

1177
1-6-77

Dr-609
ORNL/TM-5647

Loading Ion Exchange Resins with Uranium for HTGR Fuel Kernels

K. J. Notz
C. W. Greene

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

BLANK PAGE

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Energy Research and Development Administration/United States Nuclear Regulatory Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL/TM-5647
Dist. Category UC-77

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

THORIUM UTILIZATION PROGRAM (189a OH045)
Fuel Refabrication Development - Task 300

LOADING ION EXCHANGE RESINS WITH URANIUM FOR HTGR FUEL KERNELS

K. J. Notz
C. W. Greene

Date Published: December 1976

NOTICE
This report was prepared as an account of work sponsored by the United States Government under the United States and the United States Energy Research and Development Administration, and neither the employees, nor any of their activities, subscriptions, or their employees, under any authority, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. OPTIMIZED BATCH LOADING OF STRONG-ACID RESIN	2
3. CONTINUOUS LOADING OF STRONG-ACID RESIN.	9
4. BATCH LOADING OF WEAK-ACID RESIN	16
5. CONTINUOUS LOADING OF WEAK-ACID RESIN.	25
6. SUMMARY AND CONCLUSIONS.	26
7. REFERENCES	28

LOADING ION EXCHANGE RESINS WITH URANIUM FOR HTGR FUEL KERNELS

K. J. Notz and C. W. Greene

ABSTRACT

Uranium-loaded ion exchange beads provide an excellent starting material in the production of uranium carbide microspheres for nuclear fuel applications. Both strong-acid (sulfonate) and weak-acid (carboxylate) resins can be fully loaded with uranium from a uranyl nitrate solution utilizing either a batch method or a continuous column technique.

1. INTRODUCTION

High Temperature Gas Cooled Reactor (HTGR) fuel refabrication research at ORNL has resulted in the development of the uranium-loaded resin kernel process, which has been adopted as the reference method in the National Program Plan for Thorium Utilization. The loading procedure has been reported in numerous Gas-Cooled Reactor Program monthly reports, in annual progress reports,¹⁻⁶ and in technical reports,⁷⁻¹³ as well as at technical and scientific meetings.¹⁴⁻¹⁹ One patent has been granted,²⁰ and others have been submitted. The process has been demonstrated with radioactive ²³³U containing up to 250 ppm of ²³²U.²¹ When used with recycle fuel, it will be carried out by remote means in a shielded cell.

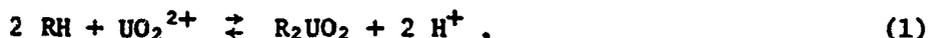
Early work was done with strong-acid (sulfonate) resins, which loaded readily but had a low uranium capacity and contained sulfur. Later, the method was adapted successfully for use with weak-acid (carboxylate) resins, which do not have the above problems but are more difficult to load. This report summarizes work done by the authors in optimizing batch loading of sulfonate resin, reviews the requirements for loading of carboxylate resin, and describes the successful demonstrations of continuous loading of both strong- and weak-acid resins.

2. OPTIMIZED BATCH LOADING OF STRONG-ACID RESIN

It has been shown previously at ORNL that strong-acid resins can be loaded to a uranium content of about 50 wt %, after carbonizing,²² by contacting them with a concentrated solution of uranyl nitrate hexahydrate (UNH). This procedure required a large excess of uranium and a minimum contact time of 2 hr at ambient temperature.²² We developed chemical flow-sheets that optimized the loading process and are also suitable for engineering scale-up. The process developed is based on batch loading of a static bed of resin contained in a conventional column.

Our first objective in utilizing column loading (rather than a stirred vessel) was to improve the efficiency of uranium utilization with sulfonate resins. To correlate data on this basis, we defined the "efficiency ratio" as the number of milliequivalents of uranyl nitrate required for full loading per milliequivalent of resin bed capacity; thus, a ratio of unity represents the maximum attainable efficiency. In the earlier work, an efficiency ratio of only 5 to 7 had been realized (i.e., a 400 to 600% excess of uranyl nitrate was required to achieve full loading). Our objective was to attain an efficiency ratio close to unity.

The use of dilute uranyl nitrate solutions gave a significant improvement in efficiency. The loading reaction, starting with the acid form of the resin, may be written as:



where

R = resin.

Since hydrogen ion is a product of the reaction, decreased acidity will favor the forward reaction, and the hydrolytic acidity of uranyl nitrate solutions decreases with decreasing concentration. Also, from the expression for the equilibrium constant for this reaction,

$$K = \frac{[\text{R}_2\text{UO}_2][\text{H}^+]^2}{[\text{RH}]^2[\text{UO}_2^{2+}]} , \quad (2)$$

it can be seen that, in order to maximize the R_2UC_2/RH ratio, the H^+/UO_2^{2+} ratio must be minimized. Use of a lower solution concentration will aid in this minimization since $[H^+]$ enters as a squared quantity. Figure 1 illustrates the advantage of using a dilute uranyl nitrate solution for improved uranium utilization. The quantities of uranium fed to the column are plotted vs the pH of the column effluents, thus providing a convenient way to follow these reactions by means of the evolved H^+ . When the reaction is complete, the pH levels off at the value for the feed solution. The data shown in this figure are for 50 ml of 20-50 mesh Dowex 50W-X8 resin contained in a column 1.4 cm in diameter and 33 cm long. A flow rate of 5 ml/min was used for each concentration. A major improvement in uranium utilization is realized by going to about 0.1 M uranyl nitrate solution. Although an even lower concentration gives further improvement in efficiency, it is offset by the larger volume of solution that is required.

A second objective was to optimize the flow rate of the uranyl nitrate solution. The data shown in Fig. 2 were obtained by using a column of the same size and containing the same resin as that which yielded the data in Fig. 1. For the data in Fig. 2, a uranium concentration of 0.172 M was used. Although the maximum efficiency is obtained at the slowest flow rate, an intermediate rate of 5 to 10 ml/min provides optimum performance since a very slow flow requires excessive time. A flow rate of 5 to 10 ml/min is equivalent to 6 to 12 bed volumes per hour, or 3.3 to 6.6 ml $min^{-1} cm^{-2}$. Two physical factors related to the flow rate are channeling and density streamers. Both of these become significant at flow rates of 3 ml/min or less but can be alleviated by flowing the uranyl nitrate solution upward; however, at flow rates of 5 ml/min or greater, downward flow presents no problems.

A third factor investigated was the effective column length. Proper control of column length permits essentially 100% efficiency in uranium utilization; that is, no uranium need ever be recycled. If the column is long enough, the upper part of the resin bed can be fully loaded before any uranium breaks through. For strong-acid resins and the optimum uranyl nitrate concentration and flow rate given earlier, a threefold increase in column length accomplishes this. A simple way of attaining the necessary

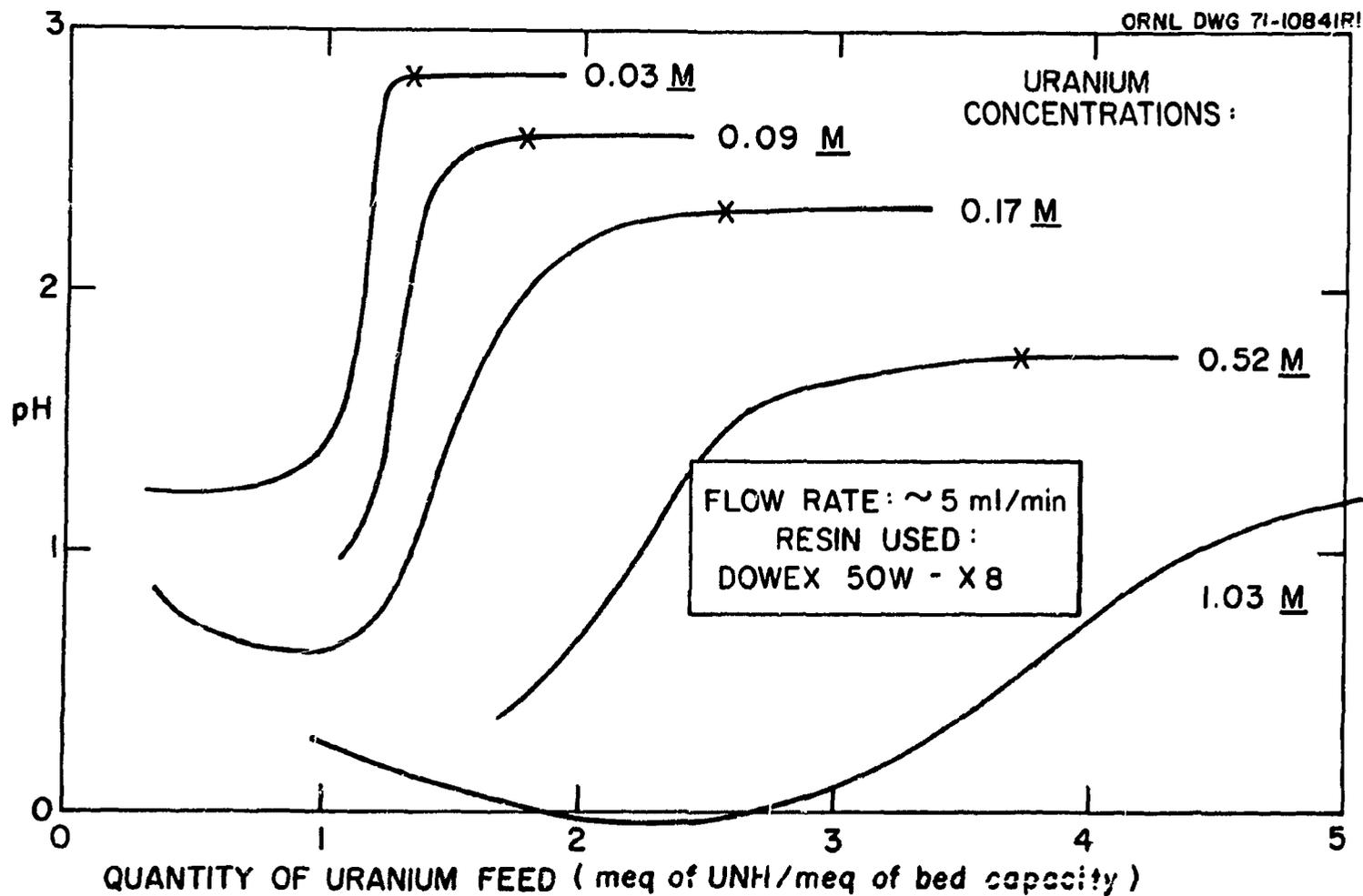


Fig. 1. Effect of uranium concentration on resin loading efficiency.
(X indicates approximate full loading and is the efficiency ratio for that concentration.)

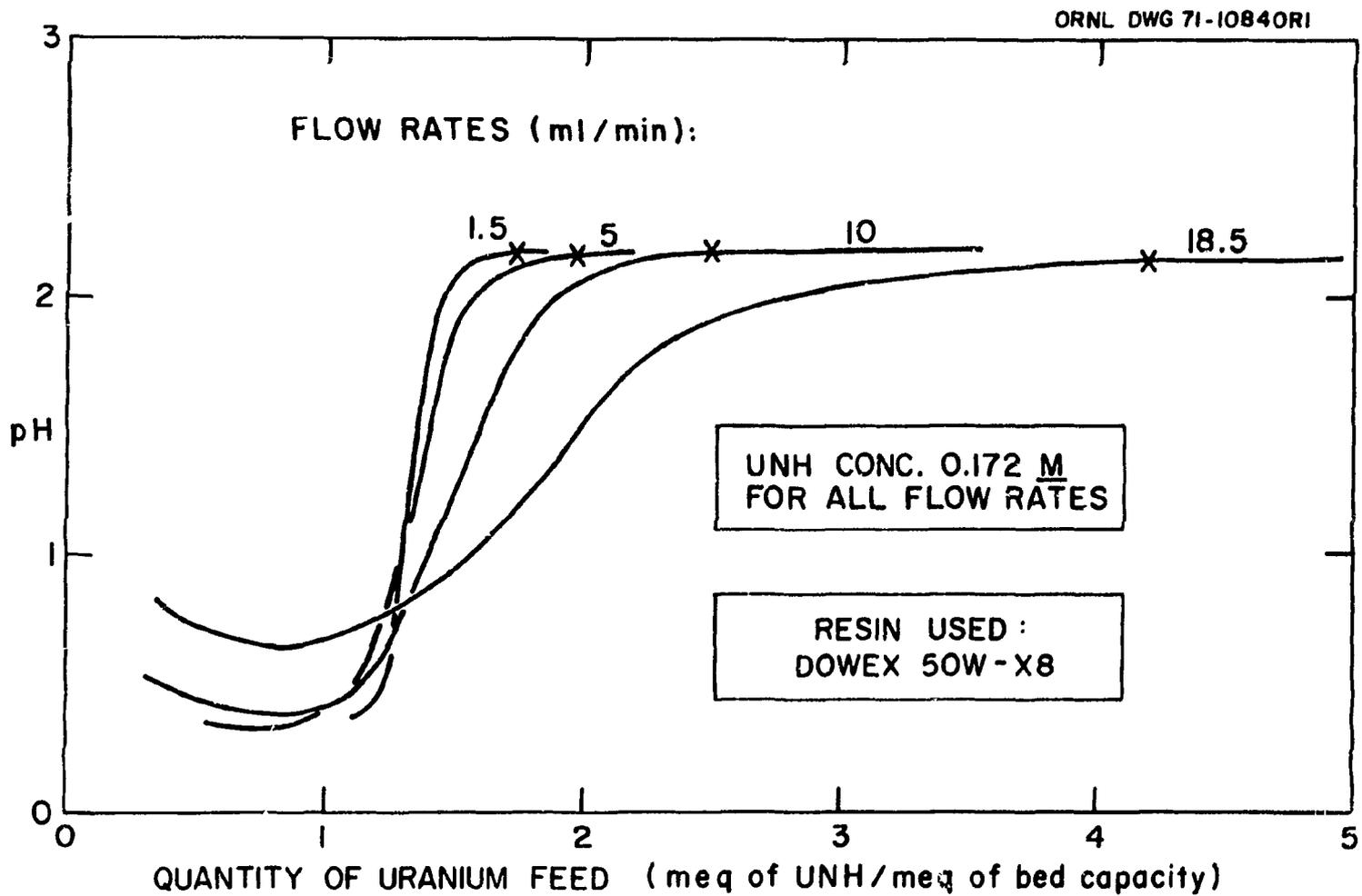


Fig. 2. Effect of flow rate on resin loading efficiency.
(X indicates approximate full loading and is the efficiency ratio for that concentration.)

increase in length is to connect three 33-cm-long columns in series. The first column will then be fully loaded before any uranium breaks through the third (determined via pH measurement). At this point, the first column is removed, and a fresh one is placed in the third position. This procedure can be continued indefinitely, with no uranium losses or recycle. (A more elegant way of achieving the same results on a continuous basis is to move the resin countercurrently by means of a Higgins-type contactor, as discussed in Sect. 3.) A three-column line was set up, after scaling up the cross section by a factor of 5 (Fig. 3), and operated as described above to produce about 800 g (after calcination) of uranium-loaded resin beads using enriched uranium. These products are described in Table 1.

Full loading of resin beads requires diffusion of the uranyl ion to the center of each bead. From data obtained in the flow rate runs, it was possible to estimate a minimum diffusion time of 1.1 hr for 20-50 mesh Dowex 50W-X8 beads at 25°C and 0.17 M uranyl nitrate. Increasing the temperature would increase the diffusion rate and decrease the minimum time required for loading. Observation of breakthrough volumes indicates that about 75% of the uranium required for full loading diffuses into the beads in about 15 min. This corresponds to 37% penetration along the radius of an average-sized sphere, which is in reasonable agreement with the minimum diffusion time.

Approximately 20 samples were loaded using Dowex 50W-X8 or the corresponding Bio-Rad resin. After calcination, the uranium contents varied between 46.3 and 48.8 wt % (av, 47.2). This corresponds to 96.7 to 104.3 wt % (av, 100.3) of the theoretical capacity, as determined by direct titration of the acid-form resin with standard alkali. Starting with 100 ml of acid-form resin loaded into a column by the usual fluidizing method, the following volumes (and weights) were noted: at start of loading (solution downflow), 98 ml; after uranium loading, 93 to 96 ml; after air drying, 50 ml (65 g); after calcination at 1100°C; 26 ml (46 g).

ORNL-DWG 71-12621

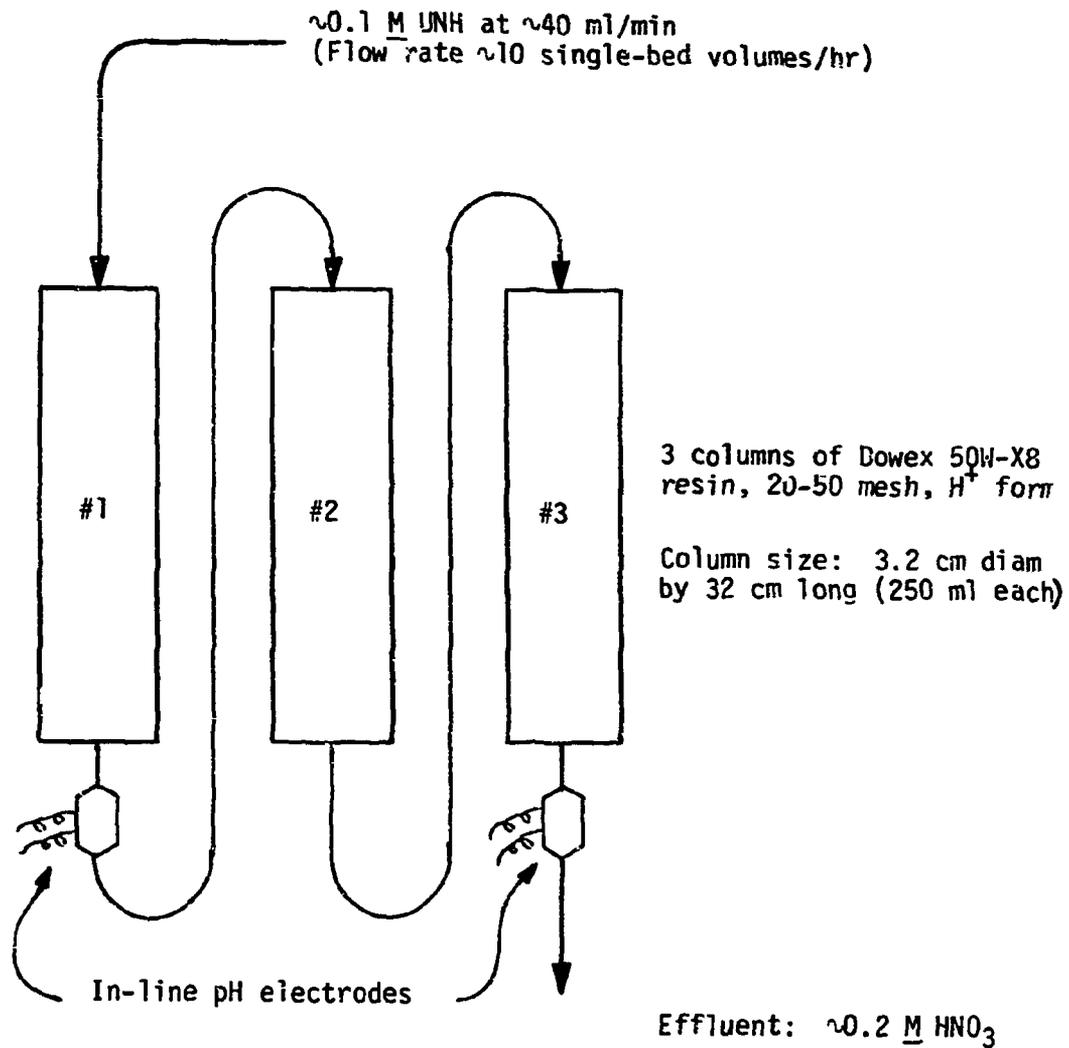


Fig. 3. Flowsheet for laboratory-scale multiple column loading of strong-acid resin beads.

Table 1. Dowex 50W-X8 resin (20-50 mesh) fully loaded with uranium, using various enrichments of ^{235}U

Desired enrichment, at. % ^{235}U	7.35	7.35	20	30
Quantity of wet resin (acid form), ml	750	500	250	250
1100°C calcined products				
Yield of uranium-loaded resin beads, g	347	232	113.2	113.6
Isotopic enrichment, at. % ^{235}U	7.32	7.32	20.3	30.0
Total U, wt %	47.2	46.9	47.7	46.6
Carbon, wt %	36.6		36.4	35.9
Sulfur, wt %	11.4		9.9	10.4

3. CONTINUOUS LOADING OF STRONG-ACID RESIN

The continuous operation of resin columns was pioneered at ORNL by Higgins et al. in the early 1950s²³⁻²⁴ and later as a private enterprise.²⁵⁻²⁷ There has been a continuing interest in this type of operation²⁸⁻³² where the emphasis is, of course, on the conventional use of ion exchange resins, namely, either to deplete a solution of some ion or to effect a separation of ions but, in any event, to regenerate the resin and continue the operation. Also, in these conventional operations there is no need for, nor benefit in, fully loading the resin. For our particular application, it is necessary to fully load the resin, but regeneration of the resin is not required since the fully loaded resin is the desired product. It is also desirable to completely deplete the uranyl nitrate solution of uranium so that the effluent can be processed as a simple nitric acid waste (i.e., for acid recovery or for discard).

The above criteria are met in a pulsed column based on the Higgins system. This column, which is made of 1-in.-ID Pyrex pipe and has an overall height of 7 ft, is shown schematically in Figs. 4 and 5 and depicted in Fig. 6. Its active loading length, 6 ft (between the "feed solution" inlet and the "spent liquor" outlet), determines the maximum throughput since the exposure time of the resin must be at least 2 hr (at ambient temperature) to allow sufficient time for diffusion to the centers of 600- μ m resin beads. The air-operated ball valves are solenoid controlled, as are the cutoff valves on the four aqueous streams. Variable-flow pumps provide the desired flow rates on the three input streams. The entire operating cycle is controlled by a pair of adjustable timers (see Fig. 6). An electrical schematic of the timers is shown in Fig. 7. A typical time cycle is a 10-sec pulse (to move the resin) every 5 min. During the remaining time the wash water and feed solution flow in, while the spent liquor is discharged. With a strong-acid resin, the feed is a uranyl nitrate solution (~ 0.1 M) and the effluent is dilute HNO_3 essentially free of U. The progress of the loading reaction and the condition of the column are monitored by means of conductivity probes inserted at appropriate locations (marked by white tabs in Fig. 6). Figure 8 shows a typical start-up profile and the attainment of steady-state conditions.

ORNL DWG 72-3205

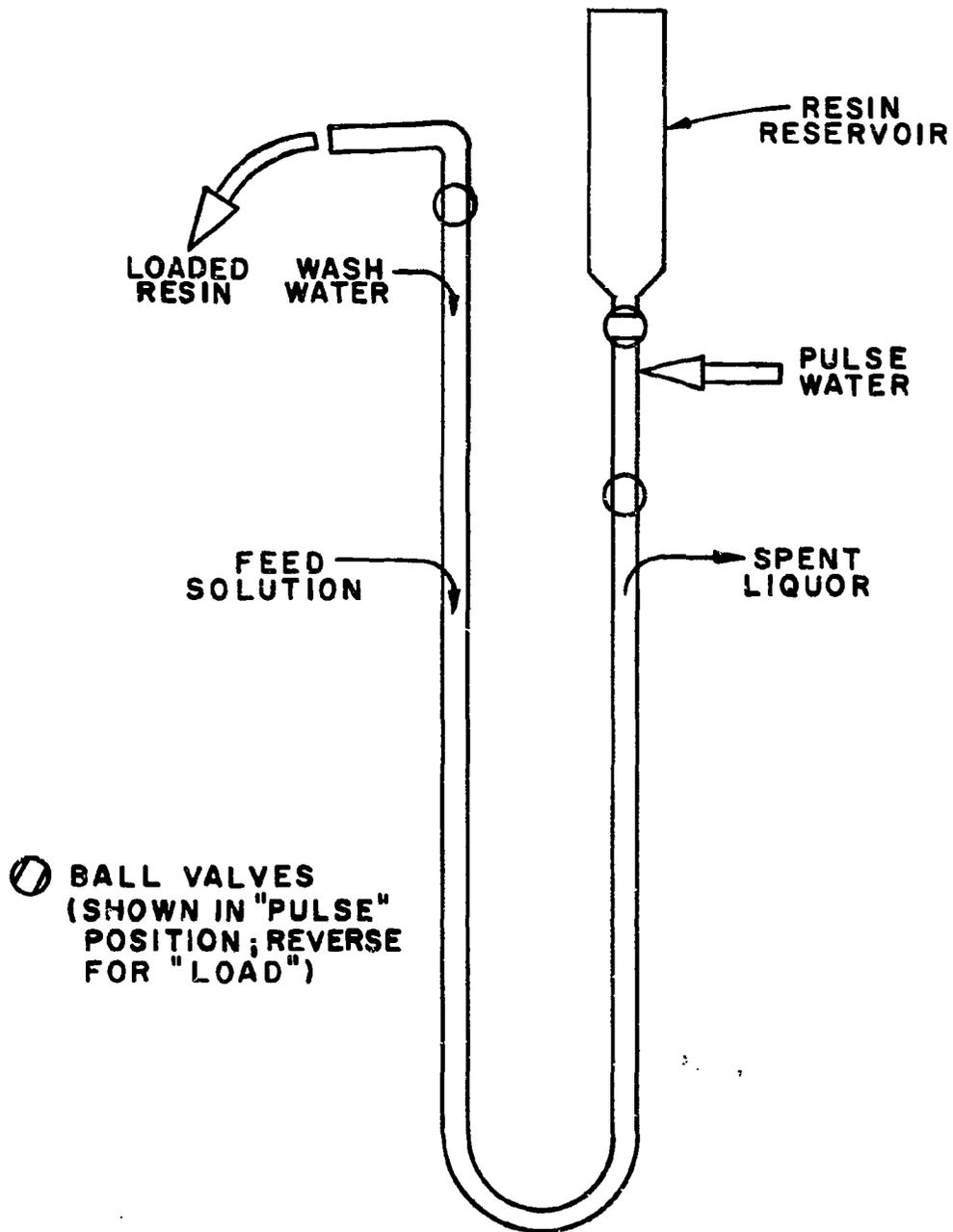


Fig. 4. Schematic drawing of pulsed resin loading column.

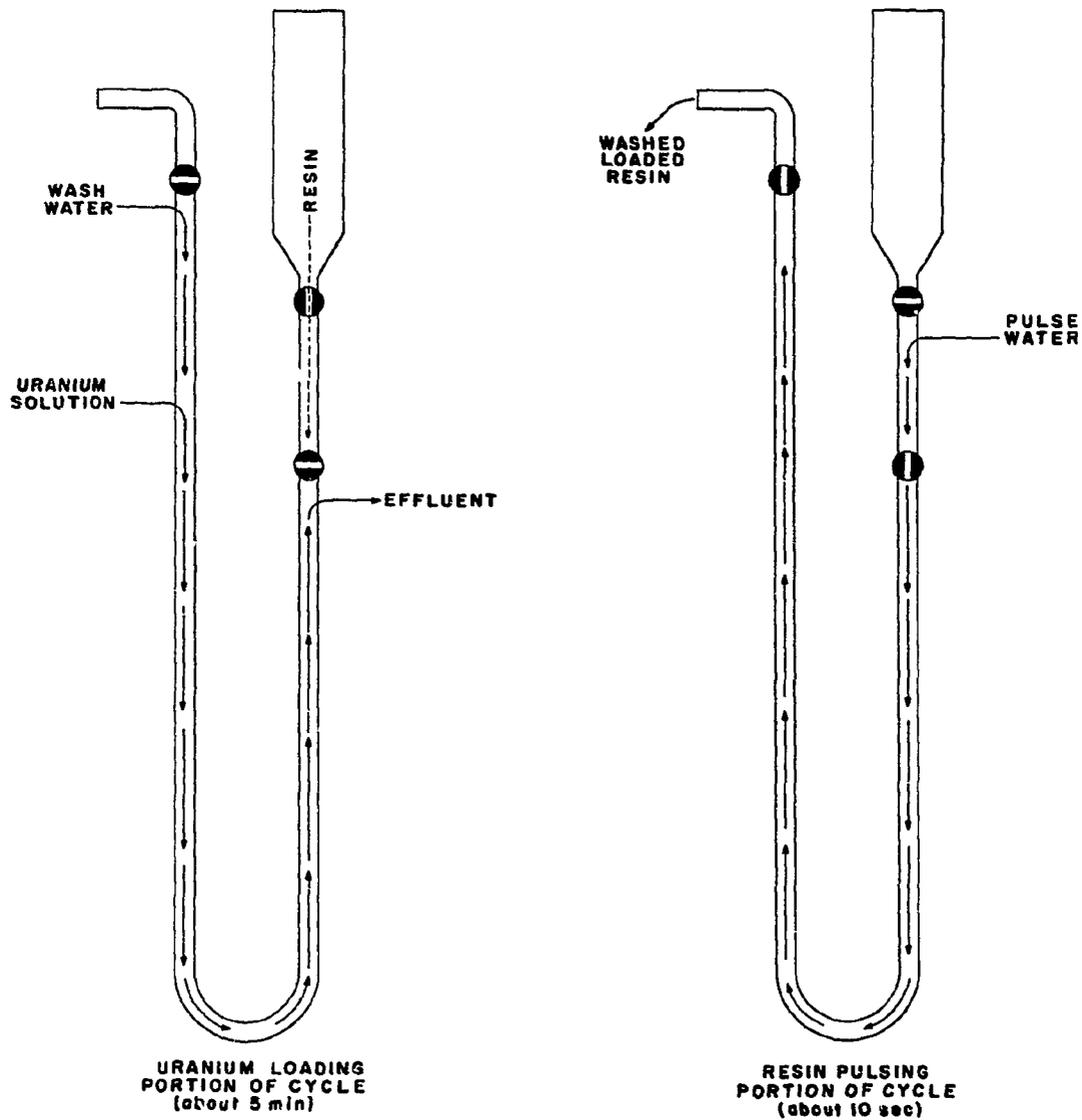


Fig. 5. Schematic drawing of continuous column in load and pulse positions.

ORNL PHOTO 0785-72A

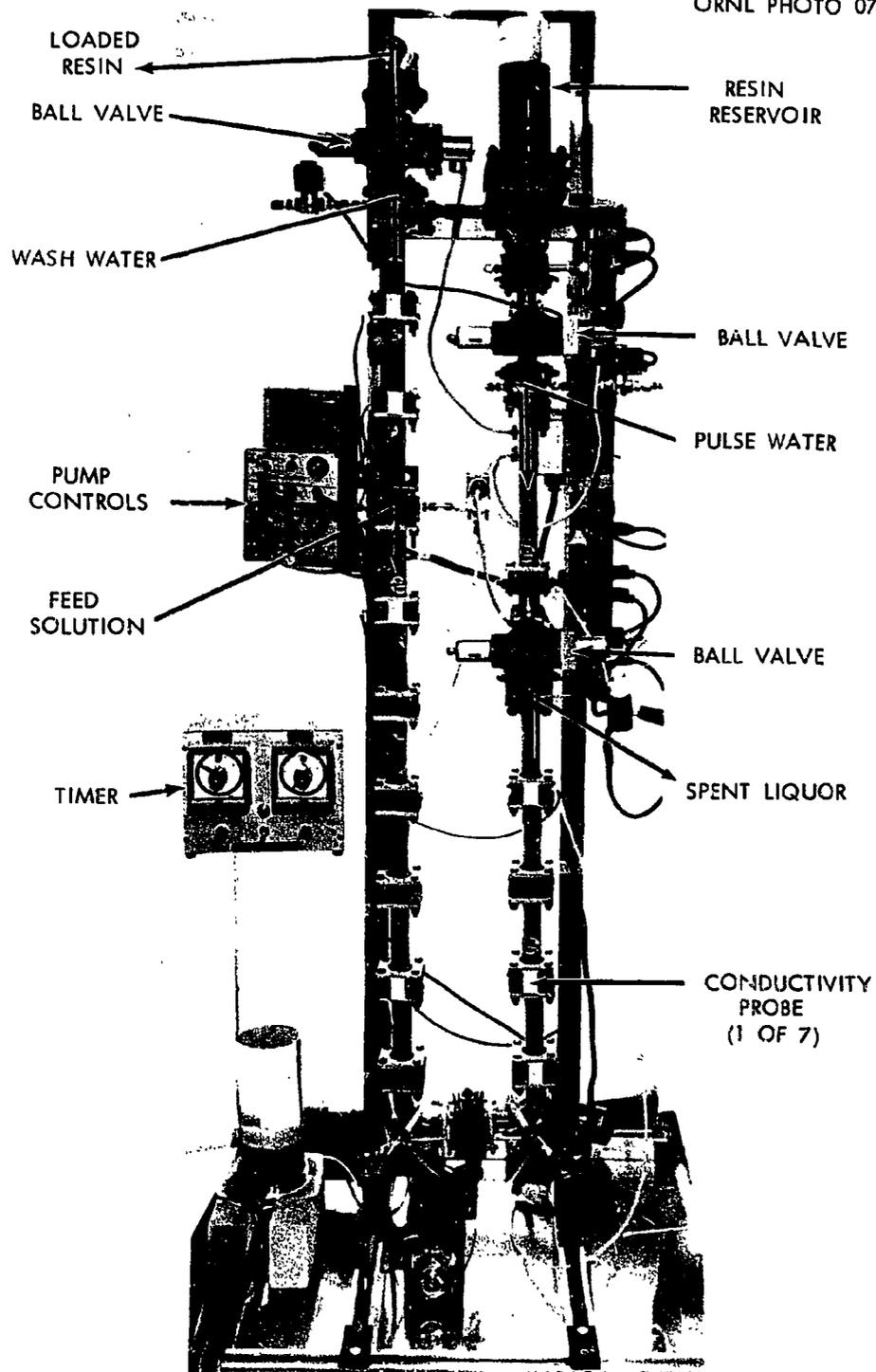
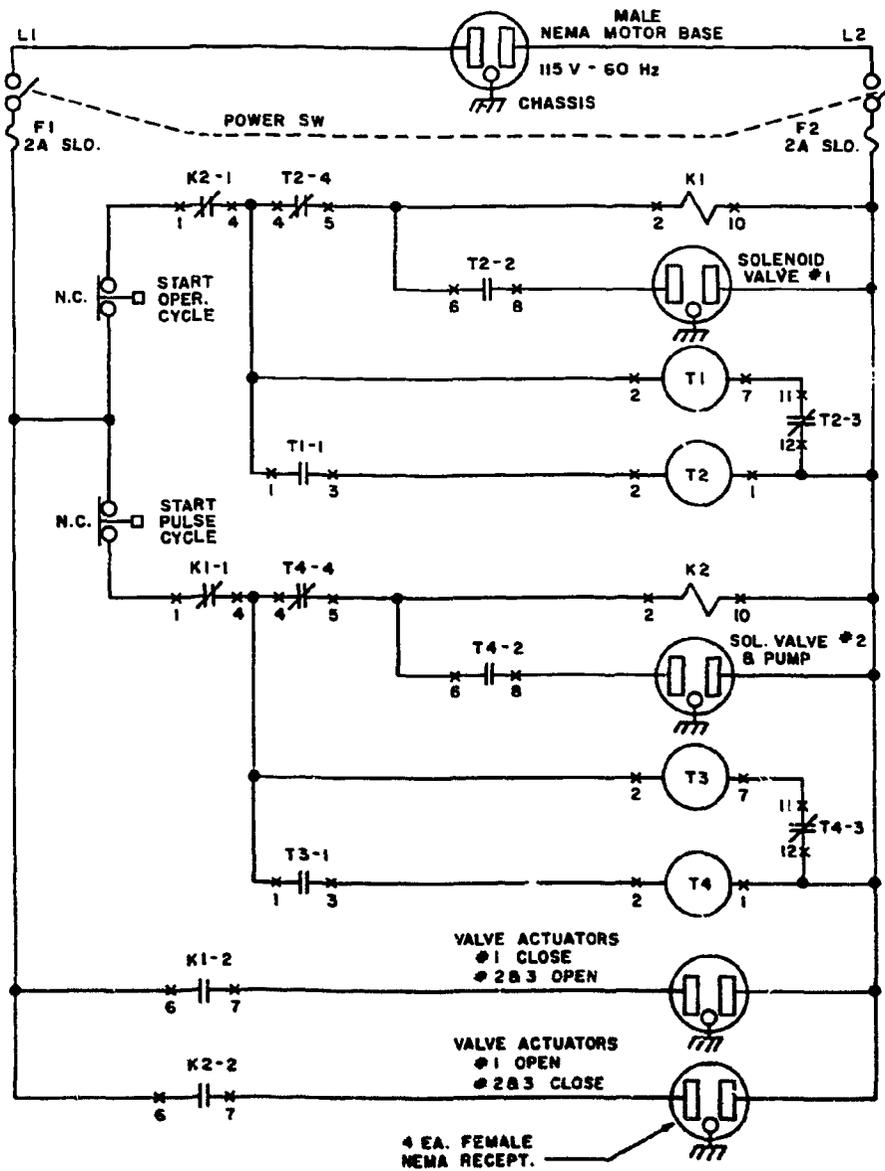


Fig. 6. Photo of pulsed, continuous resin loading column.



NOTES

- 1 - K1 & K2 ARE 115V-60 HZ OPDT RELAYS. (SIGMA KRPI4AC OR EQUIV.)
- 2 - T1 & T3 ARE SYRACUSE DELAY TIMERS MODEL TER-00311 (0-60 SEC.)
- 3 - T2 IS EAGLE CYCL-FLEX TIMER NPS SERIES (0-10 SEC.)
- 4 - T4 IS EAGLE CYCL-FLEX TIMER NPS SERIES (0-30 MIN.)

Fig. 7. Electrical circuitry for column timer.

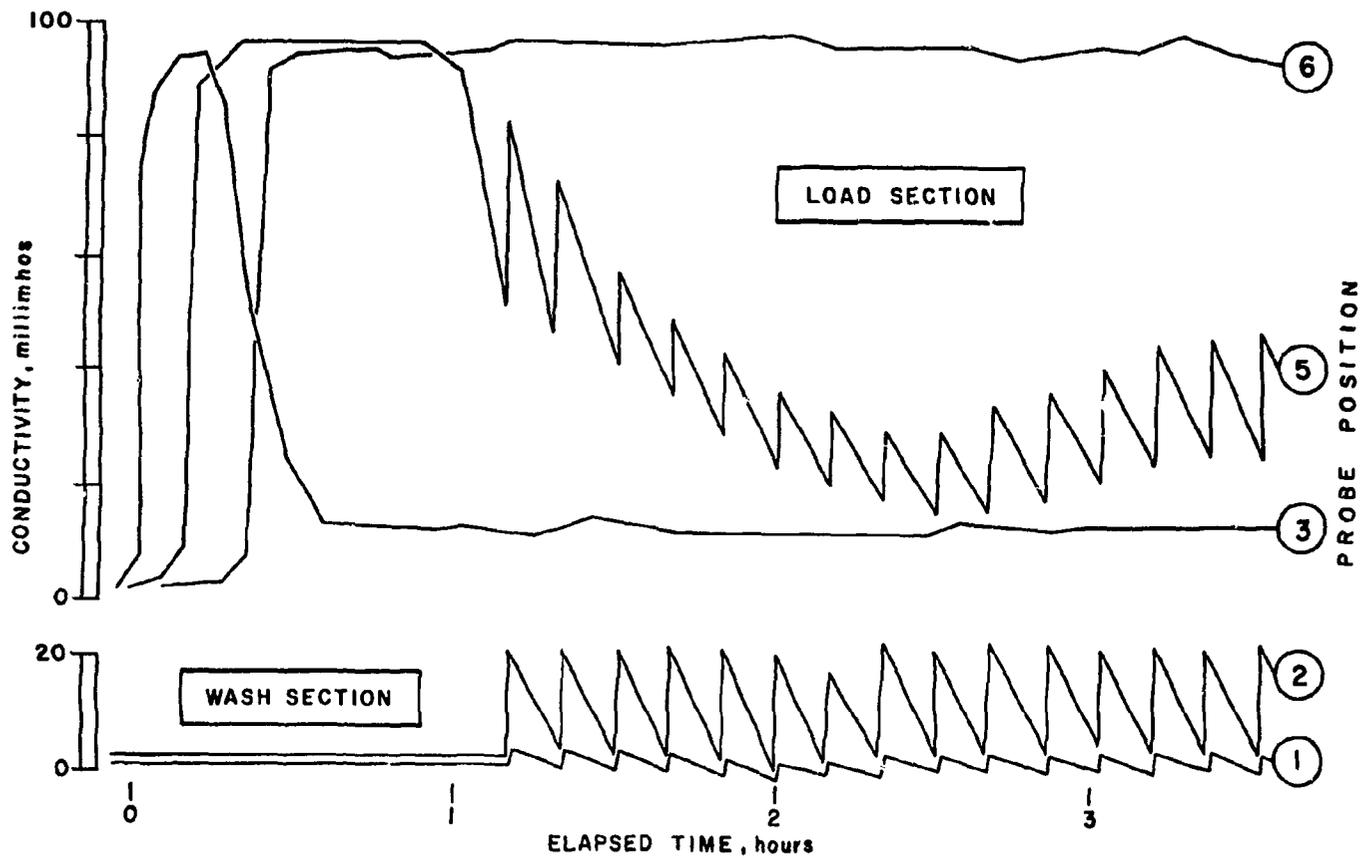


Fig. 8. Conductivity curves for the pulsed column during start-up and steady-state operation with strong-acid resin (Dowex 50W-X8).

The run shown in Fig. 8 was made with 20-50 mesh Dowex 50W-X8 resin. However, our application will require monosized resin, which has less favorable hydraulic properties. Therefore, a run was made using presized Dowex 50W-X8, obtained from Bio-Rad Laboratories, in the 30-35 mesh range (in the acid form). This material was loaded successfully in a 9-hr run very similar to the one for which data are shown in Fig. 8. Two problems that occur to a very minor degree with 20-50 mesh resin become more pronounced with monosized resin. These are: a greater tendency to pack or plug, thus resisting pulsed movement, and a much greater tendency toward a skewed interface (i.e., a loading front not at right angles to the column axis). The packing problem is readily handled; during operation, the cycle time is shortened to 5 min (vs the 10-min cycle used in Fig. 8). To start a run after a prolonged shutdown overnight or over a weekend, longer, more frequent pulses are used to break the packed resin loose; after the resin has loosened, a normal cycle can be resumed.

The skewed interface, which is readily observable by the color of the resin, could be stretched out to more than 1 ft of column length by inappropriate operation. To minimize skewing, the following steps should be taken:

1. hang the column perfectly plumb;
2. keep the interface out of the U-bend;
3. avoid a very fast flow rate (we used a 40-ml/min uranyl nitrate feed solution rate and a 10-ml/min wash water rate);
4. use a relatively long cycle, with corresponding pulses (5 min per cycle and 10 sec per pulse minimized both skewing and packing).

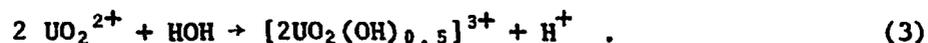
A helpful physical modification to the column is to place a partial restriction at the bottom of the U-bend. We used a gasket with an oval hole (oriented with the long axis in a horizontal position) which restricted the area by about 15%. This compensates for the bed expansion and settling both during and after pulses.

The column described above has a demonstrated loading capacity of 3000 ml of strong-acid resin per 8-hr day, or 640 g of uranium. This can be scaled up by a factor of 150 and still meet criticality limitations by

using a 5-in.-ID column, doubling the active column length, and going to a 24 hr day. The corresponding output, 100 kg of uranium, would be adequate to produce fissile particles from uranium (^{235}U or ^{233}U) from a reprocessing plant handling 2 tons of heavy metal per day [equivalent to about fifty 1100-MW(e) large HTGRs].

4. BATCH LOADING OF WEAK-ACID RESIN

Weak-acid (carboxylate) resins are preferred over strong-acid (sulfonate) resins for reasons mentioned in Sect. 1; however, the exchange reaction to load U is much less favorable. The loading reaction, starting with acid-form resin [see Eq. (1)], proceeds quite satisfactorily with sulfonate resins. In fact, as described in previous sections, both full loading and full utilization of uranium may be achieved in a counter-current process. However, with carboxylate resins, the normal reaction range is pH 5 to 14,³³⁻³⁴ whereas uranyl nitrate solutions have a pH of about 1 (varying with concentration) due to the hydrolysis of UO_2^{2+} . Nonetheless, it is possible to partially load the carboxylate resins from a uranyl nitrate solution; more importantly, it is possible to fully load these resins from an acid-deficient uranyl nitrate solution by utilizing mass action to drive the reaction to completion. Full loading is possible because the uranyl ion can be hydrolyzed to about 25% acid deficiency without precipitation in a nitrate solution, if the evolved acid is removed:



The necessary neutralization of H^+ or removal of H^+ (as HNO_3) could be accomplished in various ways, as follows:

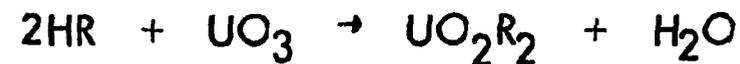
1. by reaction with UO_3 ;
2. by neutralization with NH_4OH (or other base);
3. by extraction with an amine;
4. by thermally driving off HNO_3 ;
5. by reacting with formaldehyde;
6. by dialysis.

The critical factor is that, at the achievable acid deficiency, full loading of the resin with divalent uranyl ion can be attained at a pH of about 3. Equilibrium loading curves for the two preferred resins (Amberlite IRC-72 and Duolite C-464) have been obtained by Shaffer and Greene over a range of temperatures, throughout the complete pH and concentration ranges of interest.⁹⁻¹²

In practice, selection of a process to achieve the necessary acid deficiency involves many factors. The UO_3 method¹⁹ is very clean because it does not introduce foreign cations or any other reagent; it is also very amenable to simple and/or small-scale operations and generates no waste (other than water). However, it does require the preparation of UO_3 , which is a rather difficult process to carry out in a hot cell. Neutralization with NH_4OH ⁸ introduces a foreign cation, some of which remains in the product and eventually gives rise to ^{14}C (via neutron capture by ^{14}N ; neutralization with $NaOH$ introduces Na which is even less desirable); also, it results in the generation of NH_4NO_3 waste, which must be disposed of or processed to recover HNO_3 . Amine extraction,⁹ by operating through an intermediate liquid-liquid extraction stage, avoids contamination of the product but requires more complex equipment. Again, a nitrate waste is generated; however, one can choose between NH_4NO_3 or $NaNO_3$ since the bases are equally capable of regenerating the amine. Partial thermal decomposition,³⁵⁻³⁷ which drives off only the required amount of HNO_3 , is potentially the most promising method, even though it requires engineering development; its chemical feasibility has been shown. The feasibility of dialysis and reaction with formaldehyde must still be demonstrated. At this time, the reference method is the amine extraction process. However, we strongly recommend further consideration of partial thermal denitration, since, in principle, (1) relatively simple equipment should be required, (2) the evolved nitrate can be recovered as nitric acid and can be recycled internally, and (3) this method can be used for either batch or continuous loading with equal effectiveness.

The reactions involved in the UO_3 and amine methods are shown in Figs. 9 and 10. Note that some nitrate is required in the UO_3 method (since the

THE OVERALL REACTION WHERE HR REPRESENTS THE RESIN IS:



THIS OVERALL REACTION IS THE SUM OF:

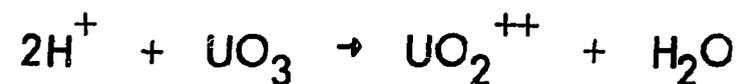


Fig. 9. Reactions for the loading of resin via UO_3 . (Nitrate is required to balance the charge on the uranyl ion, but nitrate does not enter into the reaction.)

URANIUM LOADING OF WEAK-ACID RESINS VIA
AMINE EXTRACTION OF NITRATE

CHEMICAL EQUILIBRIUM:



ACID REMOVAL:



LOADING REACTION:



Fig. 10. Uranium loading of weak-acid resins via amine extraction of nitrate.

loading reaction requires the uranyl ion); however, this amount of nitrate is fixed and remains as a heel after each batch and is reused. Chemical Technology Division personnel have performed numerous batch loadings of ^{235}U and ^{238}U by these two methods, as well as demonstration loadings of ^{233}U . About 6 kg of ^{235}U and 100 kg of ^{238}U have been loaded via UO_3 ,^{38,39} about 200 kg of ^{238}U via amine extraction,³⁹ and several hundred grams of ^{233}U via UO_3 .²¹ Most of these loadings were done with Amberlite IRC-72 resin, which is received in the Na^+ form, converted to the H^+ form (with dilute HNO_3), and then loaded. Table 2 summarizes the volume changes that the resin undergoes due to loading and subsequent processing. Its appearance at various stages is shown in Fig. 11. Duolite C-464 behaves in a similar manner.

Uniformity of kernel composition is important with regard to core physics, accountability, and quality assurance. In terms of uranium loading, uniformity is of concern on at least four levels:

1. the uniformity of uranium loading along the radius within a single resin bead;
2. the uniformity of uranium loading from bead to bead within a single loading batch;
3. the uniformity of uranium loading from one loading batch to another (or, for continuous column loading, from one time period to another) within a single source of resin;
4. the uniformity in capacity from one batch to another for a single type of resin.

Within a single bead, the uranium density along the radius appears to be constant. Knowledge of resin manufacture and structure would predict this, and the relative constancy of percent uranium loaded onto different diameter beads of the same resin provides indirect evidence that this is so; also, radiographs of loaded beads confirm it within the limits of capability of this technique. Further, electron microprobe scans of sectioned beads give direct evidence of a constant U concentration throughout each bead. It has also been shown that outer-shell loading of uranium, leaving an unloaded center, could be done with

Table 2. Volume relationships for Amberlite IRC-72 resin bead kernels

	Measured data	Calculated bead diameter ^b
Initial (wet) volume		
Na ⁺ form	200 ml	790 μ
H ⁺ form ^a	100 ml	627 μ
Loaded (dry) volume		
At 110°C	76 ml	561 μ
At 130°C	70 ml	556 μ
Fired (final) volume at 1000°C	26 ml	400 μ
Final (fired) weight at 1000°C	53 g	
Particle density		
At 1000°C (70 wt % U)	3.4 g/ml	400 μ
At 1250°C (75 wt % U)	3.7 g/ml	380 μ
At 1750°C (90 wt % U)	5.3 g/ml	317 μ

^aLoading: 100% of capacity with UO₂²⁺ (3.4 meq/ml wet resin in H⁺ form).

^bCorresponding diameters of individual, monosized beads, starting with the size shown.

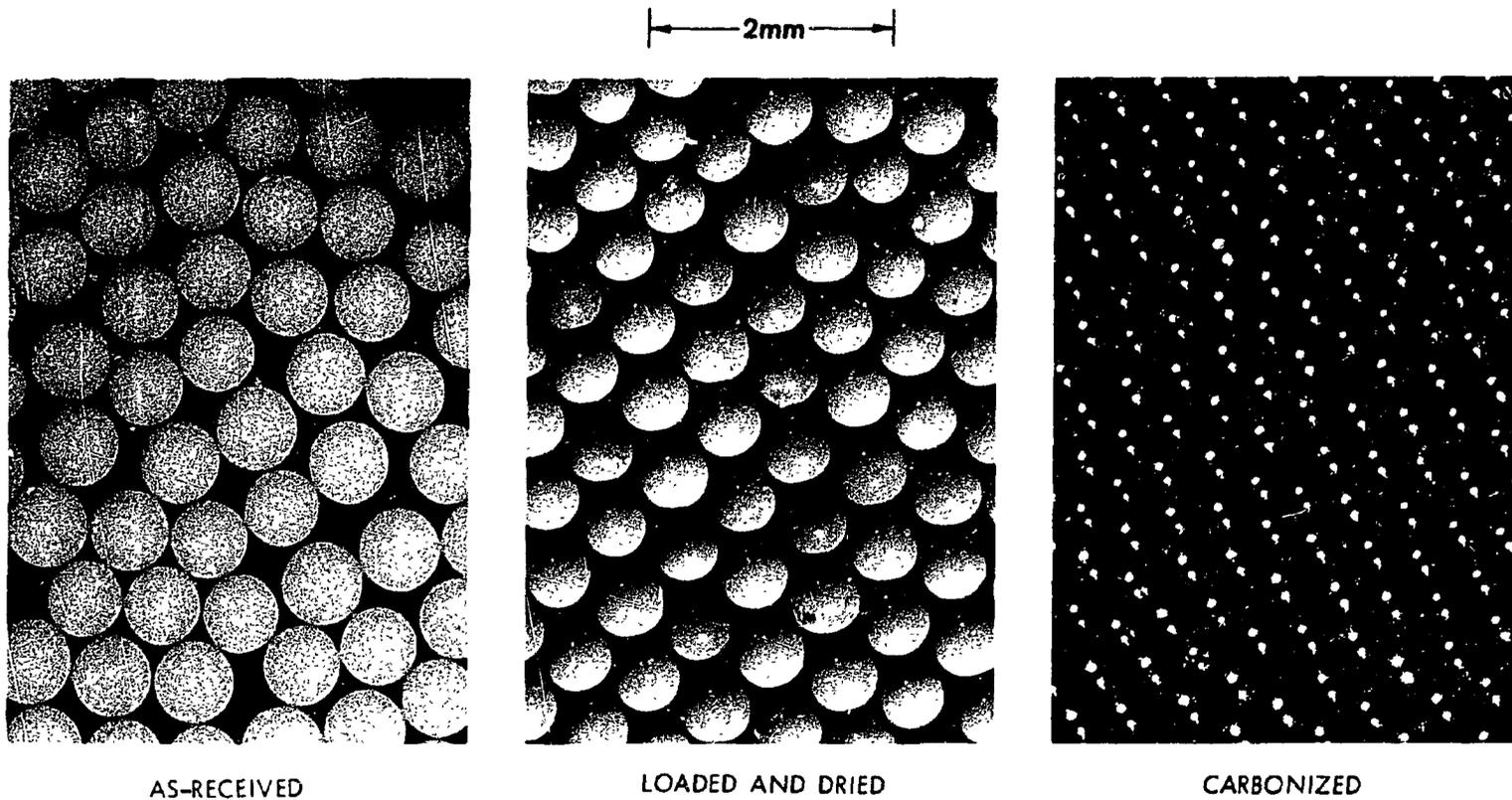


Fig. 11. Appearance of weak-acid resin kernels at various stages.

weak-acid resin in the Na^+ or NH_4^+ form for exchange times of less than 1 hr but, conversely, that such shells were not obtained with strong-acid resin, or with weak-acid resin in the H^+ form, or with weak-acid resin in Na^+ or NH_4^+ forms for exchange times greater than 2 hr.²

Within a single loading batch, or for different loading batches within a single source of resin, uniformity of loading from bead to bead was inferred by the relatively constant density for individual beads (Table 3). These densities were determined in a gradient column⁴⁰ using resin beads that had been selected at random from four different batch loadings, all of which used a common source of 32-38 mesh carboxylate resin; loading was done by reaction with UO_3 . In each case, the loaded resin was washed thoroughly to remove any uranyl nitrate and stored wet. Densities were measured on wet beads that had been blotted to surface dryness. Wet beads were used to be certain that all the internal porosity was entirely filled with pure water; if the beads had been dried first, uncertainties would have been introduced from variations in the degree of dryness, the amount of trapped air after immersion in the density gradient column, and the actual density of the column fluid that did penetrate the voids. Because the density of the dried beads is about 1.7 g/ml and the volume shrinkage due to drying is about 20%, one can calculate that the wet beads contain about 75 vol % water, which includes the void volume in the dry beads plus the swelling of the resin itself from imbibition of water. From the very narrow range of these data, one can conclude that both the uranium content and the void volume are constant from bead to bead within a single loading batch and also within a single batch source of resin. A similar conclusion can be reached from the work of Knoll,⁴¹ who analyzed individual kernels loaded with enriched uranium for their ^{235}U content and normalized his data on a volume basis.

For a given type of resin, the variations from batch to batch will need to be established over a period of time. Recent data, although limited, suggest that these variations are small, that is, on the order of 2% difference in uranium content. Variations of this magnitude can be accommodated in subsequent carbonization and conversion steps so that the final product will not be affected.

Table 3. Densities^a of individual weak-acid resin beads fully loaded with uranium

	Batch			
	A	B	C	D
	2.093	2.115	2.112	2.124
	2.097	2.126	2.121	2.124
	2.101	2.127	2.135	2.126
	2.104	2.129	2.135	2.126
	2.105	2.130	2.136	2.128
	2.105	2.131	2.136	2.128
	2.105	2.135	2.138	2.128
	2.107	2.135	2.138	2.128
	2.108	2.135	2.139	2.129
	2.108	2.138	2.138	2.129
	2.109	2.138	2.139	2.129
	2.109	2.139	2.142	2.129
	2.110	2.144	2.143	2.130
	2.110	2.145	2.143	2.130
	2.112	2.146	2.144	2.136
	2.113	2.148	2.149	2.136
	2.114	2.150	2.152	2.136
	2.117	2.152	2.152	2.137
	2.118	2.152	2.153	2.140
	2.119	2.152	2.154	
	2.120	2.153	2.157	
	2.120		2.201	
	2.127			
	2.128			
Mean	2.1107	2.1391	2.1436	2.1303
Std Deviation	0.0085	0.0106	0.0166	0.0047

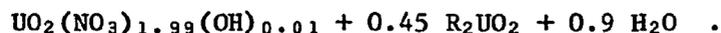
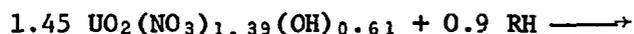
^aDensities measured in g/cm³, as determined in a density gradient column.

5. CONTINUOUS LOADING OF WEAK-ACID RESIN

The technique described in Sect. 3 for the continuous loading of strong-acid resin is also suitable for use with weak-acid resins, with three modifications: (1) the loading solution must be acid deficient, (2) the effluent will contain a large fraction of the influent uranium, and (3) this effluent uranium will have to be recycled to the acid removal step and then back to the loading column again. The sequence, shown as unbalanced equations and using reaction with UO_3 to obtain the acid deficiency, is:



This was demonstrated with acid-deficient uranyl nitrate prepared by equilibrating uranyl nitrate with excess UO_3 , which yielded a solution 0.668 M in uranium and 0.929 M in nitrate, with a NO_3^-/U ratio of 1.39. This solution, which was fed to the column at 34 ml/min, yielded an effluent that was 0.403 M in uranium and 0.800 M in nitrate, with a NO_3^-/U ratio of 1.99. (The effluent was more dilute in nitrate than the feed because of dilution by wash water and pulse water; there is no gain or loss of nitrate.) The loading reaction was:



The ratio of uranium utilization was 0.45/1.45, or 31%. The balance, contained in the effluent, would have to be recycled through a UO_3 contactor in a continuing operation.

At steady-state operation the influent feed rate was 30 to 40 ml/min, which is equivalent to 88.5 to 118 g of uranium loaded on resin per hour. The resin feed rate was ~ 250 ml/hr. Scaled up to a column with 50 times the capacity (5-in. diam and 12 ft of working length, vs 1 in. and 6 ft for our demonstration column), this is equal to between 106 and 142 kg of uranium per 24-hr day, which is even greater than the rate demonstrated earlier for strong-acid resin.

A uranium concentration profile was obtained at the conclusion of the run by siphoning out resin samples at 6-in. intervals. These were then dried at 130°C and analyzed for uranium content. Figure 12 shows the results in terms of both the dry resin weight per 10 ml of wet resin and the wt % uranium in the dried resin; the dry weight basis closely follows the actual analysis. From this profile, it is evident that a larger safety margin was allowed than needed. Of the total 6 ft of column length, only 4 ft (points 5 through 13) was utilized for loading; the last 2 ft (points 1 through 5) accomplished no additional loading. On the other hand, the maximum uranium utilization was not realized since the uranium content of the resin did not drop to zero in the available length. Optimum operation would move the curve 1 or 2 ft to the left, which can be done in a controlled fashion by means of the conductivity probes. At maximum utilization, some free acid would be present in the effluent. Detailed studies of the equilibrium show that the maximum NO_3^-/U ratio at which loading occurs on fresh resin is about 2.3, depending on the uranium concentration.⁹

6. SUMMARY AND CONCLUSIONS

The highlights of this study, and the conclusions that can be drawn from it, are as follows:

1. Batch loading of strong-acid resins was optimized in terms of concentration and feed rate, so that only a small excess of uranium was required to achieve full loading in 2 hrs.
2. Loading of strong-acid resin in a continuous column was demonstrated, and complete uranium utilization at a loading rate equivalent to 100 kg of uranium per day in a single 5-in.-diam column was achieved. The only effluent was dilute HNO_3 .
3. Requirements for the loading of weak-acid resin with uranium were discussed, and six methods for achieving the necessary acid removal were reviewed. The uniformity of uranium loading was demonstrated, both within a loading batch and from batch to batch for a given resin.

ORNL DWG 73-2531R1

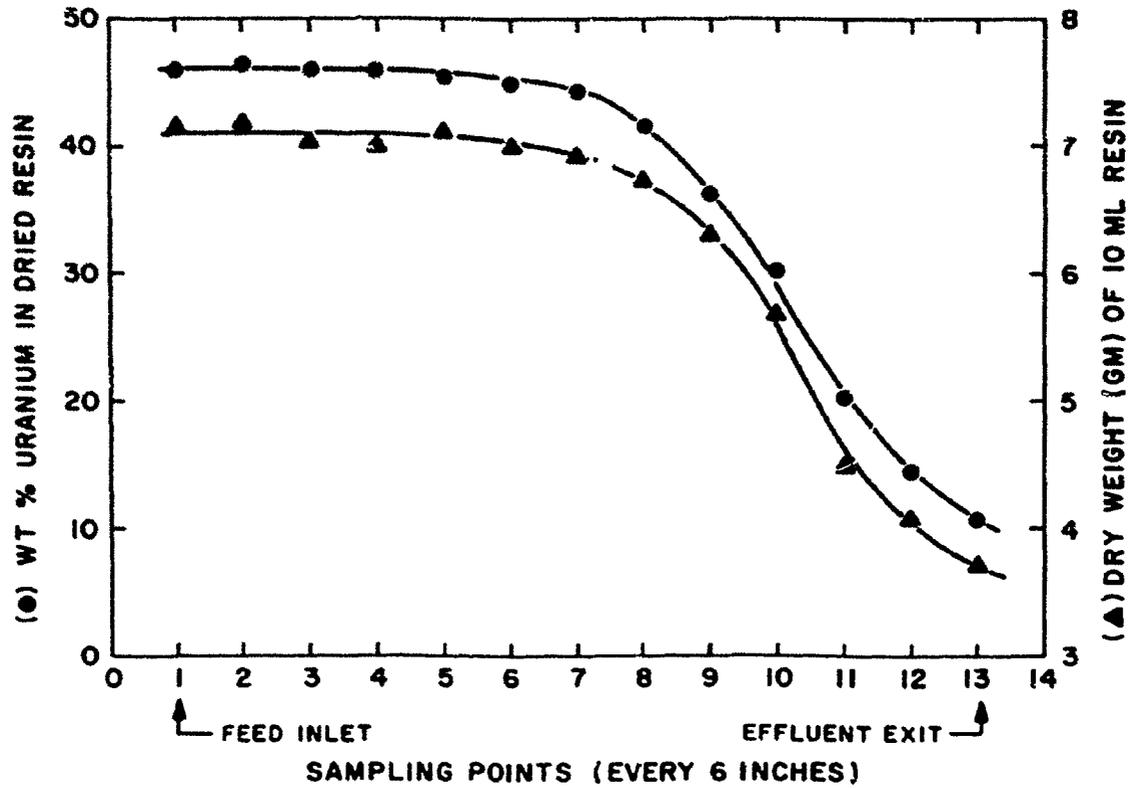


Fig. 12. Uranium profile for continuous loading of weak-acid resin.

4. Loading of weak-acid resin in a continuous column was demonstrated at a rate equivalent to over 100 kg of uranium per day in a single 5-in.-diam column. Recycle of uranium (to the acid removal step) is necessary when weak-acid resin is used.

7. REFERENCES

1. P. R. Kasten, J. H. Coobs, and A. L. Lotts, Gas-Cooled Reactor and Thorium Utilization Programs Ann. Prog. Rep., Period Ending Sept. 30, 1971, ORNL-4760 (January 1973), pp. 40-43.
2. P. R. Kasten, J. H. Coobs, and A. L. Lotts, Gas-Cooled Reactor Programs Ann. Prog. Rep., Period Ending December 31, 1972, ORNL-4911 (March 1974), pp. 27-31.
3. P. R. Kasten, J. H. Coobs, and A. L. Lotts, Gas-Cooled Reactor Programs Ann. Prog. Rep., Period Ending December 31, 1973, ORNL-4975 (April 1976), pp. 18-22.
4. A. L. Lotts and P. R. Kasten, Gas-Cooled Reactor Programs Thorium Utilization Program Prog. Rep., January 1, 1974 - June 30, 1975, ORNL-5128 (May 1976), pp. 109-42.
5. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1972, ORNL-4794, pp. 47-51.
6. Chem. Technol. Div. Annu. Prog. Rep. Mar. 31, 1973, ORNL-4883, pp. 48-51.
7. P. A. Haas, HTGR Fuel Development: Use of UO_3 to Load Cation Exchange Resin for Microsphere Preparation, ORNL/TM-3817 (September 1972).
8. Internal memorandum by P. A. Haas, HTGR Fuel Development: Loading of Uranium on Carboxylic Acid Cation-Exchange Resins from UO_2^{2+} - NH_4^+ - NO_3^- Solutions, GCR: 75-3 (April 1975).
9. P. A. Haas, HTGR Fuel Development: Loading of Uranium on Carboxylic Acid Cation-Exchange Resins Using Solvent Extraction of Nitrate, ORNL/TM-4955 (September 1975).
10. Internal memorandum by J. H. Shaffer and C. W. Greene, Reactions of Uranyl Nitrate Solutions with Carboxylic Acid Cation Exchange Resins I. Amberlite IRC-72 at 30°C, GCR: 75-7 (May 1975).
11. Internal memorandum by J. H. Shaffer and C. W. Greene, Reactions of Uranyl Nitrate Solutions with Carboxylic Acid Cation Exchange Resins. II. Duolite C-464 at 30°C, GCR-76/13 (June 1976).

12. Internal memorandum by J. H. Shaffer and C. W. Greene, Reactions of Uranyl Nitrate Solutions with Carboxylic Acid Cation Exchange Resins. III. Amberlite IRC-72 at 40°C, GCR-76/14 (June 1976).
13. Internal memorandum by J. H. Shaffer and C. W. Greene, Reactions of Uranyl Nitrate Solutions with Carboxylic Acid Cation Exchange Resins. IV. Duolite C-464 at 40°C, GCR-76/16 (June 1976).
14. K. J. Notz and P. A. Haas, "Resin-Based Fuels for HTGR's: Part II - Uranium Loading of Resins," presented at the Joint Fall Meeting of the American Ceramic Society, Philadelphia, Pa., Sept. 24-27, 1972; Am. Ceram. Soc., Bull. 51(8), 655 (1972).
15. K. J. Notz and P. A. Haas, "Uranium Loading of Ion Exchange Resins for HTGR's," presented at the 75th National Convention of the American Ceramic Society, Cincinnati, Ohio, April 29-May 3, 1973; Am. Ceram. Soc., Bull. 52, 400 (1973).
16. K. J. Notz and C. B. Pollock, "Nuclear Fuel Microspheres Derived from Ion Exchange Resin Beads," presented at the Joint Regional and Nuclear Division Fall Meeting of the American Ceramic Society, San Francisco, Oct. 30 - Nov. 2, 1973; Am. Ceram. Soc., Bull. 52(9), 721 (1973).
17. K. J. Notz, J. H. Shaffer, and C. L. Fitzgerald, "Loading ^{233}U on Ion Exchange Resins for HTGR Fuel Kernels," presented at the Joint Fall Meeting of the Nuclear and Basic Sciences Divisions, American Ceramic Society, Williamsburg, Va., Sept. 29-Oct. 2, 1974; Am. Ceram. Soc., Bull. 53(8), 621 (1974).
18. K. J. Notz and P. A. Haas, "Uranium Loading of Recycle Fissile Fuel Kernels," presented at the 77th Annual Meeting of the American Ceramic Society, Washington, D.C., May 1975; Am. Ceram. Soc., Bull. 54(4), 442 (1975).
19. Paul A. Haas, "Resin-Based Preparation of HTGR Fuels: Uranium Loading Development Studies," Trans. Am. Nucl. Soc. 22, 317-18 (1975).
20. Paul A. Haas, "Loading a Cation Exchange Resin with Uranyl Ions," U.S. Patent 3,800,023 (Mar. 26, 1974).
21. Internal memorandum by J. H. Shaffer, C. L. Fitzgerald, and K. J. Notz, Loading of Weak-Acid Ion Exchange Resin with Uranium-233 Containing up to 250 ppm Uranium-232, GCR: 75-22 (October 1975).

22. P. R. Kasten, J. H. Coobs, and A. L. Lotts, Gas-Cooled Reactor and Thorium Utilization Programs Semiannu. Prog. Rep. Sept. 30, 1970, ORNL-4637 (July 1971), pp. 3-7.
23. I. R. Higgins, Mechanical Features of the Higgins Continuous Ion Exchange Column, ORNL-1907 (Sept. 29, 1955).
24. C. W. Hancher, I. R. Higgins, and J. S. Taylor, Uranium Recovery from Ore by a Higgins Ion-Exchange Contactor at Grand Junction Pilot Plant, ORNL-2508 (June 17, 1957).
25. I. R. Higgins, "Counter-Current Liquid-Solid Mass Transfer Method and Apparatus," U.S. Patent 2,815,322 (Mar. 31, 1954).
26. I. R. Higgins, "Continuous Ion Exchange Equipment ... Adapted to Water and Dilute Waste Treatment," *Ind. Eng. Chem.* 53(8), 635-37 (1961).
27. I. R. Higgins, "Downflow Ion Exchange," U.S. Patent 3,580,842 (Apr. 8, 1968).
28. R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick (eds.), Perry's Chemical Engineers' Handbook, 4th ed., Sect. 16, pp. 20-23, McGraw-Hill, New York, 1963.
29. R. McNeill, E. A. Swinton, and D. E. Weiss, "Continuous Ion Exchange," *J. Met.* 7, 912-21 (August 1955).
30. "New Try for Continuous Ion Exchange," *Chem. Week* 78, 74-90 (June 9, 1956).
31. R. L. Hobart, Control of a Continuous Ion Exchange System, ARH-SA-82 (Oct. 20, 1970).
32. Harris Gold and Ain A. Sonin, "Design Considerations for a Truly Continuous Moving-Bed Ion Exchange Process," pp. 48-58 in Adsorption and Ion Exchange, ed. by Imre Zwiebel and Norman H. Sweed, AIChE Symp. Ser. No. 152, Vol. 71 (1975).
33. J. A. Dean, Chemical Separation Methods, p. 87, Van Nostrand, Princeton, N. J., 1969.
34. Rohm and Haas Company, Amber-Hi-Lites (January 1971).
35. Internal memorandum by K. J. Notz, Partial Thermal Denitration of UNH: Preliminary Experiments, GCR-74/16 (July 1974).

36. Internal memorandum by R. H. Rainey, Denitration of Uranyl Nitrate Solutions by Steam Stripping, GCR-74/17 (September 1975).
37. Internal memorandum by P. A. Haas, HTGR Fuel Development: Preparation of Acid-Deficient Uranyl Nitrate by Steam Stripping of Nitric Acid from Molten Uranyl Nitrate, GCR-75/2 (March 1975).
38. J. H. Shaffer, personal communication.
39. P. A. Haas, personal communication.
40. W. R. Laing, Analytical Chemistry Division, ORNL, data partially reported in ref. 3.
41. R. W. Knoll, Measurement of the Relative ^{235}U Concentration and the Absolute ^{235}U Content of Individual HTGR Fuel Particles, ORNL/TM-5436 (July 1976).