 70°C with stirring:

288 ml or 910 meq Amberlite IRC-72 resin
in the H form
144.2 g or 1013 meq UO_3 (93% ^{235}U)
93 meq HNO_3
 H_2O to make about 400-ml total volume

After 1 hr at 70°C, the UO_3 was all dissolved and the solution pH was 2.8. The loaded resin was filtered and dried at room temperature to give the following:

106 meq of U in solution
907 meq of U on resin (by difference) or 100% loading
245.5 g of loaded resin of 43.5 wt % U

Example 4: Amberlite IRC-72 (106 cc, or 350 meq) was warmed in water to 70°C; 365 meq U was added as UO_3 , and 78 meq U as uranyl nitrate. After 1 hr at 70°C, solution was slightly hazy, and the pH was 2.55, indicating full loading of the resin. The final pH at 25°C was 2.9. The resin was washed and air dried to give 94.7 g of dried resin of 43.3 wt % U.

The results for maximizing the uranium loadings are discussed separately in Section 3.3. In general, the carboxylic acid cation resins require acid-deficient uranyl nitrate solutions (NO_3^-/U mole ratios of less than 2.0) before useful uranium loadings are possible. If weak acid resins are equilibrated with uranyl nitrate solutions ($\text{NO}_3^- < 1 \text{ N}$), the solution pH values would be in the order: Amberlite IRC-50 < Amberlite IRC-72 < Amberlite IRC-84. Approximate solution pH values versus U loadings for Amberlite IRC-72 were determined as shown by the following (also Fig. 1):

Example 5: pH measurements were made for loading 100 ml of Amberlite IRC-72 resin, using solution which was 0.3 N NO_3^- (60 meq NO_3^- , about 200 ml solution).

Stoichiometric uranyl nitrate, no resin, pH = 2.45
After resin addition (60 meq U), pH = 1.11
After 14.5 g UO_3 addition, equilibrium pH = 1.45

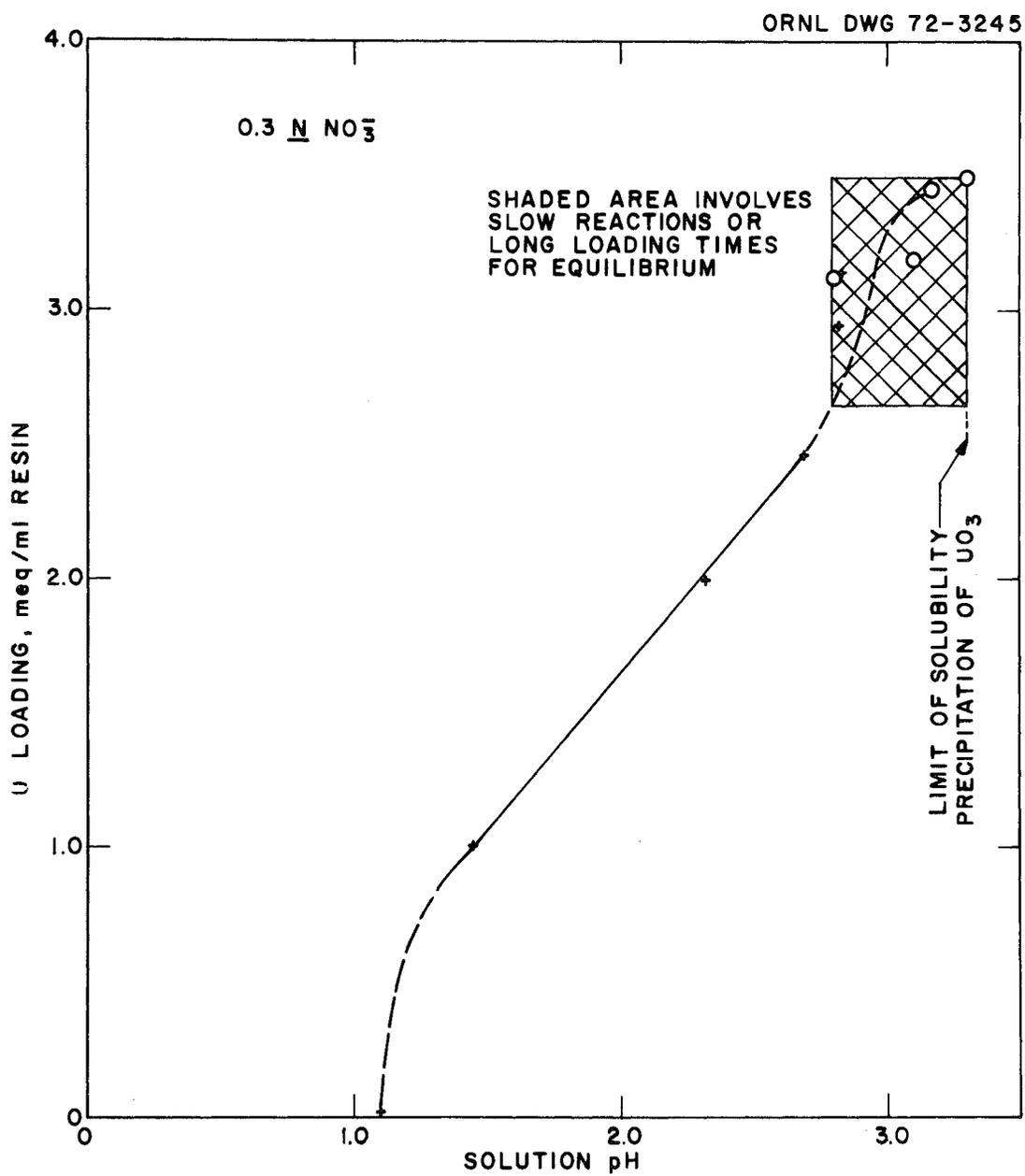


Fig. 1. Solution pH Values Versus U Loading for Amberlite IRC-72 Cation Exchange Resin.

After 29.3 g UO_3 addition, equilibrium pH = 2.32

After 36.25 g UO_3 addition, equilibrium pH = 2.68

After 43.75 g UO_3 addition, equilibrium pH = 2.82

The amount of U added along with the NO_3^-/U ratios, reported as a function of pH (Figure 2), were used to calculate the U loadings of Figure 1. This test and other results show that steady-state pH values are reached in 2 hr or less at 50 to 80°C for the lower part of the Figure 1 curve (loadings of less than 2.8 meq/ml and final pH values less than 2.8). The dissolution of UO_3 slows down for pH > 2.8; the loading slows down for loadings of 3 meq/ml or higher; and the observed points scatter as a result of inadequate time to reach equilibrium.

3.3 Maximizing Uranium Loadings

Maximizing the loading of uranium on cation exchange resins requires selecting the solution compositions which favor the highest loadings and then promoting solution-resin mass transfer until the resin approaches equilibrium with this solution concentration. Unfortunately, these solution compositions result in complex hydrolytic behavior of UO_2^{++} with no dependable information on the equilibrium constants involved. Among species which have been proposed are: $^5\text{U}_2\text{O}_5^{++}$ or $\text{UO}_2(\text{UO}_3)^{++}$, $\text{U}_3\text{O}_8^{++}$, $\text{U}_3\text{O}_8(\text{OH})^+$, $\text{UO}_2(\text{OH})^+$, $\text{UO}_2[(\text{OH})_2\text{UO}_2]_n^{++}$, and un-ionized dimers such as $(\text{UO}_2\text{F}_2)_2$.

If we designate a positively charged uranium complex by $[\text{COMP}]^{+n}$, the resin loading equation in a general form is:



This indicates that a high loading of the uranium complex is probably favored by a low H^+ concentration or high pH, but the true relationship is complex since the $[\text{COMP}]^{+n}$ concentration is also dependent on the H^+ concentration. If we assume stoichiometric uranyl nitrate with UO_2^{++} as the species which reacts with the ion exchange resin, high resin loadings are favored by diluting the uranyl nitrate to increase the pH. From reported pH values,⁶ the favorable effect of diluting the uranyl nitrate would be large for U concentrations over 100 g U/liter and would

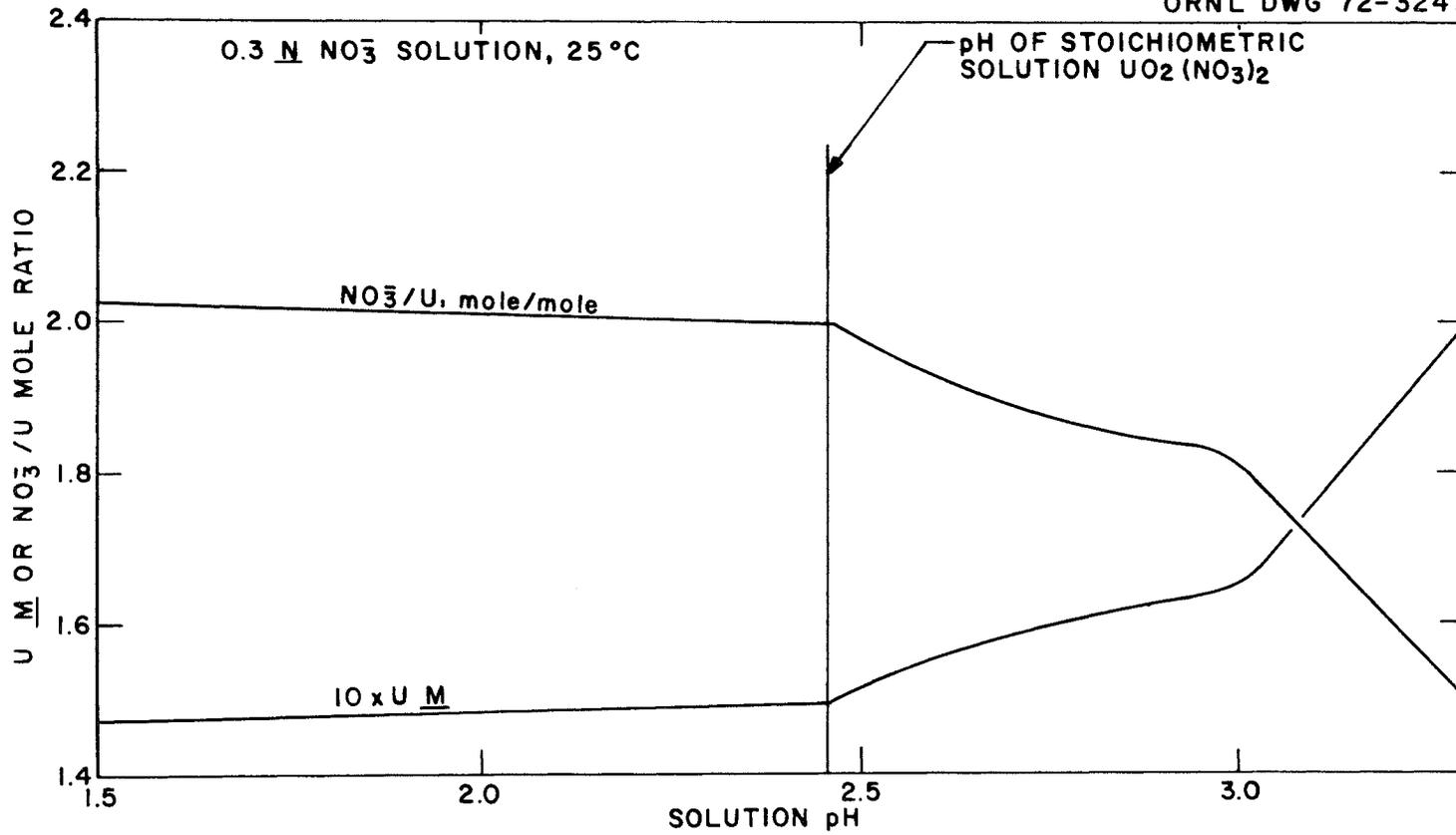
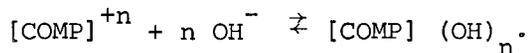


Fig. 2. U Concentrations Versus pH Values for a Constant NO_3^- Concentration.

persist to concentrations of 15 g U/liter or less. The loading of hydrogen forms of the resin produces free acid or H^+ , which gives solution pH values that are much lower than those of stoichiometric uranyl nitrate.

From the general form of the loading equation, we can promote high loadings by decreasing the H^+ and increasing $[COMP]^{+n}$. However, these are limited by the precipitation of the uranium as expressed by:



The most effective procedure for effectively decreasing H^+ and increasing $[COMP]^{+n}$ is to bring the solution into equilibrium with UO_3 [which corresponds to $UO_2(OH)_2$ for the right side of the above equation]. Other procedures, such as use of Na^+ or NH_4^+ forms of the cation exchange resin or addition of NH_4OH or $NaOH$, are fundamentally less favorable to high loadings of uranium. Any other cations compete with the uranium, and anions tend to convert the uranium to negatively charged complexes.

For this investigation, we have chosen to use nitrate as the anion in the loading solution. Nitrate does not leave any undesirable residue or impurity in the carbonized particle, it is not corrosive to stainless steel at these conditions, and it does not complex uranyl into negatively charged anionic forms as easily as many other anions.

For a uranyl nitrate solution in equilibrium with UO_3 (and no other solutes), the solution concentration at a specified temperature is fixed when the nitrate concentration is specified. That is, UO_3 [or $UO_2(OH)_2$] will dissolve or precipitate until an equilibrium U concentration is present in solution. Because of the complex hydrolytic behavior of the uranium at these conditions, the equilibrium resin loadings as a function of nitrate concentration (in equilibrium with UO_3) are uncertain. If we assume that $U/(H^+)^2$ should be maximized, the pH values reported for acid-deficient uranyl nitrate solutions⁶ indicate that the NO_3^- concentrations should be about 0.2 M. Higher nitrate (and therefore higher U) concentrations may be favorable to forming polymeric species such as $U_2O_5^{++}$, but the pH of the solution decreases, thus making the solution-resin equilibrium less favorable. The NO_3^-/U mole ratio and U molarity vs pH for 0.3 N NO_3^- are typical of those for 0.2 to 0.6 N NO_3^- (Figure 2).

From these considerations, UO_3 in equilibrium with uranyl nitrate solutions of 0.2 to 0.6 M total nitrate appears most favorable for maximizing the resin loadings. Heat and agitation are desirable to promote equilibrium between the solution and UO_3 ; UO_3 dissolves slowly in dilute nitric acid at room temperature. Experimental tests are necessary, as the information on the hydrolytic species of uranium is inadequate to allow theoretical estimations. The following tests are preliminary only and are probably not the maximum loadings possible.

Example 6: A 100-ml sample of Amberlite IRC-72 was agitated with a slurry of UO_3 in uranyl nitrate for 28 hr at about 55°C and $\text{pH} \geq 2.8$. At the end of this time, there was no visible UO_3 and the resin was filtered, washed, and dried. The final products were: 90.8 g of dried resin, 45.4% U or 3.46 meq U/ml resin, and solution of 0.4 N NO_3^- and $\text{pH} = 3.16$. The loading calculated from the UO_3 addition would be 3.52 meq U/ml resin.

The U loadings of examples 1 and 2 correspond to 2.0 and 2.01 meq per milliliter of resin, while the resin capacity by titration was 1.88 meq/ml. As would be expected from the rates of hydrolytic or polymeric reactions, loadings above stoichiometric are slow. In 7 hr, a sample was loaded to 2.28 meq/ml or over 120% of stoichiometric (Example 7). The equilibrium solution pH in the presence of UO_3 would have been more than 3.4. The pH was still decreasing when the resin was filtered from the solution; this indicates that the rate of U loading was still significant.

Example 7: A 101-ml sample of Dowex 50W-X8 was agitated with a slurry of UO_3 in uranyl nitrate solution for 7 hr at about 60°C (at $\text{pH} \geq 3$ after 2 hr). At the end of this time, there was no visible UO_3 , and the resin was filtered, washed, and dried. The final products were: 77 g of dried resin of 34.0% U or 2.18 meq U/ml resin, and solution of 0.10 N NO_3^- , $\text{pH} = 3.15$. The loading calculated from the UO_3 addition would be 2.28 meq/ml resin.

3.4 Loadings to Partial Capacity or to Prepare Mixed Oxides

Batch loading of the ion exchange resins using good agitation can be used to obtain uniform partial loadings or uniform concurrent or sequential loadings of two or more cations. These are not practical for loading with liquid flow through a bed of resin, as the differential contact in the bed favors separation of components and/or high recovery at the expense of uniformity.

Using good agitation during sequential additions would promote particle-to-particle uniformity. The possibility of annular differences within a single particle would have to be considered and might be of interest for special experiments.

The above possibilities have not been applied. The result for loading of the weak acid resin versus solution pH (Figure 1) shows how a partial loading would be controlled. The loading of strong acid resins with U, Pu, or Th has been more extensively investigated.⁷ Plutonium and thorium do not have oxides which dissolve with the ease of UO_3 . However, Pu(IV) and Th(IV) both load preferentially to UO_2^{++} . Thus, efficient loadings of Pu on weak acid resins should be possible by using UO_3 to control the solution pH during loading. The presence of some ^{238}U on a Pu fissile particle would be of no importance for an HTGR fuel and would be more acceptable than Na from use of NaOH or resin in the Na form. Also, precipitation of Pu or recycle of waste might be less troublesome for the batch loading using UO_3 than for other loading procedures.

Two tests with UO_3 and $\text{Th}(\text{NO}_3)_4$ solution were as follows:

Example 8: The following were mixed, warmed, and agitated:

49 ml of Amberlite IRC-72 resin
 59 meq Th(IV) as $\text{Th}(\text{NO}_3)_4$
 59 meq of NO_3^- [from $\text{Th}(\text{NO}_3)_4$]
 166 meq of UO_3 (UO_2^{++} basis)
 H_2O to 250-ml volume

The resin was filtered from the final clear yellow solution (pH = 2.92) to give 38.2 g of dried resin which contained 54 meq of Th and 102 meq U. This final resin loading was 3.2 meq/ml and had a Th/(Th + U) mole ratio of 0.209.

Example 9: A 49-ml sample of Amberlite IRC-72 resin was mixed with 0.8 N $\text{Th}(\text{NO}_3)_4$ solution and UO_3 . Resin was filtered from clear yellow solution (pH = 2.9) to give 36.3 g of dried resin of 15.9% U and 21.1% Th. This is equivalent to 1 meq U/ml resin and 2.70 meq Th/ml resin and to a Th/(Th + U) mole ratio of 0.576.

3.5 Scale-Up Studies

Some of the problems involved for scale-up, criticality control, and remote operation of resin loading were considered. For the schematic flowsheet (Fig. 3), the major problems for either batch equipment (Fig. 4) or continuous equipment are the metering and contacting of resin and UO_3 . The following individual discussions are limited to new information from current investigations.

3.5.1 Size Classification

Standard, commercial ion exchange resins will have to be size classified to meet the size specifications for fissile particles. The usual 20/50 mesh commercial size resin commonly has about 30 wt % in each of three screen size fractions, each of which would meet the $\pm 10\%$ of mean diameter range for reactor fuel. For Dowex 50W-X8, the 30/35 mesh or 500-590 micron resin particles would give a suitable diameter range of carbonized particle. For large-scale production, the manufacturer of ion exchange resins would probably size classify out the desired size and use the 70 wt % of smaller or larger particles for non-nuclear uses. An alternative is to adapt the fuel fabrication process to use more than one size of resin particle.

Size classification without drying, probably by wet screening, appears better than dry classification. Ion exchange resins are commonly labeled with warnings to avoid dehydration. Two weak acid

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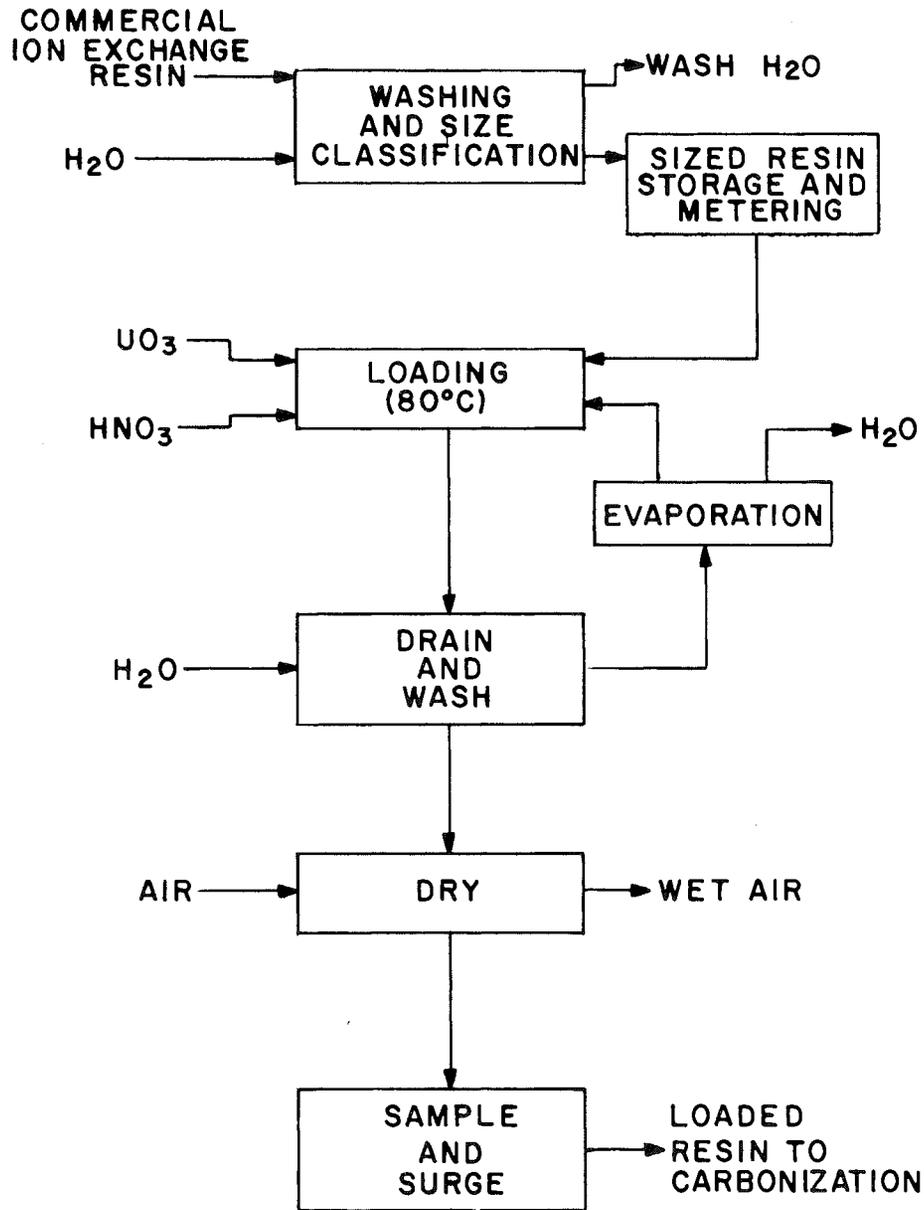


Fig. 3. Resin-Based Microsphere Preparation: Schematic Flowsheet for Resin Loading.

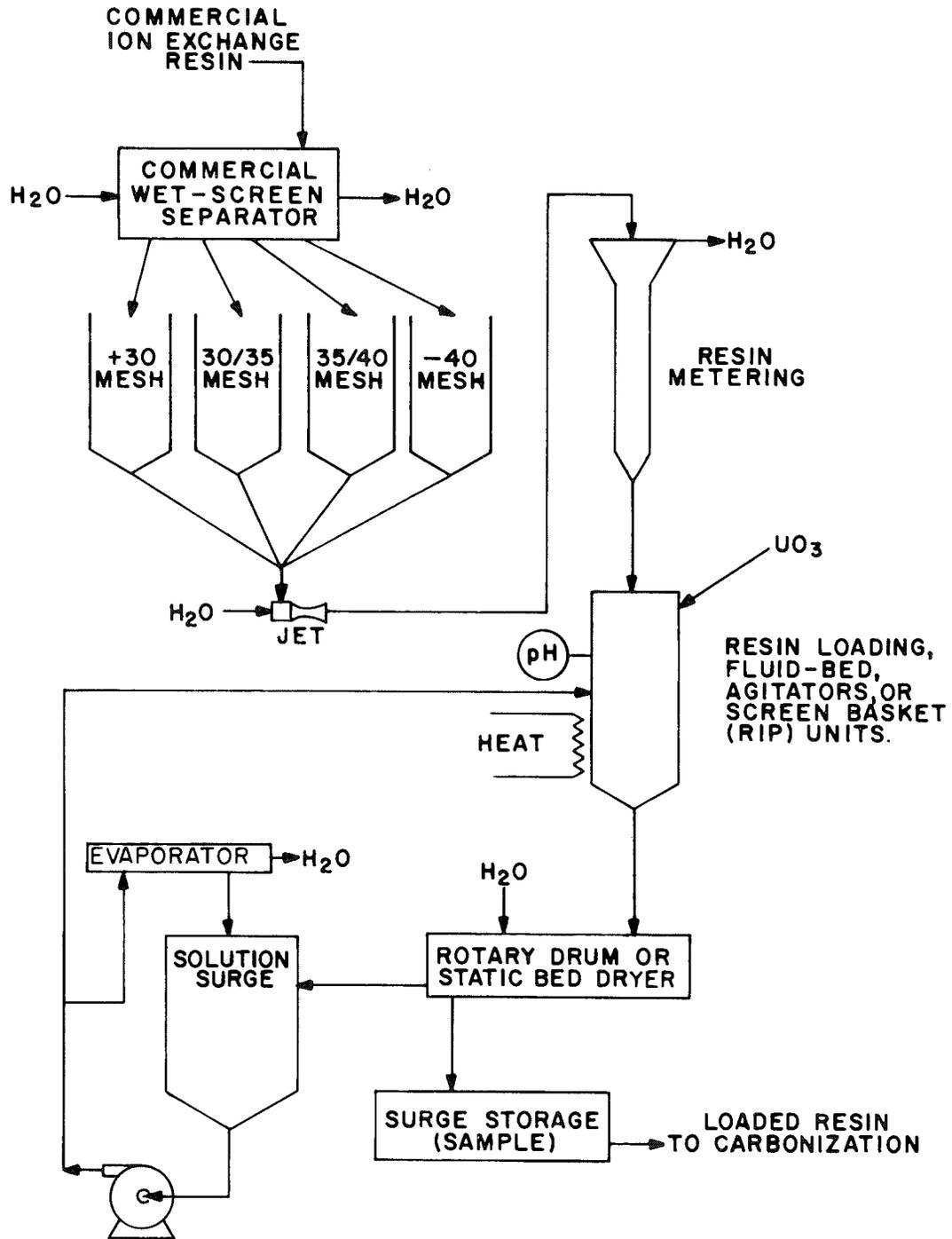


Fig. 4. Resin-Based Microsphere Preparation: Equipment Flowsheet for Resin Loading.

resins, Amberlite IRC-50 and Amberlite IRC-72, loaded significantly slower and less completely after drying in room air at room temperature. Two dried strong acid resins, Amberlite IRC-120 and Dowex 50W-X8, did not show any difference in loading U to 2 meq/ml as compared to undried resins. All of the resins are too moist for effective dry screening as received, and wet screening after addition of water appears less troublesome than a drying operation followed by dry screening.

3.5.2 Resin Metering

A satisfactory measurement of the amount of a resin is obtained by determining its wet volume (in H_2O). The water content of the resin varies somewhat from batch to batch so that weight measurements of the bulk resin are not reproducible. The moist resin as received will not settle and flow to give meaningful volume measurements. But if the resin is added to and allowed to settle in an excess of H_2O to displace air bubbles, it gives a reproducible settled volume. Therefore, the overfilling of a metering tank with an overflow to return the excess resin should provide an adequate resin metering system.

3.5.3 Loading Contactor

Several types of mixers were tested for scale-up using UO_3 , as several problems or requirements exist which do not commonly occur for loading of resins from solutions.

1. A very large change in the resin-solution density difference occurs while going from the H form of the resin to the U-loaded form.
2. Any UO_3 powder that is not mixed with an excess of solution acts as a cement and sets up in a hard cake. Settling of the thoroughly wetted UO_3 does not cause any problem.
3. Both the dissolution of the UO_3 and the loading of the weak acid cation exchange resins are very pH and temperature dependent, so that uniformity of mixing and temperature throughout are important.

4. Uniformly sized resin settles into an orderly arrangement of spheres, which is more difficult to resuspend than the resin of a usual size distribution.
5. Any pockets of unmixed material are not acceptable because the product must be uniformly loaded.
6. The loaded resin must be drained free of solution, dried, and transferred for carbonization.

The satisfactory arrangements, first, provide effective agitation where the UO_3 powder is mixed with the hot solution and, second, contact of the slurry with the whole batch of resin. Draft-tube arrangements in a beaker or a conical-bottom vessel were not satisfactory. Both solution-jet and propellers were tested with the draft-tube devices. Satisfactory operation was demonstrated with three arrangements.

1. Baffled vessels with paddle agitators are very simple. The baffles must be constructed to avoid trapping of solids, and extra equipment must be provided for the draining, drying, and transfer operations.
2. A 5-in.-diam basket (with a 40-mesh screen bottom) was mechanically jiggled to give the "resin-in-pulp" type of contactor developed for uranium ore slurries.⁸ The UO_3 was mixed with the solution separately, using agitation as a preliminary operation. The screen-bottom basket provides very convenient washing and drying. The problems of handling the resin are replaced by the mechanical jiggling and handling of the basket.
3. A tapered fluidized bed using a 40-mesh screen support for the resin was employed with a side-stream of solution through a paddle-agitated mixer for introducing the UO_3 . The screen support allows convenient draining, washing, and drying of the loaded resin.

Selection from the three satisfactory arrangements would depend on the requirements for specific applications. The baffled vessels appear simplest to use and adequate for resin batches up to 2 liters in volume, while the fluidized bed appears preferable for larger batches

requiring critically-safe geometries. The screen-bottom basket was demonstrated with 0.6 liter of resin, the baffled vessels for two liter batches, and the fluidized bed for six liter batches.

The screen-bottom basket was fabricated by clamping and welding a 40-mesh stainless steel screen between a 5-in. length and a 1/8-in. length of 5-in.-OD stainless steel tubing. The basket was jiggled by hanging it from a counter-weighted lever resting on a cam driven by a variable-speed motor. Large baskets have been extensively used for uranium ore processing.⁸ The small basket described above gave good solution-slurry-resin contact when jiggled at about 28 cycles per minute and 1-1/2 in. amplitude in a 6-in.-ID vessel. The small clearance between the vessel and the basket improves the agitation both outside and inside the basket. At the end of the loading operation, the basket was allowed to drain, jiggled in wash water and drained, and then set in a filter funnel with a rubber gasket to allow vacuum to the bottom of the basket to pull air through the basket to dry the resin.

The fluid-bed system was as shown in Figure 5. The dimensions of the glass components are not important design variables; these components were surplus equipment from other studies. The UO_3 powder disperses and circulates throughout the whole system. Some of the UO_3 disperses into almost colloidal size particles so that good mixing of UO_3 without carryover of UO_3 solids is essentially impossible.

3.5.4 Drying

Drying of loaded resin does not appear to have any critical requirements. When the liquid is first drained from the resin, the wet beads do not pour or flow--probably due to surface tension effects of liquid film. This might limit the effectiveness of a rotary drum dryer.

3.5.5 pH Measurements

A standard type of pH instrumentation with an automatic temperature compensation provides an important process control measurement. For tests with the fluidized-bed loading apparatus, the use of standard

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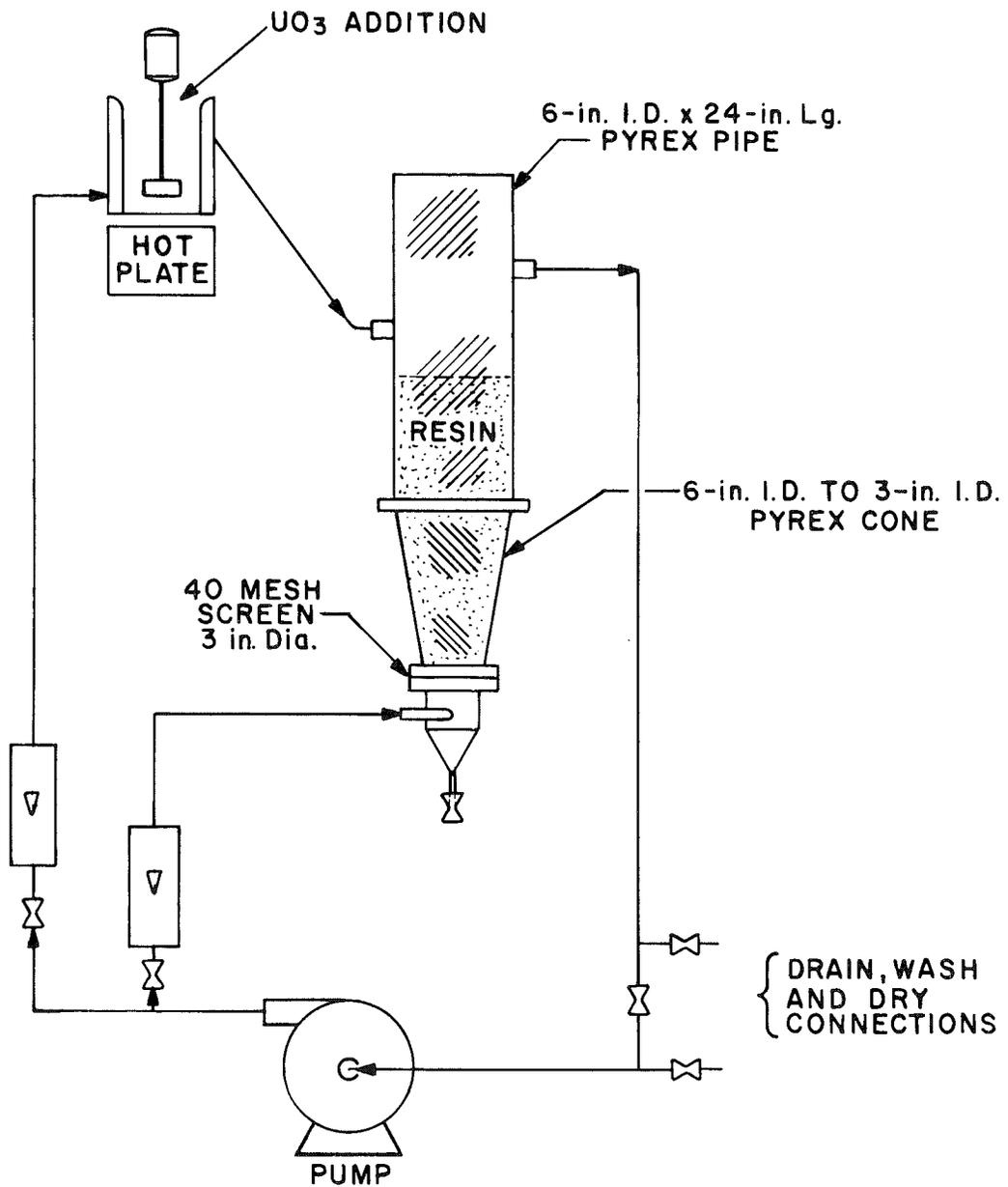


Fig. 5. Fluidized-Bed System for Loading Ion Exchange Resins Using UO_3 .

laboratory pH electrodes in the solution leaving the top of the resin bed was grossly inaccurate. The indicated pH for this arrangement was 5 to 6, while solution dipped out in a beaker gave correct readings of 1.5 to 3. This same effect on pH measurements has been observed for 2-ethyl-1-hexanol solutions above a fluidized bed of sol-gel spheres. The problem can best be avoided by locating the pH electrodes in a small, separate chamber fed from the pump. The effect does not result from electrical shorts or a lack of ground connections, but may be associated with the use of glass fluidized-bed vessels.

3.5.6 Resin Costs

Commercial ion exchange resins in large quantities commonly cost less than \$1/lb, while specially handled, purified, analyzed, or sized resins may be \$20/lb to \$100/lb or more. The cost of either commercial Dowex 50W-X8 or Amberlite IRC-72, allowing for their capacity for uranium and the usual size distribution, would be about \$6/lb of uranium if only one screen size fraction were recovered and used, or about \$2/lb of uranium if the other sizes can be sold for full value or if three screen sizes of resin can be used. Sizing of the resin, washing, and control of impurities are being investigated.

4. CONCLUSIONS

The concept of reacting cation exchange resins in the hydrogen form with UO_3 , using dilute uranyl salt solutions as a transfer medium, has important advantages for preparation of HTGR fuel particles from ion exchange resins. Of the strongly acidic cation exchange resins, Dowex 50W-X8 (with nuclear sulfonic acid exchange groups attached to a styrene-divinylbenzene polymer lattice) satisfies the product requirements better than do other strong acid resins. The sulfuric acid exchange group leaves sulfur in the carbonized particle under usual carbonizing conditions. Weakly acidic cation exchange resins with carboxylic acid exchange groups leave only carbon and oxygen after

carbonization and thus give particles more comparable with the UC_2 or UO_2 commonly used for HTGR fuels. Amberlite IRC-72 was identified as having a better combination of properties than any other weak acid resin tested. Three common problems with weak acid resins were (1) nonspherical resin particles, (2) cracking during loading of uranium, and (3) slow or difficult loading of uranium. Amberlite IRC-72 was the only weak acid resin with good performance with respect to all three problems.

The following specific results were demonstrated for reacting UO_3 with cation exchange resins in the hydrogen form using uranyl nitrate as the transfer solution:

1. Efficient and well controlled loading of strong acid resins without formation of partially diluted uranium solution. The final solution concentration can be selected and controlled by mixing the desired amounts of UO_3 , resin, and solution without any need to monitor flow rates or concentrations. The strong acid resins are easy to load with uranium. Conventional fixed-bed procedures can also be used and would probably be preferred if the uranium feed were in the form of uranyl nitrate or uranyl fluoride solutions.
2. Weak acid resins, which require NO_3^-/U mole ratios of less than 2 ("acid deficient" conditions), can be efficiently and controllably loaded. Mixing of UO_3 with the resin is the only procedure which has demonstrated practical, stoichiometric loadings of a weak acid resin with uranium.
3. The Dowex 50W-X8 resin can be loaded in excess of the "stoichiometric" amount of uranium based on two equivalents per mole U (i.e., UO_2^{++}). A typical capacity for Dowex 50W-X8 is 1.88 equivalents per liter, based on the settled bed volume of resin in the H form. Using the appropriate amounts of UO_3 and about 0.2 N NO_3^- in the solution, the U loadings at 50-80°C can be 110% of stoichiometric in less than 1 hr, 120% in 7 hr, and continue to increase slowly after that time. This is probably explained by the formation of hydrolytic species such as $U_2O_5^{++}$.

4. The Amberlite IRC-72 resin can be loaded in excess of the "stoichiometric" amount of uranium, similar to the results for Dowex 50W-X8. A typical capacity for Amberlite IRC-72 in the H form is 3.3 equivalents per liter. Using the appropriate amounts of UO_3 and about $0.3 \text{ N } \text{NO}_3^-$ in the solution, the U loadings at $50\text{-}80^\circ\text{C}$ are nearly 100% of stoichiometric in one to two hours and about 105% of stoichiometric in 24 hours.
5. Amberlite IRC-72 weak acid resin was loaded with mixtures of Th and U by using UO_3 with $\text{Th}(\text{NO}_3)_4$ solutions. The same procedure might be useful for $\text{Pu}(\text{NO}_3)_4$ and UO_3 .
6. Agitation of a resin batch during loading promotes uniform and rapid loading of the complete resin charge. This allows uniform partial loadings or uniform concurrent or sequential loadings of two or more cations.
7. Satisfactory mixing of resins, UO_3 , and uranyl nitrate solution was demonstrated in agitated, baffled vessels, in a screen-bottom basket of the resin-in-pulp type of contactor, and in a fluidized resin bed with a separate mixer for the addition of UO_3 . The mixing conditions must allow for the following effects:
 - a. A very large change in the resin-solution density difference as the resin loads with uranium.
 - b. Any masses of UO_3 that are not quickly dispersed as a slurry will set up in a hard chunk, which will dissolve very slowly.
 - c. Much of the UO_3 initially disperses as a fine, very slow-settling slurry, which reaches any part of the system accessible to the solution.

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6. APPENDIX

Table A-1. Batch Loadings of Dowex 50W-X8 Strong Acid Resins Using UO₃

Resin Mesh	Size of Resin (μ)	Capacity (meq/ml)	Resin (ml)	Feed		Final Solution		U Loaded (meq/ml resin)		Loading Time (hr)
				U (meq/ml resin)	NO ₃ ⁻ (meq/ml resin)	NO ₃ ⁻ (Na)	pH	From UO ₃	From Product Weight	
20/50	300-840	1.88	40	2.160	0.190	0.13	2.17	2.00	—	0.25
			50	2.054	0.200	0.07	1.92	1.97	1.80	2.80
			50	6.430	4.050	2.00	1.76	2.04	2.06	1.90
			50 ^b	6.430	4.050	2.00	1.72	2.04	—	1.90
			100	3.220	0.670	0.50	3.20	2.45	2.21	29.00
			101	2.560	0.220	0.10	3.15	2.28	2.20	7.00
			1960	2.075	0.076	0.08	1.72	2.01	—	1.00
6000 ^c	2.800	0.600	0.23	2.95	2.02	2.01	2.00			
30/35	500-590	1.88	100	2.070	0.170	0.17	2.57	2.06	—	1.00
			1400	2.250	0.200	0.24	2.50	2.03	—	1.50
			1400	2.260	0.200	0.12	2.50	2.03	1.97	7.00 ^d
			1400	2.270	0.200	0.12	2.60	2.03	—	7.00 ^d
			2000	3.500 ^c	1.200 ^c	0.25	2.90	2.00	1.90	1.00 ^c
			2000	3.480 ^c	1.200 ^c	0.25	2.60	2.03	2.06	1.00 ^c

^a Nitrate concentrations are approximate; volumes vary with the use of wash water.

^b Resin dried in room air at room temperature before loading.

^c Fluidized-bed system with large liquid inventory.

^d Different mixer, which gave poor mixing of UO₃.

Table A-2. Batch Loadings of Several Strong Acid Resins, Using UO_3

Resin	Capacity (meq/ml)	Resin (ml)	Feed		Final Solution		U Loaded (meq/ml resin)		Loading Time (hr)
			U (meq/ml resin)	NO_3^- (meq/ml resin)	NO_3^- (N^a)	pH	From UO_3	From Product Weight	
Dowex 50W-X8	1.88	50	6.43	4.05	2.00	1.76	2.04	2.06	1.9
		1400	2.25	0.20	0.24	2.50	2.03	—	1.5
Amberlite IR-120	1.90	49	9.70	7.45	3.60	1.10	1.88	1.92	1.7
		62	7.65	7.45	2.50	0.50	1.81	—	1.5
		62	7.60	7.45	2.50	0.40	1.76	1.93	0.6
		62 ^b	5.26	3.14	2.30	1.30	1.80	1.80	3.9
Duolite C-25	1.50	295	1.88	0.40	0.30	2.80	1.45	1.45	4.5

^a Nitrate concentrations are approximate; volumes vary with use of wash water.

^b Resin dried in room air at room temperature before loading.

Table A-3. Batch Loadings of Weak Acid Resins, Using UO₃

Resin	Capacity (meq/ml)	Resin (ml)	Feed		Final Solution		U Loaded (meq/ml resin)		Loading Time (hr)
			U (meq/ml resin)	NO ₃ ⁻ (meq/ml resin)	NO ₃ ⁻ (N ^a)	pH	From UO ₃	From Product Weight	
Amberlite IRC-72	3.3	50	4.12	0.84	0.40	2.80	3.10	2.90	1.5
		50 ^b	4.10	0.84	0.40	2.80	<2.40	—	2.5
		50 ^b	4.10	1.48	0.50	3.20	<2.40	<2.00	5.0
		100	4.32	0.60	0.40	3.16	3.50	3.46	28.0
		106	4.19	0.72	0.50	2.90	3.30	3.28	2.0
		243	3.51	0.31	0.23	3.10	3.20	3.20	1.5
		288	3.48 ^c	0.32	0.30	2.80	3.14	3.10	1.0
		400	3.72	0.35	0.40	2.73	3.33	3.20	4.3
		600 ^d	3.60	0.30	0.30	3.05	3.10	3.10	3.0 ^d
		2000 ^e	4.80	1.40 ^e	0.30	3.00	3.10	3.04	5.0 ^e
		6000 ^e	3.90	0.60	0.23	3.30	3.20	3.05	5.0 ^e
Relite CC	3.3	101	3.16	0.26	0.13	3.30	2.85	3.00	6.0
		605	2.77	0.15	0.20	2.63	2.60	2.60	5.2
Amberlite IRC-50	3.5	49	7.60	4.17	2.30	2.00	3.20	2.90	3.1
		49	9.05	6.20	3.80	1.90	2.10	2.50	4.5
		49	10.80	7.60	3.40	1.60	2.60	2.74	3.6
		49	5.10	2.04	1.00	2.40	2.84	2.80	20.0
		49	9.73	6.14	3.00	1.70	2.90	3.10	20.0
		76 ^b	4.86	2.65	2.00	2.20	1.80	1.50	4.0
Amberlite IRC-84	3.5	50	6.50	5.00	0.70	2.60	1.10	0.88	24.0
		50	2.48	0.40	0.10	3.10	<1.60	—	22.0
		50	4.10	2.00	0.60	2.70	1.90	1.62	48.0
		50	2.72	0.76	0.35	2.90	1.90	1.56	66.0
		51	5.72	4.58	2.90	2.00	<0.60	0.50	48.0
		51	8.77	7.28	3.70	1.70	<0.60	0.30	3.5
		52	3.62	1.87	1.00	2.90	1.60	1.60	48.0
		99	3.30	0.81	0.50	3.30	2.10	1.75	70.0
Duolite CC-3	3.5	50	3.42	0.78	0.30	2.90	<2.00	1.50	72.0

^a Nitrate concentrations are approximate; volumes vary with the use of wash water.

^b Resin dried in room air at room temperature before loading.

^c 93% ²³⁵U for irradiation specimens.

^d Screen-bottom basket used as "R-I-P" type mixer.

^e Fluidized-bed system with large liquid inventory; separate mixing of UO₃.

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