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DESIGN OF A CRITICALLY SAFE ²³³U BATCH

DISSOLVER FOR BUILDING 3019

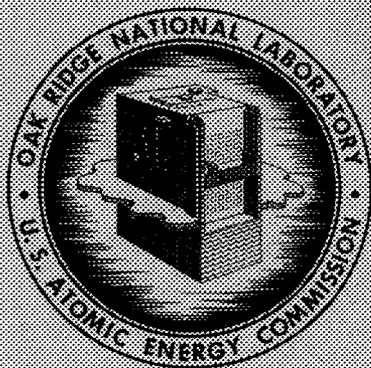
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CHEMICAL TECHNOLOGY DIVISION

DESIGN OF A CRITICALLY SAFE ^{233}U BATCH DISSOLVER
FOR BUILDING 3019

A. M. Rom

OCTOBER 1966

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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ABSTRACT

A critically safe small-scale ^{233}U dissolver system for dissolving gram quantities of ^{233}U was needed for the ^{233}U storage and distribution facility at ORNL.

Criticality requirements were satisfied by limiting equipment diameters to 4 in., except for a 5-in. heating jacket on the dissolver, restricting the mass of bulk fissionable metal pieces permitted in the dissolver, and spacing the various equipment components with respect to each other and with existing equipment in the cell. The dissolver system, with its nominal 16-liter volume, can dissolve ^{233}U in amounts ranging from a few grams to 5 kg or more per day equally well.

This new 4-in. dissolver, designated S-15, supplements the Thorex dissolver S-1, which is 54 in. OD and more than 67 in. high.

INTRODUCTION

This report describes the work that was begun in June 1965 to design a critically safe ^{233}U dissolver system to supplement the old Thorex S-1 dissolver. Dissolving solid forms of fissionable ^{233}U to produce nitrate solutions is a necessary part of the ^{233}U storage and distribution operation at ORNL. Uranium-233 received for storage usually arrives as oxide powder, metal turnings, metal scrap, or metallurgical slag and is canned in aluminum and shielded as necessary. It can be stored in Building 3019 either as a solid or a liquid; however, the storage capacity for liquids is much greater than that for solids. In addition, and perhaps more important, ^{233}U is much more conveniently handled immediately after solvent extraction has removed the hard-gamma-emitting radionuclides, primarily ^{208}Tl and ^{212}Bi , that are present as a result of ^{232}U decay (some ^{232}U is always formed along with ^{233}U in a nuclear reactor).¹⁻⁴ Hence, even if ^{233}U is initially stored as a solid, its dissolution will eventually be necessary to allow removal of ^{208}Tl and ^{212}Bi .

With the Thorex S-1 dissolver (550-gal capacity), which is 54 in. OD by 67 in. long, it is necessary to limit the amount of dissolved ^{233}U to 10 kg, to limit the concentration of the product to 8 g/liter, and to dissolve the ^{233}U in a neutron-absorbing $\text{Th}(\text{NO}_3)_4$ solution containing 280 to 300 g of $\text{Th}(\text{NO}_3)_4$ per liter. The thorium serves both as a neutron poison during dissolution and as a salting agent during solvent extraction.

The large-sized S-1 dissolver and associated 6-kg/day Kilorod Solvent Extraction Facility were unsuitable for processing low-gram amounts of ^{233}U . Now, requests for small amounts can be conveniently met with the critically safe batch dissolver S-15 described herein and the 1-kg/day Single-Cycle Solvent Extraction Glove Box Facility described elsewhere.⁵

Criticality is controlled by limiting all vessel diameters to 4 in., except for the dissolver heating jacket, which is 5 in. in diameter, and also by carefully spacing the equipment so that a chain reaction between the contents of individual components or with other existing equipment is avoided. In addition, a mass limitation is imposed where the material to be dissolved is in the form of bulk metal pieces.⁶

Information on the critically safe S-15 dissolver system is discussed in this report under the following headings: stoichiometry; dissolver design, including steam jacket, slide valves, inner basket, draft tube, and instrumentation; liquid-vapor separator and condenser. A drawing of the equipment as finally evolved is shown in Fig. 1.

The author acknowledges the assistance of many during this assignment, particularly J. P. Nichols, for his advice on criticality matters, J. R. Parrott for supplying basic information concerning the problem, and E. L. Nicholson and H. E. Goeller for reviewing the preliminary draft of this report.

DISSOLVER

Design requirements for the new ^{233}U dissolver system, which, along with dissolver S-1, is located in cell 5 of Building 3019, were that it be (1) critically safe, (2) "contained," and (3) able to dissolve ^{233}U in amounts ranging from a few grams to 5 kg per day. The concentration of ^{233}U in solution was not to exceed 150 g/liter.

Uranium-233 in oxide form is received in aluminum cans that are 10 in. long by 2-3/4 in. OD, with 0.040-in. wall thickness, each of which contains approximately 450 g of ^{233}U . This material currently constitutes the major portion of the dissolving load and was therefore used as the design basis. However, the capabilities of the critically safe dissolver are not limited to this material; other materials such as mixed thorium and uranium sol-gel fuels may be dissolved, or chopped stainless steel or zirconium fuel elements may be leached.

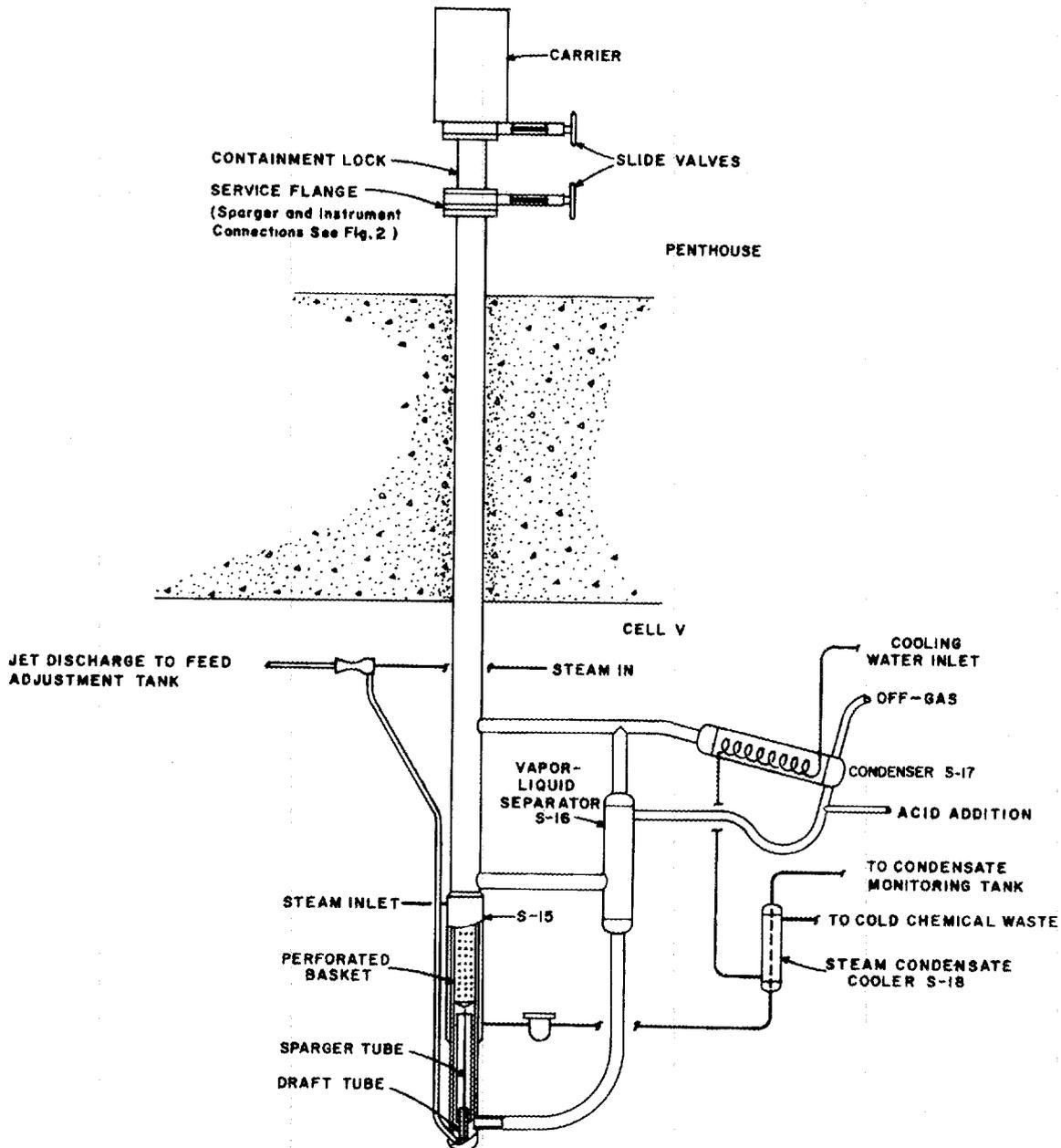
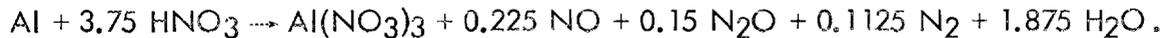


Fig. 1. Critically Safe ^{233}U Dissolver System.

Stoichiometry

Mercury-catalyzed HNO_3 (6 to 8 M HNO_3 plus an amount of mercuric nitrate equal to 5% of the weight of aluminum to be dissolved) is used to dissolve the aluminum can; excess HNO_3 dissolves the uranium oxide. The following equation has been proposed to describe the dissolution reaction for the aluminum can:⁷



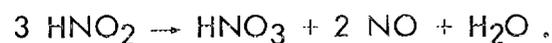
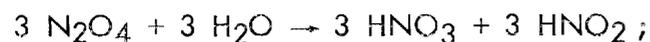
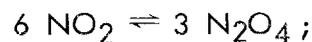
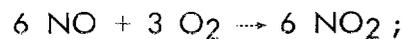
The exact proportion of the various oxides of ^{233}U present inside a can is not known precisely; however, since $^{233}\text{UO}_2$ constitutes, by far, the largest percentage, 100% $^{233}\text{UO}_2$ was assumed for design purposes. Uranium dioxide and HNO_3 react to form uranyl nitrate in a manner that may be described by the following simplified reactions recorded in the literature:⁸



or



Our design, through the use of a cocurrent-flow, downdraft condenser, prolongs the contact time between the nitrogen oxides and the condensate to favor better utilization of nitric acid. The chemical reactions describing this have been proposed as follows:⁸



The oxidation of NO to NO_2 is believed to occur rapidly; absorption of the NO_2 (or N_2O_4 , as the case may be) in water is believed to take place less rapidly and therefore is favored by the increased residence time in the cocurrent-flow, downdraft condenser.

The true stoichiometry of the dissolver will be determined only by actual operation of the dissolver system.

Dissolver Design

The dissolver, known as S-15 and shown in Fig. 2, is a jacketed thin cylinder with a removable, internal, perforated basket for supporting the fuel, and an air-actuated draft tube for resuspending settled fines. The dissolver extends through the

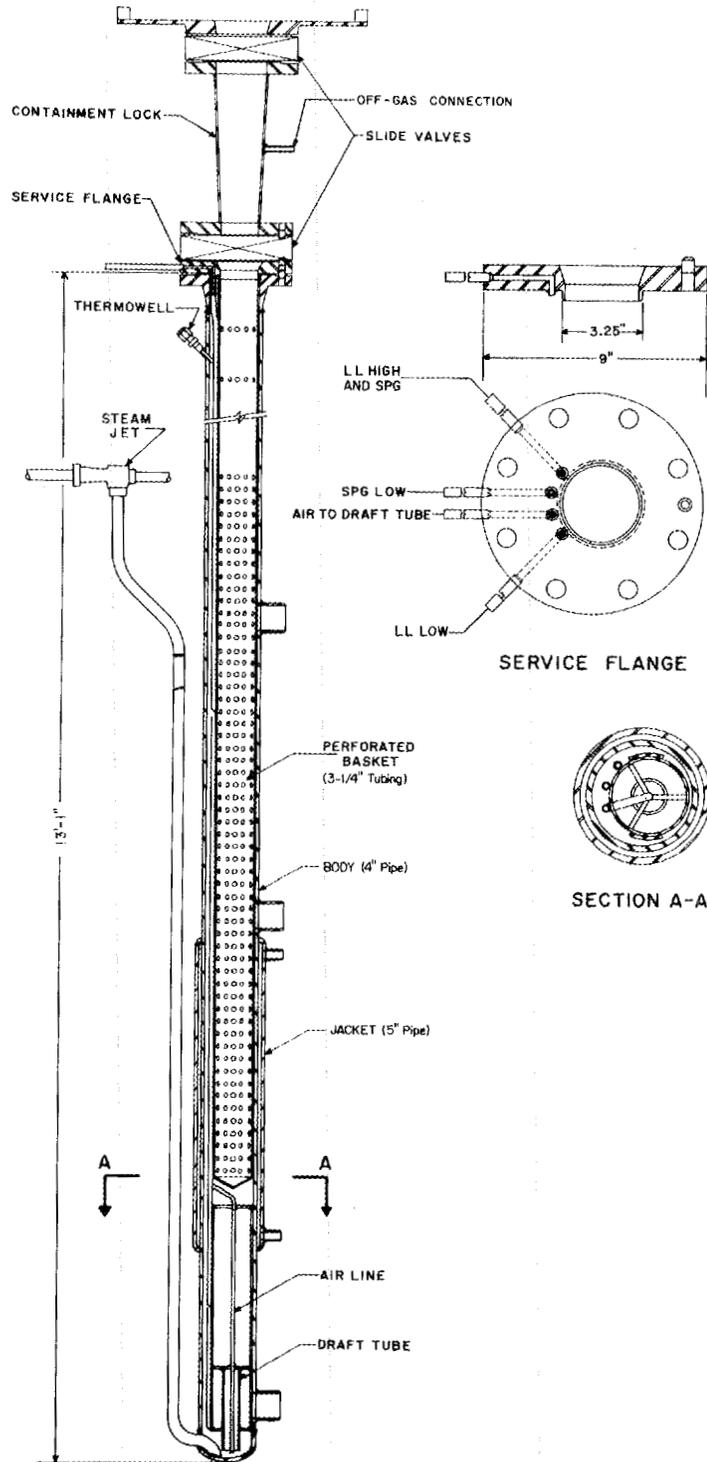


Fig. 2. Dissolver, S-15.

roof of the cell; the top portion, which is outside the cell, is fitted with two slide valves that enclose a chamber between them, forming an air-lock system to ensure containment during loading. Adjuncts to the dissolver, which will be discussed separately, are the liquid-vapor separator and downdraft condenser.

Outer Body

The dissolver body is 13 ft 1-1/16 in. long; it was fabricated from 4-in., sched-40 stainless steel (304L) pipe, with a welding cap used for the bottom and a welding-neck flange forming the top. The dissolver extends through a 5-in.-diam hole that was core-drilled through the 4-1/2-ft-thick concrete roof of the cell, and only its upper 16 in. protrudes.

Steam Jacket. — The bottom 1 ft 5-5/16 in. of the outer body is bare; the next 2 ft up are jacketed for steam service. The jacket is made from 5-in. stainless steel (304L) pipe, with the ends swaged down to 4-1/2 in. ID for welding onto the dissolver body.

A heat duty of 4240 Btu/hr was calculated for the jacket; this value was based on a calculated 2.23 ft² of heat-transfer area, an assumed overall heat-transfer coefficient U of 100 Btu hr⁻¹ ft⁻² °F⁻¹, a temperature of 250°F for the 15-psig steam, and an inside temperature of 231°F corresponding to boiling 36% or 7 *M* HNO₃ for an overall ΔT of 19°F. Heat is supplied to drive the reaction and to generate a thermosiphon by induced density differences between solution in the body and that in the liquid-vapor separator leg. Mixing and agitation are also promoted by the air-actuated draft tube discussed later.

Slide Valves. — The top of the dissolver body is fitted with a pair of De Zurik slide valves and a 13-7/8-in.-long, flanged, type 304L stainless steel spool piece between the valves to serve as a containment lock for introducing cans of material into the dissolver without breaking the containment. The valves used (De Zurik Bulletin 302, Fig. 457) were 4-in. nominal diameter, knife-gate, hand-wheel-operated, and bonnetless, and had a ring seal seat. The valve body was made from type 304L stainless steel; the seating material was Hycar RS-26; and the packing was Teflon-impregnated, type C, which is suitable for use at 450°F.

Piping Connections. — A jet suction line, made from 1/2-in. stainless steel (304L) pipe, runs along the outside of the dissolver to a height about 1-1/2 ft below the ceiling, inside the cell. The line penetrates the dissolver body at a point 1-3/4 in. from the bottom, and the open end extends to about 1/4 in. from the bottom to minimize the heel volume left by the jet. The suction line is serrated on the end to keep it from plugging, although it is not believed that solids in sufficient quantity or size will be present to cause plugging.

Dissolver Internals

The dissolver was designed for maximum versatility by simplifying the removal and the replacement of the internal basket, draft tube, and instrument tube assembly.

Inner Basket. — The inner basket is made from specially procured type 347 stainless steel tubing (3-1/4-in.-OD by 0.120-in.-wall aircraft tubing). The basket measures 11 ft 2-5/16 in. from the flange to the cone tip and is used to support fuel cans during dissolution. The lower 3 ft of the basket is drilled with 1/4-in. holes on 1-in. centers to permit free access of dissolvent to the fuel cans. To vent the upper reaches of basket to the dissolver body, the upper 8 ft of basket has a row of 1/4-in. holes on 2-in. centers occurring every 2 ft along the length.

Instrument Lines. — Three instrument air probes and a draft-tube air supply, 1/4 in. OD, are attached to the outside of the basket and connected to radial holes drilled in the top flange for connection to appropriate supply headers.

Draft Tube. — Earlier work indicated a need for keeping finely divided fuel material from settling to the bottom of the dissolver, where it may be difficult to dissolve. The most satisfactory of several arrangements that were tried and reported⁹ was one that used a 6-1/2-in. length of 1-1/2-in.-OD tubing that protruded 1-1/2 in. below a concentric 18-in. length of 3-1/4-in. tubing. A 1/4-in. air supply line centered within and concentric with the other tubes extended 1/4 in. beyond the 1-1/2-in. tube to within 1/2 in. of the dissolver bottom. The end of the 1/4-in. air supply tube was plugged, and three 0.020-in. holes were drilled 120° apart, 3/4 in. from the plugged end. An air rate of 0.15 scfm in a draft tube of identical design adequately kept a 1.6-kg charge of -16 mesh ThO₂-UO₂ suspended.⁹ Design details are shown in Fig. 2 and in ORNL drawing E-58125 (see Appendix).

DOWNDRAFT CONDENSER

The downdraft condenser, S-17, shown in Fig. 3, functions to return condensed vapors to the dissolver while permitting noncondensable gases to pass into the off-gas system for Building 3019.

The condenser is inclined downward in the direction of flow and exits condensed liquid at the lower end, with the cocurrent flow of gas and liquid enhancing the absorption of nitrogen oxide for more efficient acid utilization.

The condenser body is 24 in. overall, made of 4-in., sched-40 stainless steel (304L) pipe, with elliptical welding caps forming the ends. It is fitted with an internal, helically wound 3-in.-OD coil made from 5/8-in.-diam stainless steel (304L) tubing with a 0.035-in. wall thickness. Cooling water runs inside the coil; process vapors are in the shell. The vapor inlet is a 2-in.-diam nipple; the outlet for noncondensable gases is 1-in. nominal diameter, as is the condensate return. The condenser is fitted with a standard 1/4-in. thermowell on the downstream end.

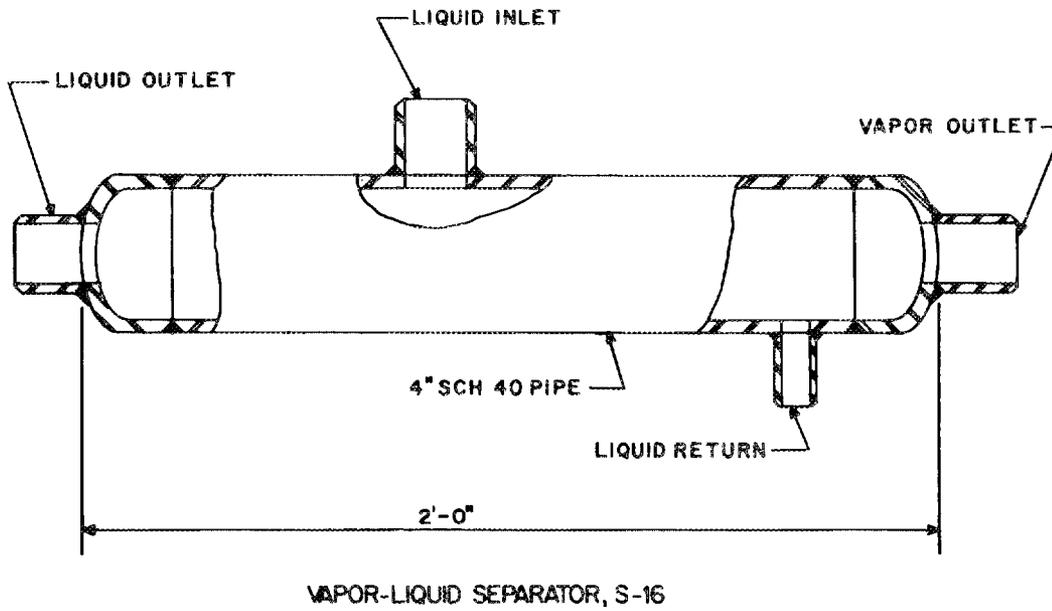
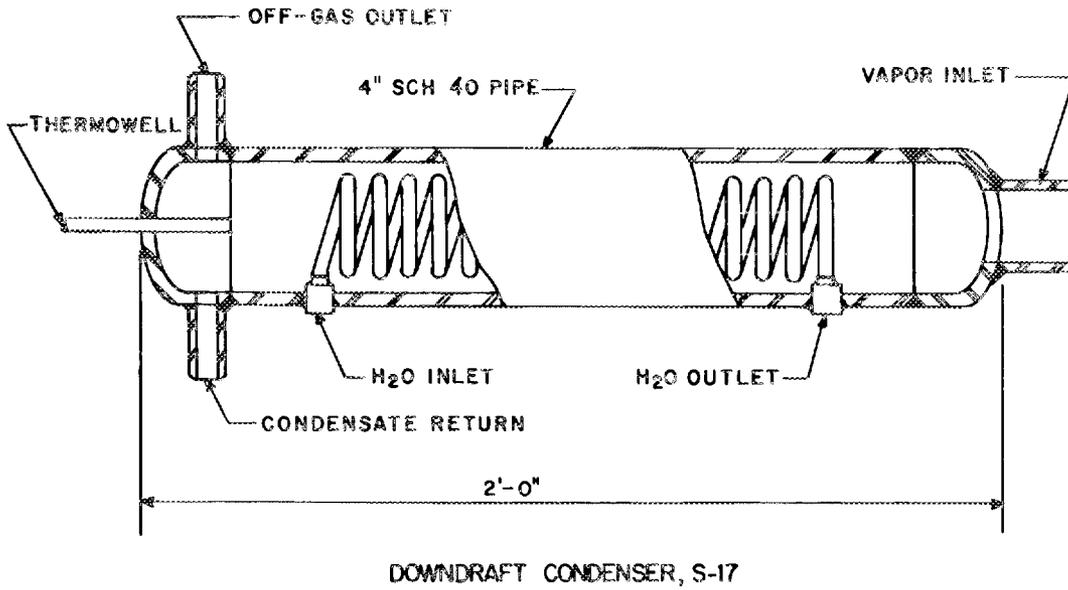


Fig. 3. Auxiliary Equipment for Critically Safe ²³³U Dissolver System.

The cooling coil has a heat-transfer area of 1.62 ft². A required area of 1.37 ft² was calculated, based on an overall heat-transfer coefficient, $U = 100 \text{ Btu hr}^{-1} \text{ ft}^{-2} \text{ }^\circ\text{F}^{-1}$, a ΔT of 100°F, and a heat duty, $q = 4240 \text{ Btu/hr}$.

LIQUID-VAPOR SEPARATOR

The liquid-vapor separator, S-16, also shown in Fig. 3, is the cold leg of the thermosiphon loop. It also provides a place for noncondensables to leave the system and serves as a receiver for condensate coming from the downdraft condenser (S-17). The liquid-vapor separator, which was fabricated from 4-in. stainless steel (304L) pipe, is 2 ft in overall length, with elliptical welding caps at either end. Two 2-in.-diam nozzles, one at the lower end and one 10 in. from the bottom, connect it into the thermosiphon loop. A 2-in. connection at the top vents it into the condenser, and a 1-in.-diam nozzle 6 in. from the top receives condensate.

COST

Overall construction cost for the S-15 dissolver system was about \$10,000, of which approximately \$5,700 was spent to provide materials for, and to fabricate, the dissolver (S-15), the liquid-vapor separator (S-16), and the downdraft condenser (S-17). The remainder, \$4,300, was used for their installation in cell 5, Building 3019.

The availability of existing instruments in the parallel S-1 dissolver system helped to keep the equipment cost low. The new dissolver was connected to these existing instruments, and operating versatility was preserved by using isolation valves in the instrument lines, which permitted operation of either the new or the old equipment but not both simultaneously.

The installation costs are for work in a radioactive area, which is more cumbersome and is therefore more costly than that in a nonradioactive area. Although the installation had to be scheduled at convenient times, such as when the intermittently operated Kilorod Solvent Extraction Facility in cell 5 was inactive, this was handled routinely and did not significantly increase installation costs.

INITIAL OPERATION

The first few months of operation indicate that design objectives were met, if not exceeded. Experience with dissolving ²³³U oxide canned in aluminum, in approximately 1-kg batches, shows that five to six such dissolvings may be possible per 24-hr day.¹⁰

Acid utilization data for this process are not available, since only a uranium balance is necessary for adequate dissolver operation. Qualitative observations indicate that less-than-stoichiometric amounts of acid are being added, as is evidenced by the usual acid deficiency of the final solutions. Preferential dissolution of ^{233}U oxide seems likely, since the oxide dissolves completely, while some of the thick aluminum end caps remain undissolved. In our particular operation, significant benefits could be derived by eliminating some of the aluminum used in canning. Present aluminum: uranium molar ratios are 6:1, thereby making aluminum the controlling factor in current dissolver operations.

Initial operation also indicated avenues for equipment improvement. A greater separation between the vapor outlet from the dissolver to the condenser and the liquid overflow from the dissolver to the liquid-vapor separator is desirable in future designs to avoid flooding the vapor outlet through boilup observed during dissolvings.

APPENDIX

Eleven engineering drawings were made for the design and installation of the critically safe ^{233}U dissolver system. These are listed below:

D-58111	^{233}U Dissolver Process Flowsheet
D-58123	^{233}U Dissolver Layout
E-58124	Dissolver Body (S-15)
E-58125	Dissolver Internals (S-15)
D-58126	Liquid-Vapor Separator (S-16)
D-58127	Downdraft Condenser (S-17)
D-58128	Spool Piece and Detail Sheet No. 1
D-58129	Carrier Support and Installation - Detail
E-58140	Dissolver (S-15) Assembly
P-12165-CP-014	^{233}U Dissolver Installation, Cell 5, As-Built 2/17/66
I-20327-QE-022	Instrument Application Tabulation for ^{233}U Dissolver, Building 3019, Cell 5

REFERENCES

1. A. T. Gresky and E. D. Arnold, Products Produced in Continuous Neutron Irradiation of Thorium, ORNL-1817 (Feb. 6, 1956).
2. A. T. Gresky and E. D. Arnold, Products Produced in Batch Neutron Irradiation of Thorium, ORNL-1818 (Dec. 27, 1955).
3. E. D. Arnold, "Radiation Hazards of Recycled ^{233}U —Thorium Fuels," ORSORT Chemical Technology Course Reference Notes (1963-64 Session).
4. E. D. Arnold, "Radiation Limitations on Recycle of Power Reactor Fuels," Proc. U. N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958, vol. 13, P/1838, 237-50 (1958).
5. J. Klitgaard, personal communication, Nov. 2, 1964.
6. H. C. Paxton, J. T. Thomas, A. D. Callihan, and E. B. Johnson, Critical Dimensions of Systems Containing ^{235}U , ^{239}Pu , and ^{233}U , TID-7028 (June 1964).
7. R. E. Blanco and C. D. Watson, "Head-End Processes for Solid Fuels," p. 73 in Reactor Handbook, Vol. II, Fuel Reprocessing, ed. by S. M. Stoller and R. B. Richards, Interscience, New York, 1961.
8. J. B. Adams, A. M. Benis, and C. D. Watson, Comparative Cost Study of Processing Stainless-Steel-Jacketed UO_2 Fuel: Mechanical Shear-Leach vs Sulfex-Core Dissolution, ORNL-3227, p. 23 (Apr. 6, 1962).
9. C. D. Watson, B. A. Hannaford, F. L. Rogers, and D. E. Willis, "Power Reactor Fuel Processing" in Unit Operations Section Monthly Progress Report - January 1964, ORNL-TM-798, pp. 41-54 (July 1964).
10. J. R. Parrott, personal communication, Aug. 1, 1966.

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