Resin-Based Preparation of HTGR Fuels: Operation of an Engineering-Scale Uranium Loading System

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ENGINEERING-SCALE URANIUM LOADING SYSTEM

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ABSTRACT

The fuel particles for recycle of ^{233}U to High-Temperature Gas-Cooled Reactors are prepared from uranium-loaded carboxylic acid ion exchange resins which are subsequently carbonized, converted, and refabricated. The development and operation of individual items of equipment and of an integrated system are described for the resin-loading part of the process. This engineering-scale system was full scale with respect to a hot demonstration facility, but was operated with natural uranium. The feed uranium, which consisted of uranyl nitrate solution containing excess nitric acid, was loaded by exchange with resin in the hydrogen form. In order to obtain high loadings, the uranyl nitrate must be acid deficient; therefore, nitric acid was extracted by a liquid organic amine which was regenerated to discharge a NaNO_3 or NH_4NO_3 solution waste. Water was removed from the uranyl nitrate solution by an evaporator that yielded condensate containing less than 0.5 ppm of uranium. The uranium-loaded resin was washed with condensate and dried to a controlled water content via microwave heating. The loading process was controlled via in-line measurements of the pH and density of the uranyl nitrate. The demonstrated capacity was 1 kg of uranium per hour for either batch loading contactors or a continuous column as the resin loading contactor. Fifty-four batch loading runs were made without a single failure of the process outlined in the chemical flowsheet or any evidence of inability to control the conditions dictated by the flowsheet.

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1. INTRODUCTION

The reference fuel kernel for recycle of ^{233}U to High-Temperature Gas-Cooled Reactors (HTGRs) is prepared by loading carboxylic acid cation exchange resins with uranium and carbonizing at controlled conditions. The carbonized products must be spheres containing high uranium concentrations and only carbon and oxygen as the other major constituents.

A process that would give acceptable loaded spheres was initially developed using the hydrogen form of the cation resin and UO_3 to maintain acid-deficient uranyl nitrate.^{1,2} The purified $^{233}\text{UO}_2(\text{NO}_3)_2$ solution from a fuel reprocessing plant contains excess nitric acid (NO_3^-/U ratio ~ 2.2). When the requirements for remote operation, accountability, and control of nuclear criticality were considered, the usual processes for preparing UO_3 and the in-cell use of UO_3 did not seem acceptable. Therefore, an amine extraction process was developed for resin loading.

The reference flowsheet for a ^{233}U recycle fuel facility at Oak Ridge National Laboratory uses solvent extraction of nitrate by a 0.4 M secondary amine in a hydrocarbon diluent to prepare acid-deficient uranyl nitrate (ADUN) solutions. This nitrate extraction, along with the resin loading and amine regeneration steps, was demonstrated in 14 runs³ utilizing components and procedures developed in previous sol-gel studies. Conditions expected to be satisfactory were used without any systematic optimization of variables. The engineering-scale resin loading system described here was the next stage of the development program following the process demonstration studies,³ but prior to the design of a remotely operated pilot plant.

1.1 Scope

It was considered necessary to obtain results from the operation of a complete, integrated resin loading system prior to designing a fuel recycle facility for HTGR fuels. The recycle of ^{233}U imposes certain requirements relative to remote operation, control of criticality, treatment of wastes, and material accountability which do not apply to the

process demonstration with natural uranium. The engineering-scale resin loading system was intended to provide information on concepts necessary to meet these requirements; however the engineering-scale system did not meet such requirements in detail and was limited to natural uranium.

The engineering-scale resin loading system is full scale with respect to the proposed fuel recycle pilot plant. The capacity of the recycle pilot plant is one batch per day, with 4 kg of ^{233}U per batch. The individual process operations were intended to be much shorter, with a maximum of 4 to 6 hr per batch. This allows sequential operations with a minimum number of personnel in the pilot plant. It also means that scale-up to a commercial recycle plant capacity of about 25 kg of ^{233}U per day would not require any increase in equipment size. Alternate operation of two batch loading contactors would give 24 kg of ^{233}U per day (six 4-kg batches using a nitrate extraction system, an evaporator, and a resin dryer of the same sizes as the engineering-scale units).

This report on the engineering-scale resin loading system will present results for the complete system and will provide details on individual processes or operations only when they are not reported elsewhere. The design, fabrication, and testing of the microwave dryer for uranium-loaded resin and of the evaporator for the ADUN have been reported separately in detail. The cocurrent contactors used in the amine regeneration system were designed, fabricated, and described as part of the sol-gel development. Laboratory studies of the equilibrium and kinetics of the resin loading reactions are being reported by Shaffer et al.⁴

1.2 Acknowledgments

The operation of the engineering-scale resin loading system was part of the Thorium Utilization Program and was dependent on interactions with, or contributions from, many individuals assigned to this program. Among these were: K. J. Notz (Program Director for the Chemical Technology Division); J. H. Shaffer (chemical flowsheet studies); J. P. Drago, D. L. Million, and R. D. Spence (equipment development); and R. D. Arthur, T. V. Dinsmore, and J. R. Parrott, Jr. (system operation). R. D. Arthur supervised the initial installation of equipment. The dried, uranium-loaded resin was used and evaluated by W. J. Lackey, J. A. Carpenter, Jr., and others of the Metals and Ceramics Division.

2. DESCRIPTION OF THE PROCESS

The purified $^{233}\text{UO}_2(\text{NO}_3)_2$ feed from a fuel reprocessing plant contains excess nitric acid (NO_3^-/U ratio ~ 2.2) and introduces uranium, nitrate, and water to the resin loading system. The cation exchange resin is fed as a slurry of acid- (hydrogen-) form resin spheres in water. The uranium leaves the resin loading system as the dried uranium-form resin. Excess water is removed from the uranyl nitrate as condensate from an evaporator. The nitrate extraction system uses a regeneration by caustic solution (NaOH , NH_4OH , or $\text{Na}_2\text{CO}_3\text{-NaOH}$) to discharge nitrate as NaNO_3 or NH_4NO_3 waste solution. These operations can be integrated (Fig. 1) into an efficient system for conversion of the uranyl nitrate solution into loaded, dried resin.

The uranyl nitrate feed, including the excess nitric acid, is introduced into a central surge tank (Fig. 1). One stream of solution is pumped

"ADUN" INDICATES ACID-DEFICIENT URANYL NITRATE ($\text{NO}_3/\text{U} < 2$, MOLES/MOLE)

Fig. 1. Schematic reference flowsheet for uranium loading of resin.

to a resin loading operation where part of the uranium is removed by exchange with the resin and a less acid-deficient uranyl nitrate returns. Another stream is pumped to the evaporator where some of the water is removed and a concentrated stream returns. A third stream is pumped to a nitrate extraction system and returns with a reduced nitrate concentration. The engineering-scale resin loading system is concerned with integrated, simultaneous operation of the processes shown in Fig. 1.

2.1 Chemical Flowsheet

From the usual concepts for ionic solutions, uranyl nitrate would be expected to give UO_2^{2+} , $\text{UO}_2(\text{NO}_3)^+$, and NO_3^- ions. However, the conditions used for our resin loading process result in complex hydrolytic behavior of the uranium. Among the species that have been proposed are: $\text{U}_2\text{O}_5^{2+}$ or $\text{UO}_2(\text{UO}_3)^{2+}$, $\text{U}_3\text{O}_8^{2+}$, $\text{U}_3\text{O}_8(\text{OH})^+$, $\text{UO}_2(\text{OH})^+$, or $\text{UO}_2[(\text{OH})_2\text{UO}_2]_n^{2+}$. High anion concentrations can result in negatively charged complexes of uranium of the type $\text{UO}_2(\text{NO}_3)_4^{2-}$. The existence of these complex species will be ignored during our discussion of the chemical reactions for resin loading and nitrate extraction. The simple reactions correctly give the overall net effect; however, attempts to use them to correlate the equilibrium and kinetic behavior will give anomalous results.

2.1.1 Resin loading reactions

The net effect of resin loading is to exchange one uranyl ion for two hydrogen ions. When the carboxylic acid resin equivalent to one exchange site is indicated by R, the net exchange reaction is:

Although it is useful to discuss the concentrations and write an equilibrium constant as if this were a simple chemical reaction, the inaccuracies of this approach should be recognized. The uranium in solution is hydrolyzed or otherwise complexed and is only partly present as UO_2^{2+} . The resin is a porous solid, and activities and volume concentrations are either very difficult to measure or of doubtful significance.

The exchange of UO_2^{2+} for H^+ in the feed resin is limited by the back-reaction as H^+ accumulates in the solution. The accumulation of H^+ can be controlled by using a salt form of the resin or adding base to the solution. Ammonium ion is mostly volatilized (as ammonia) when the resin is carbonized, while metals generally remain as unacceptable impurities in the final product. For the original development of UO_2^{2+} -loaded carboxylic acid resins, the H^+ concentration was controlled by reaction with UO_3 as follows:^{1,2}

The purified ^{233}U from a fuel reprocessing plant would be uranyl nitrate containing some excess nitric acid. The preferred procedure for using uranyl nitrate solution feed is to remove nitric acid from the solution and thus control the H^+ concentration according to the following reaction:

The reference process for resin loading, and the process used in the engineering-scale system, is to extract nitric acid with a liquid organic amine (see Sect. 2.1.3).

While stoichiometric uranyl nitrate has a NO_3^-/U mole ratio of 2.0, nitric acid can be extracted from uranyl nitrate solutions to give ratios as low as 1.5 without precipitation of uranium. The same low ratios can be obtained by dissolving UO_3 according to Eq. (2). These solutions are commonly called ADUN, and the average composition for a NO_3^-/U ratio of 1.5 would be $\text{UO}_2(\text{OH})_{0.5}(\text{NO}_3)_{1.5}$. Stoichiometric uranyl nitrate will only allow about 80% exchange of UO_2^{2+} for H^+ , while ADUN is necessary for the high (>95%) conversions required for resin-based fuel preparation.

The equilibrium data for the exchange of UO_2^{2+} for H^+ have been investigated experimentally and correlated by Shaffer et al.⁴ The results are presented as equilibrium quotients for Eq. (1), with the temperature and the resin type as parameters. As a result of the complex uranyl species in solution, the equilibrium quotients are also functions of the nitrate ion concentrations. The typical result is shown for conditions near those most commonly used in our engineering-scale system runs (Fig. 2). The H^+ concentrations are calculated from pH measurements, and the resin concentrations are given in moles per liter of wet resin.

Process control for the engineering-scale system is maintained through in-line measurements of ADUN pH. Shaffer's data can also be presented as the resin loading (that is, the percent exchange of UO_2^{2+} for H^+) vs ADUN pH with NO_3^- concentration as a parameter (Fig. 3). The data of Shaffer et al. for pH vs percent loading can be combined with data for the ADUN solution (see Sect. 2.1.2) to give NO_3^-/U ratios vs percent resin loading (Fig. 4). For 0.2, 0.6, and 1.0 N NO_3^- , there was no significant difference between the Amberlite IRC-72^{*} and Duolite C-464^{**} resins or the temperatures

^{*}Trademark of the Rohm and Haas Co.

^{**}Trademark of the Diamond Shamrock Co.

Fig. 2. Equilibrium quotient for uranium loading vs nitrate concentration (Amberlite IRC-72 at 40°C). (See ref. 4.)

Fig. 3. Equilibrium loading of uranium vs solution pH (Amberlite IRC-72 at 41°C). (See ref. 4.)

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Fig. 4. Equilibrium loading of uranium vs solution NO_3^-/U ratio (Amberlite IRC-72 or Duolite C-464 at 30 or 40°C).

of 30°C and 40°C. For the controlling region of above 70% loading, all the conditions of importance to the engineering-scale resin loading are represented by a single curve of percent loading vs NO_3^-/U ratio. This is an important simplification for the purpose of making calculations.

2.1.2 Properties of ADUN solutions

The densities, pHs, and conductivities of ADUN solutions were measured experimentally and correlated by Botts with uranium concentration, NO_3^-/U ratio, and temperature as variables.⁵ The ranges of interest to the engineering-scale resin loading are less than 0.5 M uranium, 25 to 50°C, and NO_3^-/U ratios of 1.5 to 1.9. For this range, the density data are adequately represented by:

$$\rho(\text{ADUN}) = \rho(\text{H}_2\text{O}) + 0.324 [\text{U}] , \quad (4a)$$

$$[\text{U}] = 3.10 [\rho(\text{ADUN}) - \rho(\text{H}_2\text{O})] , \quad (4b)$$

where

$\rho(\text{ADUN})$ = density of ADUN, g/cm^3 ;

$\rho(\text{H}_2\text{O})$ = density of H_2O at the same temperature;

$[\text{U}]$ = uranium molarity.

The experimental measurements of Botts⁵ for pH at 50°C are shown with a log scale for uranium molarity (Fig. 5) to facilitate interpolation at the lower uranium concentrations. For the acid-deficient concentrations (NO_3^-/U ratio <2), the reported pH values averaged 0.22 unit higher at 25°C and 0.22 unit lower at 75°C as compared with the values at 50°C. As a result of the uranium complexes present, attainment of an equilibrium pH requires a long time compared with that for simple ionic solutions.

Fig. 5. ADUN pH values as a function of uranium concentration and NO_3^- ratio.

Samples removed from the engineering-scale system frequently show rapid pH changes for several minutes and small, slow changes for much longer times. The conductivity of the ADUN is very dependent on temperature, uranium concentration, and NO_3^-/U ratio. The equations given by Botts would allow the conductivity measurement to be used for computer control of a resin loading process, but the density and pH give the two important concentrations $[\text{U}]$ and $[\text{NO}_3^-/\text{U}]$ more conveniently and directly from Eq. (4b) and Fig. 5.

2.1.3 Nitrate extraction reactions

Equations of importance to the nitrate extraction system include the following, where X_2NH represents the Amberlite LA-2^{*} secondary amine (N-lauryl-N-trialkylmethylamine):

Both the reaction for nitrate extraction, Eq. (5), and the reactions for regeneration Eqs. (6)-(8), are very favorable chemically and can be forced to completion with essentially 100% utilization of one of the reactants. Since excessive extraction of HNO_3 will precipitate uranium in the ADUN solution, the nitrate extraction contactor is always supplied with a large excess of ADUN. One theoretical stage of contact would provide complete conversion of the amine to the nitrate salt form. Although

^{*}Trademark of the Rohm and Haas Co.

the spray column used for the nitrate extraction contactor is not designated for high efficiency, it results in greater than 99% conversion.

The conditions in the regeneration contactor are selected to improve phase separation. Phase separation is poor at high pH values with stable emulsions being formed in the presence of large excesses of NaOH. In the first demonstration of this resin loading process,³ the amine was completely regenerated by using an excess of base. Use of an excess of NaOH was not practical in the engineering-scale system because of the emulsion problem; therefore, the regeneration was carried out with equimolar mixtures of NaOH and Na_2CO_3 . Partial regeneration of the amine using an excess of amine nitrate has important advantages, and the results are reported in Sect. 6.

The uranium in uranyl solutions can form negatively charged complexes which can react with the amine. Equation (9) is included to illustrate this type of reaction but does not mean that a complex of the formula indicated was known to be present. Any uranium complexes which reach the amine regeneration contactor result in losses of uranium to the aqueous waste. Thus, high uranium concentrations or high NO_3^-/U ratios in the ADUN are undesirable since they favor the formation of such complexes. Aqueous scrubs of the amine nitrate can be used to recover both uranium complexes and entrained ADUN before they reach the amine regeneration contactor.

2.1.4 Composition of the resin

The composition of the dried, UO_2^{2+} -loaded resin depends on the average formula of the feed resin, the extent of loading, the drying

conditions, and the presence of impurities. Both Amberlite IRC-72 and Duclite C-464 are prepared by polymerizing acrylic acid with divinylbenzene (DVB) to provide cross-linkage and thereby improve the physical properties of the resin. Amberlite IRC-72 is manufactured to contain 10 wt % DVB, which is supplied as a commercial mixture containing a smaller amount of ethylvinylbenzene (EVB) and slight amounts of other constituents. The resulting resin polymer thus contains 10 wt % DVB plus varying amounts of EVB, depending on the mixture; the balance is relatively pure acrylic acid (molecular weight, 72.064). The active group for cation exchange is the carboxylic acid (-COOH), and capacities or "equivalent weights" are for equivalents of carboxylic acid.

The composition of one batch of Amberlite IRC-72 in the hydrogen form is equivalent to the following: 10.000 wt % DVB, 7.982 wt % EVB, and 82.018 wt % acrylic acid. The equivalent weight is then $72.064/0.82018$, or 87.86 g. The calculated cation exchange capacity (CEC) in milliequivalents per gram (meq/g) of dry, hydrogen-form resin is $1000/87.86$, or 11.38. Complete cation exchange results in 86.86 g of resin combining with 1 equiv of the cation that replaces the hydrogen.

The measured CEC values for Amberlite IRC-72 were generally 10.3 to 10.7 meq per gram of dry, H^+ -form resin. The uranium-loaded carboxylic acid resins contain uranium, carbon, hydrogen, and oxygen as the only major constituents. Spectrochemical analyses show about 300 ppm (based on uranium) of total metallic impurities. The standard uranium and carbon analyses are accurate and relatively simple, while oxygen and hydrogen are more troublesome. Analyses of two uranium-loaded Amberlite IRC-72 samples were:

<u>Analysis</u> <u>(g/g dry resin)</u>	<u>Sample 1</u>	<u>Sample 2</u>
Uranium	0.4656	0.481
Carbon	0.2340	0.2216
Hydrogen	0.0335	0.0372

The loaded resin has carbon/uranium mole ratios of about 9, in agreement with about 95% exchange of uranyl ion for hydrogen. Other analyses indicate about 2 moles of water per mole of uranium at the standard Loss On Drying (LOD) conditions of 110°C. The hydrogen- and sodium-form resins do not retain water at these LOD conditions; the water with the uranyl-loaded resin is probably bound with the cation as $\text{U}(\text{OH})_4^{2+}$, $\text{UO}_2(\text{H}_2\text{O})_2^{2+}$, or some similar structure. The average structure per uranium atom might be represented by $\text{UO}_2(\text{H}_2\text{O})_2\text{H}_{0.1}(\text{C}_{4.6}\text{H}_{4.7}\text{O}_2)_{2.1}$.

2.2 Product Specifications

In general, the primary product specifications are those for the carbonized and/or coated kernels; in addition, the dried, uranium-loaded resin must be suitable for carbonization, conversion, and coating to meet those primary specifications. Secondary specifications for resin loading have not been written. The size, shape, sphericity, and some impurities are determined and controlled by resin feed preparation. The specifications of greatest importance to the loading of the resin require the following:

1. A high uranium content; that is, nearly complete exchange of UO_2^{2+} for H^+ in the resin exchange sites. For some fuel loadings, the usual uranium content of resin-based kernels is just adequate; that is, lower uranium contents would require other preferred conditions to be compromised.

2. Reproducibility of a specified loading is required to meet specifications for chemical composition, uranium content, and uniformity. The range of allowable chemical compositions is not very restrictive, and variations in loading would probably compromise the uranium content or the uniformity of loading before the chemical composition failed to meet specifications.
3. Uniformity of uranium loading from particle to particle. The effects of nonuniformity have not been determined. A high degree of uniformity is preferred since determination of the allowable extent of nonuniformity would require a major experimental program.
4. Uniformity within a particle. Nonuniformity could result from variations in resin capacity that occur because of voids or shell structure, or from nonuniform loading of uranium due to mass transfer effects. The comments for (3) also apply to this item.
5. No material should be added that would distribute impurities to the carbonized kernels or that would result in uncontrolled variations in carbon and oxygen contents after carbonization. Both the neutron cross sections and the chemical effects during refabrication and irradiation are important in considering the effects of impurities.
6. The shape of the kernels must not be degraded by cracking, clustering, or other changes.
7. The average uranium content of one fuel kernel should be about 65×10^{-6} g.

The general approach for the first five items has been to develop a practical resin loading process and then determine whether the products are acceptable. The final secondary specifications would then require products known to be acceptable rather than determination of the minimum acceptable specifications. Irradiation tests are currently in progress to provide information for a minimum acceptable shape specification (item 6).

3. RESIN LOADING

During the resin loading step, uranyl ion is exchanged for hydrogen ions as represented by Eq. (1). This cation exchange process is controlled by the reactions, kinetics, and equilibria discussed in the previous section. The resin discharged from the loading contactor must meet the product specifications, and the uranium loading rates must be compatible with satisfactory operation of the remainder of the system.

The resin loading method for preparing HTGR fuel differs from the more common ion exchange processes in a distinct and significant way. Here the resin is the product, whereas the solution is the product in most ion exchange processes. As a result, all of the resin must be uniformly loaded. The solution, on the other hand, is recycled, and a large excess or poor utilization of it is of little importance. Charging and discharging the resin are part of the routine operation and must be done without significant residues or losses. Figure 6 shows a diagram of the uranium and resin flows.

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Fig. 6. Process flows of uranium and ion exchange resin for resin loading.

3.1 Batch vs Continuous Resin Loading

Carbonization and conversion of the uranium-loaded resin must be carried out batchwise in order to provide a complex sequence of process conditions,⁶ and the amount of material in each process is dictated by nuclear criticality limitations. The daily capacity of a recycle fuel pilot plant or small commercial plant is equivalent to 1 to 10 g of uranium per minute; such quantities are too small for efficient continuous operation. Therefore, the engineering-scale resin loading was developed for batch loading with 4 kg of uranium per batch.

The process operations associated with the extraction of nitric acid are most conveniently done in a continuous mode. The volumes or amounts of solvent, ADUN solution, and uranium are excessive for batch nitrate extraction with a loading of 4 kg of uranium per batch. Therefore, a continuous nitrate extraction system was combined with a batch resin loading contactor. A nitrate extraction capacity equivalent to the loading of 1 kg of uranium per hour was convenient for several reasons. A 4-hr loading time allows a convenient schedule of batch operations and easily meets the minimum kinetic requirements for full loading. Smaller capacities would not result in any significant reductions in the cost or space requirements for the nitrate extraction system. Finally, the 1-kg-of-uranium-per-hour capacity for nitrate extraction could be increased to 24 kg/day if two batch loading contactors were used alternately to achieve continuous operation. The engineering-scale resin loading system for testing this approach is nearly full scale with respect to a commercial recycle plant.

Continuous ion exchange contactors have been developed and might be used with the continuous nitrate extraction to give continuous resin loading. Two principal advantages could be realized from this combination. One is that the resin loading could be operated at steady state throughout without the fluctuations inherent in batch operation. In practice, however, this is not necessarily a simplification or improvement since the control of rates to give steady-state operation is more complicated than operating at a fixed rate to a selected end point. The second advantage is easier control of nuclear criticality for larger capacities. One continuous loading system of critically safe dimensions could give capacities that would be equivalent to 20 to 50 batches per day for batch loading contactors. However, a commercial ^{233}U recycle plant would only require six to eight batches per day.

It appears that either continuous or batch loading contactors could be efficiently used for 25 kg of uranium per day. Batch loading would probably be more efficient for capacities less than 25 kg/day, while continuous loading would be more efficient for capacities greater than 25 kg/day.

3.2 Batch Resin Loading Contactor

Descriptions of the design and the fluidization behavior of the batch loading contactor are given here. The overall process behavior and control of the complete system are described in Sect. 7.

The batch resin loading contactor was a 5-in.-ID, 60-in.-long cylinder with a cone bottom and a 120-mesh stainless steel screen top (Fig. 7). The 5-in.-ID dimension was the maximum allowable for control

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Fig. 7. Cross-sectional view of batch loading contactor.

of nuclear criticality. The 60-in. cylinder length gives a total volume of 20 liters, while the settled volume of one batch of resin is 11 to 13 liters. The extra volume is necessary to allow reasonable initial ADUN flows without packing the resin against the exit screen.

Some design details of the test unit are shown in Fig. 7; however, the pilot plant would use different materials and assembly details. The top flange and screen assembly was essentially identical to that designed and described for the resin dryer (see Sect. 4.3). The transparent walls allowed observation of the hydraulic and mixing behavior, but this is not necessary since a schedule of flow rates can be specified without observation of the resin.

The batch loading contactor generally shows several mixing cells instead of one uniformly mixed bed. The center entry and the cone bottom result in a spouting bed type of operation in the bottom one-fifth of the contactor. Above this, there are two or more cells with upflow at the center, downflow at the walls, and center-to-wall or wall-to-center flows at the top and bottom of each mixing cell. The poorest mixing occurs at the bottom corner between the cylinder and the bottom cone. While mixing in this region is incomplete during the initial period of low ADUN flow, satisfactory results are obtained after the ADUN flow is increased.

Plugging of the 120-mesh top screen by resin fines was detectable but did not cause operating problems. In pilot-plant operation, the feed resin would be more carefully screened and would therefore contain a much smaller fraction of fines. The screen mesh could be changed to a larger opening size to eliminate accumulation of fines on the screen.

3.3 Continuous (Higgins) Resin Loading

A continuous, 2-in.-ID resin loading contactor of the Higgins type was tested as a replacement for the batch loading contactor in the engineering-scale resin loading system. The results have been reported elsewhere⁷ and thus will only be summarized here. The results indicate that the 2-in.-ID Higgins contactor can easily load 25 kg of uranium per day, implying that a 4-in.-ID Higgins contactor can load 100 kg/day. The process control requirements were investigated with particular emphasis on remote operation. In addition, the 2-in.-ID Higgins contactor was successfully used to convert sodium-form resin to the acid form. The conclusions as reported⁷ include the following:

1. Adequate process control has been demonstrated for the continuous loading of cation exchange resin with uranium.
2. Remote operation appears to be feasible with existing instrumentation.
3. The existing equipment can supply an acceptable resin product at the rate of 1.4 kg of uranium per hour.
4. Scaling up to 100 kg of uranium per day can be achieved by using a 4-in.-ID Higgins contactor of critically safe dimensions.

4. DRYING OF URANIUM-LOADED RESIN

The selection, design, and testing of a microwave-heated dryer as part of the engineering-scale resin loading system have been reported.⁸

Microwaves are electromagnetic waves in the frequency range of 300 MHz to 300 GHz, with corresponding wavelengths of 1 m to 1 mm. Microwaves have many of the same characteristics as light waves; that is, they

can be generated, reflected, transmitted, and absorbed. Of course, there are basic differences in the materials that transmit and absorb them, as well as in the manner in which each is generated. When an electromagnetic wave is propagated in a dielectric material, the wave is attenuated and power is thereby dissipated in the material in the form of heat. Water has certain molecular properties that enable it to absorb microwave energy.

Microwave drying has several advantages over conventional heating, which relies primarily on conduction-convection. These include instant "on-off" capability, moisture leveling (i.e., preferential heating of the wettest material), and a shorter drying cycle without high temperatures. Microwave heating has satisfied our needs better than any other methods considered for this application with geometry restrictions, poor thermal conductivity of the resin, and uniformity requirement.

4.1 Capacity

The engineering-scale resin loading system is designed for batch loading of resin at 4 kg of uranium per batch. While the pilot-plant capacity is based on one batch per day, the resin loading operations require 4 hr per batch or less. The nitrate extraction system is continuous with a uranium capacity equivalent to at least 1 kg/hr. If the complete cycle for the resin dryer (including loading, washing, drying, and unloading) does not exceed 4 hr, a single dryer could serve a continuous nitrate extraction system with either multiple batch contactors or a continuous resin loading contactor. About 2 kg of water should be evaporated to dry one batch of resin to a preferred water content (discussed in Sect. 4.2).

4.2 Specifications for Dried Product

These specifications remain to be determined or to be verified. In general, the primary specifications are those for the carbonized and/or coated kernels; in addition, the dried, uranium-loaded resin must be suitable for carbonization, conversion, and coating to meet those primary specifications. The size, shape, sphericity, uranium content, and impurity content of the kernels are determined and controlled by resin feed preparation and resin loading operations. The specifications of greatest importance to the drying of the resin are as follows:

1. The shape of the kernels must not be degraded by cracking, clustering, or other changes during drying.
2. Any material added should be free of impurities that would change the composition of the carbonized kernels or that would result in uncontrolled variations in the carbon and oxygen contents after carbonization.
3. The water content of the dried resin should be within an optimum range for the requirements for accountability, handling, and carbonization.

Specification of the water content for the dried, uranium-loaded resin is now 10 to 20% LOD from a compromise of conflicting requirements. The water content is generally determined as a percentage LOD for overnight exposure to ambient air at 110°C. The primary requirement for accountability is that the LOD be reproducible and uniform. Treatment of the carbonization off-gases, including control of criticality, is simplified by minimizing the amount of water charged to the carbonization furnace.

These two requirements resulted in an initial selection of less than 0.1 wt % LOD as a specification for dried resin. For less than 0.1 wt % LOD, the dried resin shows static charge effects which make handling and transfer very troublesome. The resin literally climbs the walls of all surfaces exposed to it and cannot be poured or transferred pneumatically without leaving some of the particles behind on surfaces. Addition of graphite powders was tested, but this only alleviates the problem without eliminating it and is an undesirable process complication. Empirical tests showed that 10 to 20% LOD for uranium-loaded Amberlite IRC-72 results in acceptable handling properties. Static charge problems become increasingly noticeable as the LOD decreases below 10 wt %. The resin appears to become increasingly sticky from dampness as the LOD increases above 20 wt %. The alternate resin, Duolite C-464, is slightly more porous and shows the same behavior at a slightly higher LOD; 12 to 24 wt % gives optimum handling behavior.

4.3 Description of the Microwave Dryer

A microwave energy system for drying uranium-loaded ion exchange resin was purchased from a commercial manufacturer^{*} and tested. A schematic diagram illustrating the components of the microwave dryer system is shown in Fig. 8. The microwave cavity (applicator) is constructed of 0.16-cm-thick type 304 stainless steel and has dimensions of 1.2 m high x 1.2 m wide x 0.9 m deep. The resin container is a 13.0-cm-OD x 0.3-cm-wall x 1.2-m-long Pyrex tube. The column is a vessel of safe geometry with respect to nuclear criticality and provides ample freeboard to allow fluidization and mixing of the resin. At static conditions, the reference

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^{*}Gerling Moore, Inc., Palo Alto, Calif.

Fig. 8. Microwave-heated dryer used in the preparation of uranium-loaded ion exchange resin.

11-liter resin batch occupies approximately 75% of the column. The width and depth of the cavity, as well as the location of the column, were selected by the microwave system manufacturer. Provisions for solids addition and withdrawal (as well as liquid or vapor only, through screens) are incorporated in a special flange assembly (Fig. 9). This flange has a conical ($\sim 45^\circ$ slope), 120-mesh screen with a hole at the apex. A 1.9-cm ball valve is secured to the plate to allow retention and transfer of solids. The flange and screen are fabricated from type 304 stainless steel. During the drying cycle, air is passed through the resin bed to aid in water vapor removal and to promote mixing of the material. The saturated air leaving the column is passed through a condenser, and the condensate is collected.

A recirculating hot air system reduces heat transfer from the resin column to the surroundings during the drying cycle. A 2-kW space heater and blower directs heated air into the cavity. The temperature inside the cavity is maintained at approximately the steady-state temperature of the column exit gas stream (typically, 70 to 80°C) during the microwave heating period. (The outside top and side walls of the cavity were insulated.) When this heater is not operated, water condenses on the glass column.

The microwave power source (magnetron) is a variable-power generator with an operating range of 0 to 2.5 kW at 2.45 GHz. The 2.45-GHz band was selected over the 915-MHz band because the higher frequency produces a shorter wavelength (and therefore more modes in a given cavity size) and consequently a more uniform heating. A standard rectangular rigid

Fig. 9. End sections of resin dryer in microwave cavity.

waveguide, bends (elbows), and a 1-m length of flexible waveguides were used to couple the power supply to the cavity. A quartz window diaphragm is located between the waveguide flange and the cavity wall to prevent material from entering the waveguide. Flexible waveguide is manufactured from silver-plated interleaved brass and can be fabricated in any length up to 1.5 m. This flexible waveguide can make a 90° twist or bend in 31-cm lengths. Standard rectangular waveguide is commonly fabricated from aluminum. The straight waveguide is available in stainless steel; however, the flexible waveguide cannot be purchased in this form.

4.4 Results Obtained by Microwave Drying

Microwave heating was successfully demonstrated to give controlled and reproducible drying of 11-liter batches of uranium-loaded (4 kg of uranium) resin in a vessel of safe dimensions for nuclear criticality (12.4 cm ID). The dried resin should have a water content of 10 to 20 wt % to minimize handling problems. The microwave heating evaporates water throughout the resin bed, with preferential heating of the wettest resin, and allows short drying cycles.

A standard drying procedure and methods for determining the duration of microwave heating, in order to obtain the desired water content, were developed. Use of an experimentally derived drying factor or monitoring the amount of water removed from the wet resin has been found to provide reproducibly acceptable dried product. Temperature or reflected power was not reliable in obtaining resin of the preferred moisture content.

A heat balance on the resin dryer system and the coupling efficiencies of the microwave energy with the wet resin were calculated and found to be

in good agreement with experimental results and the manufacturer's literature respectively. The minimum fluidization velocity was also calculated and found to compare favorably with experimental observations. Mixing of the material was found to be required in order to ensure a uniform moisture content. No significant operating difficulties were encountered. Detailed results and procedures have been reported elsewhere.⁸

5. EVAPORATOR

Design, fabrication, and testing of a thermosiphon evaporator as part of the engineering-scale resin loading system have been reported.⁹

Figure 10 is a schematic flowsheet of the vertical thermosiphon evaporator. Uranyl nitrate is supplied by a centrifugal pump to the evaporator feed nozzle located near the liquid inlet of the reboiler. The feed rate is usually two to three times the condensate rate. Concentrated uranyl nitrate is cooled to the resin system process temperature before returning to the UNH surge tank via a fixed jackleg (overflow weir). Vapor passes through the disengaging section and a wire-mesh mist eliminator. The entrainment-free vapor is condensed and the condensate collected. The overflow weir and condensate tank are on a common vent line. The type 304L stainless steel evaporator is of all-welded construction.

The thermosiphon evaporator was simple and easy to control. The fixed jackleg maintains a constant liquid level in the evaporator and permits continuous circulation through it. The evaporation rate (and hence the uranium concentration in the resin loading system) was controlled by regulating the steam pressure while maintaining a constant rate

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Fig. 10. Vertical thermosiphon evaporator.

of feed flow to the evaporator. A high-quality condensate containing less than 0.5 ppm of uranium, for an overall decontamination factor of greater than 5×10^5 , is obtained by utilizing a tangential vapor entry to the large vapor disengaging section and a wire-mesh mist separator. The decontamination factor was not a consistent function of the condensate rate for rates of 17 to 79 liters/hr. This evaporator design is acceptable for meeting the HTGR fuel recycle pilot plant requirements. Details of the design and results have been reported.⁹

When highly acid-deficient uranyl nitrate is heated to temperatures above 100°C, precipitation of uranium occurs. This precipitate is easily dissolved at lower temperatures or higher NO_3^-/U ratios. The normal operating procedure for the engineering-scale resin loading system limited evaporator operation to periods of higher NO_3^-/U ratios and used continued flow through the evaporator at lower temperatures to dissolve any precipitated uranium. In future systems, the evaporator should probably be fed with the more acidic uranyl nitrate from the resin loading contactor in order to further minimize precipitation of uranium.

6. NITRATE EXTRACTION

The nitrate extraction system consists of a series of five cocurrent (one theoretical stage of contact each) contactors (Fig. 11). A single solvent stream (0.4 M Amberlite LA-2 secondary amine) is pumped once and flows, via gravity, through all five contactors back to the solvent surge tank. An aqueous stream is metered to each contactor and exits through a jackleg and weir to control the aqueous-organic interface level. The mixing sections are organic continuous to improve the phase separation,

and the organic-air interface level is controlled by a weir for the exit organic. In the engineering-scale resin loading system, the highest contactor to which the organic is pumped is a spray column for extraction of nitric acid from the ADUN. The other four contactors have high organic/aqueous flow ratios and require mechanical agitation to improve their efficiencies. The first two are water scrubs to recover uranium for return to the ADUN tank. The third is the regeneration contactor with NaOH (or other base) solution feed. The final contactor has a water feed to scrub entrained aqueous waste from the solvent. The aqueous effluents from the third and fourth contactors are waste solutions with approximately neutral pH values.

The nitrate extraction system components had been designed, fabricated, and operated earlier for sol-gel processes. The spray contactor was a modification of that used for preparing urania sols.¹⁰ The mixer-settler contactors and solvent system were designed as prototypes for the preparation of ThO_2 - $^{233}\text{UO}_3$ sols¹¹ and had been operated for demonstration runs.¹²

6.1 Nitrate Extraction Equipment

Uranyl nitrate solution from the ADUN tank was pumped through a filter, a Kates flow controller, a conductivity cell with temperature element (thermocouple), a heater, a flow element (orifice and differential-pressure cell), and a nozzle with 1/8-in.-diam holes below the solvent-air interface in the extraction column (Fig. 11). The aqueous drops flow cocurrently with the continuous organic phase down a 2-in.-ID, 36-in.-long contactor. Phase separation with interface control was achieved with several variations

of new components and is described separately, along with the results obtained, in Sect. 6.2.

The solvent regeneration contactors may be oversized with respect to meeting the flowsheet requirements. Each mixer-settler (Fig. 12) is made of 3-in.-diam glass pipe to permit observation of the process streams and operating characteristics. It is divided into six compartments, each of which has a mixing impeller; these impellers are mounted on a common shaft with a variable-speed drive. The aqueous and organic phases enter at the top and flow cocurrently down through the six compartments to give the effect of mixing vessels in series. This arrangement ensures good stage efficiency. Since the mixer is designed to remain filled with organic, the aqueous phase is dispersed into the organic phase (organic continuous) to minimize emulsification. At shutdown, the aqueous phase drains to the bottom; consequently, only the organic phase is present in the mixer at startup, and the aqueous stream is easily dispersed as it enters. Each mixer is equipped with two U-shaped sections of stainless steel tubing through which hot water is circulated to maintain the organic and aqueous phases at about 50°C. As initially installed, phase separation occurs in the section located below the mixer. The position of the interface is controlled by adjustable weirs on both the aqueous and the organic overflow lines. The nominal volumetric holdup of the mixing section is 2.0 liters, while that of the settler is 2.8 liters of organic phase and 1.5 liters of aqueous phase. An improved arrangement, which was installed and tested, is recommended for in-cell use. This is described separately in the following section.

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Fig. 12. Mixer-settler for solvent scrub and regeneration stages.

6.2 Phase Separation and Interface Control

Separation and control of the two phases after leaving the mixers are necessary in order to achieve satisfactory operation. Carry-over of organic into aqueous wastes would make waste handling more troublesome and would require replacement of the lost solvent. Organic in the ADUN to the resin loading would accumulate on the resin and, when present in large amounts, would interfere with the loading of uranium. Small carry-overs of aqueous streams in the organic only result in small losses of efficiency since the primary nitrate extraction and amine regeneration are each followed by water scrubs which would return aqueous to the same ADUN or waste tanks. These results of poor phase separation are listed as Table 1.

Detection and feedback control of the regeneration system interfaces would be troublesome and undesirable for an in-cell system. Overflow weirs are simple, inexpensive, and less likely to malfunction than a control valve system. The solvent extraction system, as initially adapted,³ required large changes in weir heights to compensate for variations in liquid density. The largest variations were from uranium concentration changes in the ADUN and from temperature changes for the organic solvent. The liquid-liquid interface position results from a pressure balance, as follows:

$$H_o \rho_o = H_A \rho_A , \quad (10a)$$

where

H = height above interface,

ρ = density,

o,A = subscripts indicating organic and aqueous respectively.

Table 1. Effects of poor phase separation

Contactor and exit streams ^a	Effect of aqueous carry-over with organic	Effects of organic carry-over with aqueous
Nitrate extraction (ADUN and amine nitrate in DEB)	More uranium to be recovered in scrub contactors, and a minor increase in uranium losses to nitrate waste	Organic in ADUN tank (and to ADUN pump)
First H ₂ O scrub (dilute ADUN and amine nitrate in DEB)	More uranium to second scrub, and minor increase in uranium losses to nitrate waste	Organic in ADUN tank (and to ADUN pump)
Second H ₂ O scrub (very dilute ADUN and amine nitrate in DEB)	Minor increase in uranium losses to nitrate waste	Organic in ADUN tank (and to ADUN pump)
Amine regeneration (NaNO ₃ solution and 75% amine--25% amine nitrate in DEB)	NaNO ₃ to final H ₂ O scrub, and minor increase in sodium carry-over to ADUN	Loss of solvent to NaNO ₃ waste
Final H ₂ O scrub (very dilute NaNO ₃ and 75% amine--25% amine nitrate in DEB)	Minor increase in sodium carry-over to ADUN	Loss of solvent to aqueous waste

^aDEB = diethylbenzene.

Equation (10a) can be rearranged to give:

$$H_A = (H_o - H_A) \frac{\rho_o}{\rho_A - \rho_o}, \quad (10b)$$

$$H_o = (H_o - H_A) \frac{\rho_A}{\rho_A - \rho_o}. \quad (10c)$$

The usual densities (in g/cm³) are: amine solvent (ρ_o), 0.82; 1.5 M NaNO₃, 1.075; scrub water, 0.99; and ADUN [see Eq. (4a)], 1.09 for 0.3 M uranium. For fixed interface positions, $H_o - H_A$ is fixed. For the original arrangement shown by Fig. 13(a), the H_A were about 70 cm and interface variations would be as large as 15 cm for fixed weirs. Such large variations would not be tolerable. For the arrangement shown in Fig. 13(b), the H_A are about 10 cm and the resulting interface variations (up to 2 cm) are acceptable. This modification was demonstrated for both the nitrate extraction and the caustic regeneration contactors. Results were as expected; no difficulties were encountered.

The mixing requirements and the effects of temperature initially reported³ were confirmed. The phase separation, although adequate at 25°C, is visibly faster at 40°C. Since radiochemical cells are usually warmer than 25°C, the high temperature is easier to maintain than 25°C. The effects of temperature in the 40 to 60°C range are not important. Details of the contactor designs have been reported previously.¹¹ The contactors have six stages with cocurrent flow using a common agitator with a 1-3/4-in.-diam by 1/2-in.-high impeller in each stage. For the resin loading flowsheet, these agitators must be operated at 350 to 500 rpm to achieve optimum results.

Fig. 13. Interfaces in nitrate extraction and amine regeneration contactors for resin loading.

A standard centrifugal pump rotating seal (John Crane type 9) made of alumina and graphite was used for the contactors. This seal is capable of operating when the interior of the contactor is evacuated. Support for the impeller shaft is located above the rotating seal in a 2:1 right-angle speed reducer (Crown Gear Model 154). The impellers are attached to the extended low-speed shaft. A variable-speed motor and the 2:1 speed reducer limit the speed of the impellers to 875 rpm.

A membrane type of separator^{*} was tested on the ADUN flowing to the resin loading contactor to prevent organic entrainment. The ADUN was passed through a membrane which rejects organic drops. The rejected organic and excess ADUN flowed to the nitrate extraction contactor and phase separator. This unit was effective for preventing organic carry-over to the resin loading step. However, the membranes also acted as filters and showed signs of plugging during long-term use. The membrane materials are of unknown composition and might be sensitive to radiation damage from ²³²U. Simple gravity separation by an enlarged tee is recommended for in-cell use since the potential problems from the membranes are more important than a more efficient phase separation.

The amounts of organic in ADUN samples were determined by analyses for total carbon content. The results¹³ show less than 100 ppm of carbon with some removal of carbon by the ion exchange resin during the first third of the loading. The total carbon accumulated on the resin would be less than 1 g/liter, or 1000 ppm, for the dried resin. This quantity is not expected to have any significant effect on the resin composition since most of it is probably volatilized by steam-stripping during the resin drying process.

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^{*}Model LS-60-P, Selas Flotonics Corp., Springhouse, Pa.

6.3 Equipment Performance

The nitrate extraction components, including the amine regeneration system, have performed well. While the units designed for sol-gel processes were adequate for the development studies, several modifications or changes seemed desirable to adapt them to remote operation. These included the following:

1. Elimination of visual observation and control of liquid-liquid interfaces (see Sect. 6.2).
2. Changes or additions to facilitate phase separation (see Sect. 6.2).
3. Use of metal contactors instead of glass. Although glass equipment has been accepted for HETF use, demonstration of metal prototype contactors may be required as a test for future plants.
4. Use of multistage countercurrent contactor in place of the four cocurrent contactors in the amine regeneration system. Unacceptable results for a packed column will be described in this section. Pulsed columns could probably provide the more effective mixing that is required, but the tendency for emulsifications to form at the NaOH solution inlet might be troublesome. Further tests of contactors are not scheduled.
5. The solvent was metered by Micro Bellows pumps (Research Appliance Co.). These pumps use cam-operated Teflon bellows with adjustable stroke lengths to vary the flow rates. Some other liquid flow control system might be preferred for remote operation.

A 3-in.-ID by 6-ft-long packed column (3/8-in. Raschig ring packing) was fabricated, installed, and tested to replace the two co-current mixer-settler stages for recovering uranium from the nitrate extraction solvent. The packed column would be simpler mechanically, while a countercurrent contactor might provide more than two theoretical stages, thereby reducing the uranium content of the nitrate waste. During two test runs, the 6 ft of packed column gave only a fraction of a theoretical stage. The uranium losses were about 0.5% as compared with less than 0.05% for the two co-current mixer-settler stages. The aqueous scrub does not disperse into small drops in the packed column. A pulsed column contactor could probably be used as an efficient countercurrent scrubbing contactor.

6.4 Partial Regeneration of Amine

The third contactor in the regeneration system reacts the amine nitrate with aqueous solutions of base to regenerate the free amine. Excess NaOH results in the formation of emulsions and is not allowable. The initial demonstration of amine extraction¹² used equimolar mixtures of NaOH and Na_2CO_3 . The solvent/aqueous ratio was selected to give complete regeneration of the amine with complete utilization of the NaOH, but only partial conversion of the Na_2CO_3 to NaHCO_3 and NaNO_3 . The typical molar ratio of Na/NO_3^- in this waste was 1.7. Partial regeneration of the amine using NaOH (or NH_4OH) only and a NaOH/amine ratio of about 0.7 is an important process improvement. The amount of waste salt is greatly reduced; the Na/NO_3^- ratio is 1.0 mole/mole. The waste is almost neutral (pH of 7.6), and phase separation is improved. The solubility of uranium

is minimized so that any large losses of uranium can be recovered by filtration. These improvements for partial regeneration were demonstrated using both NaOH and NH_4OH for regeneration. No difficulties were observed.

One effect of partial regeneration is that the steady-state rate of nitrate extraction is set by the caustic rate instead of the solvent rate. This is an advantage in that a fixed solvent rate can be used and the caustic rate is controlled by an easily maintained and checked metering system outside the cell. However, the nitrate extraction rate responds very slowly to changes in the caustic rate as a result of the solvent inventory of the system.

6.5 Uranium Losses

The waste streams from the integrated resin loading flowsheet (Fig. 1) are the air and condensate from the resin dryer, a portion of the condensate from the ADUN evaporator, and the NaNO_3 (or NH_4NO_3) solution waste from amine regeneration. The controlling amounts of uranium are present in the nitrate solution wastes from amine regeneration. The evaporator condensate contained less than 0.5 ppm of uranium (see Sect. 5). The dryer condensate showed trace amounts of uranium (~1 ppm) in a small volume of about 2 liters per batch. The amount of radioactivity in the form of particulates in the dryer off-gas would depend on the isotopic composition of the uranium, and on the type of resin feed used; only measurements of the condensate were made. An infrequent source of uranium losses would be replacement of the ADUN filter. Most of the uranium could be leached from this filter by acid and water washes, but measurements were not made.

Table 2 tabulates the uranium concentrations in the aqueous streams of the amine regeneration system for typical conditions. Since the waste is 1.5 M NaNO_3 , the 50-ppm uranium content corresponds to 0.03% of the uranium loaded. The amounts of uranium in the uranium scrub flows are equivalent to about 0.5% of the original loading. Earlier tests with one uranium scrub contactor resulted in much higher uranium concentrations in the nitrate waste solutions. In the case of complete regeneration of the amine with an excess of $\text{NaOH-Na}_2\text{CO}_3$, the uranium was soluble at 300 and 600 ppm (Table 3, runs S02, S03). For partial regeneration with NaOH or NH_4OH , the uranium precipitated and the samples for filtered waste showed uranium concentrations of 40 to 110 ppm for NaNO_3 solution and 6 to 21 ppm for NH_4OH solution. The decreased solubility of uranium for NH_4NO_3 as compared with NaNO_3 at the same pH persisted after 24 hr and has not been explained.

The very high uranium losses for run S01 (Table 3) result from the high uranium concentration of 0.7 M, which results in extraction of nitrate complexes as illustrated by Eq. (9). The uranium losses were easily controlled for uranium concentrations of less than 0.4 M and NO_3^-/U ratios of 1.45 to 1.9; these limits did not present any drawbacks with regard to the resin loading.

7. OVERALL PROCESS BEHAVIOR AND CONTROL

The uranyl nitrate feed contains only UO_2^{2+} , NO_3^- , and water as major constituents. These are removed separately in the resin loading contactor, nitrate extraction contactor, and evaporator respectively. The uranyl

Table 2. Uranium concentrations in aqueous streams from amine regeneration for typical flowsheet conditions

Solvent flow: 0.6 liter/min of 0.4 M Amberlite LA-2
in diethylbenzene

Regeneration solution: 130 cm³/min of 1.5 M NaOH

Uranium recovery scrubs: two contactors with 60 cm³/min
of H₂O to each

Final scrub: 30 cm³/min of H₂O

Run number	ADUN U (<u>M</u>)	Uranium concentrations (ppm)			
		First uranium scrub	Second uranium scrub	Nitrate waste	Final scrub
S22	0.20	2530	996	121	10
S23	0.15	1116	617	49,84,47	21
S24	-	-	-	97	10
S25	0.15	-	456	83,80	5
S31	0.25	-	-	60	-
S32	0.25	-	-	95	-
S33	0.25	-	-	52	-
S38	0.20	3450	870	65	10
S39	0.23	2650	1100	104	4
S41	0.10	-	-	30,19	-
S48	0.23	a	a	38,40	-
S49	0.20	a	a	41,42	-
S53	0.20	a	a	47	0.2
H5	0.25	770	435	42	5
H6	0.25	770	216	13	5

^a 100 cm³/min H₂O to each scrub contactor.

Table 3. Uranium concentrations in aqueous streams from amine regeneration for varying flowsheet conditions

Solvent flow: Usually 0.4 liter/min of 0.4 M Amberlite LA-2 in diethylbenzene

Uranium recovery scrub: one contactor with H₂O flow of 60 cm³/min

Final scrub: H₂O flow of 3.0 cm³/min

Run number	ADUN uranium (M)	Amine regeneration conditions	Uranium concentrations (ppm)			
			Uranium scrub	NO ₃ ⁻ waste	Filtered NO ₃ ⁻ waste	Final scrub
Complete regeneration						
S01	0.70	Excess NaOH-Na ₂ CO ₃	13200	3600	-	8
S02	0.25	Excess NaOH-Na ₂ CO ₃	2600	600	600	10
S03	0.20	Excess NaOH-Na ₂ CO ₃	1650	300	300	80
Partial regeneration						
S05	0.20	NaOH only	1800	46	28	50
S06	0.20	NaOH only	1480	60	70	33
S07	0.15	NaOH on'y	1430	56	41	32
S08	0.15	NaOH only	1520	150	72,110	60
Partial regeneration						
S11	0.10	NH ₄ OH only	1320	-	-	11
S12	0.05	NH ₄ OH only	-	155	21	-
S13	0.15	NH ₄ OH only	-	12	12	-
S14	0.20	NH ₄ OH only	-	-	7	58
S15	0.20	NH ₄ OH only	-	10	6	62
S19	0.15	NH ₄ OH only	588	20	17	56

nitrate feed is usually added batchwise before the resin loading is started. Additional water is added to the ADUN in the form of uranium scrubs from the amine regeneration system and wash solution from loaded resin. For a batch addition of uranyl nitrate and a batch loading of resin, the amount of UO_2^{2+} is controlled by the run conditions (initial ADUN and resin present), and only the NO_3^- and water are controlled as independent variables. High loadings of uranium on the resin require low NO_3^-/U mole ratios (Fig. 4) for a sufficient time to allow approach to equilibrium. Since the minimum times are greater than 1 hr, there is little advantage to using large NO_3^- removal rates to adjust the NO_3^-/U ratio in short times. Close control of water removal is also of no importance because this removal has no effect on the NO_3^-/U mole ratio.

7.1 Uranium Inventory

The rate of uranium removal for a system with a single batch resin loading contactor is high initially but approaches zero as loading is completed. For the first 70% of the uranium loaded, the ADUN leaving the loading contactor is approximately at equilibrium with the resin, and the rate of uranium loading depends on the inlet ADUN flow rate, uranium concentration, and NO_3^-/U ratio. Both the ADUN flow rate and the uranium concentration are limited at the start since the light, hydrogen-form resin can be easily packed against the exit screen of the loading contactor. Because of these complex relationships and requirements, attempts to match a continuous uranyl nitrate feed rate with the uranium removal rate would be difficult and unnecessary. Addition of

uranyl nitrate at a continuous, constant rate over a period of about 2 hr could be used to minimize the uranium inventory.

The routine procedure for the engineering-scale resin loading has been batch additions of uranyl nitrate prior to resin loading. The uranium inventory or heel remaining after a batch of resin has been loaded is usually about equal to that in one batch (4 kg of uranium). This quantity is convenient for two reasons. Mixing of this heel (NO_3^-/U mole ratio of ~ 1.6) with the same amount of uranyl nitrate feed (NO_3^-/U of ≤ 2.2) results in an average NO_3^-/U mole ratio of less than 2. Ratios above 2 are undesirable because they result in increased extraction of uranium by the amine solvent. At the normal ADUN concentration, 4 kg of uranium is equivalent to about 70 liters of ADUN. This is a convenient volume to allow all normal process operations, including transfer to the dryer, to be performed without emptying the ADUN tank. Since transfer, washing, and drying of one batch of resin return about 40 liters of dilute ADUN to the tank, the system and tank must allow ADUN volume variations of this size even if a continuous feed of uranyl nitrate is used.

The uranium concentrations are determined routinely by measurement of the ADUN density and use of Eq. 4(b) (see Sect. 2.1.2). A special instrument for in-line measurement of ADUN density^{*} was installed, calibrated, and used for both batch and continuous resin loading contactor runs. The response of this instrument is immediate and continuous.

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* Dynatrol® CL-10TY series density cell and converter manufactured by Automation Products, Inc., Houston, Tex. (see Appendix A).

Temperature changes in the uranyl nitrate solution are compensated for in the output. The density provides the measurement of uranium concentration by using Eq. 4(b). To date (after 6 months of use), the instrument has proved to be stable, accurate, and sensitive to concentrations of 0.001 g/cm^3 . The specifications claim applicability to both liquids and slurries and insensitivity to ambient temperatures, process viscosity, pressure, and flow velocity. The process solution contacts only a 1/2-in.-diam U-tube which is forced to vibrate like a tuning fork. The vibration, which is measured electronically, changes as the density of the fluid in the tube varies.

7.2 Water Inventory

Since the equilibrium loading of uranium is primarily controlled by the NO_3^-/U mole ratio (Fig. 4) over a wide range of NO_3^- (or uranium) concentrations, close control of the water inventory is not important. For reasons discussed in Sect. 7.1, the usual procedure was to add uranyl nitrate feed batchwise prior to the start of resin loading. Then the evaporator could be operated to remove the water returned as scrub solution from the amine regeneration system plus the ADUN volume equivalent to the amount of uranium loaded. This would total about $(150)(0.2) + 40$, or approximately 70 liters. For the engineering-scale system, 6-psig steam would give 0.5 liter/min and require about 140 min. In most cases, the evaporator was started early in a run with about 6-psig steam and then shut off when the ADUN density or volume reached a preselected value. The precipitation of uranium when ADUN having a low NO_3^-/U ratio is heated above 100°C must be considered (see Sect. 5). To avoid difficulties from

such precipitation, operation of the evaporator at low NO_3^-/U ratios should be avoided and circulation without heat should be used to dissolve any precipitated uranium.

During batch loading runs, the evaporator was operated to achieve preselected values of ADUN volume or density. During continuous loading runs, the evaporator rate was varied slowly according to the volume in the ADUN tank. The selected volume in the ADUN tank was 35 liters; however, variations in the volume occurred from the return of wash water when resin drying runs were begun.

7.3 Nitrate Inventory

The NO_3^-/U ratio of the ADUN in the resin loading system must lie between two limits: that for precipitation of uranium (~ 1.45 at 50°C) and that for equilibrium between the ADUN and resin (Fig. 4). The removal of nitrate must be controlled to avoid the precipitation of uranium, which is undesirable. The required loading of uranium cannot be completed unless the NO_3^-/U ratio is 1.7 or less. This favorable ratio must be maintained for at least 1 hr, while 2 hr is a more dependent criterion.

For the engineering-scale system, we chose to use a nitrate extraction rate which usually allowed a run to be completed in about 180 min. A high rate of nitrate extraction is undesirable because repeated "on-off" cycles would be required to keep the ADUN within the NO_3^-/U ratio limits. When the uranium loading rate is high, the NO_3^-/U ratio increases. After the uranium loading rate decreases, the rate of NO_3^- removal becomes greater than the rate of uranium removal and the NO_3^-/U ratio decreases.

The nitrate removal is terminated before precipitation occurs and the NO_3^-/U ratio increases as loading is completed.

A simple material balance shows that the loading must be nearly complete when the nitrate removal operation is terminated if the NO_3^-/U ratio is to remain below 1.7. For 4 kg of uranium and a NO_3^-/U ratio of 1.45, the ADUN contains 17 moles of uranium and 25 moles of NO_3^- when nitrate removal is stopped. Removal of about 2 moles of uranium increases the NO_3^-/U ratio to 1.7; this indicates that loading must be at least 90% complete when nitrate removal ceases. If allowances are made for the concentration variations throughout the system, 95% or greater completion of loading is a more realistic criterion for determining whether the loading can be completed without resuming the nitrate removal operation.

The required rate of nitrate extraction can be calculated as follows:

Uranium loaded: 4 kg or 17 moles

Amount of nitrate in feed = $(17)(2.1) = 36$ moles

Nitrate extraction rate = $36/180 = 0.2$ mole/min

This nitrate extraction rate is equivalent to $4/3$ kg of uranium per hour.

7.4 In-Line pH Units to Measure NO_3^-/U Ratios

In-line pH units were purchased from three major manufacturers and used in the engineering-scale resin loading system. These units had many similarities. Each used a recommended combination of electrodes, temperature compensators, an amplifier at the in-line element, and a panel-mounted indicator with standard outputs (4 to 20 mA) to recorders. Additional descriptive details are given in Appendix A.

The in-line pH units were standardized by measuring the pH values of samples of ADUN with a standard laboratory pH meter and then adjusting the in-line units to indicate these values. Use of the ADUN as a buffered solution for calibration was found to be much simpler than the addition and removal of standard buffer solutions.

Evaluation of the in-line units showed that each is adequate to meet the resin-loading process requirements. No gross errors were observed. Changes between calibrations were usually small; in a few instances, corrections of 0.2 to 0.4 pH unit became necessary after shutdowns of several days to several weeks. The Leeds and Northrup system proved to be the most satisfactory since the other two systems displayed minor faults. The Beckman system showed differences of up to 0.2 pH unit from the other two in-line pH measurements and the laboratory meter as a result of changes in temperatures and flow rates. The Foxboro system showed slower responses to changes in pH which appeared to result from channeling of the ADUN flow without complete displacement of the solution in the meter. Also, the Foxboro in-line element was much larger and heavier than the other two. The suitability of the seals, electronic components, and case materials for in-cell radiation exposures has not been evaluated. Any differences in these or other attributes might be more significant than the minor differences mentioned above.

The NO_3^-/U ratios were determined from the pH measurements by using graphical correlations (Fig. 5). These correlations show that NO_3^-/U ratios vary only moderately with uranium concentrations and that the determination of uranium concentrations from densities is more than adequate.

Numerical data in Appendix D show the importance of the final NO_3^-/U ratio and the small effect of uranium (or NO_3^-) concentration.

7.5 Experimental Results

The control and behavior of the ADUN concentrations during resin loading result from the addition and removal of three components. The ADUN volume is determined by the addition and removal of water. The uranium concentration varies as a result of uranium additions or removals and changes in volume. Changes in the NO_3^-/U ratio arise from the addition or removal of nitrate and uranium (but not water). The uranium removal rate depends on the ADUN tank NO_3^-/U ratio, the resin loading exit (equilibrium) NO_3^-/U ratio, and the ADUN flow rate. The water removal rate is set by the evaporator rate. The nitrate removal rate is set by the rate at which caustic is introduced to the regeneration contactor after the nitrate extraction system has attained steady state; however, changes in solvent or caustic flow rates result in complex unsteady-state rates. The material balances were used to calculate these concentrations throughout a typical run (Table 4) and two other runs (Tables 5 and 6).

The changes during a run are illustrated by graphs of ADUN concentrations vs time. In a normal or typical run (Fig. 14), the initial and final uranium concentrations are approximately the same, with a minimum occurring at some intermediate time. A large volume decrease is required to correspond to the removal of uranium by the resin. The NO_3^-/U ratio starts at an intermediate value (resulting from the addition of uranium feed before the run is started) and goes through a maximum as a result of high initial uranium removal rates.

Table 4. Calculations of ADUN concentrations and uranium loading rates for run S51

Product resin: 8997 g, 37.09 wt % uranium, 28.0 equiv uranium

Time Clock	Run (min)	ADUN data			ADUN calculated			Incremental ^a NO ₃ ⁻ removed (moles)		Exit pH	Resin loading		Uranium loading rate (equiv/liter)		Uranium loaded (equiv)	
		Volume (liters)	U conc. (N)	pH	NO ₃ ⁻ /U ratio (mole/mole)	NO ₃ ⁻ (moles)	U (equiv)	From flows	From pH		Exit NO ₃ ⁻ /U	Flow (liters/min)	Calc. ^a	Ave. ^a	Incremental ^a	Total
0900	-15	138	0.41	2.75	1.80	50.9	56.6	-	-	-	2.6	-	0.126	-	-	-
0920	5	139	0.405	2.75	1.80	50.7	56.3	0	0.2	0.95	2.5	1.9	0.113	0.120	1.14	1.14
0940	25	132	0.38	2.55	1.91	47.9	50.2	1	2.8	1.10	2.4	1.9	0.078	0.095	1.61	4.75
1000	45	124	0.37	2.55	1.93	44.3	45.9	3.7	3.6	1.18	2.35	1.9	0.066	0.072	2.74	7.49
1020	65	118	0.36	2.57	1.93	41.0	42.4	3.7	3.3	1.23	2.35	1.9	0.064	0.065	2.47	9.96
1040	85	112	0.36	2.63	1.90	38.3	40.3	3.7	3.7	1.31	2.3	1.9	0.063	0.064	2.44	12.49
1100	105	106	0.36	2.68	1.88	35.3	38.2	3.7	2.4	1.36	2.3	1.9	0.066	0.064	2.44	14.82
1120	125	100	0.35	2.75	1.82	31.9	35.0	3.7	4.0	1.74	2.1	to 4.9	0.047	0.058	2.20	17.02
1140	145	94	0.35	2.87	1.75	28.6	32.9	3.7	3.6	2.78	1.85	4.9	0.021	0.034	3.33	20.35
1200	165	88	0.35	3.00	1.68	25.9	30.8	3.7	2.7	2.91	1.8	4.9	0.023	0.022	2.16	22.51
1220	185	82	0.36	3.18	1.55	22.7	29.5	3.7	3.2	3.09	1.65	4.9	0.024	0.023	2.25	24.77
1240	205	76	0.37	3.30	1.48	20.8	28.1	1.9	1.9	3.23	1.55	4.9	0.017	0.020	1.96	26.73
1300	225	70	0.41	3.30	1.45	20.8	28.7	0	0	3.25	1.48	4.9	0.008	0.012	1.18	27.91
1320	24	70	0.40	3.32	1.45	20.3	28.0	0	0.5	3.25	1.48	4.9	0.008	0.008	0.78	28.69
1450	335	70	0.40	3.35	1.45	20.3	28.0	0	0	3.31	1.46	4.9	0.003	0.004	1.76	30.45

^a Incremental amounts are from previous run time to listed run time.

Table 5. Calculations of ADUN concentrations and uranium loading rates for run S44

Product resin: 10,377 g, 39.57 wt % uranium, 34.5 equiv uranium

Time	Run	ADUN data			ADUN calculated			Increment (l ¹) NO ₃ ⁻ removed (moles)			Resin loading		Uranium loading rate		Uranium loaded	
		Volume (liters)	U conc. (N)	pH	NO ₃ ⁻ /U ratio (mole/mole)	NO ₃ ⁻ (moles)	U (equiv)	From Flows	From pH	Exit pH	Exit NO ₃ ⁻ /U	Flow (liters/min)	Calc. ^a	Ave. ^a	Incremental ^b	Total
0820	-10	100	0.41	3.07	1.60	32.8	31.0	-	-	-	2.6	1.9	0.158	-	-	-
0840	10	102	0.38	3.1	1.60	31.0	30.8	1.3	1.8	3.1	2.5	1.9	0.137	0.158	2.81	2.81
0900	30	106	0.32	3.01	1.70	28.8	33.9	2.7	2.2	3.25	2.45	1.9	0.098	0.12	4.56	7.37
0920	50	98	0.29	3.02	1.72	26.5	28.4	2.7	3.3	3.3	2.4	1.9	0.082	0.09	3.42	10.79
0940	70	90	0.27	3.03	1.74	24.1	25.3	2.7	3.4	3.5	2.35	1.9	0.070	0.076	2.89	13.68
1000	90	82	0.25	3.1	1.69	17.3	20.5	2.7	3.8	3.55	2.3	1.9	0.066	0.068	2.58	16.26
1020	110	74	0.23	3.16	1.65	14.1	17.0	2.7	3.2	3.64	2.3	1.9	0.065	0.065	2.37	18.63
1040	130	66	0.21	3.05	1.75	12.1	13.9	2.7	2.0	2.55	2.05	3.9	0.031	0.05	4.35	23.08
1100	150	58	0.18	3.11	1.74	9.1	10.4	2.7	3.0	2.9	1.9	3.9	0.015	0.023	2.25	25.33
1120	170	50	0.17	3.30	1.62	6.9	8.5	2.4	2.3	3.1	3.78	3.9	0.013	0.013	1.42	26.81
1140	190	42	0.165	3.29	1.60	5.5	6.9	1.9	1.4	3.2	1.7	3.9	0.010	0.013	1.27	28.08
1200	210	33	0.15	3.41	1.52	5.1	6.8	1.9	0.5	3.3	1.65	3.9	0.012	0.011	1.08	29.16
1300	270	33	0.13	3.41	1.54	5.5	5.9	0	0.6	3.35	1.5	3.9	0.005	0.008	2.35	31.5
1500	390	45	0.11	3.38	1.60	5.0	5.0	0	0.5	3.38	1.60	3.9	0	0.003	1.76	33.26

^aIncremental amounts are from previous run time to listed run time.

Table 6. Calculations of ADUN concentrations and uranium loading rates for run 543
Product resin: 9972 g, 41.61 wt % uranium, 34.9 equiv uranium

Time	ADUN data		ADUN calculated			Incremental ^a		Resin loading ^a		Uranium		Uranium loaded (equiv) Incremental ^a Total	
	Run Volume (liters)	U conc. (N)	NO ₃ ⁻ /U ratio (mole/mole)	NO ₃ ⁻ (moles)	U (equiv)	NO ₃ ⁻ removed (moles) From flow	Exit pH	Exit NO ₃ ⁻ /U (liters/min)	loading rate (equiv/liter) Calc.	Ave. ^a			
0900	-10	105	0.55	3.17	1.46	42.2	57.8	-	-	2.6	1.9	0.241	-
0920	10	105	0.53	3.04	1.58	43.9	55.7	0	-1.7	1.2	1.9	0.181	0.21
0940	30	106	0.49	2.72	1.78	46.2	51.9	0	-2.3	1.4	1.9	0.094	0.14
1000	50	110	0.44	2.65	1.84	44.5	48.4	3.7	1.7	1.5	1.9	0.064	0.08
1020	70	103	0.41	2.68	1.85	39.1	42.2	3.7	5.4	1.7	1.9	0.016	0.05
1040	90	94	0.39	2.70	1.85	33.9	36.7	3.7	5.2	2.4	4.9	0.029	0.033
1100	110	85	0.39	2.74	1.82	30.2	33.2	3.7	3.7	2.5	4.9	0.024	0.027
1120	130	76	0.39	2.85	1.76	26.1	29.6	3.7	4.1	2.7	4.9	0.019	0.022
1140	150	78	0.37	2.99	1.68	24.2	28.9	3.7	1.9	2.9	4.9	0.017	0.018
1200	170	80	0.45	3.13	1.58	22.1	28.0	3.7	2.1	3.0	4.9	0.025	0.021
1220	190	80	0.44	3.23	1.50	20.4	27.2	2.0	1.7	3.1	4.9	0.021	0.023
1400	290	80	0.34	3.19	1.54	20.9	27.2	0	0	3.15	4.9	0.004	0.010
													4.90
													31.26

^aIncremental amounts are from previous run time to listed run time.

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Fig. 14. Acid-deficient uranyl nitrate concentrations and volumes for a reference batch loading run.

The end-of-campaign loading procedure (discussed in more detail in Sect. 7.6) gives different curves (Fig. 15). The uranium concentration is reduced to a low final value by using a longer run time. The initial NO_3^-/U ratio is low as a result of small additions, if any, of uranium feed before the run. The final ADUN volume is the minimum that allows continued operation.

The desired conditions for operation with continuous resin loading (the Higgins column) are constant inventories of nitrate and uranium. With these inventories constant, the NO_3^-/U ratio will be constant and the uranium removal and nitrate removal will equal the feed rates. The water inventory (ADUN volume) will vary as a result of returns of wash water from resin drying, but this should not change the NO_3^-/U ratio. Values for one period of operation with the Higgins column are shown in Fig. 16.

The measured ADUN values and material balance calculations used in preparing Figs. 14 and 15 are listed in Tables 3-5. The uranium concentrations were obtained from density measurements and Eq. (4b). The pH values from the in-line instruments are used with Fig. 5 and similar plots to estimate NO_3^-/U ratios. The ADUN volumes are interpolated from several measurements performed during the runs and from the known evaporator and scrub rates. The nitrate removal rates obtained from the difference in calculated amounts of nitrate are in reasonable agreement with those calculated from the caustic regeneration rate.

Uranium loading rates can be calculated from the ADUN concentrations and flow rates for the resin loading contactor. Integrating these rates or determining the differences in ADUN uranium inventory gives 80 to 110%

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Fig. 15. Acid-deficient uranyl nitrate concentrations and volumes for an end-of-campaign loading run.

Fig. 16. Acid-deficient uranyl nitrate concentrations and volumes for a continuous (Higgins column) loading run.

of the amount of uranium shown by analyses of dried resin. These are reasonable checks when one considers the many approximations in both measurements. The uranium material balances generally show that 50 to 75% of the uranium has been loaded when the ADUN flow to the loading contactor is increased; this observation is consistent with the equilibrium data (Fig. 4). The calculated uranium loading rates near the end of the runs are of poor accuracy since they depend on pH differences of less than 0.1 unit.

The engineering-scale resin loading system was operated for 54 batch loading runs and 22 batches of resin from the continuous (Higgins) contactor tests to prepare more than 600 kg of dried, uranium-loaded resin. Some of the results are tabulated in Appendix D. This program was completed without a single failure of the process outlined in the chemical flowsheet or any evidence of inability to control the conditions dictated by the flowsheet. Every batch of resin was processed through the desired loading cycle; several runs which were interrupted by mechanical problems (e.g., a leak of the ADUN solution or an instrument failure) were simply shut down and then resumed after mechanical repairs had been completed. The only incompletely loaded resin batches resulted from tests of short duration, end-of-uranium batch conditions, or other special circumstances which explain the results. One batch loading run per 8-hr day was made for six successive workdays (runs S29 through S34) to demonstrate operation of the complete engineering-scale system. The failure of the initial Higgins column tests stemmed from mechanical problems⁷ which have no significance for the batch resin loading flowsheet.

7.6 End-of-Campaign Loading Procedures and Results

For ^{233}U recycle, the ^{233}U destined for use with different isotopic compositions or in different reactors would have to be refabricated in separate campaigns. Thus the uranium remaining at the end of the last resin loading run for a campaign would have to be removed from the system and subsequently shipped or stored. Tests were made to demonstrate that special loading runs could be made to minimize this final inventory. In these tests, a resin volume was selected that would leave less than 1 kg of uranium inventory after a full loading of the resin. The rate of nitrate extraction was reduced and longer run times were used so that resin loading could be carried out to low uranium concentrations. The minimum ADUN volume was about 40 liters during resin loading. Almost half of this volume is in the loading contactor. After loading and drying had been completed, nitric acid was added to increase the NO_3^-/U ratio to about 2. The ADUN was concentrated to the minimum volume that allowed normal operation of the evaporator. Using these procedures, a 7.3-liter batch of resin was loaded to a normal uranium content (run S41), leaving 0.8 kg of uranium in solution. A normal size batch of resin was loaded to a slightly low uranium content (run S44, Table 4), leaving 0.5 kg uranium in solution. The NO_3^-/U ratio increased after the nitrate extraction had ceased (see discussion in Sect. 7.3). A short period of additional nitrate extraction and a longer run time would probably have loaded sufficient additional uranium to achieve the normal uranium content. These results indicate that the proposed end-of-campaign procedures are adequate.

8. EFFECTS OF FEED RESIN VARIABLES

The variables for the feed resin have only small effects on the operation of the engineering-scale resin loading system. Numerical results are tabulated in Appendix D. The amount of uranium loaded per unit volume of feed resin is about 20% greater for Amberlite IRC-72 than for Duolite C-464. The size and shape of the resin particles can result in $\pm 5\%$ variations in capacity as a result of their effects on packing density or void volume between particles. The loading and nitrate extraction are controlled by the concentrations of the ADUN; therefore, the variations in resin capacity do not require any control measurements or actions.

A 50- μ -rated filter is used to remove solids from the ADUN. The Amberlite IRC-72 has fine resin particles when received, but most of these are removed by wet and dry screening in a resin feed preparation facility. One lot of the Duolite C-464 released small chips or pieces apparently generated by erosion of the surface of the resin spheres. The 0.6-ft² filter cartridges in the engineering-scale system filter was usable for many runs with Amberlite IRC-72 resin but showed significant plugging after several runs with this lot of Duolite C-464 resin. Plugging was not noticeable in later runs made with another lot of Duolite C-464.

Variations in particle size or shape of the resin feed are carried through to the uranium-loaded product but do not have any effect on the mode in which the engineering-scale resin loading system must be operated.

9. MECHANICAL COMPONENTS, RESIN TRANSFERS, AND EQUIPMENT SELECTION

This section will briefly report results and observations from operation of the engineering-scale resin loading system which do not fit in elsewhere but need to be considered during the design of a remotely operated facility. The engineering-scale resin loading system is not a prototype system; that is, some of the components are either not optimum or are unsuitable for a remotely operated pilot plant.

9.1 Pumps and Liquid Metering

The ADUN pump is a standard type of canned-rotor centrifugal pump^{*} with graphite bearings. A similar pump with special aluminum oxide bearings was reserved for use in case the graphite bearings presented problems; however, no difficulties have been encountered. The graphite bearings would probably have a longer life under normal process conditions; on the other hand, the aluminum oxide bearings would allow pumping of hot, nitric acid solutions at concentrations which would attack the graphite.

The only special problem with metering the ADUN solution involved the effects of entrained resin fines. These fines were removed by use of standard filter cartridges of 25- μ m or 50- μ m rating between the ADUN pump and the flow metering and control instrumentation. The amounts of fines were small for Amberlite IRC-72 resin processed in the resin feed preparation facility, and use of the resin for ten runs did not decrease the filter flow capacity.

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^{*}Chempump Model SF-3/4-3/4S.

The nitrate extraction solvent was metered and pumped by cam-operated Teflon bellows pumps^{*} using gage glasses with stopwatches to check the flow rates. These pumps, which were initially selected for the prototype SOLEX equipment,¹¹ were completely trouble-free. However, the Teflon bellows and the gage glass and cam adjustment for flow control might not be acceptable for remote operation.

9.2 Temperature Control

The nitrate extraction system was provided with a hot-water temperature control system carefully engineered to meet SOLEX process requirements.¹¹ While temperatures of 40 to 60°C improve phase separation and provide more favorable kinetics for resin loading, the temperatures are much less critical than for SOLEX. Two heat exchangers, one for the ADUN flow from the pump and one for solvent to the caustic regeneration contactor, would provide adequate control for resin loading.

9.3 Resin Transfers

The resins in either the hydrogen- or uranium-loaded forms can be transferred very easily by a small excess of water over that present in a settled bed, or by air after drying to remove all surface liquid. Gas or liquid pressures of less than 10 psig were used for routine transfer through 20 ft of 1/2-in.-ID tubing, including numerous bends and ball valves. However, there are two situations in which transfers can be impossible and these must therefore be avoided. If liquid is drained from between the resin particles, the surface films of liquid hold the

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^{*}Research Appliance Co. Micro Bellows pumps.

particles together and restrict movement. Therefore, wet resin flows very poorly as compared with either dry resin or resin in an excess of solution.

The second situation that should be avoided is settling or packing of resin into a line since any restriction, even a very minor one, may make resumption of flow impossible. To avoid this problem, all resin reservoirs were provided with valves as close to the reservoir as possible for bottom connections. All transfers of resin were followed by a volume of liquid or gas to empty the transfer lines of resin particles. The characteristics of a packed bed of resin are such that high pressure drops cannot overcome the effects of the flow restriction on a line. If no restriction exists, fluid flows between the resin spheres and refluidizes the line starting at the leading edge of the packed resin. If a restriction does exist, the resin packs tighter at the point of restriction and high pressures can cause formation of a plug -- perhaps from deformation and locking together of the porous plastic spheres. One special example of a restriction is the bed of resin in the batch loading contactor. If the ADUN flow is shut off without closing the valve at the bottom of the contactor, resin settles into this line. Once this has settled completely, the weight of the resin in the contactor restricts the return of resin from the line. Consequently, solution pressure is not effective for return of the resin into the loading contactor against the settled bed. For this reason, the shutoff valve near the contactor must be closed first before the pump is shut off, or the flow is otherwise interrupted.

10. DISCUSSION AND CONCLUSIONS

A complete engineering-scale system was installed and tested for the uranium-loading part of a resin-based preparation of HTGR fuels. The system was full scale (4 kg of uranium per batch) for the Hot Engineering Test Program (HETP) facility planned for the Thorium-Uranium Recycle Facility. The procedure that was developed requires about 4 hr of solution-resin contact time for loading and less than 4 hr for the associated operations including resin drying. The engineering-scale system with alternate use of two batch loading contactors would have the capacity for a commercial recycle facility (24 kg of ^{233}U per day), and would not require scale-up.

The engineering-scale resin loading system developed and tested the concepts critical to meeting the requirements for remote operation with ^{233}U . It was operated with natural uranium and was not a prototype system. Manually operated or observed valves, fluid metering, and fluid control devices were used since the resin loading process does not impose any special requirements on these components.

The uranium feed to a resin loading system is uranyl nitrate containing some excess nitric acid. The uranium is removed from solution by exchange of UO_2^{2+} for H^+ in carboxylic acid cation exchange resins. The reference contactor is a 5-in.-ID fluidized bed with 11- to 13-liter batches of resin. An evaporator specially designed and fabricated for this system removes the water as condensate containing less than 0.5 ppm of uranium. The nitrate is extracted as nitric acid by an amine solvent with regeneration of the solvent to give a NaNO_3 waste solution. The uranium content of this waste amounts to 0.03% of the total uranium

loaded on the resin. The solvent extraction equipment was that previously developed for sol-gel processes.^{10,11} The optimum water content of dried, uranium loaded resin was found to be 10 to 20 wt %. A microwave-heated dryer was installed and tested to provide controlled and uniform drying for this range of water content.

Satisfactory control of the resin-loading system was demonstrated. The resin loading reactions result in both equilibrium and kinetic limitations on the process. The procedures for the engineering-scale resin loading system were chosen so as to allow operation to preselected end points for each batch. The uranium feed (4 kg of uranium per batch) is charged and mixed with about an equal amount of uranium remaining as process holdup between batches. The three removal processes (for UO_2^{2+} , HNO_3 , and H_2O) are started approximately simultaneously. The evaporator is operated until the volume of solution is reduced to a predetermined value. The nitrate extraction is operated until in-line pH instrumentation indicates that the NO_3^-/U ratio is reduced to a preselected value. The resin loading is continued for about 4 hr until a preselected combination of time and solution pH has been satisfied. Although the uranium concentrations could be adequately predicted by material balances, they were confirmed by in-line measurements of solution density. This combination of process control procedures has given trouble-free operation and excellent control of the resin loading. The in-line pH and density measurements are dependable and of adequate sensitivity. Small modifications of the loading procedure allow reduction of the uranium inventory as solution at the end of the special run to less than 1 kg of uranium.

Fifty-four batch loading runs were made without a single failure of the process outlined in the chemical flowsheet or any evidence of inability to control the conditions dictated by the flowsheet.

The reference Amberlite IRC-72 resin and the alternate Duolite C-464 resin do not require any differences in resin loading conditions. The Duolite C-464 resin has 10 to 20% lower capacities for uranium expressed as either milliequivalents of uranium per gram of dry H^+ -form resin or as equivalents of uranium per liter of resin.

The engineering-scale resin loading system was also operated with a 2-in.-ID Higgins type of continuous resin loading contactor in place of the batch contactor. Resin loading was good, with excellent steady-state control of the addition and removal of uranium, water, and NO_3^- . The demonstrated capacity of more than 1 kg of uranium per hour indicates that a single, critically safe system could easily load more than 100 kg of uranium per day.

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12. APPENDIXES

12.1 Appendix A: Descriptions of In-line pH and Density
Instrumentation for ADUN Solutions

Three in-line pH instrumentation systems were purchased as follows:

(1) Beckman Instruments, Inc. (Vendor)

- (a) Digital pH meter, Model 3500
Range: 0 to 14 pH
Temperature compensation: 0 to 100°C
- (b) pH Analyzer Model 940A
Lower range limit: 0 to 12 pH continuous adjustable
Span: Sel 2, 10, or 14 pH
Temperature compensation: 0 to 50°C
Recorder output: 4-20 mA
Scale: 0 to 5
- (c) pH Electrode Assembly Series 300
Cat. #300-2-0-17-1-1-1-0

(2) Foxboro Company (Vendor)

- (a) pH electrode flow through holder
Series 85C-2 with electrodes
- (b) pH to current converter, 699-FN-2J
Range: 2 to 14 pH
Operating range: 0 to 5 pH
Temperature compensation: automatic 0 to 50°C
Recorder output: 4 to 20 mA

(3) Leeds and Northrup Company (Vendor)

- (a) pH electrodes, transmitter and mounting assembly
Model 7773-1-1-02-2
- (b) pH receiver, 7073-11-03-402-6-20
Range: 0 to 4 pH
Output: 4 to 20 mA

The in-line density instrumentation was purchased as follows:

Automation Products, Inc. (Vendor)

Density Specific Gravity Instrumentation "Dynatrol"
Density-SFG Control Type CL-10HY Combo Series 300G
Process connection: 1/2 in. NPT
Material: Stainless steel
Specific gravity range and access: 1 to 1.5 $\pm$ 0.1%
Flow rate: 1 to 5 liters/min
Output: 4 to 20 mA

12.2 Appendix B: Scale-up for Commercial Recycle Plants

Full-scale commercial reprocessing and refabrication of HTGR fuels would require capacities of about 1.2 kg/hr or 30 kg/day for both ^{233}U and recycle ^{235}U . This capacity was demonstrated during tests of the Higgins continuous loading contactor (Sect. 3.3). The purpose of this appendix is to suggest a flowsheet for the scale-up using batch loading contactors.

The minimum cycle duration for a batch uranium loading contactor is the sum of three times, as follows:

1. The time required to pass enough uranium (ADUN solution) through the resin to complete about 80% of the uranium loading. Both the ADUN uranium concentration and the ADUN flow rate are limited if the resin is to be fluidized. The diameter or cross section for flow is limited to permit control of criticality. Operation under conditions which pack the resin against the exit screen are undesirable because refluidization is difficult.
2. The time to complete the last 10 to 20% of uranium loading. This time, which is 2 hr, cannot be significantly shortened. Although this time is almost independent of the batch size, the ADUN must be at a favorable acid deficiency.
3. The time required to discharge the uranium-loaded resin, charge fresh resin, etc. During this period, the contactor is "off-stream" and does not require ADUN flow.

While operation to discharge one resin batch containing 4 kg of uranium every 3 hr is not impossible, a cycle with 8 kg every 6 hr appears much more practical. Two pairs (a total of four) of resin loading

contactors of the size tested (5 in. ID, 4 kg of uranium per batch) could be operated alternately with one pair "on-stream" at a time with a controlled ADUN flow to each contactor. The same cycle could be used with two critically safe contactors (slab, annulus) of twice the cross-sectional area of the 5-in.-ID contactors and 8 kg of uranium per batch. The 6-hr cycle time allows a well-controlled approach at a moderate rate to the preferred ADUN concentrations. A 3-hr cycle time allows little time for correction and may require overlapping cycles.

12.3 Appendix C: Operating Schedule for a 4-hr Cycle

The process operations for resin loading can be carried out in many different sequences. The example shown as Table 7 would allow alternate operation of two loading contactors to discharge a batch of loaded resin (4 kg of uranium) every 4 hr. For a smaller daily capacity, the addition of uranyl nitrate feed, the return of wash water, and the resulting ADUN volume adjustments might be done between resin loading operations in order to minimize the process changes during resin loading.

12.4 Appendix D: Tabulated Run Conditions and Results

Some run conditions and data for different resin types and batch numbers are tabulated (Table 8). The size and shape separation treatments of feed resin did not have any significant effects on the uranium loading results and are therefore not included. The results of end-of-campaign procedures and other process variations are shown, along with results for the most similar run without such variations (Table 9).

Table 7. Schedule and flow rates for amine extraction process

Time (min)	Process criteria or operation
0	Start ADUN flow to resin loading, 1.7 liters/min.
3	Start UNH feed flow, 0.5 eq/min.
6	Start scrub flows to amine regeneration, 0.1 liter/min.
8	Start solvent flow to amine regeneration, 0.8 liter/min.
10	Start caustic flow to amine regeneration, 0.16 liter/min.
15	Start steam to evaporator at 0.6-liter/min condensate rate.
40 to 60	Receive approximately 30 liters of transfer and wash solution from resin dryer.
~71	Stop UNH feed (approximately 4 kg of uranium added).
~90	When resin exit pH ≥ 1.6 , increase resin loading flow to 5 liters/min.
~120	Receive overflow from charging new batch of feed resin to other resin loading contactor (~12 liters).
~150	When ADUN concentration or volume reaches preselected value, turn off evaporator.
~156 ~158 ~160	When pH of ADUN from surge tank has pH ≥ 3.2 , shut off amine regeneration system in reverse order (caustic, solvent, scrub).
235	Shut off resin loading contactor (check pH of ADUN to confirm loading).

Table 8. Some resin loading results with reference batch loading flowsheet procedures

Equipment: engineering-scale resin loading system

Feed resin Type	Lot No.	Run No.	Final ADLN		Uranium loading	
			pH	NO ₃ /U (mole/mole)	wt % U (dry basis)	meq U ml resin (wet)
Amberlite IRC-72	2-5990	S02	3.25	1.50	49.3	3.22
		S07	3.10	1.60	48.3	3.12
		S08	3.15	1.60	48.3	3.12
Amberlite IRC-72	2-5612	S14	3.15	1.60	46.3	3.13
		S17	3.20	1.50	45.9	2.89
		S18	3.20	1.50	47.4	2.95
Amberlite IRC-72	2-3947	S23	3.45	1.40	46.2	2.88
		S29	3.00	1.70	46.3	2.95
		S30	3.15	1.50	47.5	3.10
		S31	3.05	1.60	46.7	3.08
		S32	3.05	1.60	46.8	3.09
		S33	3.10	1.60	46.8	3.04
		S34	3.15	1.55	47.5	3.11
		S46	3.30	1.45	47.5	3.00
Amberlite IRC-72	2-6681	S50	3.30	1.50	48.5	3.21
		S51	3.40	1.45	48.5	3.15
		S52	3.40	1.45	48.6	3.22
		S54	3.35	1.45	50.6	3.33
Duolite C-464	1-4J	S04	3.15	1.60	44.4	2.40
		S05	3.05	1.65	44.4	2.30
		S06	3.15	1.60	43.1	2.30
Duolite C-464	2-60	S45	3.60	1.40	43.3	2.41
		S48	3.35	1.45	43.4	2.59
		S49	3.35	1.45	43.6	2.49
		S53	3.40	1.45	44.5	2.51

Table 9. Effects of some flowsheet variations on resin loading

Feed resin		Run No.	Flowsheet variable and values	Uranium loading		
Type	Lot No.			wt % U (dry basis)	meq U ml resin (wet)	
Amberlite IRC-72	2-5990	S01	Final U conc.	0.42 $\underline{\text{M}}$ U	48.5	3.17
		S02		0.21 $\underline{\text{M}}$ U	49.3	3.22
		S11		0.11 $\underline{\text{M}}$ U	47.2	3.02
Amberlite IRC-72	2-3947	S44	Low final U	500 g	46.2	2.81
		S41	inventory (see	800 g	48.4	3.05
		S43	Sect. 7.6)	3200 g	48.7	3.16
Amberlite IRC-72	2-3947	S37	Time at NO_3^-/U	1.7 hr	45.98	2.78
		S38	ratio of 1.7	2.2 hr	46.41	2.87
Amberlite IRC-72	2-5612	S17A		2.0 hr	45.89	2.89
		S17B		3.1 hr	45.83	--
		S18A		1.8 hr	47.42	2.95
		S15B		3.8 hr	47.71	--
		S18C		10 hr	47.73	--
Amberlite IRC-72	2-3947	S36	Final ADUN	1.77 mole/mole	44.4	2.61
		S38	NO_3^-/U ratio	1.62 mole/mole	46.4	2.87
		S40		1.50 mole/mole	48.8	3.28
		S46		1.45 mole/mole	47.5	3.00
		S23		1.40 mole/mole	46.2	2.88