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Nuclear Fuel Dissolution and Rinsing Studies Using a Continuous Rotary Dissolver

W. D. Holland
C. O. Reiser
R. B. Heimdahl
W. S. Groenier

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NUCLEAR FUEL DISSOLUTION AND RINSING STUDIES USING A CONTINUOUS ROTARY DISSOLVER

W. D. Holland

C. O. Reiser*

R. B. Heimdahl**

W. S. Groenier

*Professor of Chemical and Nuclear Engineering, Arizona State University, Tempe, Ariz. 85281
**Present Address: Bingham - Willamette Co., Front Street, 2800 Northwest, Portland, Ore. 97210

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
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ABSTRACT

An experimental study of a small-scale continuous rotary dissolver is described. The unit is essentially a 1-ft (0.305-m)-diam horizontal drum divided axially into five 5-in. (0.13-m)-wide compartments. Solids are periodically advanced from compartment to compartment while liquid dissolvent flows countercurrent to the solids.

Experimental runs were made to determine rinse efficiencies and the amount of solids that accumulated within the unit. Metal and ceramic powders were used to simulate insoluble fines, and water was used to simulate the liquid dissolvent. The unit was further tested by dissolving UO_2 from metal hulls with HNO_3. The capability of the dissolver for processing large metal pieces (representing sheared pieces of shroud) was also examined.

Results indicate satisfactory overall performance of the dissolver unit. A few minor operating problems were found, but these appear to be easily correctable.

1. INTRODUCTION

During the past three years, the Chemical Technology Division at ORNL has been engaged in a development study of continuous rotary dissolvers. This type of unit is envisioned as being the central component in a primary dissolution system in the recycle process for LMFBR fuel elements. A large portion of this study has been concerned with the rinsing efficiency of the dissolver in regard to fine, relatively insoluble solid particles which are expected to be present in the system.

In an effort to understand and quantify the potential problem areas, a small-scale continuous rotary dissolver was designed, constructed, and tested in the laboratory. The results of many of these tests have been presented in program progress reports and informal memoranda. The purpose of this report is to collect all the information obtained during the

program into one source document which will be useful in the design and testing of larger-scale units of a similar type.

The overall recycle process for LMFBR fuel elements is presently envisioned as consisting of the following steps:

1. Shearing, in which the fuel rods are cut into approximately 1-in. (25-mm)-long sections.
2. Voloxidation, in which the sheared elements are heated in an oxidizing atmosphere in a rotary kiln.
3. Dissolution, in which the fissile material (approximately 80% UO_2--20% PuO_2) is dissolved (or leached from the stainless steel hulls) using hot 6 to 8 M HNO_3.
4. Further treatment steps (e.g., solvent extraction), in which the uranium and plutonium are separated and recovered from the acid solution.

The dissolution step is complicated by the following factors:

1. The solids charged to the dissolver will probably be extremely heterogeneous since they are a mixture of sheared fuel elements (some with partially closed ends), sheared spacer wires, loose powdered fuel, and pieces of stainless steel shroud material ranging in size up to 12 in. (0.305 m).
2. Previous studies have indicated that more than 10% of the PuO_2 in some mechanically blended UO_2-PuO_2 fuels may be insoluble in HNO_3. To recover this insoluble fraction of PuO_2 requires its separation and transport from the stainless steel hulls and dissolution in a more corrosive environment.
3. The gases evolved during dissolution are highly radioactive and must be extensively processed. This processing is greatly simplified if the gases are generated at a more or less constant rate over a period of time.

Consideration of the above factors led to the decision to develop a continuous countercurrent-flow rotary dissolver. This unit, designed and patented by Odom and Kunselman[1] at ORNL, basically consists of a horizontal drum divided into a series of compartments by perforated walls. While the full-size dissolver will probably be approximately 4 ft (1.2 m) in diameter and consist of eight to ten compartments, a fourth-scale unit

[1 ft (0.305-m) in diameter having five compartments] was fabricated for carrying out the initial tests.

A loading compartment, three dissolution/rinsing compartments, and a solids discharge compartment make up the five sections of the drum. Each compartment is approximately 5 in. (0.13 m) wide. The first dissolution/rinsing compartment and the discharge compartment have glass walls to permit visual observation of the solids-liquid interactions in these stages. The remainder of the unit is constructed of stainless steel, with the exception of Teflon face seals on each end. The unit was designed to provide a countercurrent flow of liquid and solids, with positive control of the residence time of the solids in the dissolution/rinsing stages. The residence time of the solids is controlled by the use of sloped axial transfer ducts, which permit advancement of the hulls to the next compartment only while the unit is rotating in a clockwise direction. The normal, counterclockwise direction of rotation, designated as the agitation mode, is used for the dissolving/rinsing operations. After the desired residence time in a compartment, the drum is reversed in direction for one revolution, thus advancing the solids to the next compartment. Perforations in the bulkheads that separate the compartments allow the liquid to continuously flow countercurrent to the solids.

A motor and chain-sprocket drive arrangement and a pump and associated piping for providing a through-flow of liquid are also parts of the overall system.

Figure 1 is a photograph of the 1-ft (or one-fourth scale) rotary dissolver. All of the tests conducted in this unit were primarily concerned with studying the behavior of solids during the dissolution step.

2. METAL POWDER RINSING TESTS [2-4]

The method used in the rinsing tests consisted of adding a measured mass of metal (either nickel or lead) powder to approximately 0.5 kg of 1/4 in.-(6.35-mm)-OD, 1-in. (25.4-mm)-long stainless steel hulls and 60-mil (1.52-mm), 1-in. (25.4-mm)-long spacer wires in the loading compartment of the unit. A flow of rinse water was established, with the discharge being from the loading compartment. The water level in the dissolver was

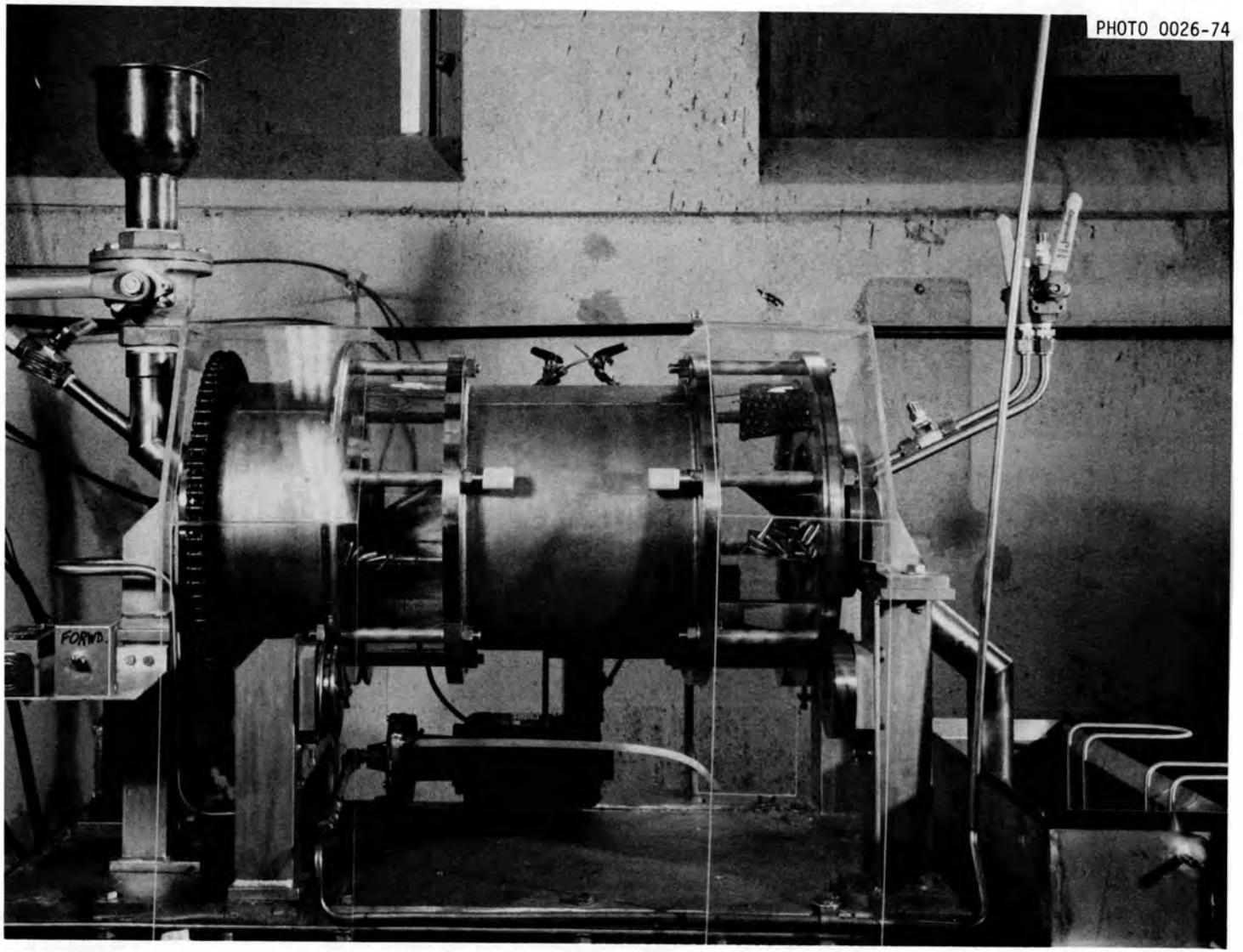

Fig. 1. Twelve-inch-diameter rotary dissolver.

maintained at approximately 4 in. (0.10-m). The drum was rotated in the agitation mode for a prescribed time, effecting the transfer of the solids into the first stage for rinsing. After the prescribed time in the first dissolution/rinsing stage, the drum was rotated clockwise for one revolution, advancing the solids to the next stage. This cycle was repeated until the solids were discharged from the unloading compartment and collected for analysis. The amount of metal powder in the discharged solids was determined by leaching the discharged solids in 1 liter of 6 $\underline{M}$ HNO_3 and analyzing the solution for its nickel or lead content. The results of the analyses for metal concentration allowed the rinse efficiency to be calculated from the following relationship:

$$\text{Rinse Efficiency} = [1 - \frac{M_f}{M_i}] \times 100,$$

where

M_f = mass of the metallic powder (nickel or lead) in the discharged solids

M_i = mass of powder which was added to the dissolver.

Table 1 summarizes the conditions and results for the rinse tests made with -325 mesh ($<44\ \mu$) nickel powder. Tests DB4 and DB5 were conducted by adding three different loads of stainless steel hulls and nickel powder in succession as the previous load was advanced to the next stage. This more nearly simulated the conditions expected to be encountered when operating the dissolver continuously. A total of 10 g of nickel powder was added per feed charge in all tests except DB1 and DB2; 20 g per feed charge was added in the latter two tests. The rinse efficiency, which was higher than 99.6% in each test, appeared to increase as the liquid flow rate increased.

Flow visualization tests using fluorescein dye and water were also made. Results of these tests indicated that a considerable amount of backmixing was occurring between compartments. The backmixing, which was caused by the pumping action of the transfer and agitation baffles in each of the stages, along with the perforations in the bulkheads, was disruptive to the countercurrent flow of solids and liquid. Several attempts were made to eliminate this problem, including reducing the rotational speed of the drum from 9 rpm to 5-1/2 rpm, plugging some of the perforations in the bulkheads, and increasing the free area of the transfer and agitation baffles.

Table 1. Results of rinse tests using -325 mesh nickel powder

Test number	Rinse water flow rate (gpm)	Rinse time per stage (min)	Rinse Efficiency (%)
DB1	0.77	20	99.95
DB2	0.34	20	99.9
DB3	0.34	60	99.95
DB4-1	0.34	20	99.6
-2	0.34	20	99.7
-3	0.34	20	99.9
DB5-1	0.77	20	99.8
-2	0.77	20	99.9
-3	0.77	20	99.95

Each of these changes resulted in a significant reduction in the degree of backmixing observed, so that finally the annular clearance of approximately 1/64 in. (0.4 mm) between the drum walls and the outer edge of the bulkheads was the only place for reverse flow to occur.

After the annular clearances between the bulkheads and drum walls had been coated with a silicone sealant, rinsing studies were continued. Generally, three or four batches were transferred through the dissolver in a given rinse test. Both lead and nickel powders were used in these tests.

The rinse efficiences determined in 11 tests in which nickel particles were used as the simulated insoluble particles ranged from 99.84 to 99.96%, averaging 99.92%. Very little effect was noted when the rinse flow rate was varied by a factor of 4 or the rinse time per stage was varied from 10 to 60 min. The use of -325 mesh lead particles as the simulated insoluble particles resulted in a lower rinse efficiency at given conditions of flow rate and time per stage as well as a greater range in rinse

efficiencies. The rinse efficiencies for the seven tests conducted with lead particles ranged from 99.27% at a flow rate of 0.17 gpm (0.64 liter/min) to 99.77% at 0.67 gpm (2.54 liters/min). The flow rate expected to be used in a large-scale [48-in. (1.2-m)-diam] dissolver corresponds to approximately 0.3 gpm (1.14 liters/min) in the one-fourth-scale unit, and three tests using a flow rate of 0.34 gpm (1.29 liters/min) yielded an average rinse efficiency of 99.66%. These tests indicate that, with three stages of rinsing and nominal residence time of 30 min per stage, rinsing efficiencies of at least 99.5% may be expected. Although the effect of including additional stages was not investigated, it seems logical to predict that more stages would further improve the overall efficiency. Increasing either the residence time per stage or the flow rate of the rinse liquid would also improve the efficiency.

The results of a final series of rinse tests are presented in Table 2. In four of the tests, 1-in.-diam bundles of tubing encased in a wrapper were used to simulate sheared fuel that is gathered as a chunk by an encircling strip of shroud material. The rinse efficiencies obtained with the use of the -270 +325 mesh lead particles were slightly higher than those previously found for -325 mesh lead. The efficiencies obtained with 2.2 to 3.0 μ nickel particles were the highest found to date. Tests DB32 through DB34 were conducted to determine the extent of particle buildup in the dissolver during sustained periods of rinsing. Fifteen batches of material were rinsed in tests DB32 and DB33; seven batches were rinsed in test DB34. The results of these tests indicated a gradual increase in the carry-over of particulates in the first few batches passing through the dissolver until equilibrium was reached (i.e., apparently after the fifth batch had been rinsed). Figure 2 is a plot of the nickel concentration obtained from leaching the rinsed hulls in 0.5 liter of 6 $\underline{M}$ HNO_3 vs the number of batches through the dissolver; the values shown were obtained in test DB33, during the period when all dissolver compartments contained hulls (12 to 15 batches).

Tests were also conducted to qualitatively assess the effects of foaming and particle deposition, or mudding, on the operation of the rotary dissolver. Electric heaters were used to increase the temperature

Table 2. Results of rinse tests with the rotary dissolver

Test number	Rinse water flow rate (gpm)	Rinse time per stage (min)	Number of batches rinsed	Particles used	Average rinse efficiency (%)
DB27	0.34	30	3	-270 +325 mesh Pb	99.78
DB28	0.67	30	3	-270 +325 mesh Pb	99.87
DB29	0.34	30	3	2.2 to 3.0 μ Ni	99.97
DB30	0.17	30	3	2.2 to 3.0 μ Ni	99.98
DB31	0.17	10	3	2.2 to 3.0 μ Ni	99.97
DB32	0.34	10	15	2.2 to 3.0 μ Ni	99.89
DB33	0.34	20	15	-325 mesh Ni	99.93
DB34	0.34	20	7	-325 mesh Ni	99.93
DB35[a]	0.34	30	4	-325 mesh Ni	99.95
DB36[a]	0.17	30	5	-325 mesh Ni	99.86
DB37[a]	0.34	10	5	-325 mesh Ni	99.89
DB38[a]	0.67	30	5	-325 mesh Ni	99.97
DB39	0.0	30	5	-325 mesh Ni	88.12
DB40[b]	0.34	30	5	-325 mesh Ni	97.84

[a] 1-in.-diam bundles of 1/4-in.-diam stainless steel tubing were sheared into 1-in. lengths (34 g of stainless steel per bundle).

[b] No rotation of dissolver except to advance the stainless steel hulls after each 30-min period.

of the dissolver to ~100°C. Quantities of MnO_2, fuller's earth, and $CaCO_3$ were added to the dissolver to fully coat all wetted surfaces. Except for the MnO_2, these materials were removed from all wetted surfaces after a short period of rinsing. The MnO_2 did not coat the surfaces; instead, it remained in the lower portion of the dissolver. The addition of hulls to each compartment accelerated the rinsing operation as a result of their scouring action. The addition of large quantities of wetting agents and detergents to the dissolver did not appear to have any significant effect on the operation of the unit. The agitation of the solution produced enough foam to completely fill the dissolver but had no effect on the transfer of hulls or wires.

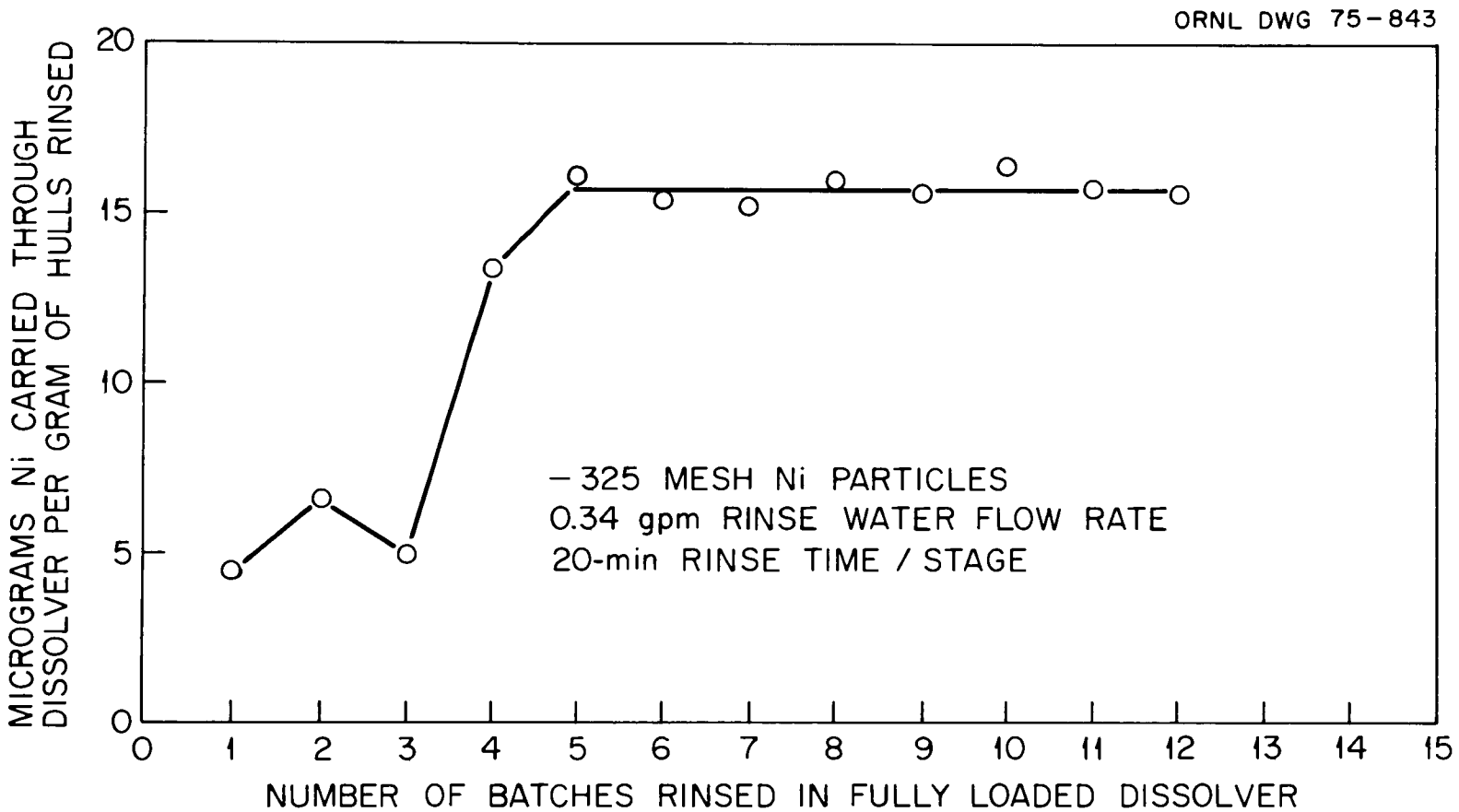

Fig. 2. Particulate carryover through the rotary dissolver as a function of time (test DB33).

3. UO_2 DISSOLUTION STUDIES[5]

On completion of the rinsing studies, a series of tests were initiated in which sheared pieces of UO_2-filled fuel elements were contacted with hot HNO_3 in the 1-ft (0.305-m)-diam rotary dissolver. In order to accomplish this, the dissolver was installed in a fume hood. Other parts of a dissolving system, including acid feed and product storage tanks, acid flow and temperature control systems, and an off-gas condenser, were assembled. Before installation, the dissolver was dismantled and the plugs used to seal the perforations in the bulkheads (described in the previous section) were removed.

The system was designed such that the liquid stream could be recycled if desired. The temperature of the liquid dissolvent could be controlled by the use of a water-cooled heat exchanger and an electrically heated section in the liquid recycle line. Additional heating of the dissolver could be accomplished using an electrical radiant heating system originally installed as part of the dissolver test unit. Provisions were also made for sampling the liquid stream, draining the system, and introducing rinse water. Figure 3 is a photograph of the dissolver system installed in the fume hood.

After several preliminary tests of the system, five dissolution runs were conducted using 0.4-in. (10.2-mm)-diam by approximately 1-in. (25.4-mm)-long pieces from sheared Zircaloy fuel elements containing unirradiated, depleted UO_2. The solvent in every case was hot 6 $\underline{M}$ HNO_3. The purpose of these tests was to gain experience in handling the UO_2-HNO_3 chemical system in the rotary dissolver and to accumulate data concerning dissolution rates of UO_2 as a function of acid flow rates and agitation, the extent of foaming to be expected, and the efficiency of the rotary dissolver in rinsing solid particles from the sheared hulls.

In general, the results of these tests confirmed that the dissolver performance was satisfactory. It was observed that the UO_2 solids separated from the hulls almost immediately after entering the dissolver and tended to remain in the first stage when the hulls were transferred to the next stage. Analysis of the recycle stream indicated that about 90% of the UO_2 dissolved in about 30 min while essentially all dissolved in 1 hr.

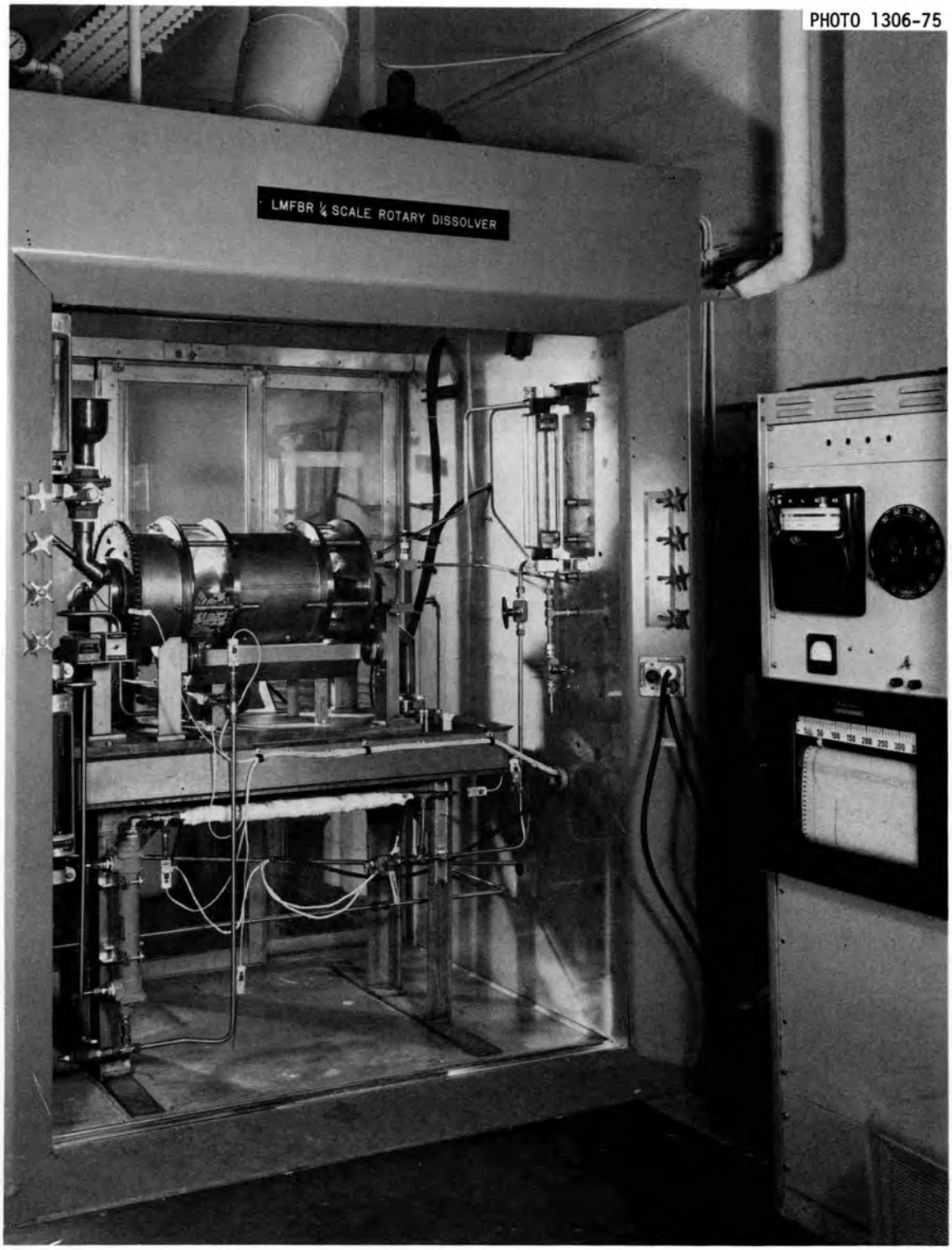

Fig. 3. Dissolver system installed in the fume hood.

Considerable bubbling action occurred when the UO_2 was added to the acid; however, very little foaming was observed. It was noted that some finely divided solids accumulated in the space between the agitation and transfer baffles in the first stage.

A summary of the test runs and the observed results is presented in Table 3 and Figs. 4 and 5. In each test, the solvent was 6 M HNO_3 at a flow rate of from 0.5 to 0.6 gpm (1.9 to 2.3 liters/min). The rotational speed of the dissolver was 5-1/2 rpm, and the depth of liquid in the dissolver was approximately 3 in. (76 mm).

Table 3. Summary of UO_2 dissolution tests

Run number	Temperature (°C)	Solvent	Volume of solvent (liters)	Comments
U-1	98	6 *M* HNO_3	5.86	Dissolved a total of 13 sheared fuel pieces (215 g of UO_2). Fuel pieces were added a few at a time. Noted that UO_2 solids fell from hulls almost immediately upon entering the dissolver. Dissolution was rapid with bubbling action; however, no foaming was apparent.
U-2	98	6 *M* HNO_3	7.24	Dissolved two batches of ten fuel pieces each (402 g of UO_2). Batches were added at 30-min intervals. When one batch was transferred, most of the undissolved UO_2 powder remained behind in the previous stage. It is estimated that over 90% of the solids were dissolved in 1 hr; about 1% remained undissolved after 2 hr.
U-3	95	6 *M* HNO_3	8.1	Dissolved three batches of 20 fuel pieces each (681 g of UO_2). Batches were added at 30-min intervals. Samples of recycle stream were taken periodically for chemical analysis. On transfer of the hulls, solid powder remained behind as in previous runs.
U-4	80	6 *M* HNO_3	7.1	Dissolved four batches of 20 elements each (1339 g of UO_2). Batches were added at 5-min intervals. The objective was to try to build up a cake of undissolved solids. An accumulation of solids between the baffles in the first stage was noted, but no operational problems were encountered. Empty hulls leaving the dissolver appeared to be well rinsed.
U-5	80	6 *M* HNO_3	6.6	Dissolved four batches of 20 elements each (1299 g of UO_2). Batches were added at 30-min intervals. Recycle stream was sampled every 5 min. Observations were similar to those for other runs.

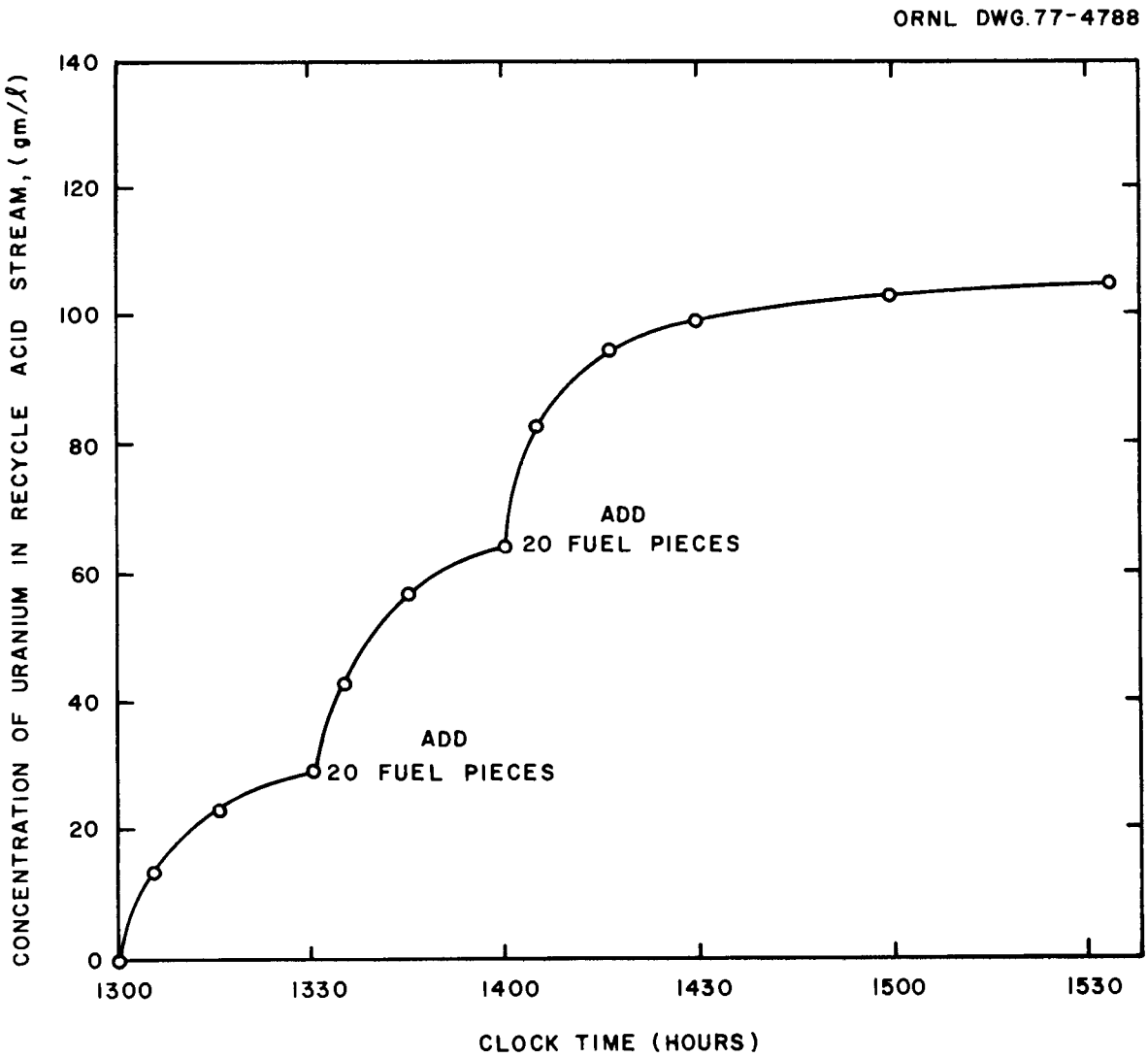

Fig. 4. Rotary dissolver results, Run U-3.

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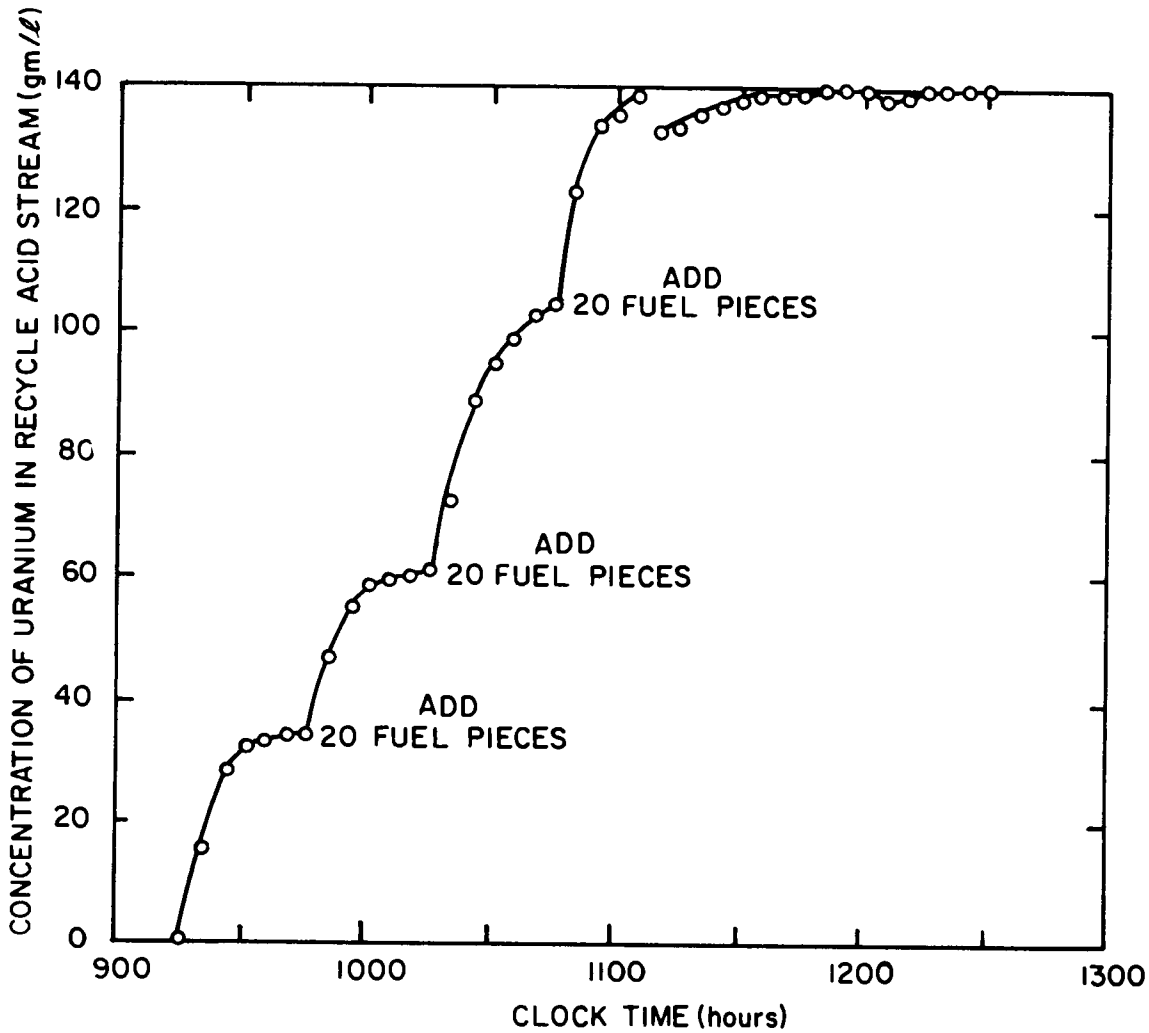

Fig. 5. Rotary dissolver results. Run U-5.

4. MUDDING TESTS WITH METAL POWDERS[6]

A series of tests was conducted to examine the problem of "mudding" in the 1-ft (0.305-m)-diam rotary dissolver. Mudding is defined as the buildup of small insoluble particles within the dissolver. The objective of these tests was to determine: (1) the location and extent of mudding, (2) the size of particles that tend to accumulate in the dissolver, (3) the effect, if any, of the accumulation on dissolver performance, and (4) the design or operational changes that might be made to alleviate observed problems.

The first series of six runs consisted of repeated additions of empty stainless steel hulls mixed with various metal powders of different size ranges. The stainless steel hulls were 0.25-in. (6.4-mm)-OD by 1-in. (25.4 mm)-long sections of tubing. The metal chips and powders included 4-mesh chromium, 40 and 325 mesh iron, 1/4-in.-diam by 1/8-in.-thick aluminum discs, and granular (≥ 40 mesh) lead. A 3-liter/min flow of water was used to simulate the dissolvent liquid. The amount of insoluble metal powder in the feed was much higher than that to be expected during normal operation of the dissolver, being 14.5 g of metal powder and 30 hulls (~35g) for each feed charge.

The results of these runs can be summarized as follows:

1. Particles in the size range from 200 to 500 μ tended to accumulate in the dissolver until a certain inventory was established. The larger metal chips (1/16 to 1/4 in.) (1.6 to 6.3 mm) passed through the dissolver along with the empty hulls. Smaller particles of iron (~20 μ) were removed with the wash liquid.
2. A steady-state inventory was attained after repeated additions of the 200- to 500-μ iron or lead particles; at this point, the rate of input of these particles was balanced by the rate of discharge with the empty hulls. Apparently the mechanism of transfer of the particles through the dissolver was a "scooping" action, in which the hulls carried the solids from one stage to another.
3. The steady-state accumulation of solid particles in the dissolver did not interfere with the transfer of hulls from stage to stage but caused some difficulties at the exit chute, which occasionally became clogged.

4. A fairly large amount of particles accumulated in the space between the agitation and transfer baffles of each stage; this is undesirable and should be corrected in future designs.

The specific test conditions used and the results obtained for each of the six runs are given in Appendix A.

Another run of this type was made using a more typical 5% insoluble metal powder content (1.75 g of iron powder and 30 hulls for each feed charge). Approximately 130 feed additions were made before iron powder appeared in the exit stage as compared with 21 additions in earlier runs using a higher proportion of powder. After 175 batches had been fed, the iron powder discharged with the hulls was sufficient to stabilize the accumulation in the final dissolver compartment at about 10 g. No plugging of the exit chute was indicated when the run was terminated after 269 charges. These results lead to the conclusion that normal amounts of insoluble fines will not clog the exit chute or interfere with routine operation of the dissolver.

5. TESTS WITH CERAMIC POWDERS[6]

The accumulation if insolubles in the dissolver was also studied by charging porcelain-filled sheared prototype LMFBR fuel and operating with a countercurrent water wash of approximately 2 liters/min. This was a long-term run in which 73 charges consisting of mixtures of ceramic-filled hulls and wires and ceramic powders were added at 20-min intervals. A rough material balance was made by calculating the difference between the inlet and outlet weights of solids.

The solids feed for the first 38 additions consisted of a mixture of 200 g of ceramic-filled hulls, wires, powder, and fragments mixed in the same proportions as was found in shearing tests of this material, plus, 50 g of ceramic powder, also blended to match the size distribution found in the shearing tests. Thus, the total weight per charge was 250 g. The complete size distribution of the feed is given in Appendix B.

The next ten feed additions consisted of 250 g of the feed material described above plus 50 g of 1-in. (25.4-mm)-long by 0.25-in. (6.4-mm)-diam empty hulls. After one further addition of 250 g of ceramic feed, 24 batches consisting of 250 g of ceramic feed and 25 g each of +325 mesh nickel powder and -325 mesh lead powder were added. Finally, nine additions consisting of 100 g of empty hulls were made.

The experimental data collected for the run are shown in Fig. 6, where the mass of feed to the dissolver and the mass of solid product from the dissolver are plotted for each separate feed addition. The difference between the total mass input and total mass output is also plotted. This quantity, which has been corrected for fines exiting in the wash liquid, is the total mass that has accumulated in the dissolver.

Although the interval between feed additions was 20 min for most of the runs, the dissolver was occasionally left to rotate for several hours between feed additions. During these periods, additional solids would exit the dissolver and the amount of accumulated solids had to be corrected by subtracting this amount from the cumulative total. These corrections are shown by vertical arrows in Fig. 6.

The weights of the solids exiting the dissolver were not measured individually for the first six batches of feed added. Consequently, the

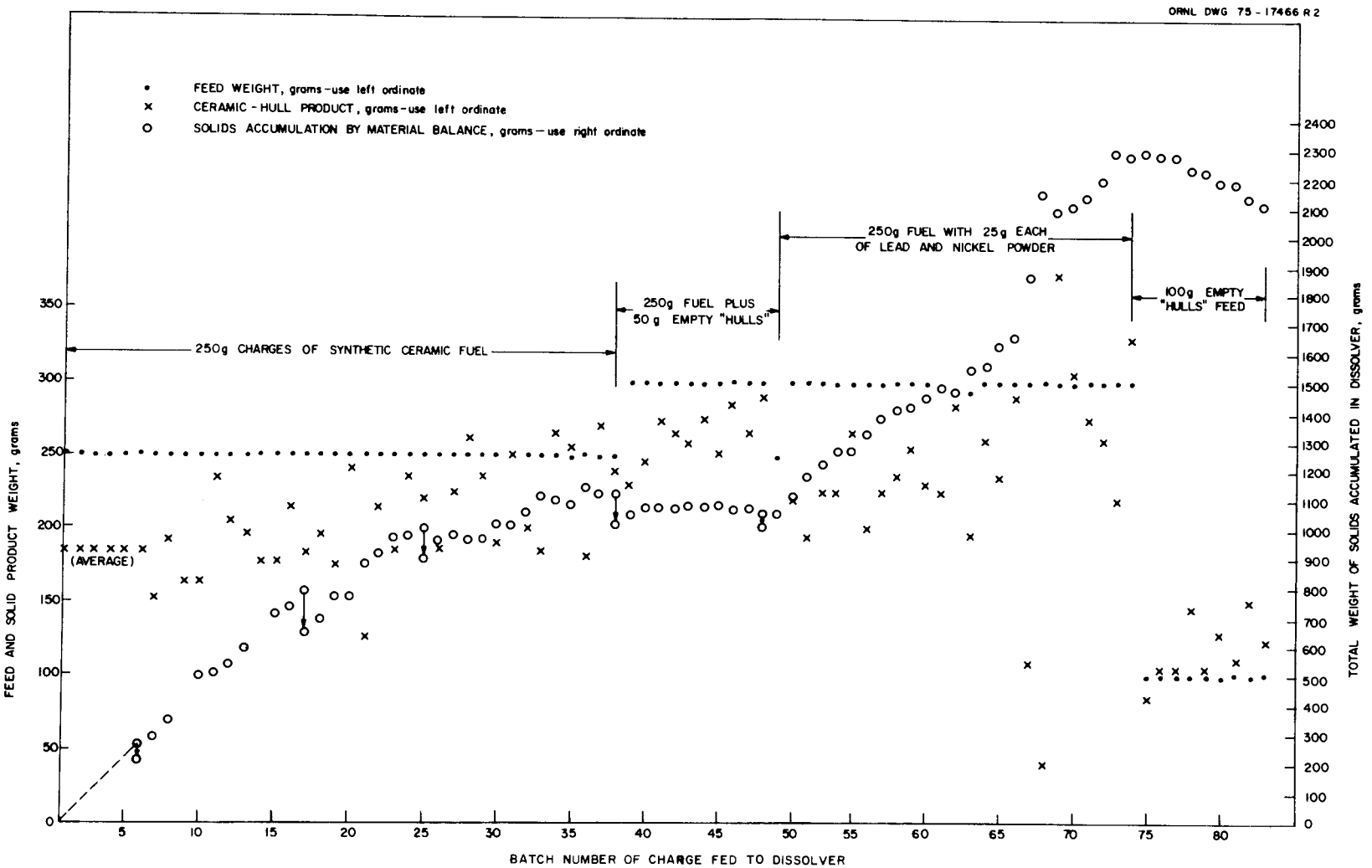

Fig. 6. Dissolver run with ceramic prototype fuel using a water wash.

average output based on the total amount of solids out after six batches is plotted in Fig. 6.

Several interesting points can be made from a consideration of the data presented in Fig. 6. The inventory of accumulated solids gradually increases, until about the 35th addition to a total of about 1100 g; at this time, a steady state seems to have been reached. During this period, the amounts of solid per batch leaving the dissolver show considerable variation. The next ten additions, consisting of a 250-g feed mixture plus 50 g of empty hulls, had essentially no effect on the solids inventory in the dissolver. When the solids feed was subsequently changed to 250 g of feed mixture plus 25 g each of +325 mesh nickel and -325 mesh lead powder, rapid and steady increase in the dissolver solids holdup occurred and an increasing percentage of metal powders adhered to the hull product. More nickel than lead was retained on the hulls, apparently because of the large size of the nickel powder.

In the final series of additions, the feed consisted of 100 empty hulls per addition. This caused a decrease in the retained solids inventory in the dissolver by as much as 50 g per charge.

On completion of this run, the dissolver was disassembled and the accumulated solids were collected. The quantity of solids found in the dissolver was only about half that expected from the cumulative material balance. The amount and nature of the solids accumulated in the dissolver compartments are shown in Table 4.

It is believed that the discrepancy between the actual amount of solids accumulated at the end of the test and that calculated by the overall material balance can be attributed to losses of fine powder in the wash water. On exiting the dissolver, the wash water flowed into a large settling tank and then was discharged into a drain. After each series of additions, the solids in the settling tank were collected, dried, and weighed. The total mass collected was divided by the number of additions, and the result, representing the average amount of solids leaving in the wash water per addition, was used as a correction term in the material balance. There is a possibility that all the solids (particularly the finer ones) did not settle in the tank and were lost with the wash water.

Table 4. Accumulated solids found in dissolver after 83 additions

Feed Section	Leaching sections			Discharge Section
	First	Second	Third	
31 g of fine ceramic powder with no metal	309 g with wide range of ceramic particles. Some wire and hulls.	284 g; ceramic powder with fewer fines. Few wires but no hulls.	382 g; more wire but ceramic powder similar to preceding stage.	138 g; ceramic powder similar to preceding stage. Less wire but more hulls.

This discussion points out the difficulty of maintaining an accurate cumulative material balance in this system. A relatively small error on each addition can lead to large discrepancies in the predicted solids inventory over many additions.

6. Additional UO_2 Dissolution Studies[6]

The purpose of this test was to study the dissolution of UO_2-containing samples at conditions more representative of actual operating conditions than those used in the earlier UO_2 dissolution runs. To accomplish this, the apparatus was modified in such a way that fresh HNO_3 could be preheated and added to the dissolver continuously.

The feed material consisted of approximately 1-in. (2.54-cm)-long chopped sections of stainless steel tubing containing depleted UO_2. These samples had been prepared several years earlier for another test program and were found to contain a mixture of two different diameters [0.305 in. (7.8 mm) and 0.35 in. (8.9 mm) OD]. Some of the samples were crimped at one or both ends.

The dissolvent for this test was 8 M HNO_3 at 92°C. Chromium powder was added to the dissolver along with the UO_2-containing hulls to simulate insoluble plutonia or fission product particles.

Three feed charges were prepared and fed to the dissolver at 1-hr intervals. The makeup of the charges was as follows:

Component	First charge(g)	Second charge(g)	Third charge(g)
Urania + Stainless Steel Hulls	1221	1221	1221
Chromium powder	45 (2μ)	45 (140 mesh)	45 (2μ) 45 (140 mesh)

Weighings of the empty hulls after dissolution of the UO_2 indicated that approximately 200 g of stainless steel hulls was present in each charge.

The dissolver was initially loaded with 6.4 liters of 8 M HNO_3 at 92°C. The first feed charge was introduced into the dissolver and allowed to react for 1 hr in the first stage before it was advanced to the next stage and the second feed charge introduced. At this time, acid flow through the dissolver was commenced. Fresh acid was introduced and spent acid was withdrawn at the rate of approximately 10 liters/hr.

After another hour, the third feed charge was introduced to the dissolver; after the following hour, the initial feed charge was withdrawn.

At this time, the acid flow was reduced to approximately 5 liters/hr. The remaining two charges were subsequently withdrawn at 30-min intervals. Throughout the 4-hr test period, acid samples were removed at the dissolvent outlet at 15-min intervals. These samples were analyzed for dissolved uranium and insoluble chromium powder contents. Figure 7 shows the feed and withdrawal schedule as well as the results of the uranium and chromium analyses.

The hull products for each withdrawal were collected, weighed and subsequently leached with hot 6 N H_2SO_4, which was analyzed to determine the uranium and chromium contents. Results of these analyses are presented in Table 5.

Table 5. Analysis of hull products

Feed charge	Mass(g)	Conc. (ppm in 500 ml)		Mass % in product	
		Uranium	Chromium	Uranium	Chromium
1	60	86	5	0.071	0.0041
2	140	111	5	0.040	0.0018
3	400	241	8	0.030	0.0010

As can be seen from Fig. 7, the residence time in the dissolver for the three feed charges were 3, 2.5, and 2 hr, respectively. The UO_2 from the first and second charges was found to be completely dissolved. Hulls from the third charge were found to contain four small pebbles of undissolved UO_2, and one tube, which was crimped at both ends, contained UO_2 that was not completely dissolved. The appearance of some 2-μ chromium powder in the exit stage was noted approximately 15 min after the first addition of feed. This was probably caused by the absence of countercurrent acid flow during the first hour and would not be characteristic of steady-state conditions.

The transfer of hulls out of the dissolver was not in correspondence to their feed rate. As shown in Table 5, the outlet masses of hulls were 60, 140, and 400 g, respectively, from three equal mass feed charges. It should be noted that all of the last mass (400 g) did not exit the dissolver

as the result of a single reversal. The dissolver rotation was repeated several times at the end of the run, and the 400 g of hulls collected represents all the hulls in the dissolver at that time.

An analysis was made of the uranium concentration data presented in Fig. 7. Assuming that each 1221-g charge contained 200 g of stainless steel hulls a uranium content of 898.5 g per feed charge was calculated. Since the first feed charge was visually observed to be almost completely dissolved in 1 hr, this would indicate a uranium concentration of appoximately 140 g/liter if the 6.5 liters of solution in the dissolver were well-mixed. The acid samples withdrawn during the first hour had a concentration of about half this value. It is believed that this discrepancy is caused the samples that were taken during the period of no acid flow and thus did not truly represent the contents of the first dissolving stage. Once the countercurrent acid flow was started, the measured uranium concentrations increased markedly.

An overall uranium balance was made for the entire run. The agreement between the total uranium input (3 x 898.5 = 2695.5 g) and the uranium output obtained by a trapezoid rule integration of the concentrations of uranium in the outlet stream times the volumetric flow rates out gave agreement within 2%.

Insoluble chromium powder in the exit acid stream was determined by filtering a sample of known volume and subsequent drying and weighing. As mentioned earlier, the 2-μ chromium powder added with the first feed charge seemed to diffuse rapidly throughout all stages in the dissolver. The addition of 45 g of 140 mesh powder along with the second feed charge did not seem to have much effect on the chromium concentration in the exiting acid solution. When 90 g of mixed powder was added with the third feed charge, a rapid increase occurred in the amount of chromium being washed out by the acid stream. Integration of the chromium concentration data in Fig. 7 indicates that approximately 70 g of chromium powder were washed out in 1 hr by the 10-liter/hr acid stream.

The effectiveness of the dissolver in rinsing the insoluble chromium particles from the hulls is evident in Table 5. The higher chromium content of the hulls from the first feed charge is probably caused by the absence of acid flow during the first hour of the test.

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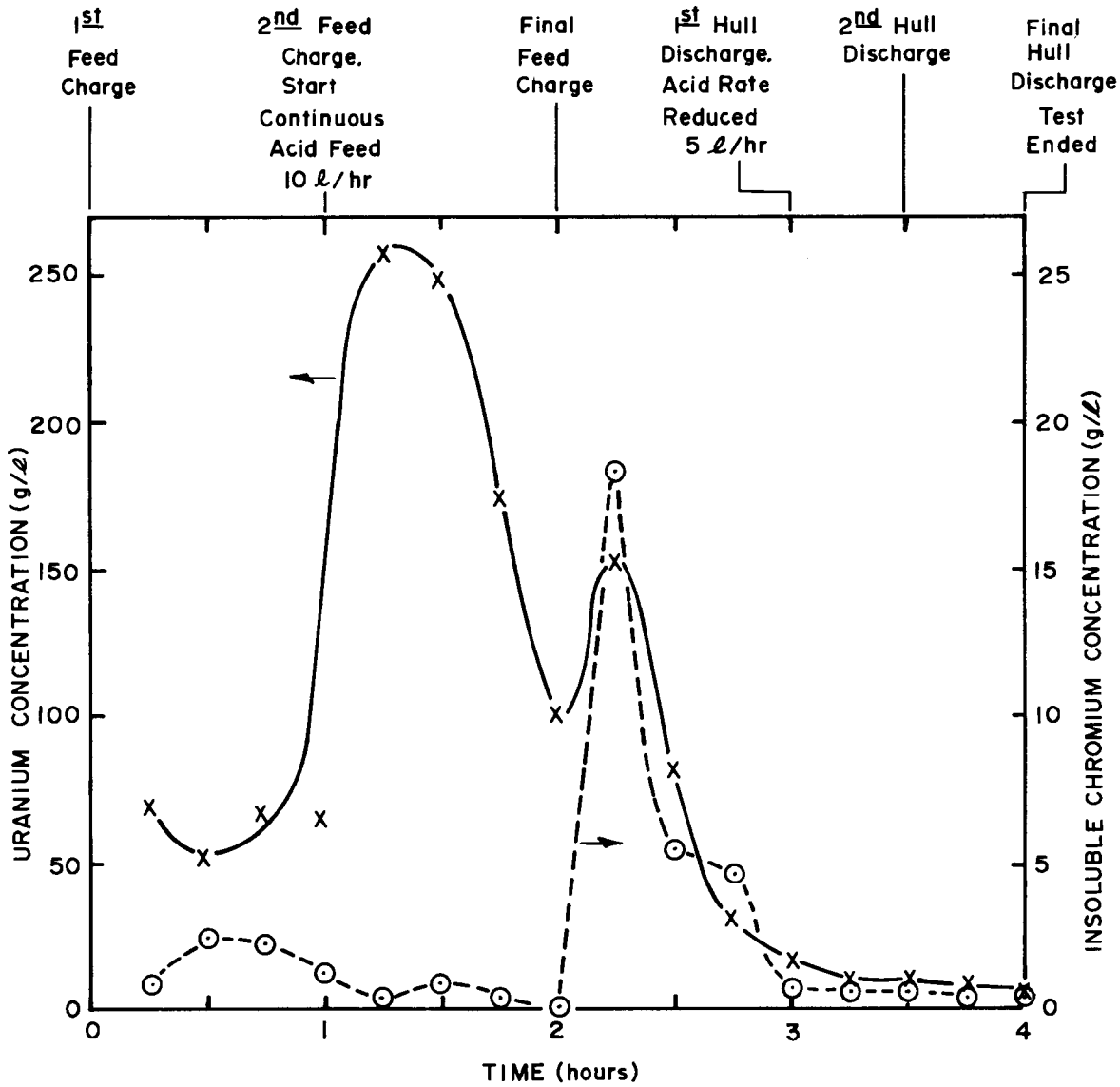

Fig. 7. Dissolution schedule and acid concentrations.

Thus the chromium particles were able to diffuse throughout the dissolver and to contact the hulls in the exit section. Such behavior was not observed when the acid flow was commenced, and backwashing tended to keep the insoluble particles away from the exit section. In this case, rinse efficiences greater than 99.9% (as found in earlier rinse tests) were obtained.

7. TESTS WITH SIMULATED SHROUD PIECES[7]

The 1-ft(0.305-m)-diam, three-stage rotary dissolver was operated to determine whether the presence of pieces of fuel element shroud or wrapper resulting from whole-element shearing would create material transfer problems in the ducting between dissolver stages. Since this experimental unit is roughly one-fourth scale, miniaturized shroud pieces were fabricated for test purposes. Stainless steel strips were cut from 22-gauge (0.74-mm) stock in three sizes: 1/4 x 2 in., 3/8 x 2-1/2 in., and 1/2 x 3 in. (6.3 x 50.8 mm, 9.5 x 63.5 mm, and 12.7 x 76.2 mm). These three sizes of strips were bent into half-hexagon shapes having major dimensions of 44, 58, and 64 mm respectively. One piece of simulated shroud material was fed to the dissolver with each charge of 1-in. (25-mm)-long sheared porcelain-filled fuel hulls and wires. The charge size was approximately 1 kg. In some cases, the shroud pieces did not transfer to an adjoining stage on the first reversal of the dissolver drum. This is not unusual, however, as some of the jagged pieces of sheared fuel also tend to skip a transfer on occasion. These delays are not caused by transfer duct plugging, but rather by the jagged material catching temporarily on perforations in the lifting baffles or on wires caught in these baffles. All shroud pieces were accounted for in the final product. The test pieces are thought to be equivalent to full-scale material having a major dimension of up to 10 in. (254 mm).

Forty-two additions of 1 kg each of sheared wires and porcelain-filled hulls plus one shroud piece of the smaller [1/4 x 2 in. (6.3 x 50.8 mm)] size were made. The weight of the discharged product ranged from 500 to 1200 g per batch. Some discharged batches contained no shroud material, while others contained two pieces. The holdup of dissolver material was greater than when operating with UO_2 because the porcelain "fines" tend to accumulate until hull pieces transport them to the solids discharge end of the unit. A static liquid inventory was maintained with no rinse flow; holdup was as high as 5.7 kg containing seven shroud pieces. The average number of shroud pieces found in the dissolver was approximately four.

Thirty-nine batch additions of fuel, each containing an intermediate-sized shroud piece [3/8 x 2-1/2 in. (9.5 x 63.5 mm)] were used in the

second test. The results were similar to those obtained in the first test; the product material ranged in weight from 500 to 1300 g per batch and contained from zero to three shroud pieces. The dissolver inventory increased to 10.6 kg with a maximum of nine shroud pieces. The average number of shroud pieces was between four and five. No plugging or other operational problem was encountered.

In the third test using the half-hexagon strips, 46 batch additions of synthetic fuel, each containing one of the largest shroud pieces [1/2 x 3 in. (12.7 x 76.2 mm)], were used. Again, no plugging of internal ducts occurred. The product material ranged in weight from 700 to 1300 g per batch and contained zero to three shroud pieces. The inventory decreased slightly (from that found in the second run) to 9.7 kg with a maximum of seven shroud pieces. The number of shroud pieces in the dissolver averaged between four and five.

In a final test, simulated shroud pieces of a different shape were used. These were made by forming 1/2 x 3 in. (12.7 x 76.2 mm) strips into a C-shape having a major dimension of 1.5 in. (38 mm). Twenty-eight additions of feed containing one or two of the simulated shroud pieces were made. Results were similar to the tests using half-hexagon pieces in that solids transfer was irregular, although no blockage of the transfer ducts was observed.

One difference noted in this test as compared with other tests using the half-hexagon pieces was the tendency for the C-shaped pieces to become permanently hung on the lip of the outlet chute. This occurred several times during the test run and eventually resulted in blockage of the exit chute. Redesign of this chute and/or of the lifting baffle that feeds the chute should solve this difficulty.

8. CONCLUSIONS

The performance of the rotary dissolver was quite satisfactory in all of the tests conducted in this study; no major problems were encountered. The results obtained in the these tests can be summarized as follows:

1. The rinse efficiency for small particles was greater than 99.5%. A unit consisting of more than the three stages used in this study should give an even higher rinsing efficiency.
2. Dissolution tests using the UO_2-HNO_3 system proceeded smoothly and efficiently.
3. Particles of a certain size (too heavy to be rinsed out with the flowing liquid and too light to transfer with the hulls) initially accumulated in the dissolver. Eventually, however, a steady-state condition occurred and these particles were transferred out of the dissolver with the hulls and wires. The presence of the particles did not seem to seriously affect the performance of the dissolver.
4. Large metal pieces sized to simulate sections of shroud were successfully fed through the dissolver; however, those having hooked ends tended to hang on the lip of the exit chute.

A few minor problems were found during some of the tests. These can be summarized as follows:

1. Solids accumulation occurred principally between the agitation and transfer baffles in each stage. This caused the perforated baffles to act as solid sections and to lift a significant quantity of liquid on each revolution. Some of this liquid then flowed back into the preceding stage, causing excessive backmixing.
2. Occasional problems were encountered with the feed and exit chutes clogging. These problems occurred when solids with an abnormally high proportion of powdered fines were fed and when the dissolver contained a large inventory of fines. Clogging was also observed when curved shroud pieces were held by the lip of the exit chute. We believe that these problems could be solved by redesign of the entrance and exit chutes.

While the results found in this study are encouraging, it should be pointed out that they were obtained using simulated feed materials in a unit approximately one-fourth the size of a full-scale model. In addition, the test times were relatively short compared with the time span necessary to demonstrate trouble-free operation of a full-scale unit. Thus, it is evident that a considerably expanded test program involving larger-scale equipment, longer testing periods, and carefully chosen simulated feed is necessary to allow actual dissolver performance to be predicted with confidence.

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10. APPENDIXES

10.1 Appendix A: Data on Mudding Tests with Metal Powders

The following metal powders and chips were used during this sequence of tests to simulate insoluble solids:

A. Chromium (Matheson Coleman & Bell)
   4 mesh
B. Iron Metal (Fisher)
   40 mesh
C. Aluminum pellets (Allied Chemical)
   1/4-in.-diam x 1/8-in.-thick discs
D. Iron (reduced) (Mallinckrodt)
   325 mesh
E. Lead metal (Fisher)
   granular (apparently 40 mesh and larger particles).

The actual test conditions and experimental observations are described below.

10.1.1 Run 1

One pound portions of each of the above materials were mixed and divided into three equal batches. The mixed powder (1.67 lb) plus 30 empty stainless steel hulls was added at 30-min intervals. A total of three batches was added. The water flow rate was 3 liters/min.

Observations - The larger chromium and aluminum pieces advanced normally with the hulls. The finer reduced iron was almost entirely washed out with the flowing water. The iron and lead metal particles (40 mesh) tended to accumulate in all four stages. After the three batches of hulls had been removed, the dissolver still contained most of the medium-sized material.

10.1.2 Run 2

A test run was made by repeadly introducing charges consisting of thirty 1-in. hulls and 14.5 g of iron metal to the 1-ft-diam dissolver. The iron metal was approximately 40 mesh. Material of this size had been found to tend to accumulate in the dissolver in a previous test. A water level of about 3 in. was maintained in the dissolver. The water flow rate was 2.9 liters/min.

Seventy-one charges were run through the dissolver over a 1-1/2-hr period. This represents a total input of 1030 g of iron powder. Very little of the powder was washed out with the flowing water.

During the initial addition of solids, it was noted that the iron powder accumulated in the first dissolving stage. (This stage has Pyrex walls.) The hulls leaving the last stage (also Pyrex) appeared to be well-rinsed; no iron powder was observed in the last stage.

As the test progressed, solids apparently began to accumulate in the other dissolving stages. However, this could not be determined with certainty because these stages have stainless steel walls and thus cannot be observed visually.

After the addition of approximately 305 g of iron powder (21 charges), iron powder was found in the Pyrex fourth (exit) stage. After 450 g had been added (31 charges), the main mechanism of transfer of the fine solids through the dissolver appeared to be a scooping action in which the "empty" hulls carried solids from one stage to another.

After powder accumulation was observed in the exit section, it was also noted that the hulls leaving the dissolver were not well-rinsed but contained many powdered iron particles.

Solids continued to accumulate in the exit section until a steady state was reached. At this point, the flow rate of solids into the dissolver was balanced by an equal flow of solids out of the dissolver. This was checked over a defined time interval and found to be approximately correct.

During the period of approximately steady-state operation, the following observations were made:

1. The operating characteristics of the dissolver with regard to transferring hulls were not affected.
2. The exit chute tended to become clogged to such an extent that hulls would not transfer out of the dissolver. This was caused by a "mud cake" of metal powder which would not flow down the exit chute. Empty hulls would become embedded in this cake and thus block the exit chute.
3. A clogging problem similar to that discussed in item (2) occurred in the entrance tube. This difficulty which was probably caused

by too-rapid feeding of the charge into the dissolver, was corrected by using slower feed rates.

4. No apparent permanent buildup of solids was observed except in a zone between two baffles in the first stage. This is the location where UO_2 particles have been observed to accumulate in earlier dissolving tests.
5. The amount of solids contained in the dissolver at steady state is estimated to be about 600 g.

On the day following the test run, the solids remaining within the dissolver was solubilized by introducing dilute HNO_3. This treatment dissolved about 90% of the solids. Most of the remaining 10% was removed in subsequent treatments with hot HNO_3 and with oxalic acid.

During the addition of oxalic acid following several nitric acid treatments, a lump of solid (apparently iron oxide), approximately 1 x 1/2 x 1/2 in., broke away in the entrance section and passed through the dissolver. This might indicate that a buildup of solids did occur in the entrance section; however this section has stainless steel walls and thus could not be observed during the test run.

10.1.3 Run 3

In this run, 75 hulls were equally distributed among the three dissolving compartments and 150 g of reduced iron was added. Water in the system was pumped around the recycle loop for 1 hr to thoroughly distribute the iron particles within the dissolver. The water in the dissolver was then pumped out into a holding tank at about 3 liters/min while fresh water was constantly fed in at the same rate.

After 22 min., all traces of iron powder in the dissolver had disappeared with the exception of some streaks on the glass in stages 1 and 4.

10.1.4 Run 4

Eighteen batches consisting of 25 hulls and 22 g of reduced iron powder were added at 5-min intervals. A water flow rate of 3 liters/min was used.

A very slight accumulation was noticed in the first stage. Well over 98% of the solids added were carried out with the water stream.

10.1.5 Run 5

Fifty-three batches consisting of 25 hulls and 50 g of lead powder were added at 5-min intervals. A water flow rate of 3.2 liters/min was used.

The solids accumulation was similar to that observed in run 2 using iron powder. An accumulation of powder in the exit stage was noted after 30 additions. The run was halted after 53 additions because the exit chute had become clogged with powder and empty hulls. A large amount of powder accumulated in the space between the agitation and transfer baffles.

10.1.6 Run 6

Twenty-seven batches consisting of 35 hulls and 50 g of lead powder and 22 g of reduced iron powder were added at 5-min intervals. A water flow rate of 2.8 liters/min was used. The water leaving the dissolver was collected in large settling tanks.

It appeared that almost all of the fine iron powder was carried out by the water stream while the larger lead particles remained in the dissolver. No solid particles were observed in the exit stage of the dissolver. Accumulation in the first dissolving stage was similar to that observed in other tests.

10.2 Appendix II: Data on Feed Used in Tests with Ceramic Powders

Composition of 250-g feed charge

Hulls	118 g
Fragments >4750 μ (+4 mesh)	40 g
Wire	24 g
Ceramic powder[a]	68 g
Total	250 g

[a]See following table.

Ceramic powder size Distribution

Screen Size	Wt. %
-4 + 10	43
-10 + 16	22.7
-16 + 20	5.9
-20 + 30	4.0
-30 + 50	7.0
-50 + 100	5.2
-100 + 200	4.3
-200 + 325	2.9
-325	5.0

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