# EFFECT OF GEOMETRICAL SHAPE ON THE CONTINUOUS DISSOLUTION OF ALUMINUM IN MERCURY - CATALYZED NITRIC ACID*

by

A. F. Boeglin and J. A. Buckham

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## A B S T R A C T

The results of a study of the effect of geometrical shape of aluminum reactor fuel elements on the dissolution rate in mercury-catalyzed nitric acid are presented. Four shapes, 1) round rods, 2) tubes, 3) flat plates, and 4) flattened tubes, were tested at five catalyst concentrations (from $1.5 \times 10^{-6}$ to $7.5 \times 10^{-4}$ molar mercury), and at each of three feed rates (280, 140, and 70 gram-moles of nitric acid per hour). Statistical analysis of the data showed that the main effects, feed rates, catalyst concentration and shape, and all first order interaction effects had a significant effect on dissolution rate. A mathematical relationship between dissolution rate and feed rate, catalyst concentration and the catalyst concentration by feed rate interaction was graphically developed for each shape. At the higher catalyst concentrations, all shapes dissolve at practically the same rate. However, flat plates and flattened tubes are much less dependent on catalyst concentration and at lower catalyst concentrations dissolve over twice as fast as round rods and tubes. Correlation of the dissolution rates of round rods with the rates obtained in previous work on cylindrical uranium-aluminum alloy fuel elements showed very good agreement. A comparison of the dissolution rate obtained in a stainless steel vessel and that obtained in a glass vessel was made; no appreciable difference was noted.

*Work done under contract AT(10-1)-205 to the U. S. Atomic Energy Commission

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# EFFECT OF GEOMETRICAL SHAPE ON THE CONTINUOUS DISSOLUTION OF ALUMINUM IN MERCURY - CATALYZED ACID

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## I. INTRODUCTION

Previous studies[1] of the continuous dissolution of aluminum and uranium-aluminum alloy in mercury-catalyzed nitric acid were made with cylindrical dummy fuel elements. The current interest in a wide variety of reactor fuel shapes prompted the undertaking of a study to determine the effect, if any, of geometrical shape on the dissolution rate of aluminum in a continuous nitric acid dissolver.

Purposes of this study were:

1. To compare the dissolution properties of various shaped elements in a continuous dissolver,
2. To correlate the results of this study with data of previous work in order to broaden the knowledge of continuous dissolution,
3. To determine the effect of acid feed rate and catalyst concentration interactions, and
4. To determine the difference, if any, of the dissolution rates in a glass vessel and a stainless steel vessel.

The study was conducted in a 2-inch diameter pyrex glass tall pipe dissolver. The aluminum used was 2-S alloy.

Four geometrical shapes were tested. They were:

1. Tubes
2. Round rods
3. Flat plates
4. Flattened tubes

These shapes have increasing surface area per unit volume of dissolver in the order listed and could be expected to exhibit increased dissolution in that order.

## II. HISTORY AND DEVELOPMENT OF PROGRAM

Extensive development work previously performed by Phillips Petroleum Company was made in flooded type dissolvers (2-inch diameter glass, 2-inch diameter stainless steel, and 5-inch diameter stainless steel tall pipe vessels) on cylindrical shaped elements. It was found that the dissolution

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(1) A. F. Boeglin, et al, Continuous Dissolution of Uranium-Aluminum Reactor Fuels, A.I.Ch.E. Journal, 2, 190 (1956) (Derived from IDO-14321).

rate varied logarithmically with the acid feed rate and the catalyst concentration, and also that an acid feed concentration of 5.6M nitric acid was satisfactory in obtaining maximum dissolution rates for both cast and extruded elements. Cast elements were found to have lower dissolution rates than extruded if all other variables were held constant. The data obtained indicated no significant increase in dissolution rate for any increase in height of packed metal above eight feet for a fully packed dissolver.

The study described herein was developed in order to determine the effect of geometrical shape on the dissolution rate as well as interactions between shape and acid feed rate, shape and catalyst concentration, and acid feed rate and catalyst concentration, and to study visually the dissolver performance. Run conditions used were an acid feed concentration of 5.6M nitric acid, a packed metal height of eight to ten feet, and extruded 2-S aluminum alloy as the metal to be dissolved.

The program consisted of two series of runs. The original program was designed as a full factorial experiment so that for each shape, three catalyst concentrations at each of two feed rates were used, giving a total of 24 runs. Results of this series indicated that interactions between shape and catalyst concentration and shape and feed rate were significant at low catalyst concentrations and high feed rates. The second series of runs was made in order to expand the factorial experiment to determine these interactions. Two lower catalyst concentrations and one higher feed rate, for each shape, were used in the second series. The overall program, therefore, was a full factorial experiment of 60 runs, testing five catalyst concentrations at each of three feed rates for each of the four shapes. Re-runs, for comparison purposes, were made of some of the above 60 runs, raising the total number of runs statistically analyzed to about 85.

For some runs the dissolver was lined with stainless steel strips welded to both top and bottom to give essentially a stainless steel vessel. Two runs with round rods and four with flat plates were made and the results were compared statistically to corresponding runs in the glass dissolver.

## III. MATERIALS AND EQUIPMENT

The aluminum alloy used for this study was the 2-S alloy which is commercially pure aluminum with less than one percent impurities. A difference in hardness due to length of cold-work time did exist between the various shapes; however, the round rods were designated as H-18 (full hard), the tubes (from which both unflattened and flattened tubes were cut) were designated as H-14 (half hard), and the sheets from which the flat plates were cut were half hard bright finish material, according to the common cold-worked temper designations. Spectrochemical analyses gave the following percentages of impurities:

Table 1

Composition of 2-S Alloys

1) Material Used in First Series of Runs

| Shape | Percent of Element | | | | | |
|---|---|---|---|---|---|---|
| | Cu | Fe | Mg | Mn | Si | Ti |
| Round Rods | 0.10 | 0.57 | 0.006 | 0.008 | 0.16 | 0.016 |
| Flat Plates | 0.14 | 0.60 | 0.014 | 0.013 | 0.21 | 0.010 |
| Tubes | 0.12 | 0.44 | 0.016 | 0.009 | 0.19 | 0.017 |
| Flattened Tubes | 0.11 | 0.45 | 0.018 | 0.009 | 0.17 | 0.016 |

2) Material Used in Second Series of Runs

| Shape | Percent of Element | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cu | Fe | Mg | Mn | Si | Ti | Ga, Ni, V |
| Round Rods | 0.13 | 0.56 | 0.004 | 0.005 | 0.13 | 0.025 | Trace |
| Flat Plates | 0.10 | 0.51 | 0.002 | 0.0086 | 0.08 | 0.011 | Trace |
| Tubes | 0.10 | 0.51 | 0.007 | 0.0045 | 0.12 | 0.0033 | Trace |
| Flattened Tubes | 0.09 | 0.41 | 0.004 | 0.004 | 0.10 | 0.0045 | Trace |

The nitric acid used was the commercially pure 60 percent (13M) acid diluted to approximately 5.6M with tap water.

The mercury used as the catalyst was obtained by adding chemically pure mercuric nitrate monohydrate to the feed acid.

The feed system consisted of a preparation tank, feed tank, pump, automatically controlled rotameter and motor valve, preheater, and an auxiliary preheater.

The dissolver system consisted of the dissolver proper including an internal cooling coil, double valve charging assembly, external condenser, condensate return system, vent line, effluent cooler, specific gravity pot, and recording instrument, and an effluent collection weigh-tank. A schematic diagram of the dissolver system is shown in Figure 1.

The dissolver bottom consisted of a two-inch diameter stainless steel cup, provided with an acid feed inlet, drain outlet, condensate return inlet, and thermocouple well. The cup was bolted through a support plate and a perforated crash plate to the dissolver body. The dissolver body was a ten-foot length of two-inch diameter pyrex glass pipe. To the top of this glass section was attached a teflon bellows (to provide for expansion of the glass) and a two-inch long stainless steel spacer containing an effluent outlet and a thermocouple well. Above the spacer was a one-foot length of glass pipe and a standard adjustable glass joint. The internal cooling coil was contained in a stainless steel section attached to the top of the adjustable glass

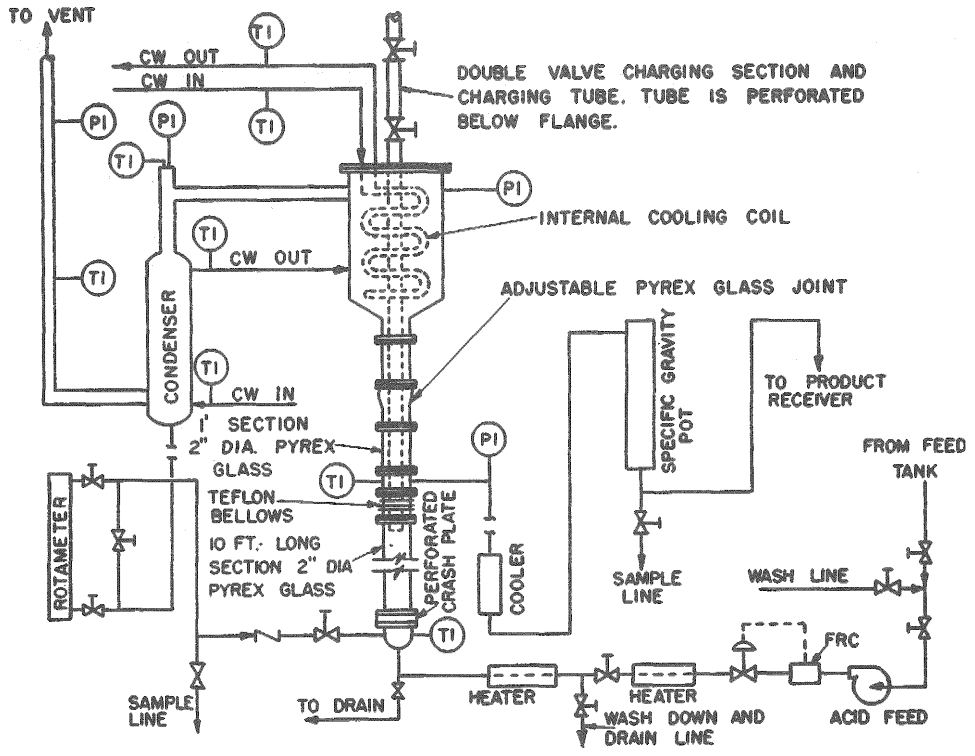



FIGURE 1

CONTINUOUS DISSOLVER SYSTEM

joint. The cooling coil was constructed from 50 feet of 3/8-inch stainless steel tubing in a double coil, the inner coil being three inches in diameter and the outer coil five inches in diameter.

The double-valve charging section consisted of a 1-1/4-inch stainless steel pipe extending down into the dissolver to a point just below the teflon bellows. To the top of this charging tube was attached the double valve section, the two quick-opening valves being separated by a two-foot length of pipe. A double-valve arrangement was used in order to eliminate the danger of acid and gas evolving from the dissolver during the charging operation.

The external condenser was a one-pass, shell and tube, vertically mounted heat exchanger. It contained a surface area for heat transfer of two square feet. The off-gas from the dissolver entered at the top and the non-condensable gases left from a side outlet near the bottom. The condensate returned to the bottom of the dissolver after passing through a rotameter (equipped with a by-pass) and a check valve.

The specific gravity pot was a two-foot length of two-inch diameter pyrex glass pipe containing two air probes (probe separation, 20.0 inches) which were connected through a differential pressure transmitter to a recording instrument. The instruments were calibrated to give a specific gravity range of 1.15 to 1.45.

Sampling outlets were provided on the condensate return line and on the effluent line just below the specific gravity pot.

Preliminary runs of the second series showed that it was necessary to modify the dissolver system in order to operate at the increased feed rate. The following modifications were made:

1. The charging section was enlarged to allow for increased metal feed rates and the stainless steel section was replaced by a glass section and glass valves in order to eliminate jamming of the small aluminum slugs in the valves.

2. The internal cooler section was offset in order to allow room for the enlarged charging section.

3. A steam jet was placed on the vent line in order to remove gases from the charging section. A contact condenser was placed in the vent system to condense the steam jet steam and allow only non-condensable gases to escape to the atmosphere.

4. The condensate return line from the external condenser was enlarged to allow for return of an increased amount of condensate.

5. The product receiver vent system was connected to the steam jet vent system in order to equalize pressure in the dissolver system so that the effluent could flow by gravity to the receiver.

6. It was necessary to place pumps in the system at two points. A pump was required to empty the product receiver against the vacuum on the receiver and a pump was also required between the specific gravity pot and the product receiver in order to obtain samples. These modifications are not shown in Figure 1. Several re-runs with flat plates were made to check the modified system and the results obtained were within four percent of previous results, showing that the system modifications had no effect on dissolution rates.

## IV. RUN PROCEDURE

The experimental runs were conducted in the following manner.

A 5.6M solution of nitric acid was made up in the preparation tank and a portion transferred to the feed tank. The desired amount of catalyst was then added to the acid feed.

The dissolver was loaded with elements to at least the eight-foot level (after dissolution began, the elements were charged intermittently to keep the metal level between eight and ten feet).

Acid feed was admitted to the dissolver with the preheater system regulated to give a feed inlet temperature between 80 and 100 degrees Centigrade.

From a half hour to two hours after the dissolving action started, the specific gravity recorder would show that a steady state condition had been reached. At this point, the liquid level in the feed tank and the weight of the receiver drum were recorded. Liquid level readings, drum weights, temperatures and a sample of the effluent were taken or recorded every half hour thereafter until at least five samples were taken.

The dissolver was shut down by shutting off the pump, feed valves, the cooling water, and the steam supply. The system was then flushed out by running tap water through one or both of the wash line inlets. This washing was done at the end of a day or between runs if the catalyst concentration was one of the run conditions to be changed. If only a change in feed rate were to be made, the flow control was changed and the run allowed to proceed.

If a new geometrical shape was to be studied the bottom would be removed from the dissolver, the partially dissolved elements dumped, the bottom replaced and the new elements charged.

The feed samples were analyzed for acid concentration, specific gravity, and mercury concentration. The effluent samples were analyzed for acid concentration, specific gravity, and aluminum concentration. All analyses were made by standard proven methods.

## V. PRELIMINARY DATA

Simulated elements used were smaller than typical fuel elements might be since the dissolver vessel used was also scaled down from a plant-scale unit. The dimensions of the aluminum pieces used are shown in Table 2.

Table 2

Dimensions of the Geometrical Shapes

| Shape | |
|---|---|
| Round Rods | 3" long by 0.25" diameter |
| Flat Plates | 5" long by 0.625" wide by 0.0625" thick |
| Tubes | 3" long by 0.625" outside diameter with 0.028" wall |
| Flattened Tubes | Same as tubes but flattened so that a small (approximately 0.03 inches) air gap existed between inside surfaces. |

The void fraction in the dissolver when fully packed with each of the shapes was determined by draining water from the eight-foot level; results are given in Table 3.

Table 3

Void Fractions in Fully Packed Dissolver

| Shape | Void Fraction: Before Dissolution (New Elements) | Void Fraction: After Dissolution (Partially Dissolved Elements) | Void Fraction: Average |
|---|---|---|---|
| Round Rods | 0.577 | 0.547 | 0.562 |
| Flat Plates | 0.600 | 0.589 | 0.595 |
| Tubes | 0.905 | 0.929 | 0.917 |
| Flattened Tubes | 0.660 | 0.756 | 0.708 |

It can be seen from Table 3 that the void fraction decreases after dissolution for the solid shapes and increases for the hollow shapes. The reason for the behavior of the hollow shapes can be seen in Figure 2, a photograph of new and partially dissolved elements. The hollow shapes in dissolving lose weight and, therefore, volume, but retain their original shape so that until they are almost totally dissolved they do not tend to pack tighter in the dissolver. The solid shapes lose their original shape and tend to pack tighter, therefore decreasing the void fraction.

The volume and surface area of a single element of each shape were determined and are listed in Table 4. A factor called the surface area factor or SAF was calculated for each shape; it gives the surface area available per foot of dissolver in a fully packed dissolver, and was obtained from the following equation:

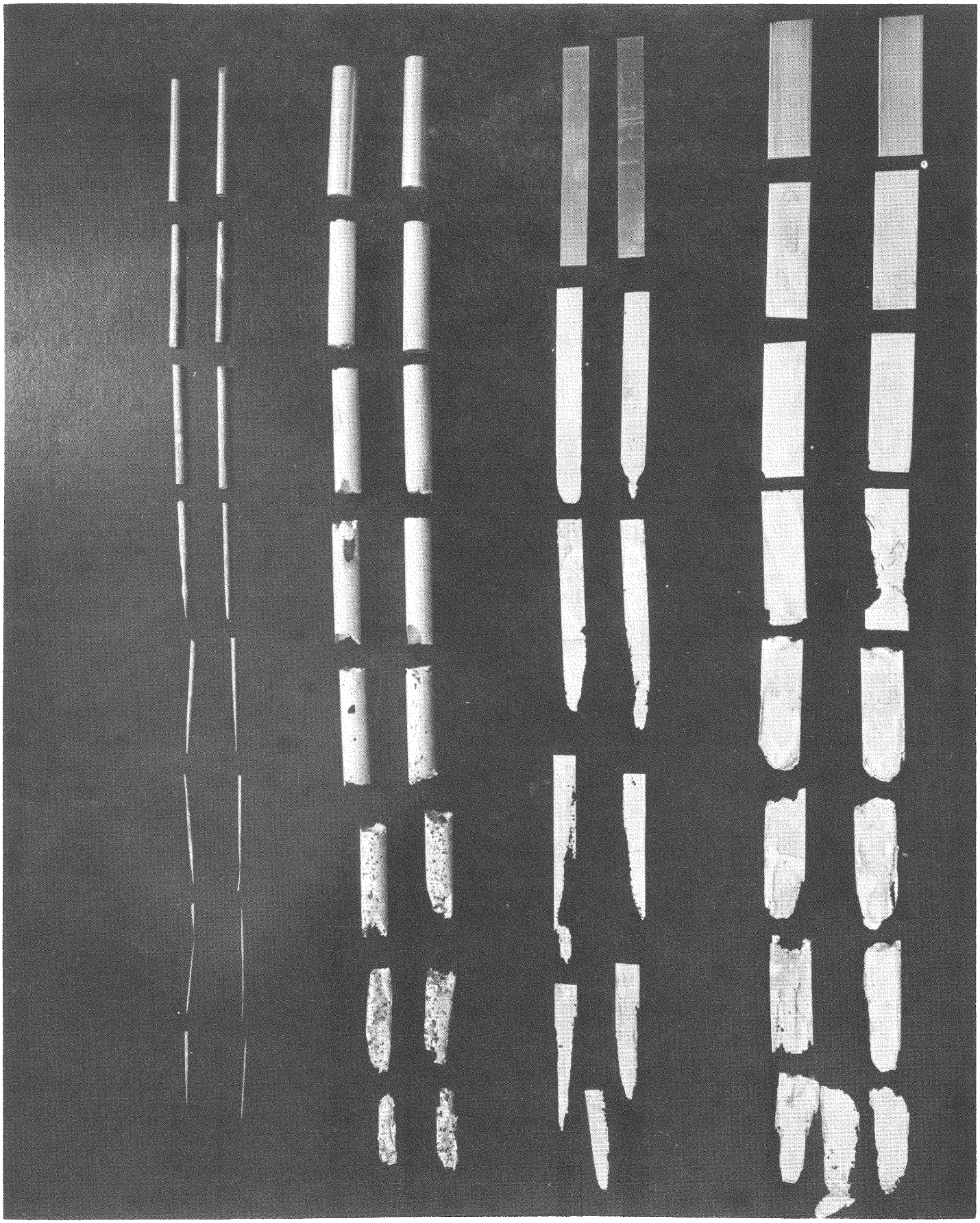
$$\frac{\frac{\text{volume of dissolver}}{\text{foot of dissolver}} \times \frac{\text{volume of elements}}{\text{volume of dissolver}} \times \frac{\text{surface area}}{\text{element}}}{\frac{\text{volume}}{\text{element}}} = \frac{\text{surface area}}{\text{foot of dissolver}} = \text{SAF}$$

The surface area factors and the ratio, S, of the surface area factors of each shape to the surface area factor of the round rods are given in Table 4. These values were determined by using the average void fraction.

Table 4

Surface Area of Aluminum per Foot of Dissolver for the Various Shapes

| Shape | Volume of Element, $cm^3$ | Surface Area of Element, $cm^2$ | At Average Void Fraction: $SAF^{cm}/ft^2$ | At Average Void Fraction: S |
|---|---|---|---|---|
| Round Rods | 2.4 | 15.9 | 1790 | 1.0 |
| Flat Plates | 3.2 | 44.4 | 3470 | 1.9 |
| Tubes | 2.7 | 72.8 | 1380 | 0.8 |
| Flattened Tubes | 2.7 | 55.6 | 3720 | 2.1 |



(a) Round Rods

(b) Tubes

(c) Flat Plates

(d) Flattened Tubes

FIGURE 2

NEW AND PARTIALLY DISSOLVED ELEMENTS

From the ratios of surface area factors for partially dissolved elements given in Table 4, it may be predicted that the dissolution rate should decrease in the following order: 1) flattened tubes, 2) flat plates, 3) round rods, 4) tubes. This prediction is only approximate as the essential values used in the determination of SAF cannot be measured very accurately.

## VI. DISSOLVER PERFORMANCE

Visual observations made during the dissolution process revealed some interesting phenomena. A cyclic surging and refluxing action caused considerable mixing of the solution throughout the dissolver. A heel of liquid varying from about two inches to eighteen inches, depending on run conditions, built up at the bottom of the dissolver; then, as the dissolution reaction proceeded, the gases and steam formed would violently lift the liquid to the top of the dissolver. The steam would condense around the internal cooling coil and condensate would reflux into the dissolver. At times there was no liquid layer at all in the dissolver proper. The amount of effluent collected over a twenty or thirty-minute period was fairly constant despite the surging action. A film of solution remained on most of the surfaces of the elements and the dissolution reaction continued on portions of the slugs which were being attacked by the acid. It can be seen from Figure 2 that the acid attacks the aluminum erratically.

There was little or no flow of condensate from the external condenser during operation indicating that the internal cooling coil was condensing most of the steam generated. The temperature of the non-condensable gases leaving the dissolver varied from 90 to 40 degrees Centigrade depending on run conditions; they were cooled to approximately 30 degrees Centigrade in the external condenser.

Jams occurred at infrequent intervals leaving large voids in the dissolver. As the reaction proceeded these jams would break, dropping the elements and filling the voids. (In previous work with large slugs, this breakup of slug jams had caused excessive glass breakage. No glass breakage was experienced due to metal jams during this study, probably due to the lightness of the individual pieces.) Tubes were much more susceptible to jamming than were the other geometrical shapes.

The specific gravity of the effluent during the high feed rate runs varied about one percent from the average while that of the low feed rate runs was essentially constant.

The packed metal level was allowed to drop below eight feet at the end of Run R-2A and a drop in the effluent specific gravity was noticed after the level had dropped to about seven feet. Earlier portions of the run had been made with a nine-foot packed metal level and the dropping of the level from nine to eight feet showed no corresponding drop in specific gravity.

## VIII. EFFECT OF FEED RATE AND CATALYST CONCENTRATION

The experimental dissolution rates, listed in Table 5, were statistically analyzed for the significance of the main effects and interaction effects. The analysis of variance, Table 6, shows the significance of each effect. The column headed "Significance of Component" gives the probability that an effect at least as large as that observed would be caused by chance alone. Table 6 shows that each of the main effects, shape, catalyst concentration, and feed rate are highly significant and that each of the first order interaction effects, shape by catalyst concentration, shape by feed rate and catalyst concentration by feed rate are also significant. It is extremely rare for an experiment of this size to yield so many significant components.

The effects of catalyst concentration and feed rate were tested for linearity and were found to have a significant higher order effect.

It was impossible to relate dissolution rate with catalyst concentration and feed rate in a simple functional form. A graphical method was used to determine a mathematical relationship. First, log-log plots of dissolution rates, Ra, versus feed rates, N, from averages of data in Table 5 at each of the catalyst concentrations were made (Figure 4 is an example), and the slopes of straight lines through the points were determined. Assuming that Ra varies as $N^b$ then the slopes of the lines of the log-log plots of Ra versus N are the values of the exponent b.

The values of b for each shape were determined at each catalyst concentration and are listed in Table 7. In general, the exponent of N decreases with a decrease in catalyst concentration. If the values of b for round rods at $7.5 \times 10^{-5}$ M mercury and for tubes at $7.5 \times 10^{-5}$ M mercury are ignored then a log-log plot of b versus the catalyst concentration, $m_f$, gives a straight line relationship. This relationship is shown in Figure 5, and is

$$b = 1.8\ m_f^{0.08} \tag{2}$$

The equation relating dissolution rate to feed rate is, therefore,

$$Ra \propto N^{1.8\ m_f^{0.08}} \tag{3}$$

for all shapes under certain limitations; namely, disregarding round rods at $m_f$ near $7.5 \times 10^{-5}$ M, tubes at $m_f$ below $7.5 \times 10^{-5}$ M, round rods and tubes at feed rates above 200 at $m_f$ near $3.75 \times 10^{-4}$ M and flat plates and flattened tubes at feed rates above 200 at $m_f$ near $7.5 \times 10^{-5}$ M mercury.

The average dissolution rates of Table 5 were normalized to a feed rate of 140 gram-moles of nitric acid per hour; i.e., the experimental dissolution rates were multiplied by the ratio

$$\left(\frac{140}{\text{experimental feed rate, } N}\right)^{1.8\ m_f^{0.08}}$$

Table 5

Dissolution Rates of Aluminum Shapes

Notes: Feed acid concentration, $n_f$: 5.2 to 5.8 molar nitric acid
Feed acid temperature: 80 to 100°C
Dissolver Diameter: 2 inches
Height of packed column: 8 to 10 feet

| | Round Rods | | Tubes | | Flat Plates | | Flattened Tubes | |
|---|---|---|---|---|---|---|---|---|
| $m_f$ Catalyst Conc. g-mols/liter mercuric ion | N Feed Rate g-mols/hour nitric acid | Ra Diss. Rate kg aluminum day | N Feed Rate g-mols/hour nitric acid | Ra Diss. Rate kg aluminum day | N Feed Rate g-mols/hour nitric acid | Ra Diss. Rate kg aluminum day | N Feed Rate g-mols/hour nitric acid | Ra Diss. Rate kg aluminum day |
| | 63 | 10.1 | 68 | 10.2 | 74 | 12.3 | 67 | 11.8 |
| | 67 | 11.9 | 70 | 11.2 | 143 | 22.3 | 134 | 24.0 |
| $7.5 \times 10^{-4}$ | 125 | 20.3 | 140 | 20.5 | 288 | 46.6 | 295 | 44.6 |
| | 130 | 22.2 | 138 | 20.6 | 276 | 23.8 | | |
| | 282 | 41.7 | 317 | 46.1 | 305 | 58.0 | | |
| | 76 | 12.0 | 77 | 12.2 | 78 | 12.8 | 73 | 13.9 |
| | 70 | 12.5 | 148 | 20.1 | 80 | 14.1 | 134 | 24.6 |
| | 71 | 13.0 | 307 | 24.0 | 71 | 13.8 | 295 | 35.6 |
| | 70 | 12.1 | | | 149 | 25.8 | | |
| $3.75 \times 10^{-4}$ | 150 | 22.9 | | | 285 | 31.7 | | |
| | 140 | 23.8 | | | 272 | 41.6 | | |
| | 281 | 16.6 | | | 296 | 45.8 | | |
| | 306 | 31.3 | | | | | | |
| | 73 | 10.6 | 74 | 9.4 | 61 | 10.5 | 71 | 12.3 |
| | 142 | 8.7 | 73 | 10.6 | 75 | 13.7 | 141 | 23.8 |
| | 142 | 11.8 | 142 | 8.0 | 142 | 22.7 | 291 | 18.6 |
| $7.5 \times 10^{-5}$ | 150 | 13.2 | 142 | 9.2 | 149 | 21.3 | 295 | 22.9 |
| | 283 | 5.8 | 146 | 6.8 | 289 | 19.1 | | |
| | 301 | 10.2 | 288 | 8.3 | 280 | 34.5 | | |
| | | | 308 | 9.2 | 295 | 17.8 | | |
| | 72 | 5.8 | 67 | 10.4 | 71 | 11.5 | 70 | 10.0 |
| | 143 | 11.7 | 137 | 18.3 | 147 | 23.2 | 148 | 21.6 |
| $1.5 \times 10^{-5}$ | 299 | 15.9 | 287 | 17.5 | 282 | 25.6 | 286 | 29.2 |
| | | | | | 277 | 32.1 | | |
| | 66 | 3.5 | 80 | 11.8 | 65 | 10.2 | 71 | 10.3 |
| | 146 | 6.7 | 70 | 4.5 | 67 | 8.7 | 147 | 17.8 |
| $1.5 \times 10^{-6}$ | 302 | 6.3 | 135 | 6.6 | 70 | 10.3 | 278 | 23.1 |
| | | | 141 | 4.5 | 135 | 13.9 | | |
| | | | 272 | 3.9 | 131 | 15.6 | | |
| | | | | | 140 | 13.8 | | |
| | | | | | 306 | 23.8 | | |

and the normalized dissolution rates for each shape were plotted on log-log paper versus the catalyst concentration. Figure 6 is an example showing the lines for tubes and flattened tubes.

The following equations were determined from the plots:

For Round Rods: $$Ra = 116 \left(\frac{N}{140}\right)^{1.8 m_f^{0.08}} m_f^{0.23} \quad (4)$$

For Tubes: $$Ra = 75 \left(\frac{N}{140}\right)^{1.8 m_f^{0.08}} m_f^{0.18} \quad (5)$$

For Flat Plates: $$Ra = 32 \left(\frac{N}{140}\right)^{1.8 m_f} m_f^{0.05} \quad (6)$$

For Flattened Tubes: $$Ra = 33 \left(\frac{N}{140}\right)^{1.8 m_f^{0.08}} m_f^{0.05} \quad (7)$$

It should be noted here that although these equations may be used over the entire range of feed rates and catalyst concentrations studied, an error as large as 50 percent may be encountered at the values of N and $m_f$ which were disregarded in plotting b versus $m_f$.

Table 6

Analysis of Variance

| Source of Variation | Degrees of Freedom | Mean Square | F Ratio | Significance of Component |
|---|---|---|---|---|
| Catalyst | 4 | 0.452 | 7.65 | 0.001 |
| Shapes | 3 | 0.303 | 6.04 | 0.005 |
| Feed Rates | 2 | 0.498 | 14.87 | 0.0005 |
| Catalyst x Shapes | 12 | 0.0674 | 15.12 | <0.0005 |
| Catalyst x Feed | 8 | 0.0467 | 10.48 | <0.0005 |
| Shapes x Feed | 6 | 0.0160 | 3.59 | 0.01 |
| Catalyst x Shapes x Feed | 24 | 0.00446 | 3.23 | 0.001 |
| Error | 24 | 0.00135 | | |

Table 7

Slope, b, of Dissolution Rate, Ra, Versus Feed Rate, N, Log-Log Plots at Constant Catalyst Concentration for the Various Shapes

| Catalyst Conc. g-mol $Hg^{++}$/liter | Slope, b | | | |
|---|---|---|---|---|
| | Round Rods | Tubes | Flat Plates | Flattened Tubes |
| $7.5 \times 10^{-4}$ | 0.95 | 0.95 | 0.95 | 0.95 |
| $3.75 \times 10^{-4}$ | 0.95* | 0.95* | 0.95 | 0.95 |
| $7.5 \times 10^{-5}$ | 0 | 0 | 0.80* | 0.80* |
| $1.5 \times 10^{-5}$ | 0.75 | 0.75* | 0.75 | 0.75 |
| $1.5 \times 10^{-6}$ | 0.6* | -0.55 | 0.6 | 0.6 |

* At values of N less than 200

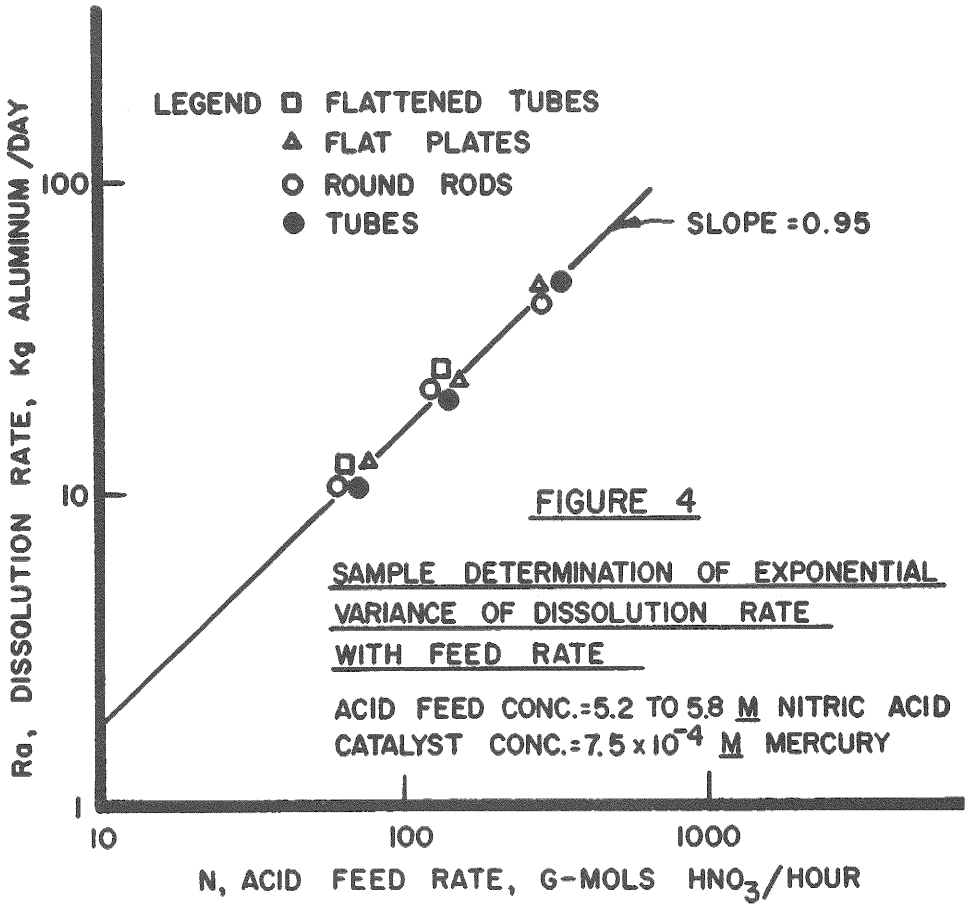



FIGURE 4

SAMPLE DETERMINATION OF EXPONENTIAL VARIANCE OF DISSOLUTION RATE WITH FEED RATE

ACID FEED CONC.=5.2 TO 5.8 M NITRIC ACID
CATALYST CONC.= $7.5 \times 10^{-4}$ M MERCURY

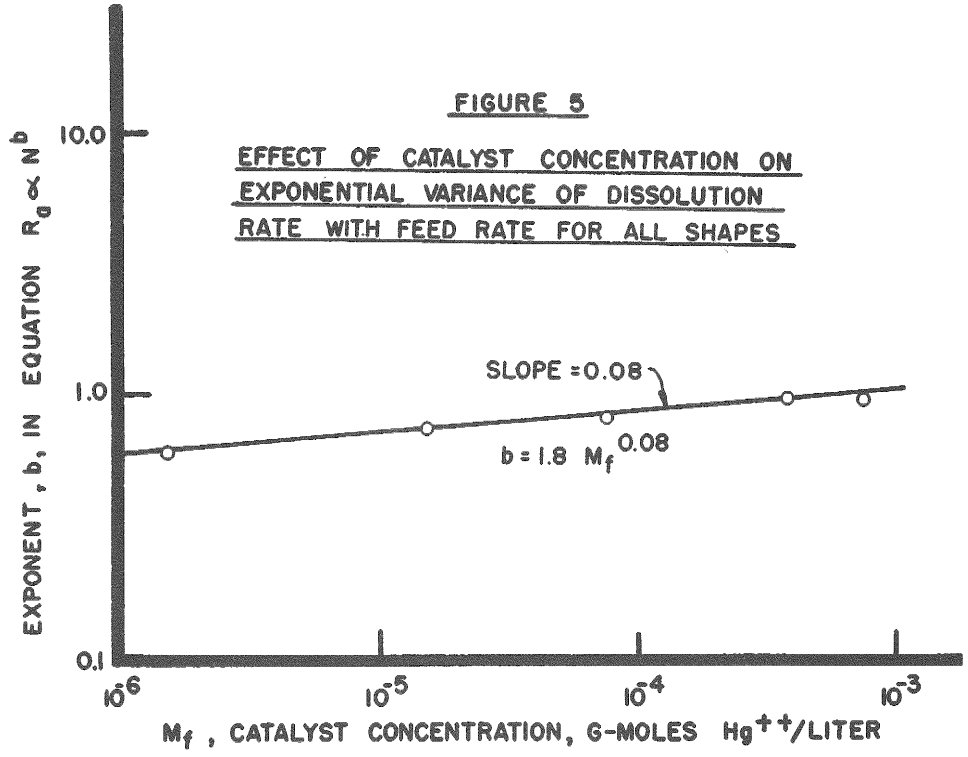
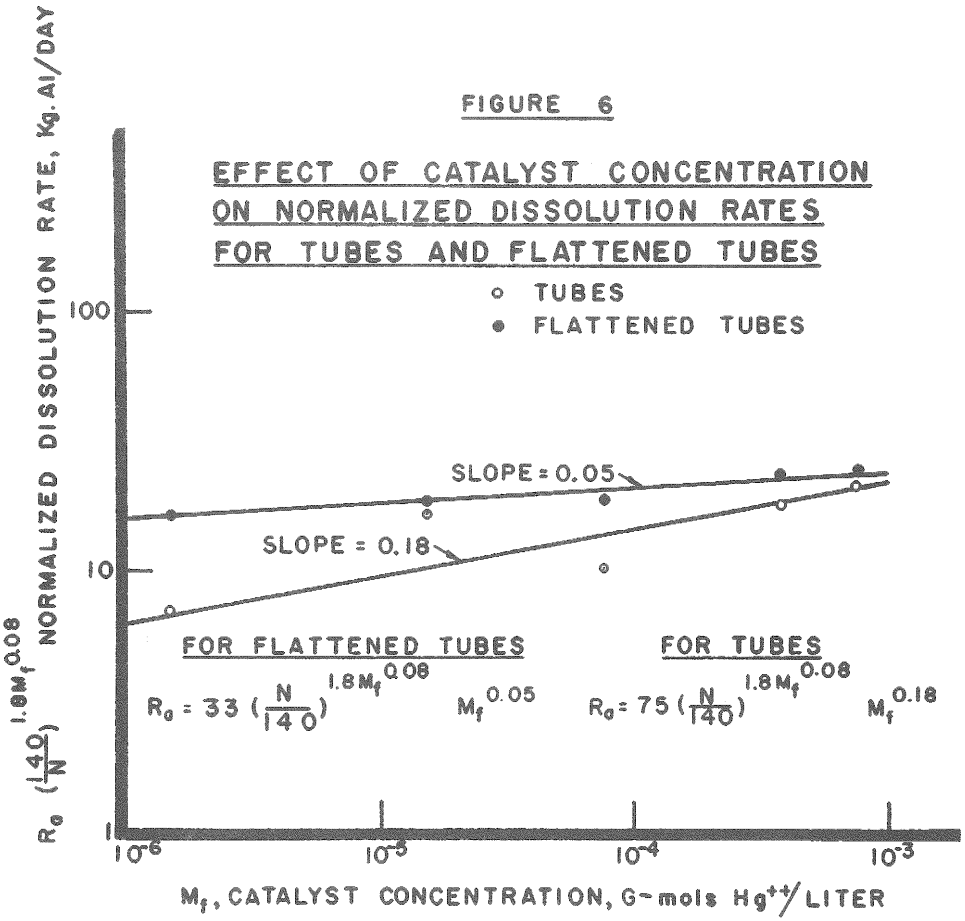



FIGURE 5

EFFECT OF CATALYST CONCENTRATION ON EXPONENTIAL VARIANCE OF DISSOLUTION RATE WITH FEED RATE FOR ALL SHAPES

FIGURE 6

EFFECT OF CATALYST CONCENTRATION ON NORMALIZED DISSOLUTION RATES FOR TUBES AND FLATTENED TUBES




## IX. EFFECT OF SHAPE

A study of equations (4) through (7) shows that round rods and tubes are much more affected by a change in catalyst concentration than are flat plates and flattened tubes. The behavior of round rods and tubes is, for all practical purposes, the same. The dissolution rate equations for flat plates and flattened tubes are also essentially identical. At high catalyst concentrations (above $7.5 \times 10^{-5}$ molar mercury) the dissolution rates for all shapes will be approximately equal. At lower catalyst concentrations, however, flat plates and flattened tubes dissolve as much as two and one-half times as fast as round rods and tubes.

The difference in behavior between flat plates-flattened tubes and round rods-tubes is in accord with the surface area ratios (S) listed in Table 3. The values of S for round rods and tubes are almost the same, being 1.0 and 0.8 respectively, and the values of S for flat plates and flattened tubes are almost equal, being 1.9 and 2.1, respectively.

The effect of shape is, therefore, dependent on the surface area and packing effect of the shape, those shapes which present a large surface area per given volume of dissolver having a greater dissolution rate for a given catalyst concentration especially at the lower catalyst concentrations.

## X. CORRELATION OF DATA WITH PREVIOUS WORK

Dissolution rates obtained in the previous work on extruded cylindrical uranium-aluminum and 2-S aluminum alloy elements in 5.0 to 6.0 molar nitric acid in the two-inch dissolvers were correlated with the dissolution rates of round rods obtained in the effect of shape study. These rates are listed in Table 8.

Four of the runs listed in Table 9 (and marked with an asterisk) were made with 2-S aluminum alloys. The dissolution rates obtained in these runs are in very close agreement with runs made with uranium-aluminum alloy at the same run conditions, showing that the addition of a small amount of uranium to the aluminum-nitric acid system has no effect on the dissolution rate of extruded material.

At those catalyst concentration levels where it was possible to plot dissolution rates versus acid feed rates this was done on log-log paper and the slope of the line determined. These plots showed that at catalyst concentrations of 0.01, 0.005, 0.003 and 0.001 molar mercuric nitrate, the dissolution rate varied as the 0.95 power of the acid feed rate. This is in agreement with the data for round rods in Table 7 which shows that the exponent of N for catalyst concentrations of $3.75 \times 10^{-4}$ molar mercuric nitrate and above is 0.95.

The previous data on cast uranium-aluminum alloy elements had indicated that the dissolution rate varied as the 0.8 power of the acid feed rate and the 0.33 power of catalyst concentration. It was assumed in previous correlations that this relationship also held for extruded elements. However, the above re-examination of the dissolution rates of extruded elements shows that the 0.95 power of the acid feed rate more accurately describes the relationship between dissolution rate and feed rate.

Thus, for the purpose of correlation, the following relationships were adopted:

$$Ra \propto N^{1.8}\, m_f^{0.08}$$ for values of $m_f$ less than $3.75 \times 10^{-4}$ M

and

$$Ra \propto N^{0.95}$$ for values of $m_f$ greater than $3.75 \times 10^{-4}$ M.

The dissolution rates for round rods from Table 5 and the rates listed in Table 8 were normalized to an acid feed rate of 140 g-moles of nitric acid per hour. The average normalized dissolution rates are shown in Table 9.

Table 8

Dissolution Rates of Extruded Uranium-Aluminum and 2-S Aluminum Alloy Round Rods

Notes: $n_f$, acid feed concentration = 5.0 to 6.0 g-moles nitric acid per hour
Feed Temperature: 80 to 100°C
Dissolver Diameter: 2-inches
Height of Packed Column: at least 8 feet

Column Headings: $m_f$, catalyst concentration, g-moles mercuric nitrate per liter
N, acid feed rate, g-moles nitric acid per hour
$R_a$, aluminum dissolution rate, kilograms of aluminum per day

| mf | N | Ra | mf | N | Ra |
|---|---|---|---|---|---|
| 0.04 | 79.1 | 17.4 | 0.003 | 114 | 20.3 |
| 0.02 | 376 | 72.7 | | | |
| | 384 | 74.8 | 0.0025 | 146 | 20.9 |
| 0.01 | 99 | 17.5 | 0.0015 | 117 | 15.5 |
| | 106 | 20.0 | | | |
| | 106 | 22.8 | 0.001 | 89 | 13.0 |
| | 366 | 67.4 | | 89 | 13.5 |
| | | | | 109 | 17.9 |
| 0.005 | 95 | 18.5 | | 111 | 15.8 |
| | 105 | 18.8 | | 111 | 15.6 |
| | 111 | 23.0 | | 262 | 24.3 |
| | 119* | 22.3 | | 293 | 24.7 |
| | 133 | 22.7 | | 384 | 47.6 |
| | 134 | 22.2 | | | |
| | 181 | 31.1 | 0.00075 | 393 | 38.6 |
| | 185* | 32.5 | | | |
| | 257 | 44.0 | 0.0005 | 107 | 13.7 |
| | 306 | 46.0 | | 110 | 12.0 |
| | 309* | 52.9 | | 375 | 27.6 |
| | 335 | 57.1 | | | |
| | 350* | 55.4 | | | |
| | 375 | 65.2 | | | |
| | 420 | 64.2 | | | |

*2-S aluminum alloy, all other runs were made with uranium-aluminum alloy

## Table 9

### Average Normalized Dissolution Rates of Round Rod Elements

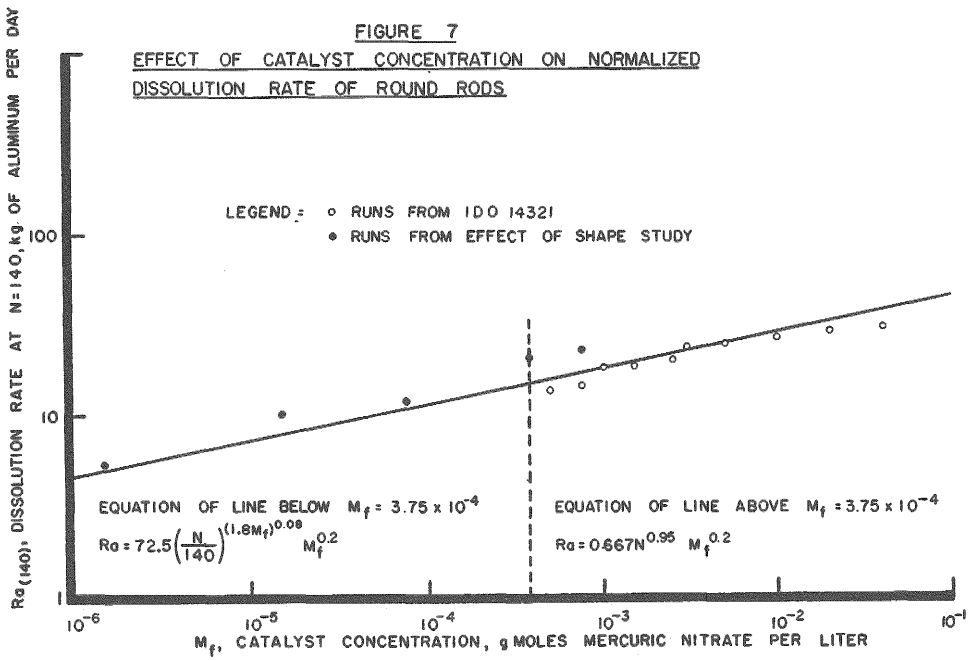
Acid Feed Rate = 140 g-moles nitric acid per hour

| $m_f$, catalyst concentration, g-moles mercuric nitrate per liter | Ra, aluminum dissolution rate, kilograms of aluminum per day |
|---|---|
| 0.04 | 30.3 |
| 0.02 | 28.6 |
| 0.01 | 26.4 |
| 0.005 | 24.7 |
| 0.003 | 23.6 |
| 0.0025 | 20.1 |
| 0.0015 | 18.4 |
| 0.001 | 18.0 |
| 0.00075 | 14.5 |
| 0.00075* | 22.8 |
| 0.0005 | 13.6 |
| 0.000375* | 20.3 |
| 0.000075* | 11.9 |
| 0.000015* | 10.0 |
| 0.0000015* | 5.3 |

* From effect of shape study; all others from IDO-14321.

The data in Table 9 are plotted in Figure 7.

FIGURE 7
EFFECT OF CATALYST CONCENTRATION ON NORMALIZED DISSOLUTION RATE OF ROUND RODS



The dissolution rate equations obtained from Figure 7 are:

For values of $m_f$ below $3.75 \times 10^{-4}$ $Ra = 72.5 \left(\frac{N}{140}\right)^{1.8} m_f^{0.08} m_f^{0.2}$ (3)

For values of $m_f$ above $3.75 \times 10^{-4}$ $Ra = 0.667 N^{0.95} m_f^{0.2}$ (9)

Dissolution rate data obtained at ORNL on extruded uranium-aluminum fuel elements in four to six molar nitric acid containing 0.005 gram-moles of mercuric nitrate per liter showed that the dissolution rate varied as the acid feed rate to the 0.98 power. The exponent, 0.95, of the acid feed rate in equation (9) compares very favorably with the ORNL exponent.

## XI. EFFECT OF DISSOLVER VESSEL MATERIAL

Stainless steel strips were welded from the discharge end of the charging tube to the crash plate at the bottom of the dissolver. Re-runs of two round rod and four flat plate runs were made in this modified dissolver. The results are listed in Table 10 along with results of the initial runs made in the unlined glass dissolver. Statistical analysis of these data indicate no difference between dissolution rates obtained in glass and those obtained in stainless steel.

Table 10

Comparison of Dissolution Rates in Glass and Stainless Steel-Lined Dissolvers

| Feed Rate g-mols $HNO_3$/hr | Catalyst Conc. g-mols Hg/liter | Shape | Dissolving Rates Kg Al/day | | Percent Change |
|---|---|---|---|---|---|
| | | | Glass | Stainless Steel | |
| 70 | $3.75 \times 10^{-4}$ | Round Rods | 11.1 | 12.5 | +12.6 |
| 140 | $3.75 \times 10^{-4}$ | Round Rods | 21.4 | 23.8 | +11.2 |
| 70 | $3.75 \times 10^{-4}$ | Flat Plates | 11.7 | 13.0 | +11.1 |
| 70 | $7.5 \times 10^{-5}$ | Flat Plates | 11.9 | 12.8 | + 7.6 |
| 140 | $7.5 \times 10^{-5}$ | Flat Plates | 22.5 | 20.0 | - 9.1 |

## XII. CONCLUSIONS

1. All variables tested (shape, feed rate, and catalyst concentration) as well as all first order interactions of these variables have a significant effect upon the dissolution rate.

2. The non-linearity of the effect of the variables and the extensive interactions preclude the use of any simple equations to describe the dissolver behavior under all conditions. However, equations have been derived which can be used with confidence over specified ranges of the variables.

3. The effect of shape on dissolution rate appears to be dependent upon the metal surface area per unit volume of dissolver; widely differing shapes having the same surface packing characteristics exhibit essentially identical behavior.

4. At high catalyst concentrations (above $7.5 \times 10^{-5}$M mercury) the dissolution rates for all shapes are approximately equal. At lower catalyst concentrations, however, flat plates and flattened tubes dissolve as much as two and one-half times faster than round rods and tubes which have only about half the free surface area per unit volume as the former two shapes.

5. The electrochemical effect of the dissolver vessel appears to be minor since no significant difference exists between dissolution rates obtained in glass and stainless steel dissolvers.

6. The fact that so many main and interaction effects are significant indicates that erratic behavior can be expected under certain conditions. It is entirely possible that at certain conditions a slight change in feed rate or catalyst concentration can greatly affect dissolution rate. Thus, care must be taken in interpreting and extrapolating the results of this work.

7. The addition of a small percentage of uranium to the aluminum-nitric acid system has no effect on the dissolution rate of the aluminum.

8. The dissolution rate of round rods varies as the 0.95 power of the acid feed rate and 0.2 power of the catalyst concentration at catalyst concentrations above $3.75 \times 10^{-4}$ molar mercuric nitrate.

The best available equations describing continuous dissolution of uranium-aluminum alloy rods in a 2-inch diameter dissolver are:

Cast Alloy $\quad Ra = 1.75\ N^{0.8}\ m_f^{0.33}$

Extruded Alloy $\quad Ra = 72.5\ \left(\frac{N}{140}\right)^{1.8}\ m_f^{0.08}\ m_f^{0.2}$ (for $m_f$ below $3.75 \times 10^{-4}$)

$\qquad\qquad\qquad\quad Ra = 0.667\ N^{0.95}\ m_f^{0.2}$ (for $m_f$ above $3.75 \times 10^{-4}$)

## XIII. ACKNOWLEDGEMENT

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## XIV. NOMENCLATURE

| | | |
|---|---|---|
| F | Feed rate of nitric acid (volumetric) | liters/hr |
| $m_f$ | Mercuric ion concentration in feed | g-mols/liter |
| N | Nitric acid feed rate (molar) | g-mols $HNO_3$/hr |
| $n_f$ | Nitric acid concentration in feed | g-mols $HNO_3$/liter |
| $n_p$ | Nitric acid concentration in product | g-mols $HNO_3$/liter |
| P | Product flow rate (volumetric) | liter/hr |
| $R_a$ | Aluminum dissolving rate | kg Al/day |
| S | Surface area factor ratio | SAF/SAF (round rods) |
| SAF | Surface area factor | $cm^2$/ft of dissolver |