# Continuous Dissolution of Uranium-aluminum Reactor Fuels

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**Extensive pilot plant studies of the continuous, mercury-catalyzed nitric acid dissolution of uranium-aluminum alloy materials similar to possible reactor fuel elements were carried out. Marked differences were observed in the dissolution rates of cast and wrought alloys. Optimum feed-acid concentrations varied with the type of alloy. At constant acid feed conditions dissolving rates varied approximately with the cube root of catalyst concentration up to a limiting concentration. The metal dissolving rate was proportional to the 0.8 power of the nitric acid feed rate. A general empirical correlation was developed.**

Nuclear reactor fuels are periodically processed to separate the fissionable material from alloying elements and from fission products which may "poison" the reactor if they are not removed. Many reactors use uranium-aluminum-alloy fuel elements of various compositions and shapes, the spent fuels being processed by batchwise mercury-catalyzed dissolution in nitric acid followed by separation of uranium from aluminum and fission products by solvent extraction. It was anticipated that operating simplifications could be achieved by continuous, as opposed to batch, dissolution. Consequently, extensive pilot plant studies of the continuous dissolution of uranium-aluminum alloys containing up to about 10 wt. % uranium were undertaken. Data and correlations are given for the portion of these investigations pertaining to the important process relationships in continuous dissolution.

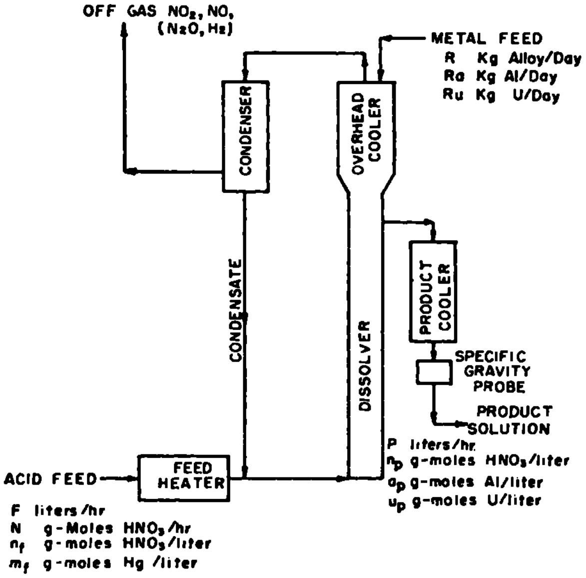

Fig. 1. Schematic drawing of continuous dissolver.

## TEST EQUIPMENT AND MATERIALS

The continuous dissolver used in the experimental work was a tall 2-in. I.D. type-347 stainless steel pipe with a cooling section at the top. This overhead cooling section and a down-draft condenser of standard design were used to condense the steam in the off-gas rising from the dissolver solution. The acid feed was continuously steam heated to near-boiling temperatures; the product was water cooled and then collected in a stainless steel drum placed on a platform scale. The acid feed rate was controlled with a rotameter and measured by liquid-level readings on the feed tank. Instrumentation for measuring the feed and product specific gravities and temperatures at various locations was available.

The reactor fuel material to be dissolved was simulated by using cylindrical slugs about 1½ in. in diameter and 8 in. long. Although not representative of M.T.R.-type fuel plates, in that the surface-to-volume ratio of such bars is much lower than that of plates, this form of material was a convenient and economical choice. Extruded 2S aluminum-bar stock and cast and extruded uranium-aluminum-alloy slugs were used in the experimental work. The slugs were loaded periodically through a pair of gate valves located at the top of the dissolver.

## GENERAL CONCEPTS

A schematic diagram of the continuous dissolver and the important auxiliary equipment is shown in Figure 1. The symbols defined on this diagram represent the important process variables and are used throughout this paper.

The nitric acid solution and mercuric nitrate catalyst solution (a separate stream if so desired) are fed at the bottom of the dissolver, and uranium-aluminum slugs are charged intermittently into the top of the vessel. The acid dissolves the slugs as it flows countercurrent to the bed of metal, and the product solution is withdrawn through an overflow pipe. At constant feed rates for slugs, acid, and catalyst the metal level will seek an equilibrium value, and a steady dissolution rate and uniform product composition should be obtained. The system is then inherently stable in that minor process fluctuations will be compensated by changes in the slug level and, hence, the surface area available for dissolution.

When slugs are added at the desired dissolution rate, the equilibrium metal level is dependent upon the quantity of acid fed and the catalyst concentration. The amount of acid fed may differ from that stoichiometrically equivalent to the metal feed rate, and the extent of this difference will be reflected in the product composition. Hence the acid feed rate required for a given dissolution rate is determined by the product composition needed for satisfactory performance in the subsequent process steps. The concentration of the acid in the feed also restricts the product composition to definite ratios of aluminum, uranium, and acid concentration. The mercuric-ion (catalyst) concentration in the feed might also be expected to affect the reaction kinetics. The effects of these three parameters (acid feed rate, feed acid concentration, and catalyst concentration) on dissolution rate are the most important dissolver process relationships that were investigated.

## DISSOLVER PROCESS RELATIONSHIPS

### General Discussion

In a correlation of the effects of the process variables aluminum dissolving rate $R_a$ (kg./24-hr. day) has been used as the major parameter. This quantity has been selected because it links results obtained with the specific uranium-aluminum alloy used in the experimental work with quantities predictable for alloys of other compositions. The alloy used in this work was approximately 10 wt. % uranium, or about 99 mole % aluminum, and so the reaction is essentially the dissolution of aluminum. In order to obtain the uranium dissolving rates for an alloy of similar composition and metallurgical characteristics from the aluminum dissolving rates presented in the subsequent correlations, one need only multiply by the ratio of percentage of uranium to percentage of aluminum.

The product nitric acid concentration is used in all correlations as an index of product composition. This property is related to the aluminum concentration by stoichiometry and can be readily converted by use of the relationships discussed below.

### Stoichiometry

A general discussion of the material-balance relationships and the reaction stoichiometry will clarify subsequent correlations of the effect of each of the process variables.

Samples of the continuous dissolver off-gas were analyzed in a number of runs. Table 1 shows the average analysis, the reactions indicated, and the calculation of the average moles of acid consumed

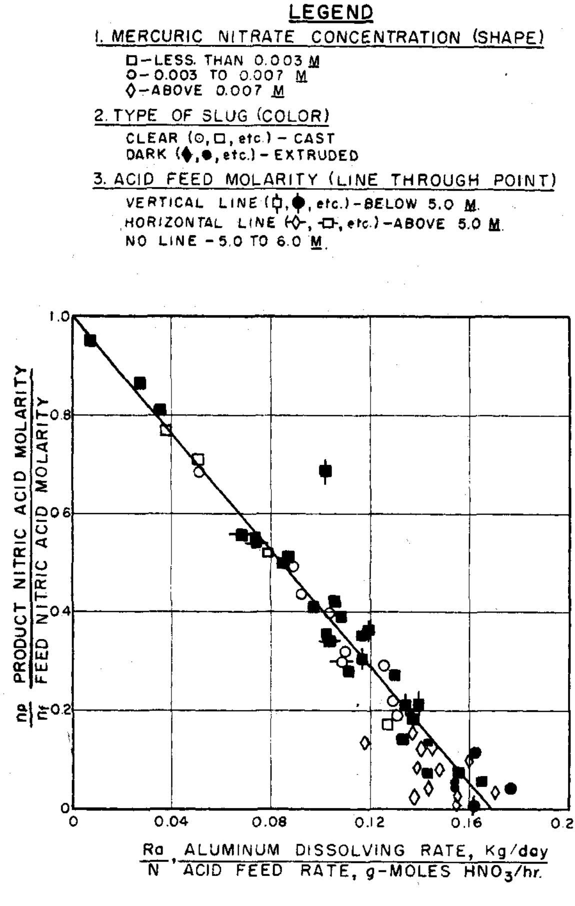

Fig. 2. Stoichiometric correlation of data.

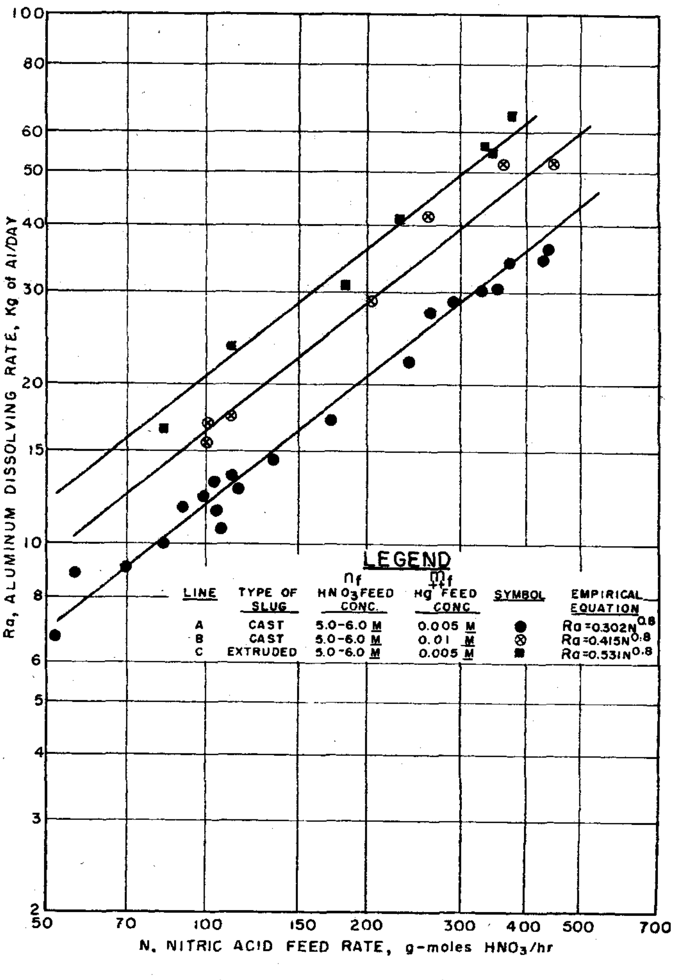

Fig. 3. Variation of dissolution rate with acid feed rate.

TABLE 1. THE MERCURY-CATALYZED DISSOLUTION OF ALUMINUM IN NITRIC ACID

| Assumed reaction | Moles of acid consumed/ mole Al dissolved | % of Al dissolved through reaction shown* |
|---|---|---|
| $Al + 6\,HNO_3 = Al(NO_3)_3 + NO_2 + 3\,H_2O$ | 6.00 | 1 |
| $Al + 4\,HNO_3 = Al(NO_3)_3 + NO + 2\,H_2O$ | 4.00 | 52 |
| $8\,Al + 30\,HNO_3 = 8\,Al(NO_3)_3 + 3\,N_2O + 15\,H_2O$ | 3.75 | 46 |
| $2\,Al + 6\,HNO_3 = 2\,Al(NO_3)_3 + 3\,H_2$ | 3.00 | 1 |

Calculated weighted-average acid consumption = 3.85

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*These values are calculated from the following average of dissolver off-gas samples: $NO_2$ = 4%, NO = 70%, $N_2O$ = 23%, $H_2$ = 3%.

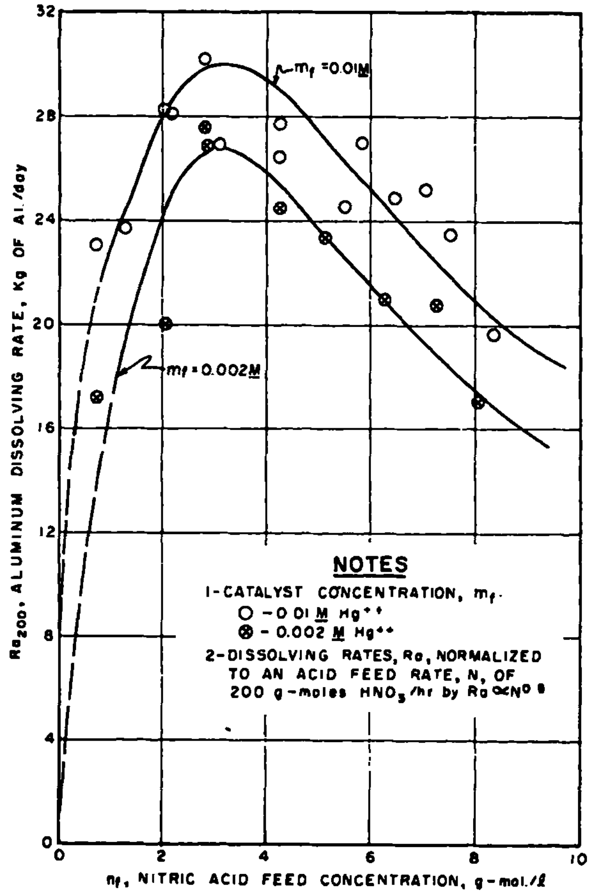


Fig. 4. Effect of feed acid concentration for cast slugs.

for each mole of aluminum dissolved; the small mole fraction of uranium in the alloy is neglected. Using this calculated value of 3.85 for the average acid consumption ratio, in conjunction with a nitric acid material balance around the dissolver, one obtains the following equation for the ratio of product acidity ($n_p$) to feed acidity ($n_f$):

$$\frac{n_p}{n_f} = 1 - 5.94\,\frac{R_a}{N} \qquad (1)$$

where $N$ is the acid feed rate in gram-moles per hour and $R_a$ is the kilograms of aluminum dissolved per day. In the derivation of Equation (1) the ratio of volumetric product rate $P$ to volumetric feed rate $F$ was set equal to 1. This is considered valid because experimental data showed that the maximum error introduced by this assumption is less than 1%.

Equation (1) is shown graphically in Figure 2, along with experimental data from a large number of pilot plant runs. The data are seen to agree closely with the line representing Equation (1). It is important to note that data from runs with wide variations in feed mercuric ion concentration, feed acid concentration, and metallurgical properties of the alloy are randomly distributed in Figure 2, showing that the reaction stoichiometry s not significantly influenced by these variables.

The nitric acid consumption for all runs averaged 4.0 moles per mole of alloy dissolved and was within 10% of this value for 85% of the runs. This further shows the validity of Equation (1) as an average representation of the reaction stoichiometry.

### Effect of Metallurgical Properties

Metallographic examination of the cast and extruded uranium-aluminum slugs used in these studies revealed significant differences in crystalline structure. The cast slugs consisted of relatively large dentrites of primary aluminum (first to freeze during solidification) surrounded by networks of eutectic of $UAl_4$ and aluminum. Examination of extruded slugs of the same composition showed a fairly uniform distribution of aluminum and intermetallic compound, with the eutectic network broken and less pronounced.

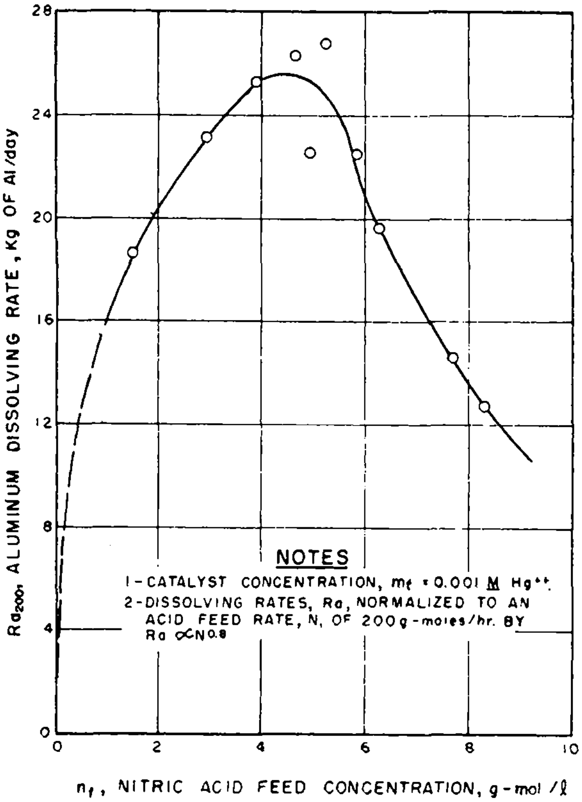
As might be expected, slugs showing such dissimilarities in alloy structure had different dissolving characteristics. At a constant feed acid composition and catalyst concentration extruded uranium-aluminum slugs dissolved about twice as fast as comparable cast material.

A number of runs were carried out with lengths of extruded aluminum rod. It was found that 2S aluminum rod dissolved at a rate very slightly lower than that for extruded uranium-alloy slugs; consequently, the runs made with the former material were considered representative of the behavior of extruded uranium-aluminum slugs. Furthermore, as the uranium contained in the extruded alloy has little effect on the dissolution rate, it may be concluded that extruded alloys of a composition somewhat different from the slugs used in this study will dissolve at comparable rates.

Differences in fabrication histories for a given alloy, however, would be expected to give significant differences in dissolution rate corresponding to differences in alloy structure. Consequently, the numerical dissolution-rate relationships presented in this paper must be considered applicable only to the specific materials used in this study. Furthermore, the effects of irradiation were not investigated.

### Effect of Acid Feed Rate

Several series of runs were made at constant feed acid and catalyst concentrations and varying acid feed rates. The results are shown in Figure 3, which is a logarithmic plot of the dissolving rate $R_a$ against the acid feed rate $N$. The slope of each of the lines is 0.8, which indicates that the dissolving rate is proportional to the 0.8 power of the acid feed rate at all conditions tested. This relationship appears to be quite general, and through its use the results from many runs have been "normalized" to a single acid feed rate to facilitate other correlations.

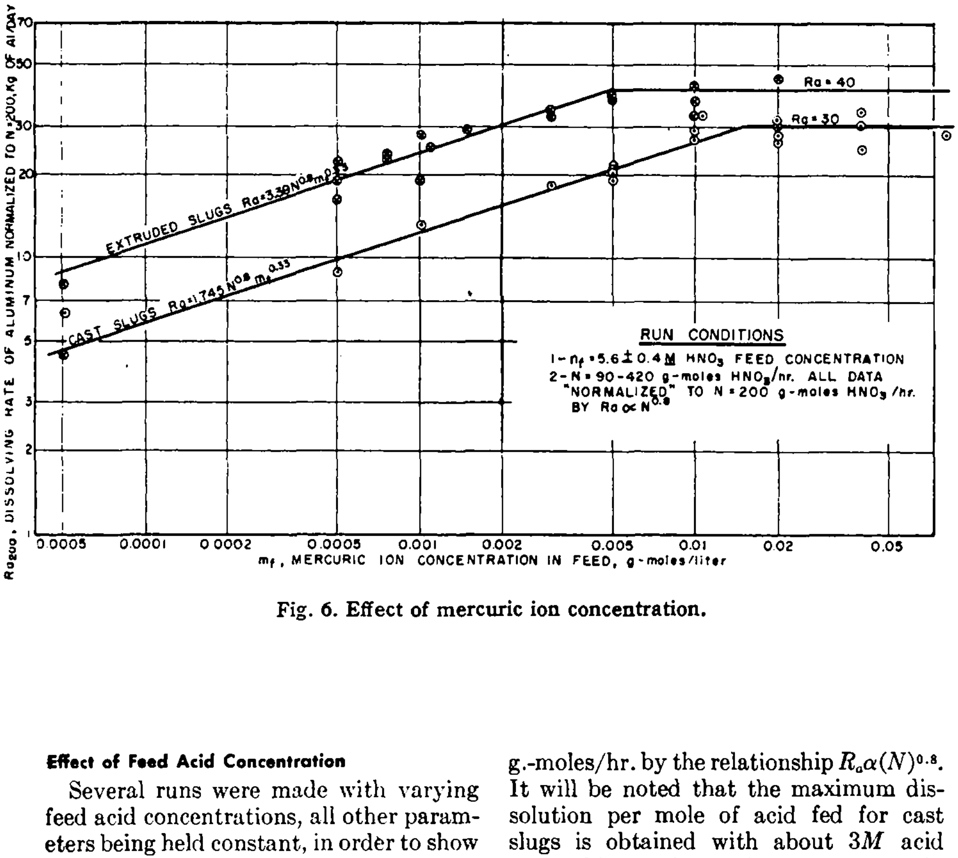


NOTES

1-CATALYST CONCENTRATION, $m_f$ = 0.001 M $Hg^{++}$.

2-DISSOLVING RATES, Ra, NORMALIZED TO AN ACID FEED RATE, N, OF 200 g-moles/hr. BY $Ra \propto N^{0.8}$

Fig. 5. Effect of feed acid concentration for extruded slugs.



RUN CONDITIONS

1-$n_f$ = 5.6 ± 0.4 M $HNO_3$ FEED CONCENTRATION

2-N = 90-420 g-moles $HNO_3$/hr. ALL DATA "NORMALIZED" TO N = 200 g-moles $HNO_3$/hr. BY $Ra \propto N^{0.8}$

Fig. 6. Effect of mercuric ion concentration.

### Effect of Feed Acid Concentration

Several runs were made with varying feed acid concentrations, all other parameters being held constant, in order to show the effect of acid concentration upon the dissolving rate. The results of such tests are shown in Figures 4 and 5, wherein the dissolving rates $R_a$ have been "normalized" to an acid feed rate $N$ of 200 g.-moles/hr. by the relationship $R_a \alpha (N)^{0.8}$. It will be noted that the maximum dissolution per mole of acid fed for cast slugs is obtained with about 3*M* acid feed; this maximum is seen to remain the same even when the feed catalyst concentration is changed by a factor of 5. The dissolving rate curve for extruded slugs was determined at only one catalyst concentration; in this case the maximum rate occurs with about 5*M* acid.

### Effect of Catalyst Concentration

Series of runs were made with both cast and extruded uranium-aluminum alloy at varying acid feed rates with 5.6*M* acid feed and a range of feed mercuric nitrate concentration between 0.00005 and 0.08*M*. The results of these runs are shown in Figure 6, wherein the acid feed rate is normalized to a standard value of 200 g.-moles/hr. by means of the 0.8 power relationship of Figure 3. It is apparent from Figure 6 that an increase in mercuric nitrate concentration in the feed results in a definite and significant increase in dissolving rate for both cast and extruded alloy up to a limiting mercuric ion concentration. Further increases in mercuric ion concentration above approximately 0.015*M* for cast slugs and 0.005*M* for extruded slugs yield no corresponding increase in dissolving rate. Below these limiting catalyst concentrations the linear relationships on the logarithmic plot of Figure 6 can be represented by the following empirical equations:

cast alloy:

$$R_a = 1.745 N^{0.8} m_f^{0.33} \qquad (2)$$

extruded alloy:

$$R_a = 3.39\ N^{0.8} m_f^{0.33} \qquad (3)$$

### General Correlation

Equation (1) can be combined with the foregoing empirical equations to include the product composition and eliminate the acid feed rate, giving the following relationships:

cast alloy:

$$R_a = 20{,}200(m_f)^{1.65}\left(\frac{n_f}{n_f - n_p}\right)^4 \qquad (4)$$

extruded alloy:

$$R_a = 557{,}000(m_f)^{1.65}\left(\frac{n_f}{n_f - n_p}\right)^4 \qquad (5)$$

These equations show the relationship between the feed and product compositions and the dissolving rate for the dissolver used in the experimental work.

Strictly speaking, Equations (4) and (5) are applicable only for 5.6*M* acid feed as Equations (2) and (3), which are used in the derivation, were determined at this concentration. However, the plots of dissolution rate as a function of acid concentration (Figures 4 and 5) show little variation in rate for acid concentrations between 3 and 6*M* for either cast or extruded slugs. Consequently, Equations (4) and (5) are approximately correct for feed acid concentrations between 3 and 6*M* and are most accurate for 5.6*M* acid.

These equations are also significant in that they can be used to show the effect of the important process variables on

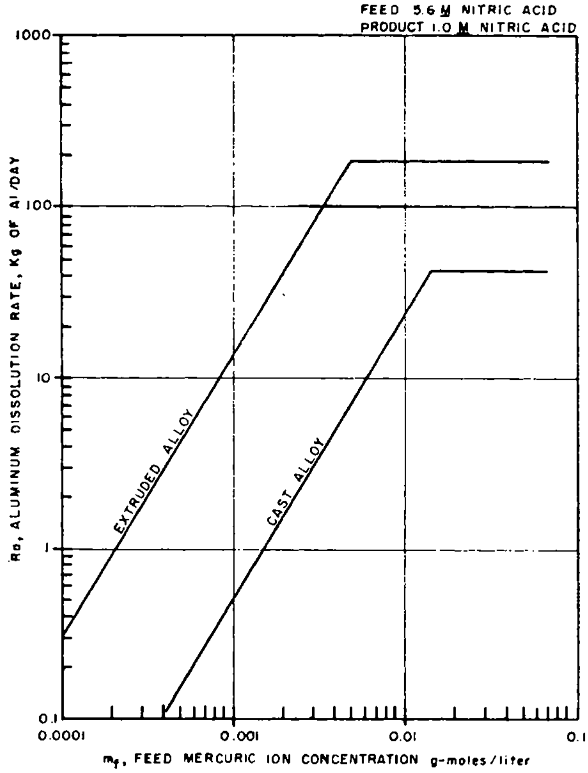


Fig. 7. General dissolver relationship.

dissolution rate at a constant product composition. The correlations developed in previous sections were obtained by keeping the feed conditions constant, except for the variable being studied, and allowing the product composition to vary at will. However, normal continuous dissolver operation would be directed toward keeping a constant product composition (within specifications for feed to a subsequent process step) and varying other conditions as necessary.

Equations (4) and (5) show that the dissolution rate varies with the 1.65 power of the catalyst concentration at constant product composition; whereas Equations (2) and (3) indicate a variation with the cube root of the mercuric ion concentration at constant acid feed rates. Beyond the limiting catalyst concentrations, an increase in mercuric ion molarity will give no corresponding increase in dissolution rate at either constant feed acid rate or a constant product concentration.

Insertion of these limiting catalyst concentrations in Equations (2), (3), (4), and (5) demonstrates that the maximum dissolution rate attainable at a constant product composition is about three times greater for extruded alloy than for cast material; whereas this ratio is only about 1.5 at a constant acid feed rate. At a given catalyst concentration below the limiting value, extruded alloy dissolves about thirty times faster than cast material for a constant product composition and only about twice as fast at a constant feed acid rate.

The effect of catalyst concentration on the dissolution rates of cast and extruded alloy for a constant product composition may be illustrated by inserting specific values for the feed and product acidity in Equations (4) and (5) and plotting the resultant relationships. For the sake of illustration, it may be assumed that a 1*M* acid product is optimum for subsequent processing. Since a 5.6*M* acid feed was used in most of the experimental work and the resultant correlations, this value is chosen for insertion in Equations (4) and (5). The resultant relationships are

cast alloy:

$$R_a = 4.42 \times 10^4 (m_f)^{1.65} \qquad (6)$$

extruded alloy:

$$R_a = 1.22 \times 10^6 (m_f)^{1.65} \qquad (7)$$

Equations (6) and (7) are plotted on Figure 7.

The significantly greater dissolution rate of extruded alloy as compared with cast material should be of special interest to those concerned with designing the fuel elements for a reactor. If there is little difference in the reactor performance of extruded and cast uranium-aluminum fuel alloys, extruded material should be specified as its considerably greater dissolution rate could result in significant savings in fuel-processing costs.

## DISSOLVER OPERATION AND CONTROL

Normally a plant-scale continuous dissolver would probably be operated with all input streams (feed acid, catalyst, and metal) controlled at selected constant rates. These rates should be chosen so that they are stoichiometrically equivalent to the desired dissolution rate and product composition. With such operation, the metal would seek an equilibrium level in the dissolver and the process would be inherently stable, as small changes in some parameter would alter the slug level (and hence the available surface area) so as to compensate for the change.

Although this inherent stability would normally give a uniform product composition, unusual conditions could occasionally yield product which did not meet specifications. Such occurrences could be detected by continuous measurement of the specific gravity of cold dissolver product; this was successfully demonstrated during the pilot plant tests.

An adjustment in operating conditions must be made whenever it is apparent that the dissolver effluent will not meet specifications for subsequent processing. Various possible methods of adjusting the product composition were tested in the pilot plant including changes in feed acid concentration, in the acid feed rate, in the dissolver temperature, in the metal feed rate, and in catalyst concentration. The last method proved most satisfactory.

This method of adjustment has the advantage of not changing the metal or volumetric throughputs, and hence nearly the entire plant would function normally regardless of the rate of catalyst addition. With such a method the catalyst should logically be injected into the feed stream separately from the dilute acid to facilitate adjustments in catalyst feed rate. Several successful pilot plant runs were made to show the effect of such changes in catalyst concentration on the product analysis and on the specific gravity as recorded on an instrument chart.

## CONCLUSIONS

Data and correlations have been given for the process relationships of concern in the continuous dissolution of certain uranium-aluminum alloys. These correlations can be used to aid in the design of a workable dissolver for processing uranium-aluminum-alloy reactor fuels at any given capacity to meet a wide range of product composition specifications.

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