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DISSOLUTION OF ALUMINUM-CLAD THORIA

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by

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ABSTRACT

A reverse codissolution process was developed to dissolve aluminum-clad thoria. In the reverse codissolution process, thoria from a previous dissolving cycle is dissolved in strong acid, then fresh aluminum-clad slugs are added to the partially spent dissolvent and the aluminum is dissolved. The advantages of reverse codissolution are: 1) high initial acid concentration enhances thoria dissolution, and 2) subsequent mercury-catalyzed dissolution of the aluminum reduces acid concentrations sufficiently to allow solvent extraction without requiring feed adjustment by steam stripping. Agitation by either submerged steam coils or air-lift circulators increased the dissolution rates from 0.9 pound ThO_2 per hour per square foot of dissolver bottom to 4.3 and 17.2 lb $ThO_2/(hr\text{-}ft^2)$, respectively. Thoria that had 1 wt % magnesia incorporated during its preparation dissolved, when agitated, at a rate of 69 lb $ThO_2/(hr\text{-}ft^2)$.

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DISSOLUTION OF ALUMINUM-CLAD THORIA

INTRODUCTION

A process was developed at the Savannah River Laboratory (SRL) for separating and purifying ^{233}U in existing plant equipment. The ^{233}U was obtained by irradiating thoria in aluminum cans in the production reactors at the Savannah River Plant (SRP). Principal steps in the process include:

- Dissolution of the fuel elements.
- Sorption of ^{233}Pa on manganese dioxide.
- Separation of ^{233}U and thorium from each other and from aluminum, protactinium, and fission products in a solvent extraction cycle. The extractant was tributylphosphate (TBP) at a concentration of 30 vol % in high purity kerosene.
- Purification of the ^{233}U from residual thorium, protactinium, and fission products in a second cycle of solvent extraction with 7-1/2 vol % TBP in high purity kerosene.
- Concentration of the ^{233}U by cation exchange.
- Precipitation of ^{233}U as ammonium uranate.
- Calcination of the ammonium uranate to uranium trioxide.
- Storage of the recovered thorium as a concentrated solution of thorium nitrate.

Laboratory-scale dissolution studies[1,2] indicated that codissolution of the aluminum can and irradiated thoria with boiling 13M HNO_3-0.025M HF-0.1M $Al(NO_3)_3$ was the most satisfactory method for preparing the feed for solvent extraction. Significant variables affecting the dissolution rate of thoria were the degree of agitation, the particle size of the thoria, and whether the thoria had magnesia (MgO) incorporated during its preparation. Experiments were conducted to determine dissolution rates and to investigate practical methods of agitation in SRP equipment for normal production grade thoria, and for thoria incorporating 1% MgO. There was no attempt to study the effect of particle size of the thoria.

SUMMARY

A reverse codissolution process was developed to dissolve residual thoria in strong nitric acid prior to the mercury-catalyzed dissolution of additional aluminum-canned thoria fuel elements. This procedure allows thoria to be dissolved at the highest acid concentration possible (thoria dissolution rate is dependent on acid concentration) and dissolves aluminum at low acid concentration (aluminum dissolution is virtually independent of acid concentration when using a mercury catalyst). This dissolving procedure produces a solution that does not require steam stripping of acid before ^{233}Pa removal on manganese dioxide (MnO_2) cake and subsequent ^{233}U recovery by solvent extraction.

The moderate agitation produced by boiling action at the surface of a horizontal steam coil buried in a bed of thoria powder increased the dissolution rate by a factor of about 5. The dissolution rate increased from 0.9 pounds of thoria per square foot of dissolver bottom to 4.3 lb $ThO_2/(hr\text{-}ft^2)$ when a steam coil was installed on the floor of the dissolver.

The thoria dissolution rate was increased by installation of two partially buried, air-lift circulators per square foot of dissolver bottom area. At circulator air flows of 3 scfm each, the thoria dissolved at a rate of 17.2 lb $ThO_2/(hr\text{-}ft^2)$.

The incorporation of 1 wt % MgO during the preparation of thoria (calcined at 2100°F for 4 hours) increased the dissolution rate four-fold to 68.8 lb $ThO_2/(hr\text{-}ft^2)$ using the air lift circulators at an air flow of 3 scfm. MgO incorporation did not increase the dissolution rate if the thoria was not agitated.

A portion (0.3 to 0.5%) of the thoria was entrained when the end of a suction pipe was located 3 to 9 inches above the settled thoria. Filtration was unsatisfactory because the entrained thoria plugged the filter; however, centrifuging decreased the entrained thoria to only 0.006% of the total thorium.

PROCESS DESCRIPTION

Laboratory studies[1,2] showed codissolution of aluminum cans and thoria to be superior to separate removal of the can by acidic or alkaline decladding. The recommended codissolvent is 13M HNO_3 containing 0.025M HF and 0.1M $Al(NO_3)_3$. The fluoride ion catalyzes thoria dissolution and is complexed by the aluminum to reduce corrosion of the dissolver vessel. When irradiated thoria was boiled for 24 hours in an acidic decanning solution [6M HNO_3-10^{-3}M $Hg(NO_3)_2$], about 20% of the ^{233}U was leached from the thoria, indicating acid decanning is probably unsuitable when the decanning solution is to be discarded. The alkaline decanning solution (4.3M $NaOH$-3M $NaNO_3$) was fairly viscous, and fine thoria particles were entrained when the spent solution was removed. Exposure to the alkaline solution retarded subsequent dissolution of thoria. Neither the acid decanning solution nor the alkaline decanning solution dissolved thoria appreciably.

Normal codissolution, i.e., adding the dissolvent to a charge of aluminum-jacketed slugs, results in an unacceptably long time cycle. This is due to the rapid dissolution of the aluminum cladding which consumes about one half of the nitric acid. The thoria dissolution rate is a strong function of acid concentration and is therefore relatively slow compared to the rate obtained with fresh dissolvent. Solvent extraction requirements prohibit the use of a larger excess of acid, and higher fluoride concentrations cause the precipitation of ThF_4.

A more efficient process is that of "reverse codissolution," which separates the initial thoria reaction from the dissolution of the aluminum cans. This process consists of: 1) dissolution of the thoria "heel" from a previous cycle in the standard boiling dissolvent, 2) cooling of the partially spent dissolvent (8M H^+ and 1M Th^{4+}), 3) charging of aluminum-canned thoria slugs, 4) addition of mercury catalyst, and 5) dissolution of the aluminum cans to a final product concentration of 1.0M Th^{4+}, 2.0M Al^{3+}, and 2M HNO_3. The thoria released from the dissolved cans remains as a "heel" for the subsequent dissolution cycle. The advantages of "reverse codissolution" are: 1) acid-dependent thoria dissolution proceeds at the highest possible rate at the high acid concentrations, and 2) subsequent mercury-catalyzed dissolution of the aluminum reduces acid concentrations sufficiently to allow solvent extraction without the need of feed adjustment by steam stripping. The concentration of the final dissolver product (1M Th^{4+}, 2M Al^{3+}, and 2M HNO_3) is high, and water is added prior to cooling to produce a soluble, more dilute solution at ambient temperatures (Figure 1).

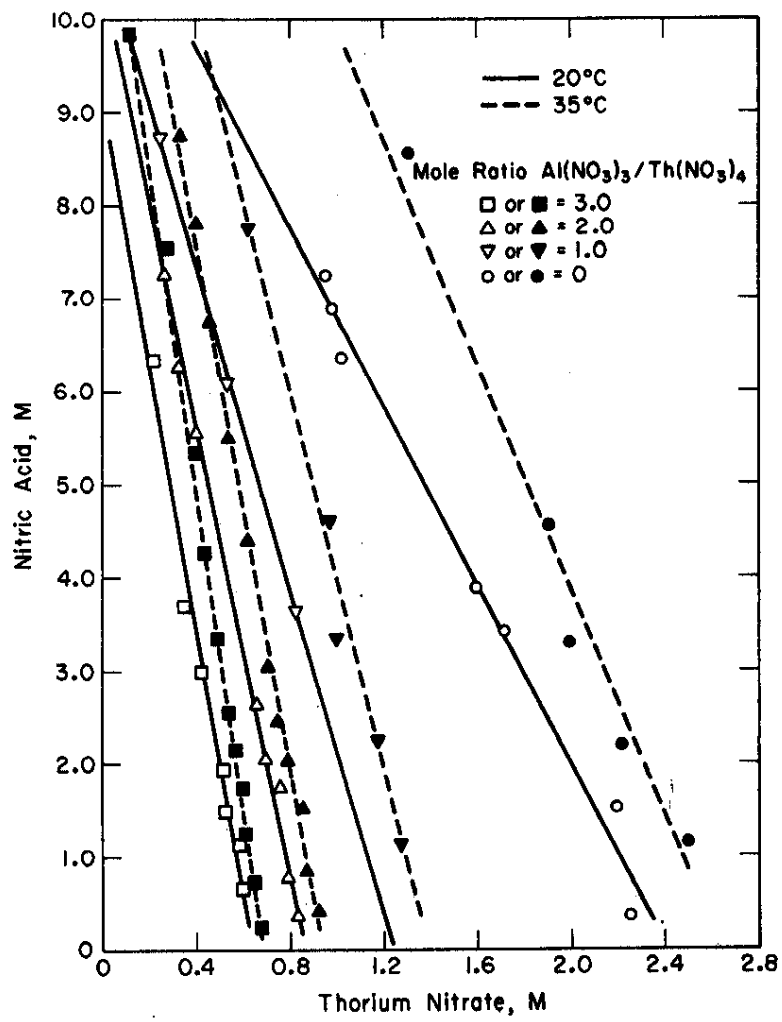


Figure 1. Solubility of Thorium Nitrate-Aluminum Nitrate in Nitric Acid

PROCESS EQUIPMENT

Either of two types of dissolvers would be used, depending on which separations plant the thoria would be processed in. In the H-Area separations plant, a normal pot dissolver would be used. An annular dissolver, which contains a high density concrete center to provide nuclear criticality protection, would be used in the F-Area separations plant.

The 11-ft-4-in. diameter H-Area pot dissolver was simulated in the SRL process studies area (TNX) with a 6-ft-diameter by 7-ft-high tank equipped with wall-mounted steam coils and a 4-ft-diameter fuel crib (Figure 2). A horizontal steam coil and protective grating (Figure 3) were added to the bottom of the tank during the tests. The steam coil was made of 1-in. Schedule 40 pipe on 3-in. centers. The cross-sectional area of the coil covered 44% of a 4-ft-diameter circle (19% of the total area of the tank bottom).

The F-Area annular dissolver (5 ft-7-in. x 10 ft-2-in. diameter annulus) was simulated with a sectional mockup. The mockup (Figure 4) was vertically similar to the plant dissolver and was rectangular (1-ft by 2-ft) at the bottom (cross-sectional area was 1/27 of the plant dissolver). The dissolver had vertical steam coils and a fence dividing the annular space into two sections: a fuel crib (inner) and a heating/cooling section (outer). A horizontal steam coil made of 1-1/2-in. Schedule 40 pipe on 2.4-in. centers (the cross-sectional area of the coil covered 79% of the bottom area) was installed on the bottom of the dissolver.

During subsequent dissolution tests with this sectional mockup, the bottom steam coils were replaced by four air lift circulators (Figure 5). The individual circulators were made of 10-inch lengths of 2-in. Schedule 40 pipe and were positioned vertically 1-1/2-in. above the dissolver bottom and evenly spaced in each of the 1-ft square "annular" sections. Four 1/4-in.-wide by 1-1/2-in.-long slots were cut into the bottom of each circulator to improve entry of the thoria-dissolvent mixture. Air was introduced through the open end of a 1/2-in. Schedule 40 pipe located below the bottom edge of each circulator. A manifold in each dissolver annulus supplied air through a restricting orifice to individual circulators. A grating was placed over the circulators in the fuel crib to protect them from damage during charging of fuel slugs.

The dissolution rate of thoria as a function of air flow rate was determined with a small funnel-shaped dissolver (Figure 6) having a 0.5-ft^2 bottom area and a single air lift circulator (described above). This small dissolver allowed a greater number of tests with the limited quantity of thoria available. The funnel shape of the dissolver returned all of the undissolved thoria particles to the 10-in.-diameter dissolving section. The dissolvent was heated by an annular steam chest located near the air lift circulator.

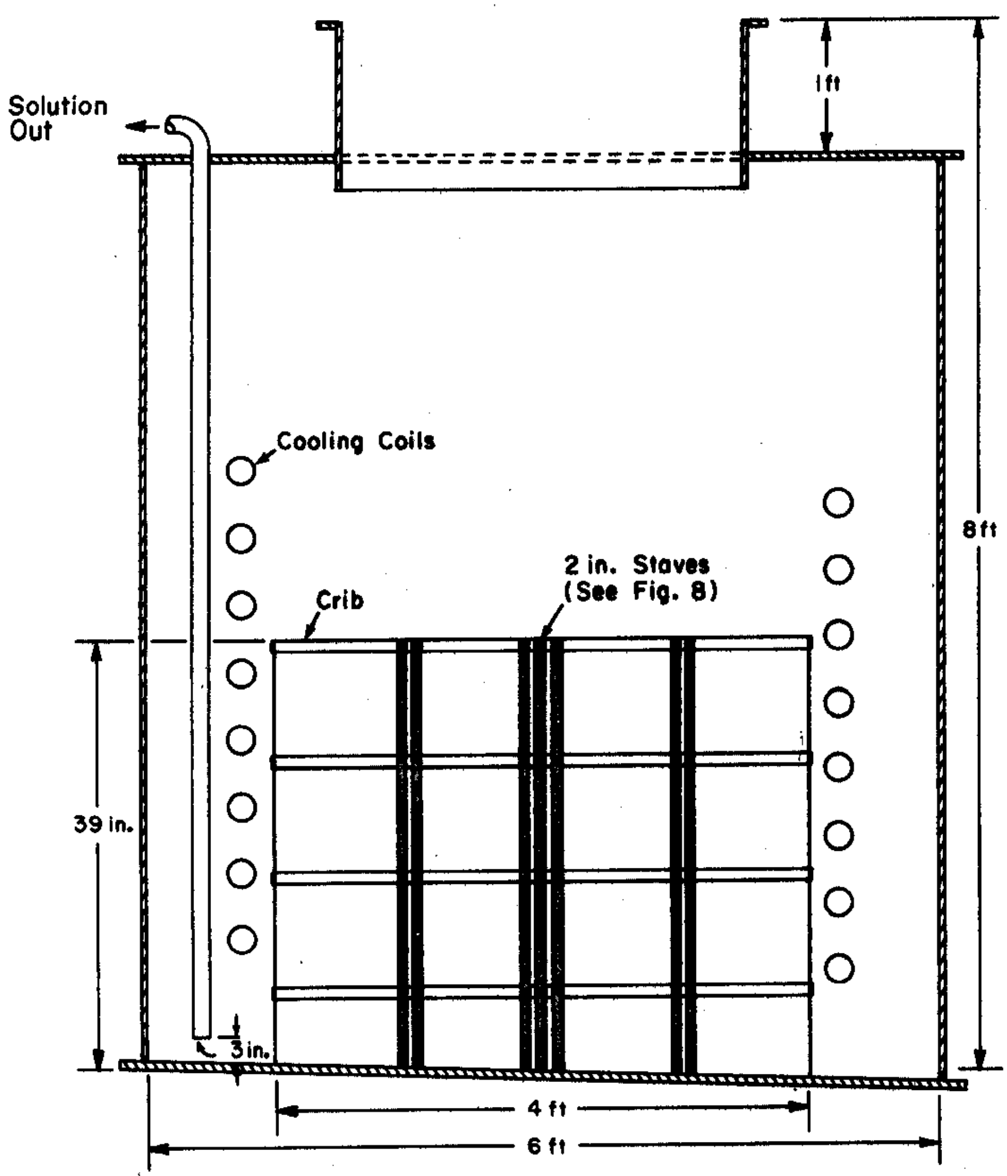
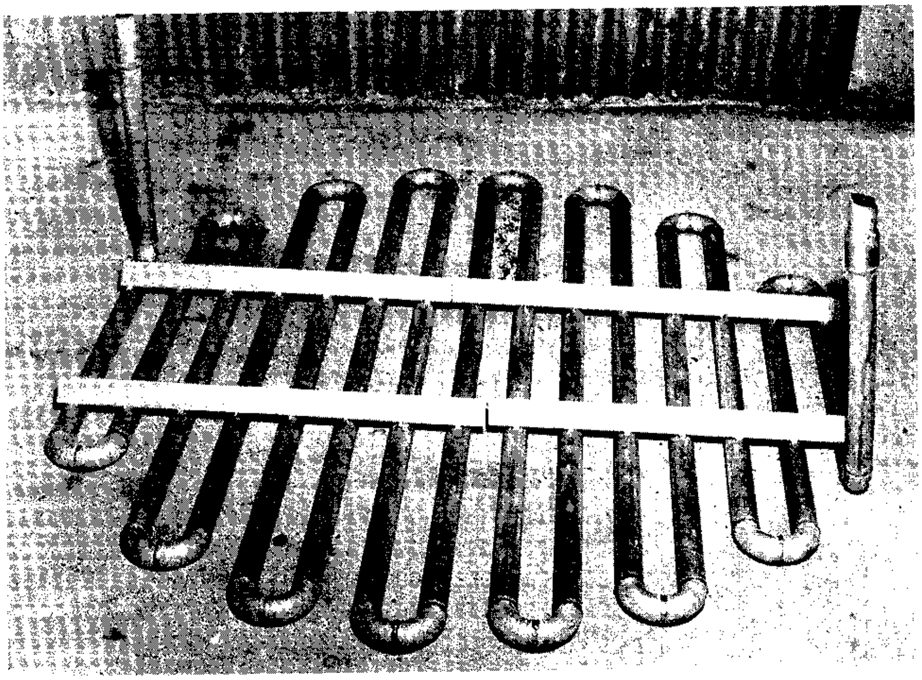


Figure 2. Semiworks Dissolver



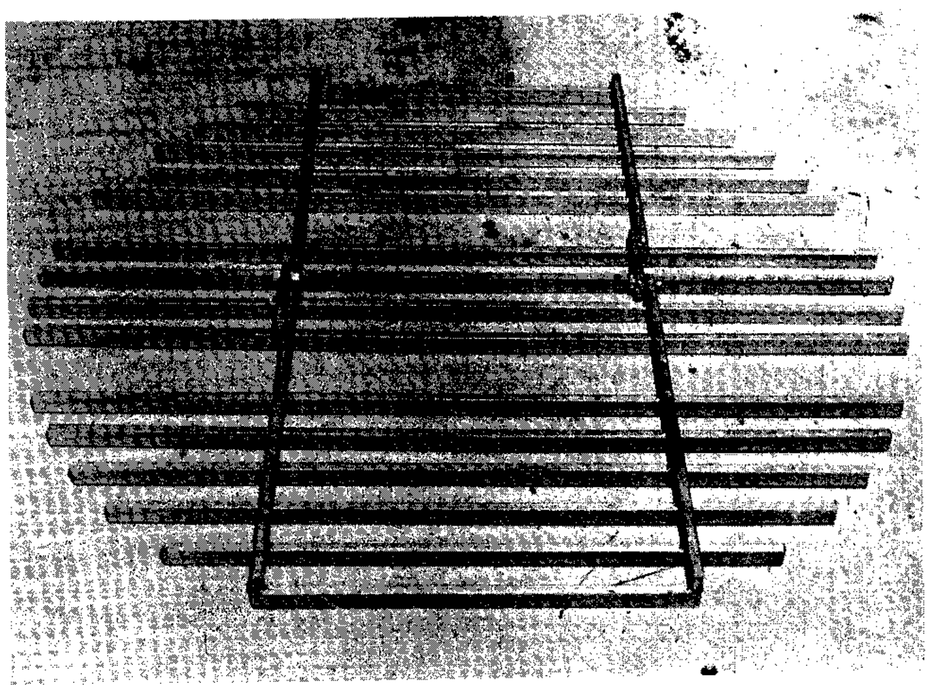


Figure 3. Horizontal Steam Coil and Protective Grating for Pot Dissolver

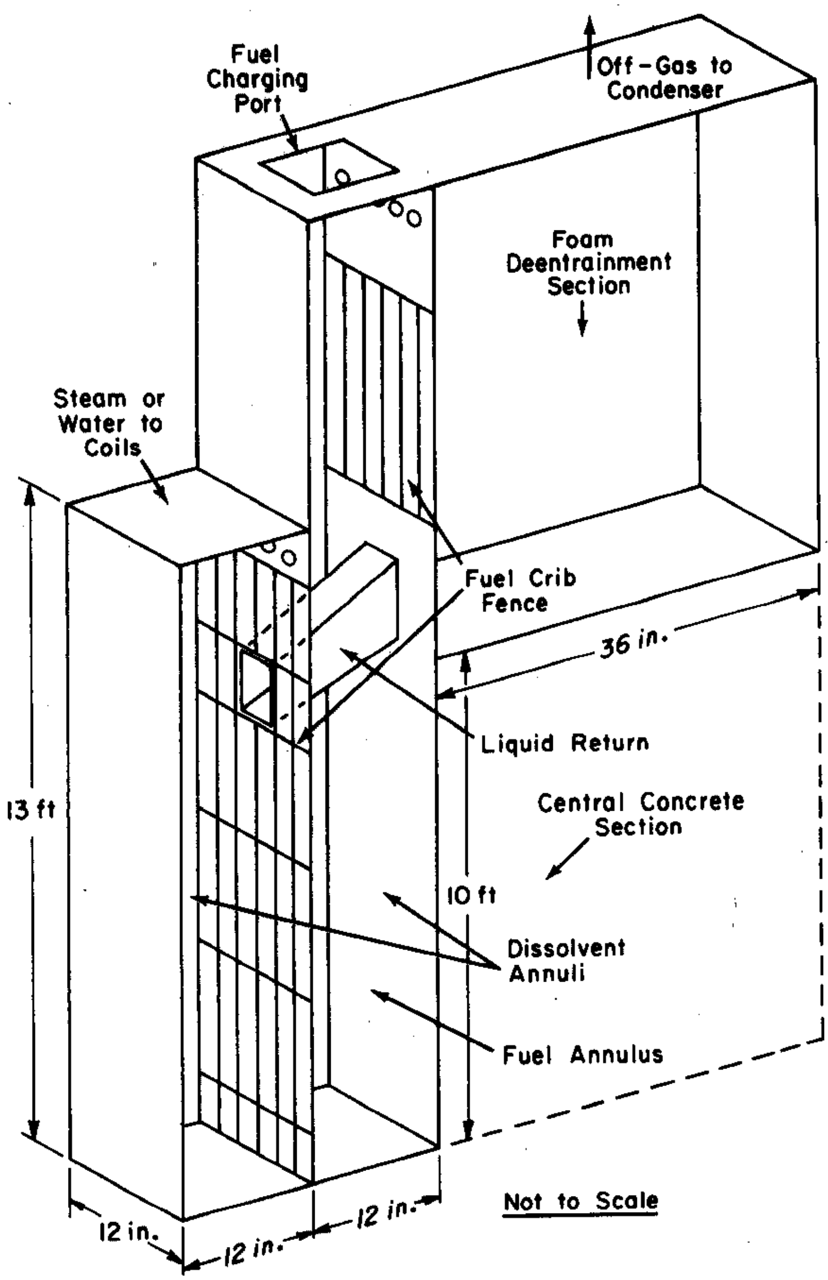


Figure 4. Sectional Mock-Up of Annular Dissolver

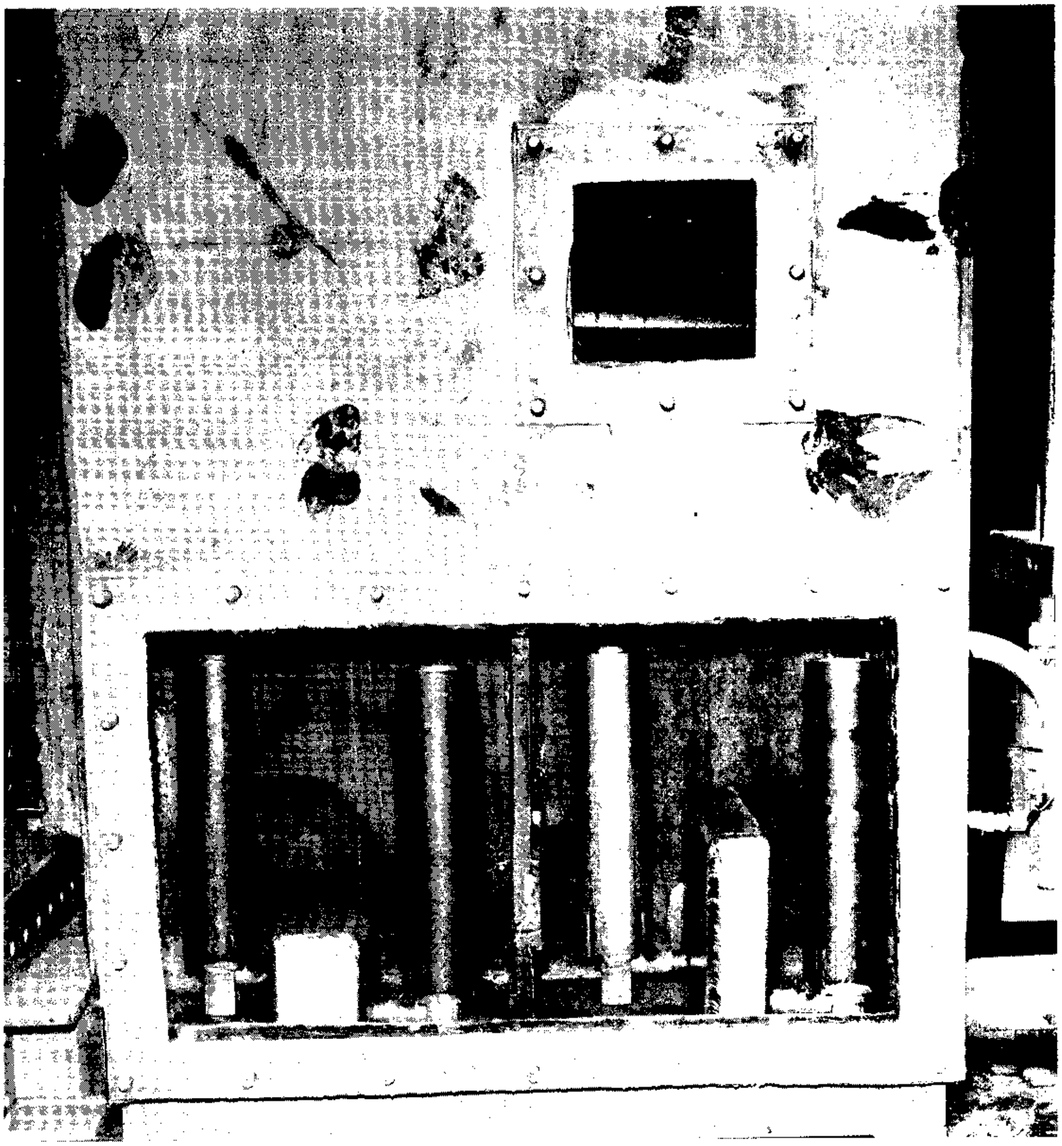
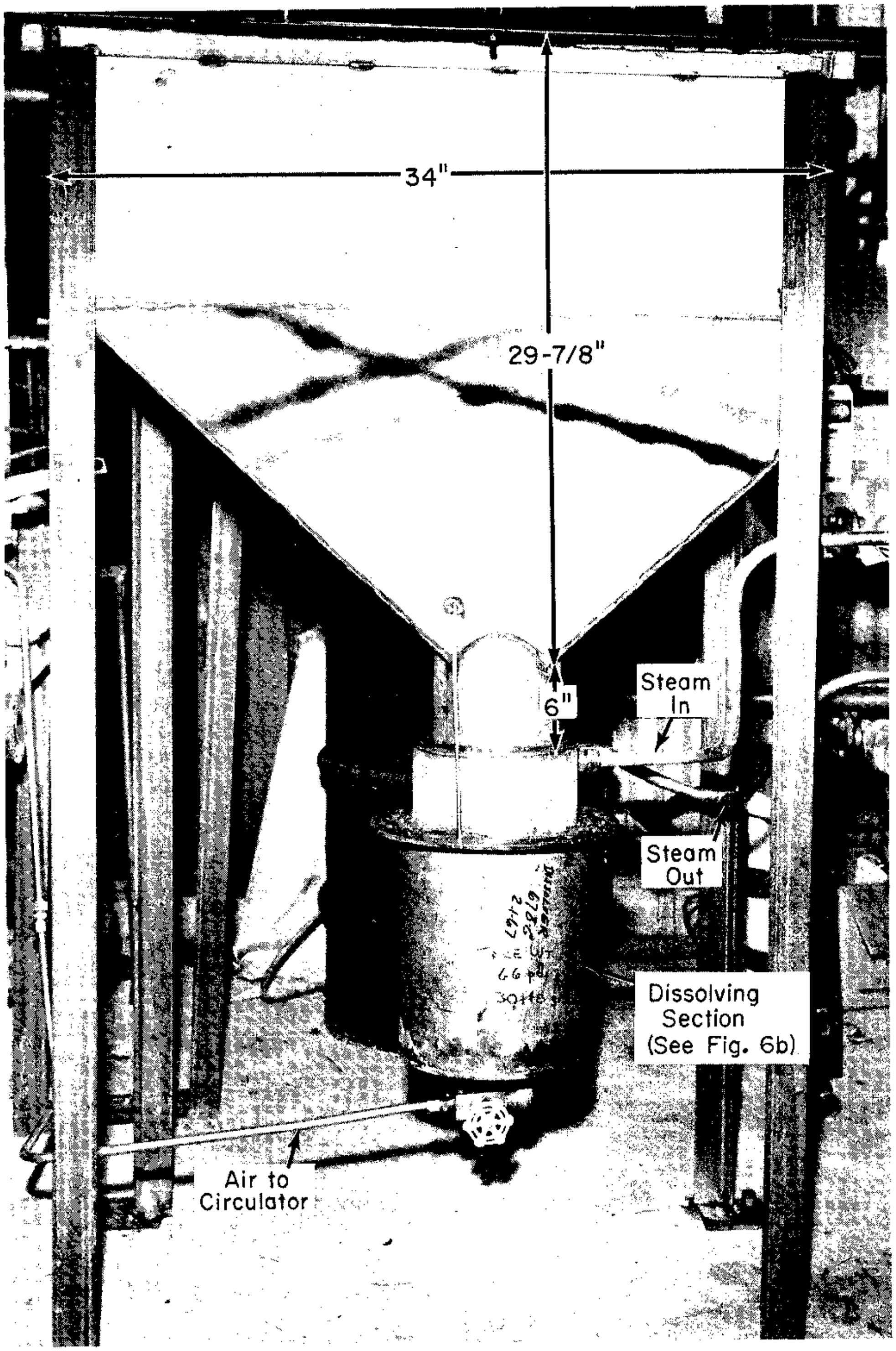
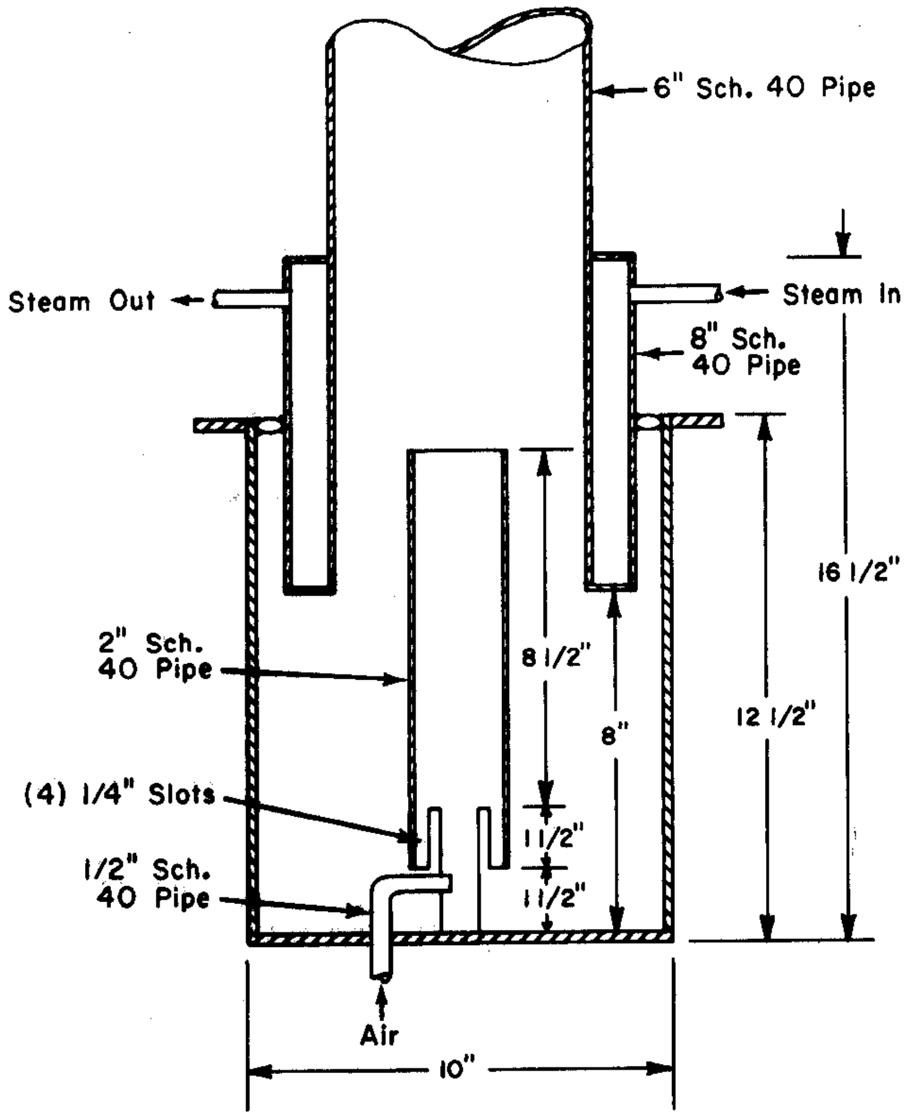


Figure 5. Air Lift Circulators in Annular Dissolver Mock-Up



a. Installed Unit

Figure 6. Funnel Dissolver



b. Dissolving Section

Figure 6. Funnel Dissolver (cont'd)

DISSOLUTION TESTS

Unagitated Dissolution Tests

Initial large-scale dissolution tests were made in the 6-ft.-diameter pot dissolver (Figure 2), which was equipped with only wall-mounted steam coils. A thoria "heel" weighing 805 pounds was left in the dissolver by chemically ($NaOH-NaNO_3$) removing the aluminum cans from a typical charge of fuel elements (Figure 7). As the aluminum cans dissolved, the dense thoria powder settled quite uniformly in a compact layer on the bottom of the dissolver (Figure 8). Additional fuel elements containing 813 pounds of thoria were charged on top of the thoria "heel," and a partial codissolution was made with 370 gallons of boiling 12.5M HNO_3-0.025M HF-0.1M $Al(NO_3)_3$ (hereafter referred to as standard dissolvent). Dissolution proceeded very slowly because the active dissolution zone was restricted to the top surface of the densely packed thoria. The calculated rate of "penetration" of the dissolvent into the thoria layer was 0.44 millimeters per hour. Three laboratory tests in 3- and 4-in.-diameter vessels verified this penetration rate with values ranging between 0.37 and 0.49 mm/hr. When a concentration of 0.5M Th^{4+}, 0.9M Al^{3+}, and 8.4M HNO_3 was reached, the average dissolution rate was 0.9 lb $ThO_2/(hr\text{-}ft^2)$, which is equivalent to a processing capacity of 0.9 ton ThO_2/day in the larger (11-ft 4-in.-diameter) H-Area pot dissolver.

Agitation by Bottom Steam Coil

To increase the thoria dissolution rate, studies were made to develop a practical means of increasing the area of contact between the dissolvent and the densely packed thoria layer. One of the proposed methods applicable to plant equipment utilized the turbulence generated by boiling at the surface of a horizontal steam coil buried in the thoria layer. Tests in glassware with a small steam coil showed that a thoria depth of about 2-1/2-in. above the top of the coil was the maximum that could be present and still allow suspension of thoria particles by boiling. Large-scale tests showed that thoria dissolution stopped when the thoria level dropped below the top of the steam coil (see Annular Dissolver Tests below). The portion of the tank bottom covered by steam coils should be as large as possible as agitation by boilup only affects the thoria directly above the coils.

Figure 7. Typical Charge of Aluminum Canned Thoria Fuel Elements

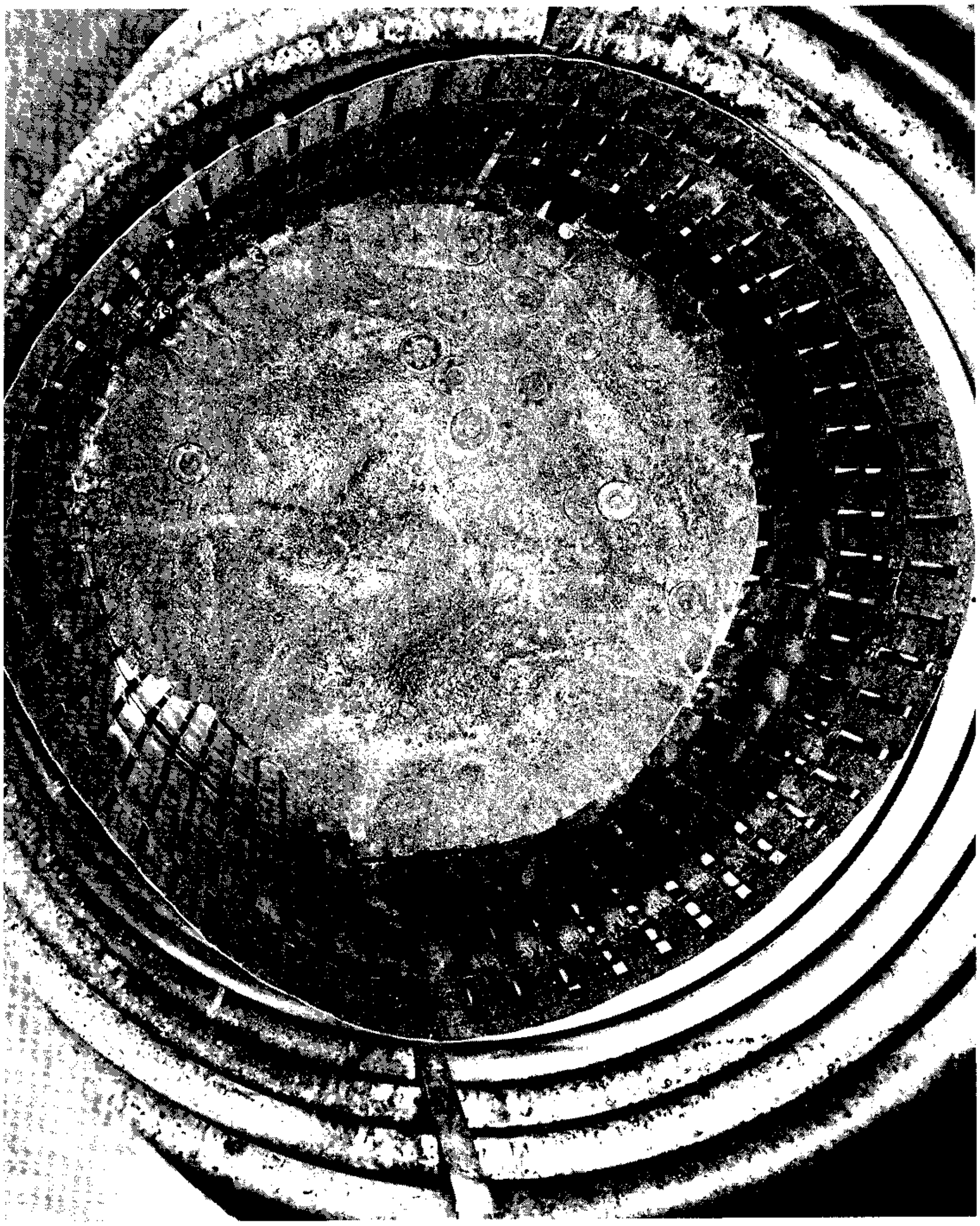


Figure 8. Typical Thoria Heel

Pot Dissolver Tests

The pot dissolver was modified to include a horizontal steam coil which covered 20 percent of the total bottom area. Two tests were made in which aluminum cans containing 850 pounds of thoria were partially codissolved with a 720-pound thoria "heel" in 800 gallons of standard dissolvent. At a product concentration of 0.05M Th^{4+}, 0.8M Al^{3+}, and 8.4M H^{+}, the dissolution rate was 1.9 lb $ThO_2/(hr\text{-}ft^2)$ a two fold increase over the unagitated tests. The aluminum cans were not dissolved completely in either test.

Because solvent extraction feed must be adjusted to 0.5M Th^{4+}, 1.0M Al^{3+}, and 0.1 to 1.0M H^{+}, further dissolution tests were made to determine whether the product acid concentration (8.5M) could be further reduced without additional processing steps such as removal of nitric acid by steam stripping. Two steam-coil-agitated dissolution tests were made in the pot dissolver. In the first test, aluminum-canned thoria fuel elements (860 pounds of thoria) were added to a 1000-pound thoria "heel" and partially codissolved in 400 gallons of standard dissolvent to which Hg^{2+} had been added as a catalyst to increase the dissolution of aluminum. The dissolution of thoria virtually ceased as the nitric acid decreased to about 3.0 molar and resulted in concentrations of 0.73M Th^{4+} and 2.0M Al^{3+}. All the aluminum dissolved. The average thoria dissolution rate was 1.4 lb $ThO_2/(hr\text{-}ft^2)$.

In the second test, a steam-coil-agitated, reverse codissolution test was made in the pot dissolver where 800 pounds of a thoria "heel" was partially dissolved in 400 gallons of boiling standard dissolvent to a concentration 0.9M Th^{4+} and 9.3M H^{+}. Empty aluminum cans weighing 160 pounds were then charged and dissolved after mercury ion addition to yield a final concentration of 0.9M Th^{4+}, 1.7M Al^{3+}, and 0.1M H^{+}. The average thoria dissolution rate was 2.5 $lb/(hr\text{-}ft^2)$, with minor thoria dissolution occurring during the aluminum decanning step.

Annular Dissolver Tests

Because the F-Area separations plant has a solvent extraction capacity of 6 tons of thorium per day as compared with 1 ton of thorium per day in H-Area, it was anticipated that large campaigns (150 tons of thorium) would be done in F-Area. Increased dissolution capacity of the annular dissolver in F-Area, which only has one-half the bottom area of a pot dissolver, was demonstrated in the previously described rectangular mockup by installing a horizontal steam coil which covered 79% of the total bottom area. In four dissolution tests, the depth of thoria above the steam coils was allowed to decrease to evaluate its effect during the first half of the reverse codissolution cycle; i.e., thoria powder was dissolved in boiling dissolvent without subsequent charging of the aluminum-canned thoria slugs.

In the first test, 714 pounds of thoria was partially dissolved in 165 gallons of standard dissolvent to a product concentration of 0.8M Th^{4+} and 6.4M HNO_3. The average dissolution rate was 4.3 lb $ThO_2/(hr\text{-}ft^2)$, and the calculated thoria depth (basis: 6.5 g/cm^3 bulk density) was reduced from 9.8 to 5.4 in. above the top of the steam coil. In the second test, the heel from the previous test was further dissolved in 163 gallons of fresh dissolvent. During the first 33 hours, the average dissolving rate was 4.2 lb $ThO_2/(hr\text{-}ft^2)$, after which it decreased markedly to that obtained in the unagitated studies.

The decrease in the dissolution rate experienced in the second test apparently occurred when the depth of thoria dropped below the top of the bottom steam coil. The boiling produced at the top surface of the steam coil could not agitate the thoria heel below it, and the average dissolution rate fell to 0.8 lb $ThO_2/(hr\text{-}ft^2)$. Measurement of the condensate from the bottom steam coil provided a basis for this explanation. During the first 19 hours when the steam coil was well covered and insulated from the bulk solution by the thoria layer, the average condensate rate was 0.2 lb/min and the moderate agitation produced an average dissolution rate of 3.6 lb $ThO_2/(hr\text{-}ft^2)$. During the period between 19 and 33 hours, more vigorous agitation produced an average dissolution rate of 4.9 lb $ThO_2/(hr\text{-}ft^2)$, and the condensate rate increased steadily to approximately 1.0 lb/min as the thoria provided progressively less insulation between the steam coil and the bulk solution. After the steam coil was completely exposed and came into direct contact with the bulk solution, the condensate rate increased slowly to 1.3 lb/min during the last 15 hours of dissolution.

The last two dissolution tests were designed to provide maximum agitation by reducing the thoria depth to the top of the bottom steam coil at a product concentration of 1M Th^{4+}. In both tests, 215 pounds of thoria, which is a calculated depth of 2.5 in. above the steam coils, was partially dissolved in 81 gallons of standard dissolvent giving an average dissolution rate of 5.8 lb $ThO_2/(hr\text{-}ft^2)$. Separate laboratory tests made in a 4-in.-dia. glass cylinder indicated thoria is thoroughly agitated by a steam coil when covered to a depth up to 2-3/4 in.

Capacity of H-Area Pot Dissolver and F-Area Annular Dissolver

Based on the time cycle summarized in Table I and shown schematically in Figure 9, a processing capacity of 1.6 tons ThO_2/day should be attainable in the H-Area pot dissolver equipped with similar steam coils using the reverse codissolution scheme.

The predicted capacity of the F-Area annular dissolver equipped with similar steam coils is 1.7 tons ThO_2/day assuming an average thoria dissolution rate of 4.3 $lb/(hr\text{-}ft^2)$, and using the same time (23.5 hr) for other processing steps as listed in Table I.

Table I. Typical Time Cycle for H-Area Pot Dissolver

Operation	Time, hours
Chemical addition	1.5
Heat to boiling point	1.0
Dissolve thoria heel [(3.3 tons at 2.5 lb $ThO_2/(hr\text{-}ft^2)$]	26.1
Cool	1.0
Charge target elements	7.0
Heat to boiling point	1.0
Dissolve aluminum cans	10.0
Dilute, cool, and transfer	2.0
Total	49.6

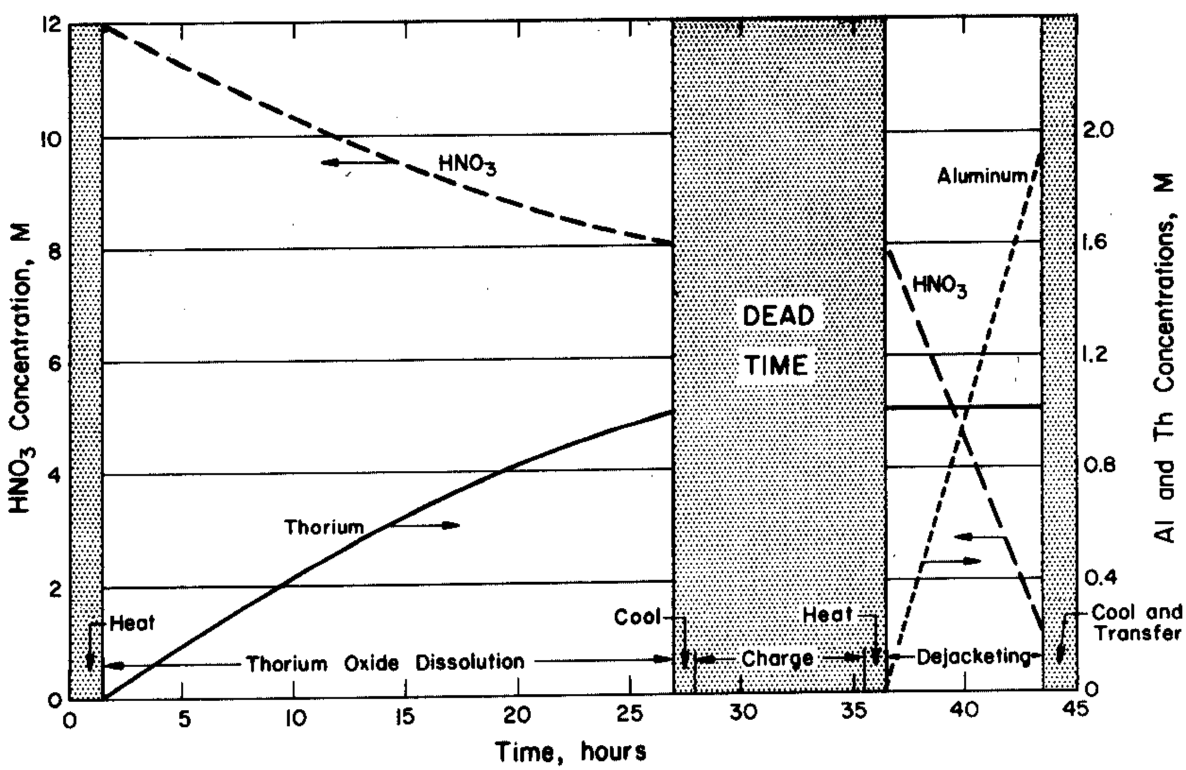


Figure 9. Typical Plant Thoria Dissolving Cycle

Agitation By Air Lift Circulators

Based on data[3] obtained from Pacific Northwest Laboratories (PNL), studies of the effectiveness of short air lift circulators for agitating the densely packed thoria layer were initiated to increase the capacity of the F-Area annular dissolver.

Design of Air Lift Circulator

The design of the individual circulators (Figure 10) was based on hydraulic tests using a transparent tank filled with thoria powder and water. Air lifts, made of short lengths of 2-in.- or 3-in.-diameter pipe, fluidized particles at the surface of the thoria layer. These particles were ejected from the top of the circulator with air flow rates as low as 2 scfm. However, the fluidization range below the bottom of the circulator was less than 1/4 in. at air flow rates as high as 5 scfm. When the bottom of the circulator was partially buried, only the thoria filling the inside of the circulator was "showered" out onto the surrounding surface.

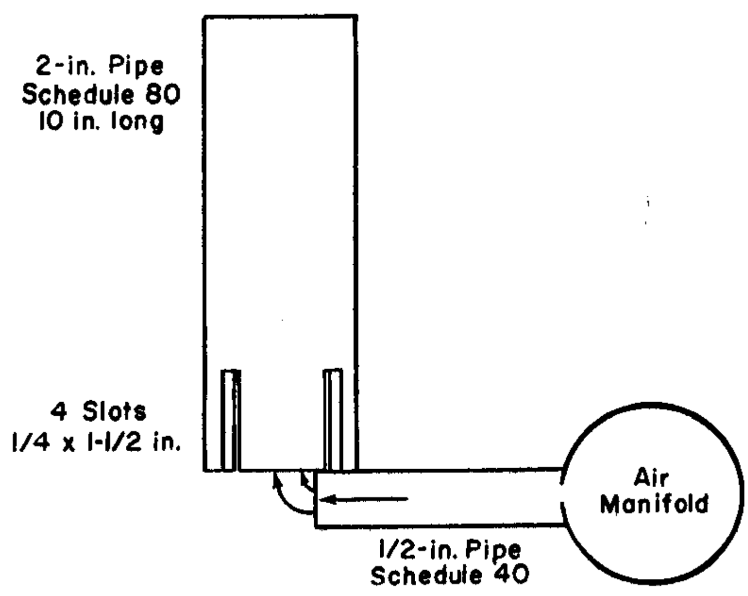


Figure 10. Air Lift Circulator Design

Vertical slots (1/4 in. wide) cut into the bottom of buried circulators allowed the thoria particles adjacent to the slots to become fluidized, resulting in a "caving-in" action. This action continued until a conical depression with a 110° apex angle was formed in the thoria layer surrounding the circulator. The bottom of this inverted cone coincided with the bottom of the circulator for slot-lengths up to 1-1/2 in. The thoria particles falling back into this conical area continued to recirculate until they settled on the surface outside the inverted cone. The diameter of the cone was 15 in. at a thoria depth of 5 in.

Two air lift circulators per square foot of dissolver bottom area enabled a large percentage of thoria surface to be affected even when the thoria depth, and thus cone diameter, was significantly reduced by dissolution. Because over a hundred air lift circulators would be required in the bottom of the annular dissolver, a large off-gas volume would be generated. The off-gas volume could be minimized by using 2-in.-dia. air lift circulators, which require about one-half of the amount of air to produce the same internal transport velocity as 3-in.-dia. air lift circulators.

Because of potential abrasive effects of fluidized thoria on the dissolver bottom, the size and discharge direction of the hole in the air supply line to each of the air lifts were evaluated. PNL[8] reported abrasion rates of 0.1 mils/hr on a stainless steel plate when air was discharged at a velocity of 220 ft/sec into a mixture of 30-mesh sand and water from a 1/4-in.-dia hole 1-1/2 in. away from the plate; they recommended that the discharge velocity be limited to 50 ft/sec.

An upward-pointing discharge hole in the air supply line eliminates abrasive effects to the dissolver bottom, but could present a serious thoria pluggage potential. 2-in.- and 3-in.-dia air lift circulators, which had downward-pointed air discharge holes with diameters of 1/2 in. and 3/4 in., respectively, produced no thoria movement when the discharge hole was located 1/2 in. above the bottom at flow rates up to 6 scfm (velocities of 74 and 33 ft/sec, respectively). During these tests, the lifting efficiency was reduced because large volumes of air escaped around the outside of the circulator body even at moderate air flow rates. Apparently the restriction to flow presented by the air supply pipe (which traverses the bottom of the circulator) combined with the slotted sides was responsible for the loss of air. The horizontal discharge of air through the end of a 1/2-in.-dia air supply pipe which enters under the bottom edge of the circulator and terminates one-third of the way across the inside of the circulator was a satisfactory compromise between pluggage of an upward-pointing hole and loss of air (plus potential abrasion) from a downward-pointing hole.

The circulators were supplied with air from manifolds containing restricting orifices to avoid reduced air flows to individual circulators that may be partially filled with thoria.

Chemical tests producing high dissolution rates at significant thoria depths suggest that the area of liquid-solid contact is increased by recirculation of fresh dissolvent down through the densely packed thoria layer; physical agitation of thoria particles is not a prerequisite for high dissolution rates. Hydraulic tests with a deeply buried (up to 10 in.) circulator produced very little "showering" of thoria particles. At shallow thoria depths, the acid recirculation continues to contribute significantly to dissolution along with the previously described thoria-showering mechanism.

The air lift circulators for the annular dissolver were installed 1-1/2 in. above the dissolver bottom and made 10-in. tall so that the tops would protrude above the settled thoria layer.

Effect of Air Flow on Dissolution Rate

A series of small-scale tests were made in the funnel-shaped dissolver to determine the dissolution rate of thoria as a function of the air flow rate. This dissolver had a bottom area of 0.5 ft^2 and was equipped with a single air lift circulator. In each of nine tests, 132 lb of thoria produced by the sol-gel process[4,5] and calcined in a hydrogen induction furnace for 2 hours at 2225°F was partially dissolved in 40 gallons of standard boiling dissolvent. The initial depth of thoria was 7.5 in. (4 in. below top of 10-in.-long circulator), and the final average "heel" depth (at a product concentration of 1M Th^{4+}) was 2.5 in. As shown in Figure 11, the dissolution rate increased from 3.7 to 44.8 lb $ThO_2/(hr\text{-}ft^2)$ as the air flow was increased from 1 to 4 scfm. These values compare with an unagitated dissolution rate of 0.58 lb $ThO_2/(hr\text{-}ft^2)$. Two tests gave unexplainably high rates even though the material used for all tests came from the same thoria lot. Air flow to each of the 104 air lift circulators installed in the F-Area annular dissolver will be limited to 3 scfm to prevent exceeding the capacity of the off-gas exhaust system.

Large-Scale Tests in Annular Dissolver Mockup

Three dissolution tests were made in the rectangular mockup of the annular dissolver (modified to include 4 air lift circulators 1-1/2 in. above the 2-ft^2 bottom) to verify the data from the small-scale tests. For each test, a 500-lb charge of thoria (7.4 in. deep) was partially dissolved in 125 gallons of standard boiling dissolvent with 3 scfm air flow to each of the circulators. At a product concentration of 1M Th^{4+} and 8M HNO_3, the average "heel" depth was 3.3 in. A typical dissolution curve is shown in Figure 12. The results of these tests are summarized in Table II.

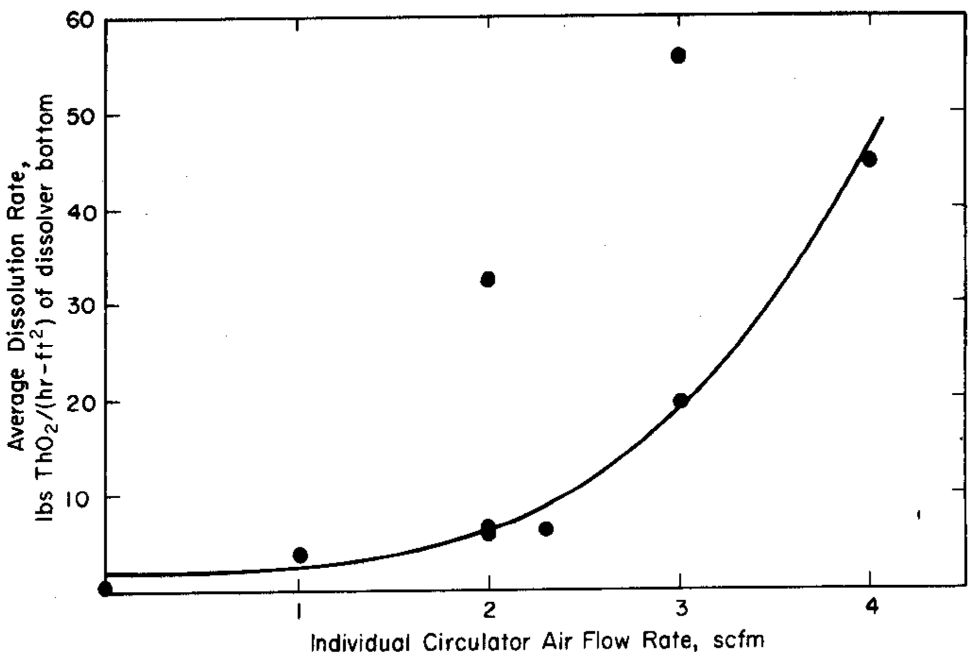


Figure 11. Effect of Circulator Air Flow on Thoria Dissolution

Dissolvent: 40 gal
Thoria: 132 lb
Std. Lab. Diss. Test: 96.6 wt % in 6 hr
Diss. Bottom Area: 0.5 ft^2
No. of Circulators: 1

Table II. Large-Scale Dissolution Tests[a] with Air Lift Circulators

Lot	Std. Lab. Diss. Test, wt % Diss. in 6 hr	Time to Reach 1M Th^{4+}, hr from steam "on"	Avg. Diss. Rate, lb $ThO_2/(hr\text{-}ft^2)$
G-71	98.2	3.20	43.0
G-81	99.9	1.66	82.9
G-105B	99.5	1.70	81.0

a. 500 lb ThO_2 in 125 gallons of dissolvent with 3 scfm per circulator (2 circulators/ft^2 of bottom).

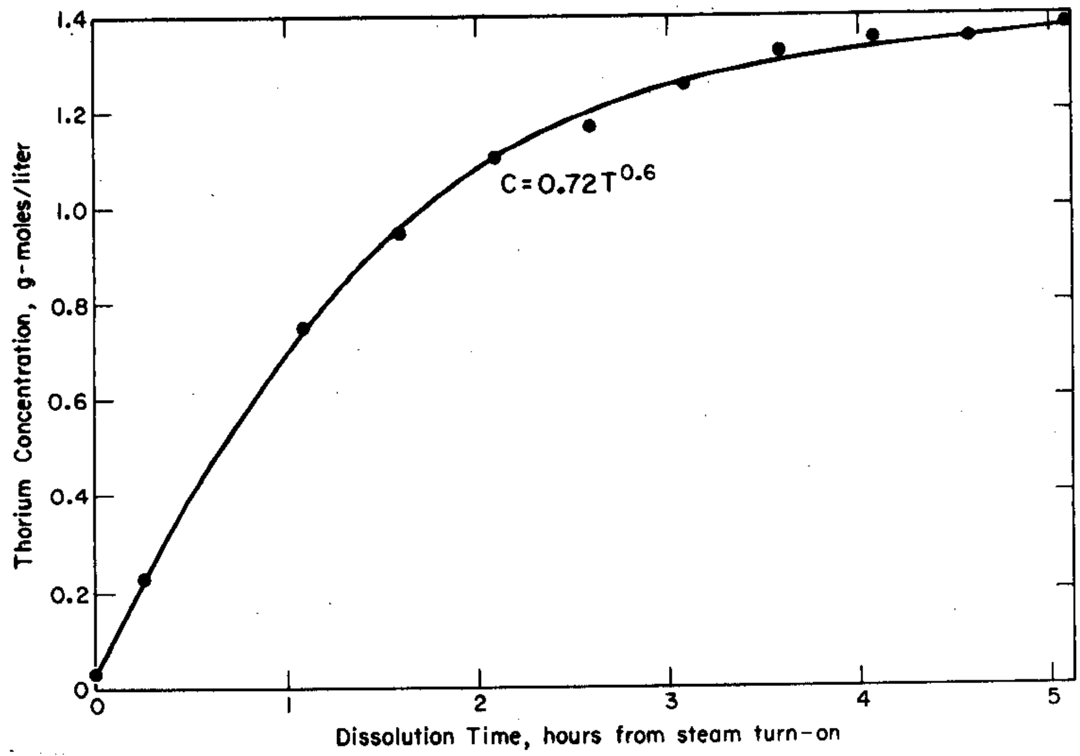


Figure 12. Dissolution of Thoria Agitated by Air Lift Circulators

Dissolvent:	125 gal
Thoria:	500 lb
Std. Lab. Diss. Test:	99.9 wt % in 6 hr
Diss. Bottom Area:	2 ft^2
No. of Circulators:	4
Air flow/Circulator:	3 scfm

The concentration of thorium (C) dissolved with agitation by air lift circulators each operating at 3 scfm can be expressed as a function of time (T) by the formula:

$$C = AT^{0.6}$$

where the constant A is dependent on the dissolving characteristics of the thoria and has a value between 0.25 and 0.75. The varying dissolution rates (Table II) observed in these three thoria lots produced under similar conditions is relatively common. The varying rates are reflected in the results of the standard 6-hr laboratory test used for the dissolution specification (20 g ThO_2 must be at least 95 wt % dissolved in 75 ml of standard dissolvent with vigorous agitation within 6 hr). Based on the results of the standard laboratory dissolution test, the thoria used in the small scale tests (funnel dissolver) gave predictably lower dissolution rates (96.6 wt % dissolved in 6 hr) than that dissolved under similar conditions in these large-scale tests.

Because previous tests with air lift circulators were made only with thoria powder, aluminum-canned thoria was tested to demonstrate the entire reverse codissolution cycle. The test was unsuccessful because the air lift circulators became plugged and resulted in a thoria dissolution rate of only 5 lb $ThO_2/(hr\text{-}ft^2)$. However, the solutions to several potential problems were revealed: 1) in order to avoid pluggage of the air supply, the circulators must be operated at all times when a thoria heel is present; however, during chemical removal of the aluminum cans in the last half of the delayed codissolution cycle, the air flow to the circulators may be reduced; 2) prior to removal of the spent dissolvent, dilution water must be added to prevent crystallization of $Al(NO_3)_3$ at ambient temperature (**Figure 1**), which causes "cementation" of the densely packed thoria heel; and 3) sufficient solution must remain in the dissolver to maintain fluidization of the thoria by the operating circulators during removal of diluted spent dissolvent.

Dissolution of Thoria Containing Magnesia

Laboratory studies[1,2] indicated that the incorporation of 1 wt % magnesia (MgO) during sol-gel preparation would greatly enhance the thoria dissolution rate. The thoria dissolution is promoted because the magnesia dissolves readily in strong acid and causes the thoria to disintegrate into fine particles with large surface area. Three thoria lots containing magnesia were prepared by the Mallinckrodt Chemical Company and were calcined under various conditions in air in an induction furnace. Three "control" lots without magnesia were calcined under similar conditions for comparison. The characteristics of these six thoria lots are shown in Table III. Because samples from five of the thoria lots were at least 99% dissolved in the standard 6-hour laboratory test, a more definitive comparison was made by determining the time to reach 95% dissolution.

Table III. Dissolution Characteristics of Thoria Containing Magnesium Oxide

Lot	MgO Content, Wt %	Calcination Conditions Temp, °F	Time, hr	Particle Size US Sieve Series	Std. Lab Diss. Test Wt % Diss. in 6 hr	Hr to Diss. 95 wt %
1339	0	2100	4	-6	97.0	6.0
				-40+100		5.0
1345	1	2100	4	-6	<99	3.5
				-40+100		2.75
1341	0	2000	1.5	-6	99	2.5
				-40+100		2.5
1347	1	2000	1.5	-6	99	1.0
				-40+100		1.25
1351	0	1950	1.0	-6	<99	0.08
				-40+100		0.5
1350	1	1950	1.0	-6	<99	0.5
				-40+100		0.75

In each test with the annular dissolver mockup with the four air lift circulators operating at 3 scfm each, a 500-lb charge of thoria was partially dissolved in 125 gallons of standard boiling dissolvent to a terminal concentration of 1M Th^{4+}. These tests (Figure 13) show that the thoria containing 1 wt % magnesia dissolved more rapidly than the thoria without magnesia. The magnesia-thoria mixture, which was calcined at the normal temperature of 2100°F for 4 hours, dissolved at a rate of 68.8 lb/(hr-ft^2) compared to 17.2 lb/(hr-ft^2) for the thoria without magnesia. The latter rate is just within the limits of the 6-hr laboratory dissolving specification. The dissolution rates increased with decreasing calcination temperatures (and length of calcination); this effect was much more pronounced with the untreated thoria. The one exception to these observations was the 1% magnesia-thoria mixture that was calcined for 1 hr at 1950°F (Lot 1350). The reason for this discrepancy is not known, but the same irregularity occurred in the laboratory test (Table III) where the -40+100 mesh sample of this thoria lot took longer to reach 95% dissolution than the

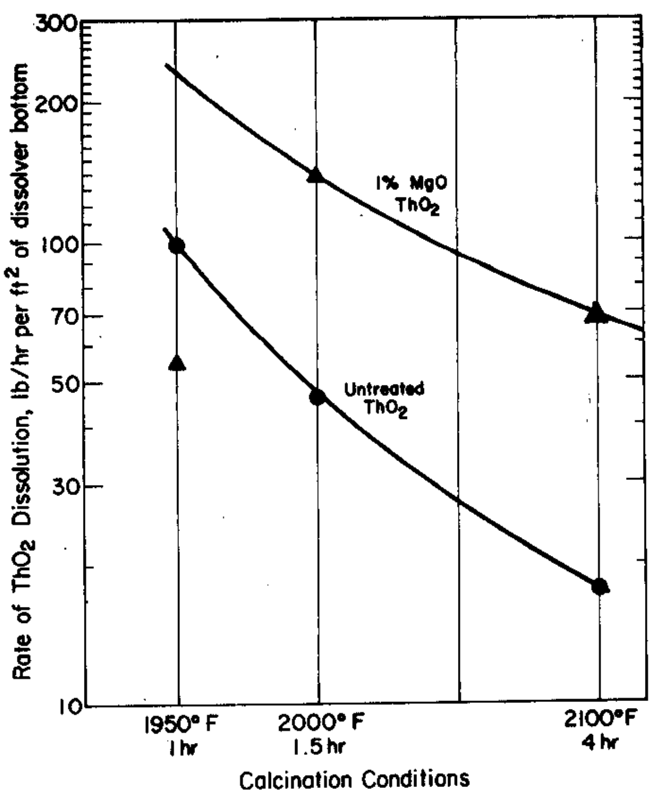


Figure 13. Agitated Dissolution of Thoria Containing Magnesia

Dissolvent:	125 gal
Thoria:	500 lb
Diss. Bottom Area:	2 ft^2
No. of Circulators:	4
Air flow/Circulator:	3 scfm

sample of the control thoria (Lot 1351).

At the end of each test with agitation, the spent dissolvent was removed, and the remaining thoria "heel" dissolved further in 80 gallons of fresh acid without agitation. The dissolution rates [less than 2 lb/(hr-ft^2)] indicate that incorporation of magnesia is not beneficial unless some means of agitation is employed (Table IV).

Table IV. Unagitated Dissolution of Thoria Containing Magnesia

Lot	MgO Content, wt %	Calcination Conditions Temp, °F	Calcination Conditions Time, hr	Avg. Dissolution Rate, lb ThO_2/(hr-ft^2)
1339	0	2100	4	1.33
1345	1	2100	4	1.14
1341	0	2000	1.5	1.15
1347	1	2000	1.5	1.12
1351	0	1950	1.0	1.83
1350	1	1950	1.0	1.51

Capacity of EM Annular Dissolver for F-Area

A total of 104 slotted air lift circulators (2-in.-dia. x 10-in. long) were installed 1-1/2 in. above the 54 ft^2 bottom of the Extra Machinery (EM) annular dissolver for the F-Area separations plant. Separate manifolds in each annulus supplied air to the air lift circulators (Figure 14), and a protective grating was placed over the circulators in the inner annulus (Figure 15) to prevent damage during fuel charging.

Operation of the air lift circulators at 3 scfm each is expected to give dissolution rates much greater than 15 lb ThO_2/(hr-ft^2). At this rate (9.9 hr to dissolve 4.0 tons of ThO_2), the predicted processing capacity would be 2.9 tons ThO_2/day using the same time for other processing steps as listed in Table I. At higher rates, the thoria dissolution time becomes relatively short, and the resulting dissolver capacity (Figure 16) is controlled by the amount of time used for other processing steps (23.5 hr). Dissolution of thoria containing magnesia calcined at 2100°F [(at a rate of 68.8 lb/(hr-ft^2)] would give a dissolver capacity of 3.7 tons ThO_2/day. The maximum capacity with instantaneous dissolution of the thoria is 4.1 tons ThO_2/day.

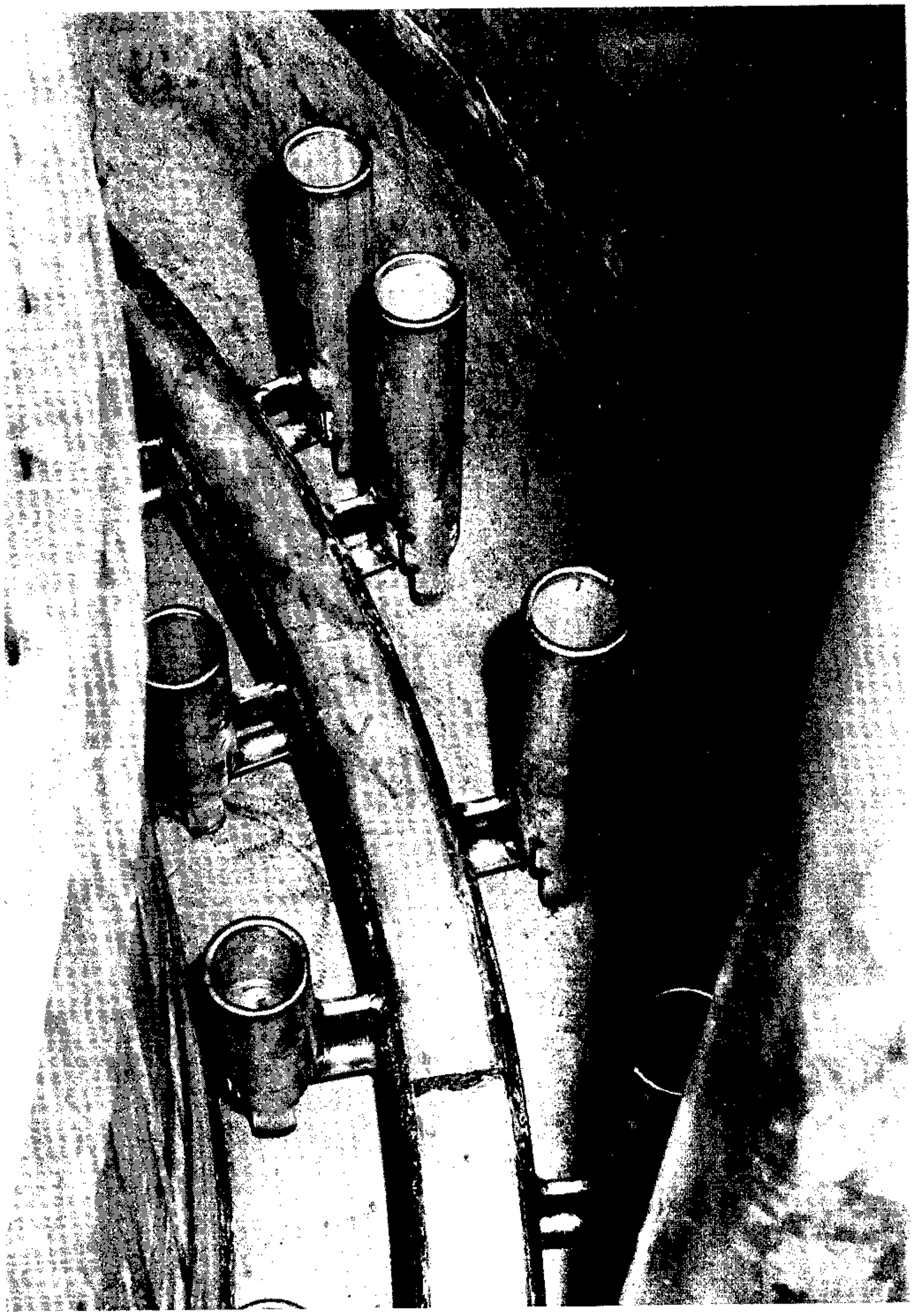


Figure 14. Air Lift Circulators in Plant Annular Dissolver

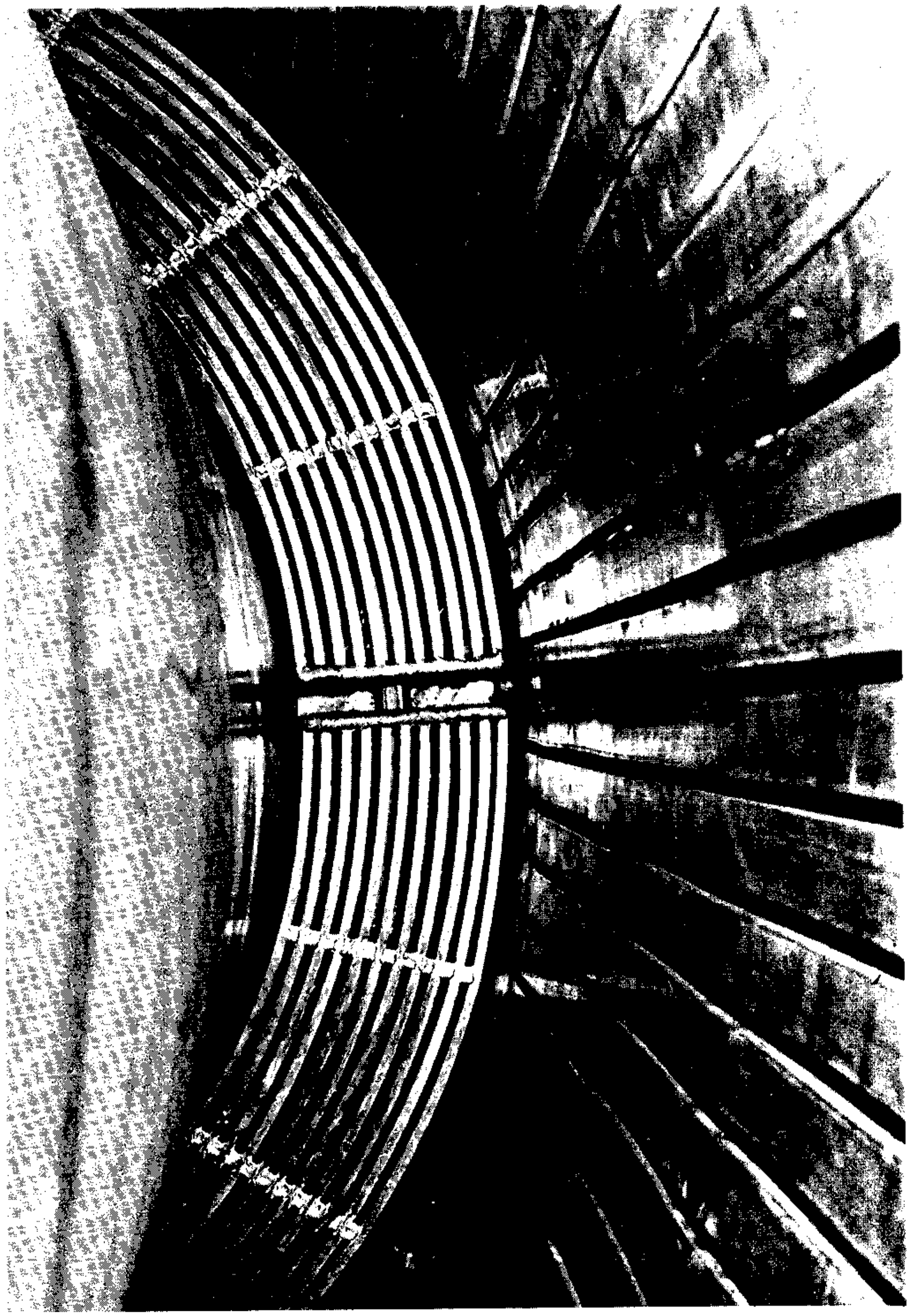


Figure 15. Protective Grating for Air Lift Circulators in Plant Annular Dissolver

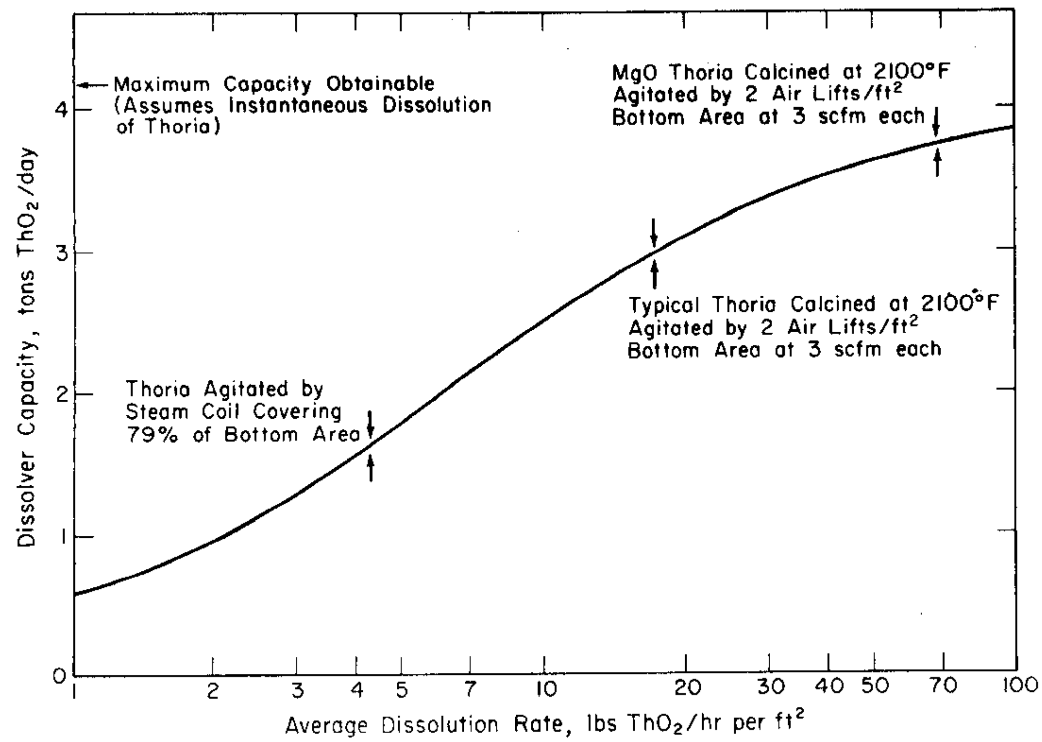


Figure 16. Capacity of Extra Machinery Annular Dissolver for F-Area

Entrainment of Thoria in Dissolver Solution

Pumping tests were made to determine how much thoria from the heel in the dissolver would be entrained in the solution removed from the dissolver vessel. With the end of the suction pipe 3 in. above the high side of the sloping (3/8-in./ft) bottom of the tank, 0.3 to 0.5% of the thoria was entrained. The same range of entrainment was observed with the suction pipe at either 5 or 9 in. from the bottom. The results are summarized in Table V.

Table V. Entrained Thoria in Dissolver Solution

Height of Suction Pipe from Bottom of Tank, in.	Flow Rate, gpm	Entrainment of Thoria in Dissolver Solution, % of thorium dissolved
3	11	0.30
3	30	0.32
5	30	0.44
9	30	0.49

Several attempts to filter the dissolver solution through two different-sized sintered stainless steel filters (98% removal at 12 μm and at 2 μm) were unsuccessful; the entrained thoria blinded the filter rapidly. Centrifugation, however, decreased the entrained thoria to a value equivalent to only 0.006% of the total thorium.

H-AREA POT DISSOLVER EXPERIENCE

A 6-ft-dia. spiral steam coil was installed on the bottom of a 11-ft 4-in.-dia. pot dissolver in the H-Area Separations plant. The cross-sectional area of the steam coil (2-in. Schedule 80 pipe on 3-in. centers) covered only 22% of the dissolver's total bottom area (79% of the 6-ft-dia crib section). During the first thoria processing campaign (88 tons of thorium), thoria dissolved at an average rate of 1.6 lb/(hr-ft^2), for a dissolver capacity of 1.2 tons ThO_2/day.[3] Although the average time required for dissolving 3.2 tons of thoria was 36 hours, this period was quite variable for apparently identical dissolving conditions. About 80% of the thoria dissolvings required 30 to 45 hours, but two dissolvings were completed in about 17 hours, and one required as much as 50 hours (a three-fold difference). The effectiveness of the steam coil during the first campaign was not clear, as several dissolvings made without steam pressure on the bottom coil gave dissolution rates similar to those obtained when the coil was in use. The effect of the coil may have been obscured by differences in the dissolving characteristics of individual lots of thoria, which have been observed to vary widely in the laboratory.

During the second thoria processing campaign (105 tons of thorium), an effect of the bottom steam coil on the dissolution rate was observed. In these dissolvings, the thoria dissolution rate without the bottom steam coil was 41 to 62% of that obtained when using the coil. However, it should be noted that this longer dissolution time decreased the dissolver capacity by only ∿10%. The thoria dissolution rate without the bottom steam coil in operation was consistently less than the dissolutions made with steam to the bottom coil. The observed increase in dissolution rate obtained with the bottom steam coil operating is consistent with data obtained during experimental tests, and contradicts results observed during the first thoria campaign. The effectiveness of the steam coil would be more apparent if the coil covered a larger fraction of the dissolver bottom.

Increased dissolving rates were also observed when 82 tons of thoria containing 1% magnesia was dissolved during the second thoria campaign. Dissolving rates were 20 to 30% faster for the four charges in which 40 to 75% of thoria targets contained 1% magnesia. Dissolving rates were not significantly faster in two charges in which magnesia-containing targets comprised 25% or less of the total charge.

The results indicated that if all thoria contained 1% magnesia, the dissolving rate would increase about 40 to 50%, and the overall dissolving time cycle would be reduced by about 10%. All tests with magnesia additive were made with steam to the bottom coil in the dissolver; greater increases in dissolution rates would be expected if agitation were provided by air-lift circulators rather than steam coils.

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