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EFFECT OF ALLOYING CONSTITUENTS ON ALUMINUM
DISSOLUTION RATES

R. D. Fletcher
M. E. Jacobson
H. R. Beard

PHILLIPS
PETROLEUM
COMPANY

Atomic Energy Division

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A B S T R A C T

In studies of the effect of alloying elements on the rate of dissolution of aluminum in mercury-catalyzed nitric acid, it was observed that copper, nickel, and silicon present at concentrations of 1-2 per cent have significant passivating effects. Iron was slightly catalytic. Passivation due to silicon was partly overcome by contacting the passive alloy with active, high purity aluminum. Increased catalyst concentration improved the rates when nickel and silicon were present. Neither approach was effective when copper was the passivating element. For application to nuclear fuel reprocessing, it is suggested that for minimum reprocessing costs the potentially passive aluminum alloys not be used in fuel elements or that, failing this, electrochemical activation techniques be applied at the processing plant.

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I. SUMMARY

In the dissolution of aluminum reactor fuel elements prior to uranium recovery, it is frequently found that either high irradiation levels or the use of certain alloys in the preparation of the fuel leads to inconveniently low dissolution rates. The likely sources of this passivation are:

1. an anticatalytic effect of ions in solution derived from the alloy,
2. passivating effects of elements in the alloy,
3. passivating effect of the metallurgical conditions of the alloy, and
4. composition and metallurgical effects in the alloy due to reactor irradiation.

Dissolution rate measurements made to evaluate the first two effects have shown that copper and nickel ions in solution significantly decrease the rate of dissolution of high purity aluminum metal in mercury catalyzed nitric acid, and that copper, silicon, and nickel as elements in aluminum alloys have a pronounced passivating effect. Other ions in solution and alloying elements, such as manganese, magnesium, zinc, and uranium were also studied and were shown to have little effect on the rate. The alloying constituents were present to the extent of less than 5 per cent in every case. Iron, at concentration levels of 1-2 per cent of the aluminum weight, was observed to be slightly catalytic for the dissolution reaction.

The passivating effect of silicon in the alloys was overcome by "contact activation," by welding or tying a piece of high purity aluminum to the passive alloy prior to the test. Passivation due to nickel or silicon was overcome by increasing the mercury catalyst concentration from 0.005M to 0.05M and maintaining the other test conditions the same. Passive effects associated with the presence of copper in the alloy could not be removed by either of these methods.

Application of these data suggests that the cost of the fuel cycle for test reactors using aluminum alloy fuels might be minimized by consideration of the effects of alloy composition on processing rates, and that materials for fuel elements might be selected with this in mind. When passive materials are found at the Chemical Processing Plant, the use of "contact activation" or other essentially electrochemical approaches for activation may be workable if the simpler, but expensive, approach of using more catalyst fails.

II. INTRODUCTION

The dissolution in nitric acid with mercury catalyst of aluminum alloy reactor fuels clad in aluminum normally proceeds at a rate characteristic of the relatively pure aluminum used in the fuel fabrication. However, there have been instances where highly irradiated, slug-type fuels have shown a dissolution rate constant in batch dissolution which was only 1 per cent of that for 1100 aluminum⁽¹⁾. It has been observed in continuous dissolution that 250 per cent excess mercury catalyst was required to maintain the same dissolution rate with irradiated material compared to unirradiated⁽²⁾. Extruded rod material has been observed to dissolve more readily than cast material of the same composition and dimensions⁽³⁾. The wide fluctuations in dissolution rates, some of them unanticipated, have led to difficulties in production scheduling, and where a rate is extremely slow, to excessive processing costs. While most indications have been that irradiation was the major factor leading to reduced rates, it has not been clear which aspect of irradiation (accumulation of fission products, disruption of the aluminum lattice, or transmutation of the aluminum to an alloying constituent which led to passivation) was responsible. Therefore, a four-phase program was initiated to study and determine the effects of several factors which might contribute to the lower dissolution rates.

- I. Catalytic or retarding effects of the ions in solution as derived from constituents of the alloy or fission products.
- II. Effect of alloy composition in the metal as well as in solution.
- III. Effect of metallurgy or working.
- IV. Effect of irradiation.

It was considered desirable to understand the simplest effects first, even though these might not be of greatest importance, so that there would be maximum possibility of successful interpretation of the results of tests with irradiated materials.

Phase I of the program consisted of batch and instantaneous dissolution rate measurements, with standard sized coupons of 99.999 per cent aluminum in 6.6M nitric acid - 0.005M mercuric nitrate at 90°C. Nitrate solutions of the typical aluminum alloying elements were added to the initial solutions to give a solution composition equivalent to that of a 1 and 2 per cent alloy at the end of the dissolution. It was

anticipated that this approach would not give a true picture of an alloy going into solution because the entire alloying constituent would be present in solution initially. However, it was expected that considerable information would be provided in certain specific areas, such as instantaneous dissolution rates at various aluminum concentrations and a qualitative indication of the effect of the alloying constituents on batch dissolution time in Phase II.

Phase II consisted of batch and instantaneous dissolution rate measurements with standard sized alloyed aluminum coupons dissolved in 6.6M nitric acid - 0.005M mercuric nitrate at 90°C. The aluminum alloy coupons were fabricated from Alcoa spectrochemical standards. The compositions were chosen to provide a significant concentration of one or two of the apparently catalytic or retarding constituents (as indicated in Phase I).

In general, the experimental results are presented in two ways: (1) the time required for batch dissolution to a given aluminum concentration under stated conditions, and (2) the instantaneous dissolution rate at a given aluminum concentration at stated conditions. These should be applicable to and interpreted in terms of batch and continuous dissolution processes, respectively. At this time, sufficient significant results have been accumulated in Phase I and II of the program to warrant review of the experimental data and consideration of the implications of these results in terms of fuel fabrication specifications and chemical reprocessing scheduling, procedures, and costs.

III. EXPERIMENTAL PROGRAM

A. Description of Techniques

1. Effect of Dissolved Cations

The first phase of the program consisted of batch and instantaneous dissolution rate measurements with standard sized (1.00" x 1.26" x 0.176") coupons of 99.999 per cent aluminum. The dissolver solution used throughout this phase was 6.6M nitric acid - 0.005M mercuric nitrate. Nitrate solutions of the typical aluminum alloying elements (copper, nickel, iron, magnesium, manganese, zinc, and uranium) were added individually to the dissolver solution prior to dissolution, to give a solution composition equivalent to that of a 1 per cent and 2 per cent alloy at the end of dissolution.

In one set of experiments strontium, cesium, zirconium, ruthenium, barium, lanthanum, and cerium were added as nitrate salts to simulate dissolved fission products. The sum of the weights of the metal ions was 1.9 per cent of the weight of the aluminum dissolved. Praseodymium and niodymium were represented by added cerium. The proportions were those found in a typical test reactor fuel but the concentrations were about three times those normally found in MTR dissolver product solution.

The details of the dissolver are shown in Figure 1. The dissolver solution was maintained at $90 \pm 2^\circ\text{C}$ by the Glascol heater, stainless steel cooling coil, and thermoregulator. Each dissolution experiment was done at least in duplicate.

2. Effect of Alloying Metals

The second phase of the study consisted of measurements of batch and instantaneous dissolution rates with standard sized (1.00" x 1.26" x 0.176") coupons machined from Alcoa spectrochemical standards. These standards are identified and related to commercially available cast and wrought products in Table 1. The compositions of the alloys are given in Table 2. In the selection of the alloys for the Phase II studies, special emphasis was given to silicon-containing alloys since silicon could not be studied in Phase I, and to alloys with iron, nickel, and copper since these had been shown to have significant effect on the dissolution rate as ions in solution in the Phase I studies. Conditions of reagent composition and temperature were identical to those for Phase I.

In addition, certain extra studies were made with passive alloys using higher temperatures and greater concentrations of mercury catalyst, 0.05M instead of 0.005M. Attempts were also made to activate passive material by contacting with pure, active aluminum.

B. Data and Mathematical Interpretation

During the course of the batch dissolutions, solution samples of very small volume relative to the total (5 ml from 250 ml) were taken periodically and analyzed for aluminum and in some cases for acid. The correction of the solution composition, due to the volume and mass decrease due to sampling, was calculated and found to be insignificantly small compared to the major errors in the analysis and measurements. The frequency of sampling was determined by the rate of disappearance of the aluminum coupon. Between 14 and 25 samples were taken during each dissolution. Typical original data for a Phase I dissolution is shown in Appendix 1 and for a Phase II dissolution in Appendix 2. Acid and aluminum concentrations obtained from a number of samples during all phases of the dissolution are plotted in Figure 2 to illustrate the stoichiometry of the dissolution reaction and to establish the typical solution concentration at every stage of the batch dissolution.

The times for batch dissolution to a predetermined aluminum concentration were read from the tabulated data or from plots of the aluminum concentration vs time. Although instantaneous rates could have been read graphically, it appeared desirable to obtain a mathematical expression for the variation of aluminum (or acid) with time and to obtain the dissolution rates by evaluating the derivative at various times or aluminum concentrations. Initially, the parabolic rate law used by Murray⁽⁴⁾

$$\frac{d(\text{Al}^{+++})}{dt} = \frac{K}{(\text{Al}^{+++})} \quad \text{Equation 1}$$

Fig. 1 Dissolver for Rate Studies

Table 1

IDENTIFICATION OF ALUMINUM ALLOYS
USED IN DISSOLUTION STUDIES

Alloy Designation in this Report	Type of Alloy ⁽¹⁾	Spectrographic Standard ⁽¹⁾	Commercial Alloys of Similar Composition ⁽²⁾	
			Wrought	Cast
1673	Iron in unalloyed aluminum	SA-1673-19	1130	(3)
1617	Iron in unalloyed aluminum	SA-1617-28	(3)	(3)
1022	Silicon in unalloyed aluminum	SAC-1022-21	(3)	(3)
774	Silicon in unalloyed aluminum	SAC-774-28	(3)	(3)
1033	142 alloy	SAC-1033-26	2218	142
1091	195 alloy	SAC-1091-26	(4)	195
2618	2618 alloy	SS-2618-A-5	(5)	(6)
5456	5456 alloy	SS-5456	(7)	(3)
6061	6061 alloy	SS-6061	6061	(3)
8001	Nickel in unalloyed aluminum	-	(3)	(3)

(1) Alcoa Spectrochemical Standards Bulletin, Alcoa Research Laboratories, New Kensington, Pa., May 1959.

(2) Alcoa Aluminum Handbook, Aluminum Company of America, 1956, pp. 35 and 163.

(3) No commercial alloy of similar composition given in reference of footnote (2)

(4) Like 2014 except that Mg and Mn are slightly low.

(5) Like 2218 except Cu is slightly low.

(6) Like B750 except Fe and Mg are slightly high.

(7) Like 5056 except Mn is high.

Table 2
COMPOSITION OF ALUMINUM ALLOYS

<u>Alloying Constituents-Per Cent</u>										
<u>Alloy</u>	<u>Cu</u>	<u>Fe</u>	<u>Si</u>	<u>Mn</u>	<u>Mg</u>	<u>Zn</u>	<u>Ni</u>	<u>Ti</u>	<u>Cr</u>	<u>Aluminum % (by difference)</u>
1673	0.01	0.60	0.10							99.29
1617	0.01	2.14	0.10							97.75
1022		0.5	1.55							97.95
774		0.5	2.91							96.59
1033	3.54	0.43	0.24	0.025	1.79	0.033	2.09	0.072		71.780
1091	4.80	0.42	1.19	0.034	0.008	0.04	0.06			93.448
2618	2.29	1.08	0.18	0.062	1.60	0.06	1.14	0.078	0.002	93.508
5456	0.06	0.16	0.14	0.82	5.12	0.055	0.011			93.634
6061	0.31	0.36	0.59	0.054	0.99	0.081	0.052			97.563
8001	0.1	0.5	0.1	0.05		0.1	1.0			98.15

Fig. 2 Stoichiometry for Aluminum Dissolution
Acid Consumption Equals 3.5 Moles of H^+ per Mole of Aluminum Dissolved

was tried, but a better fit for the data from Phase I of the study was obtained with an expression of the form,

$$(Al^{+++})^\beta = \alpha (t - t_0) \quad \text{Equation 2}$$

This allowed greater accuracy in stating the instantaneous dissolution rates while sacrificing the ability to describe the reaction by a value for a single rate constant. The constants alpha and beta for each set of experimental data were obtained by regression analysis. The mathematical value for t_0 , the induction time, was obtained by an iterative process of minimizing the error in alpha and beta. The results for the Phase II experiments gave relatively poor correlation by equation 2 and therefore equation 3 was used for these data.

$$Al^{+++} = a_0 + a_1 \log t + a_2 (\log t)^2 + a_3 (\log t)^3 \quad \text{Equation 3}$$

The coefficients of equation 3 are empirical constants which best fit the data.

One problem with equation 3 is that it is infinite at time zero. Consequently, from time zero until the time of the first sample, this function does not indicate the aluminum concentration. This should not affect the calculated rates unless the first sample was taken near 15 g/l. In some of the faster runs (in particular, pure aluminum and alloy 1673), the first sample had between 14 and 16 g/l aluminum. Consequently, the calculated times and rates of these tests are questionable. For this

reason, a regression analysis of the results of the faster tests was made using equation 4.

$$Al^{+++} = a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 \quad \text{Equation 4}$$

The specific constants are completely devoid of chemical significance.

The dissolution rates reported in this document are given in units of grams of aluminum per liter-min. Where required, these rates may be converted to rates in grams of alloy per liter-min by dividing by the purity recorded in Table 2. To convert the rates in grams of alloy per liter-min to the commonly used units of grams per cm^2 -min, the former should be multiplied by 0.25 and divided by the area of the coupon at the particular solution concentration for which the rate is being calculated. Up to 30 grams of aluminum per liter the area of the coupons may be calculated by the expression:

$$A = A_0 - 0.22 [Al^{+++}]$$

where A_0 is the initial area, 21.4 cm^2 , $[Al^{+++}]$ is the aluminum concentration of the solution in g/l. These conversions were not made here for all of the data since it has been observed in the course of the present work and elsewhere⁽⁴⁾ that the rate of aluminum dissolution was frequently more closely correlated with the initial metal surface area than with the instantaneous surface area.

C. Discussion of Results

1. Effect of Dissolved Cations

The length of time for batch dissolution to a concentration of 40 grams of aluminum per liter was taken as one criterion of dissolution rate. Table 3 shows those ions in solution which significantly affected the dissolution time for pure aluminum. Iron was found to be mildly catalytic. Copper and nickel ions increased the dissolution time significantly and the fission product mixture and uranium increased the batch dissolution period to a lesser degree. The 2 per cent concentration level corresponded to 0.8 gram of the added ion per liter. As shown in the tabulation of the complete data in Appendix 3, the following ions had no significant effect at the given concentration level: 1 per cent copper, 0.1 per cent nickel, 1 and 2 per cent manganese, magnesium, and zinc.

For another criterion of dissolution rate, the instantaneous dissolution rates were calculated at 30 grams of aluminum per liter from the concentration vs time equations. The rates for solutions containing added copper and nickel were significantly less than those for pure aluminum. The catalytic effect of ferric ion and the anticatalytic effect of fission products and uranium were not significant in a test in this case. These results are summarized in Table 3, and the complete data and statistical analysis are given in Appendix 4.

Table 3

EFFECT OF IONS IN SOLUTION ON BATCH DISSOLUTION TIME AND INSTANTANEOUS
DISSOLUTION RATE FOR PURE ALUMINUM

		<u>Ion</u>	<u>Ion Concentration % of Al at 40 g Al/l</u>	<u>Batch Dissolution Time to 40 g Al/l as % of Time for Pure Al</u>	<u>Significance Level of Effect</u>	<u>Dissolution Rate at 30 g Al/l as % of Rate for Pure Al</u>	<u>Significance Level of Effect</u>
Catalyst:	Iron		2	86	0.05	114	> 0.05
			1	89	0.05	110	> 0.05
	Pure Aluminum		0	100	-	100	-
Anticatalysts:	Copper		2	168	0.01	67	0.01
	Nickel		2	160	0.01	77	0.02
			1	133	0.01	75	0.02
	Fission Products		2	122	0.01	85	> 0.05
	Uranium		8	116	0.02	89	> 0.05

2. Effect of Alloying Elements

The aluminum alloys of the Phase II tests were selected for their simplicity of composition and content of potential passivating or catalytic elements. These studies with alloys represented the first opportunity to study the effect of silicon, since it had not been possible to introduce this element as an ion in the Phase I experiments. The various alloys are described completely in Tables 1 and 2. In most cases, it was not possible to obtain alloys of accurately known composition with only one element of particular interest present in significant amounts. Therefore, most of the observations are confounded by the presence of more than one alloying agent believed to affect the dissolution rate. In spite of this, the passivating effects of silicon, nickel, and copper, and combinations of these are fairly well proved by the experimental results.

The batch dissolution times of the various alloys to 20, 30, and 40 grams of aluminum per liter are given in Table 4. The data are given in still greater detail in Appendix 5. A test for the results of alloys 1673 and 5456 compared to those for the unalloyed aluminum indicated that the batch dissolution times for these, as well as all of the others, were significantly different from the time for unalloyed aluminum. The instantaneous dissolution rates for aluminum in $\text{g-l}^{-1}\text{-min}^{-1}$ at aluminum concentrations of 15 and 30 grams per liter are also shown in Table 4. The complete data are given in Appendix 6. Those alloying elements which appeared to contribute to the rate effect are also shown in Table 4. A plot of the instantaneous dissolution rate at 15 grams of aluminum per liter vs the percentage of impurities in the alloys is shown in Figure 3. This presentation of the data indicates that passivation is not due simply to alloying, but rather that the identity of the alloying element is of major importance. Alloy 5456, in which magnesium is the principal alloying constituent, shows a significant, but relatively small decrease in dissolution rate compared to pure aluminum. Silicon, copper, and nickel in alloys of equivalent or greater purity, show greater reductions in dissolution rate. Qualitatively, silicon appears to be the most effective passivating element of those studied. The behavior of iron is more complex. A catalytic effect is observed with alloy 1673 which contains about 0.6 per cent iron. Alloy 1617, containing 2.14 per cent iron, is slightly passive.

The data of Table 4 and Figure 3 suggest the chemical state of the alloys at 90°C in the particular reagent used. Alloys 1673 and 5456 and unalloyed aluminum are clearly active. Alloy 1617 may be described as slightly passive. Alloys 774, 1033, 1091, 2618, and 8001 are clearly passive. Alloys 6061 and 1022 are probably passive under the test conditions, but the unusual behavior in test 1 with 6061 and test 2 with alloy 1022 suggests that these metals might be active under conditions very close to the conditions held in the experiments. Minor variations in the operating or composition variables might have allowed the alloys to become active for a portion of the dissolution cycle in the first case and for all of the cycle in the second case. Sporadic vigorous dissolution activity could be observed on some of the passive samples during the tests, suggesting that the sample might be readily activated

Table 4

BATCH DISSOLUTION TIMES AND INSTANTANEOUS DISSOLUTION
RATES FOR ALUMINUM ALLOYS

<u>Alloy</u>	Batch Dissolution Times (min) to Aluminum Concentration of			Instantaneous Dissolution Rates ($\text{g-l}^{-1} \text{ min}^{-1}$) at Aluminum Concentrations of		<u>Important Alloying Elements</u>
	<u>20 g/l</u>	<u>30 g/l</u>	<u>40 g/l</u>	<u>15 g/l</u>	<u>30 g/l</u>	
Unalloyed	4	8.6	17.2	4.5	1.4	-
1673	3.8	7.2	14.8	5.2	1.8	0.6% Fe
1617	12	36.8	> 85	1.2	0.25	2.1% Fe
1022	660	1030	>1000	0.031	0.022	1.5% Si
774	920	1460	>1400	0.023	0.017	2.9% Si
1033	430	700	> 900	0.044	0.032	3.5% Cu
1091	170	340	> 460	0.10	0.05	4.8% Cu-1.2% Si
2618	100	170	> 270	0.22	0.11	2.3% Cu-1.1% Ni
5456	5.8	13.5	> 35	3.2	0.67	5 % Mg
6061	330	500	-	0.052	0.03	0.6% Si
8001	1000	1600	>1800	0.021	0.015	1 % Ni

Fig. 3 Alloy Dissolving Rate as a Function of Alloy Composition

The activation of several of the passive alloys was attempted by contacting the alloy with high purity aluminum during the initial stage of the dissolution. Two methods were used for attaching the high purity aluminum to the alloy, one was to tie the two together with a piece of Nichrome wire and the second was to spot weld the two together. The results of these tests are given in Table 5. In the Table, the criterion for dissolution rate is the time required for the dissolver solution to reach 30 grams of aluminum per liter. It may be observed that activation by this technique was successful in those cases where silicon was the apparent passivating component. It was not successful for the two alloys in which the copper was the passivating element.

Several of the passive alloys were tested in experiments in which the mercuric nitrate catalyst concentration was increased from 0.005M to 0.05M. Other conditions remained the same. The batch time to 30 grams of aluminum per liter for unalloyed aluminum was not increased by the increase in catalyst concentration. Under these conditions, the alloys passivated by nickel and silicon dissolved with rates characteristic of active alloys. The alloys containing 3.5 and 4.8 per cent copper remained passive. Even these could be activated temporarily at the higher catalyst concentration by raising the temperature to 98°C, but the effect was not reproducible.

in the environment, but that vigorous reaction could not be sustained.

3. Activation of Passive Alloys

Since the experiments of Section III-C suggested that certain of the aluminum alloys were only borderline passive in the test environment, a few measurements were made to illustrate the possibility of activation of these metals by either the use of additional mercury catalyst or intimate contact with pure aluminum. A study of the effects of variation in the dissolution conditions was not an objective of this work and, therefore, the results reported below are very limited. The observation that certain passive alloys can be activated by contact with pure aluminum is probably of process interest.

Table 5

ALLOY DISSOLUTION IN CONTACT WITH HIGH PURITY ALUMINUM
OR WITH INCREASED CATALYST CONCENTRATION

<u>Alloy</u>	<u>Standard^(a) Test</u>	<u>Attached to High^(c) Purity Aluminum</u>	<u>Higher Catalyst^(b) Level</u>	<u>Important Alloying Elements</u>
(Batch Dissolution Times [Minutes] to 30 g Aluminum Per Liter)				
Unalloyed	8.6	-	10	-
1022	1030	47 (Al spot)	-	1.5% Si
774	1460	80 (Al piece)	15	2.9% Si
1033	700	passive (Al spot)	passive	3.5% Cu
1091	340	passive (Al piece and spot)	passive	4.8% Cu-1.2% Si
6061	500	48 (Al piece)	-	0.6% Si
8001	1600	-	14.5	1 % Ni

(a) Standard Conditions - 6.6M HNO_3 , 0.005 M mercuric nitrate, 90°C.

(b) Higher Catalyst - 0.05M mercuric nitrate, other conditions the same.

(c) "Al piece" indicates that the high purity aluminum was tied to the alloy with Nichrome wire.

"Al spot" indicates spot welding of a small piece of high purity aluminum to the alloy.

IV. PROCESS IMPLICATIONS AND CONCLUSIONS

The direct conclusions of the experimental work reported here are:

1. Iron, either as an ion in solution or as the element in the aluminum alloy, can exert a slight catalytic effect in the mercury catalyzed dissolution of aluminum in nitric acid.
2. Silicon, copper, and nickel, the last two as ions in solution and all three as elements in an alloy, can exert a passivating effect on the same reaction.
3. A quantitative or semiquantitative measure of the degree of this effect and the specific conditions can be obtained from the detailed data presented here.
4. Where passivation is experienced, it may sometimes be overcome by increased reaction temperature, higher catalyst concentration, or activation of the passive alloy by physical contact with pure aluminum.
5. Of the elements which passivate the aluminum, silicon appears to have the greatest effect per unit weight in the alloy, and its passivating effect was most readily overcome by increasing the catalyst concentration.

In a chemical processing plant, it may be possible to improve the accuracy of predicting the dissolution rate of aluminum alloy fuels, and therefore the processing time, from a knowledge of the fuel composition and the effect of composition on the dissolution rate. As has been noted earlier, the composition of the alloy is only one of several factors affecting the dissolution rate. However, these data indicate that very important effects are possible due to this factor alone. Variation in concentration of mercuric nitrate catalyst has been used successfully to control the dissolution in continuous dissolvers for some time and very high concentrations of catalyst have been used in attempts to speed the batch dissolution of very passive fuels in process. The use of catalyst concentrations up to 0.05M for this purpose is not new; but the possibility of attaching high purity or other active aluminum metal to the refractory fuel elements prior to charging to the dissolver or of charging such active aluminum into the fuel bed in a continuous dissolver to overcome passivation, is an interesting possibility, which is parallel to the use of mild steel wool to activate stainless steel fuel elements during dissolution in sulfuric acid. The latter is common practice at the Idaho Chemical Processing Plant. It seems very likely that the charging of scraps of high purity aluminum might be less expensive than the use of additional mercuric nitrate catalyst for securing activation of passive aluminum alloys.

With regard to the design of test reactor fuel elements, it may be inferred from the data presented here that care in the selection of the aluminum used, to avoid those compositions which are obviously difficult to dissolve, could result in a reduction in the overall fuel cycle cost.

V. SUGGESTIONS FOR FURTHER WORK

The results reported here do not suggest any experimental or interpretative difficulty which would reduce the value of continuing this study, as planned, with dissolution rate measurements made on alloys of varying metallurgical and irradiation history. The problem of defining a standard "metallurgical state" for the alloys and of securing reproducible variations from the standard is a difficult one but probably not insurmountable. The gross effects of neutron irradiation are of immediate process interest, while the separate effects of metallurgical changes, accumulation of activation products, and accumulation of fission products would be of long term interest.

The possibility does exist that specific rate effect values could be assigned to each alloying element with the hope of quantitative application of these to untested alloys. The data collected to date are not extensive enough, and the effects of interactions are probably too great to allow this. If additional information is secured, this may be profitable.

Electrochemical measurements might have been used to supplement or replace the rate measurements made here. For successful dissolution, the alloy cannot be passive as defined by these rate measurements or as defined by polarization measurements. Certainly, the study of the passive alloys could have been accelerated greatly by the use of polarization measurement. This approach also offers the possibility of nondestructive evaluation of the dissolution properties of unknown or possibly even irradiated alloys.

In most cases, the dissolution reaction appeared to be first order with respect to nitric acid. However, when a reaction was stopped for a period of several hours, as the experiments with the very passive alloys were, the first order rate constant was invariably different before and after the interruption. Also, there were periods when no simple kinetic expression could be applied. It was hoped that the experimentally observed induction periods might be correlated with the induction periods derived from the mathematical expressions for the dissolution and both of these associated with some property of the alloy. No general correlation of this type appeared to be possible. The interpretation of these experimental results could have been greatly simplified if a reliable kinetic expression for the reaction had been available. Neither the first order expression, nor the parabolic rate law used by Murray⁽⁴⁾ described the data as well as the empirical equations actually used. More fundamental studies of the mercury-catalyzed reaction of aluminum in nitric acid are required before rate measurements can be closely associated with dissolution mechanism or kinetic theory.

VI. LITERATURE CITED

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VII. ACKNOWLEDGEMENT

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Appendix 1

TYPICAL DISSOLUTION DATA SHEET - PHASE I EXPERIMENT

Al Sample Weight 9.9455 Gms.		Run No. Al-Zn-1	
Alloying Impurity Added to Solution- <u>Zn</u> <u>2</u> Per Cent			
Observed Time to t_o - 4 Sec.			
<u>Sample</u>	<u>Time (min)</u>	<u>Temp.</u>	<u>Al</u>
Al-Zn-1-1	2	91.5	12.3 $\pm$.5
Al-Zn-1-2	4	91.5	18.8 $\pm$.5
Al-Zn-1-3	6	91	23.6 $\pm$.9
Al-Zn-1-4	8	89.5	27.4 $\pm$.9
Al-Zn-1-5	10	88	30.1 $\pm$.9
Al-Zn-1-6	12	89	34.0 $\pm$.9
Al-Zn-1-7	14	89	39.0 $\pm$ 1.2
Al-Zn-1-8	16	89	40.0 $\pm$ 1.2
Al-Zn-1-9	18	89.5	41.7 $\pm$ 1.2
Al-Zn-1-10	20	88.5	42.1 $\pm$ 1.2
Al-Zn-1-11	22	89.5	42.1 $\pm$ 1.2
Al-Zn-1-12	24	89	42.0 $\pm$ 1.2

Appendix 2
TYPICAL DISSOLUTION DATA SHEET - PHASE II EXPERIMENT

Al Sample Weight-9.5481 Gms. Run No. Al 5456-2
Alloying Impurity 6.4918 Per Cent
Observed Time to t_0 - 5 Sec.

<u>Sample</u>	<u>Time (min)</u>	<u>Temp. °C</u>	<u>Al g/l</u>	<u>H⁺ (M)</u>
Al-5456-2-1	2	87.5	12.9	5.00
Al-5456-2-2	4	88.5	17.7	4.34
Al-5456-2-3	6	89.0	20.3	3.88
Al-5456-2-4	8	88.5	23.4	3.46
Al-5456-2-5	10	88.5	26.2	3.10
Al-5456-2-6	12	88.0	28.1	2.78
Al-5456-2-7	14	90.0	30.2	2.54
Al-5456-2-8	16	89.0	32.3	2.27
Al-5456-2-9	18	87.5	33.7	2.07
Al-5456-2-10	21	87.5	35.4	1.82
Al-5456-2-11	24	88.0	36.4	1.65
Al-5456-2-12	27	87.5	37.8	1.50
Al-5456-2-13	31	89.0	38.9	1.40
Al-5456-2-14	34	87.0	39.1	1.33
Al-5456-2-15	38	89.0	38.7	1.33

ALLOY COMPOSITION

Cu	.060
Fe	.16
Si	.14
Mn	.82
Mg	5.12
Zn	.055
Ni	.011
Al	Remainder

Appendix 3

BATCH DISSOLUTION TIMES AND ANALYSIS FOR PHASE I STUDIES

Test	Composition	Time to 40 g/l Min.	Average	Variance in Average	σ^*	Δ Minutes	t^{**}	Significance Level ***		
								0.05 (2.78)	0.02 (3.75)	0.01 (4.60)
Al 1	99.999% Al	18	17.2	1.8						
2	99.999% Al	17½								
3	99.999% Al	16								
5	99.999% Al	17½								
Cu 1	2%	31	28.8	9.7	1.7	+ 11.6	7.8			S
2	2%	26½								
Fe 1	2%	14	14.8	1.3	0.88	- 2.4	3.1	S	N	
2	2%	15½								
Mg 1	2%	16	16.8	1.3	0.88	- 0.4	0.52	N		
2	2%	17½								
Zn 1	2%	16	16.5	0.5	0.76	- 0.7	1.1	N		
2	2%	17								
Ni 1	2%	28	27.5	0.5	0.76	+ 10.3	16			S
2	2%	27								
Mn 1	2%	17	17.5	0.5	0.76	10.3	0.45	N		
2	2%	18								
Cu 3	1%	18	17.5	0.5	0.76	+ 0.3	0.45	N		
4	1%	17								
Ni 3	1%	23	22.8	0	0.67	+ 5.6	9.6			S
4	1%	22½								
Fe 3	1%	15½	15.3	0	0.67	- 1.9	3.3	S	N	
4	1%	15								
Mg 3	1%	16½	16.5	0	0.67	- 0.7	1.2	N		
4	1%	16½								
Zn 3	1%	15	16	0.5	0.76	- 1.2	1.8	N		
4	1%	17								
Mn 3	1%	18½	19	0.5	0.76	+ 1.8	2.7	N		
4	1%	19½								
Ni 5	0.1%	18	18	0	0.67	+ 0.8	1.4	N		
6	0.1%	18								
U - 1	8%	20½	20	0.5	0.76	+ 2.8	4.2		S	N
U - 2	8%	19½								
FP-2	2%	22	21	0.5	0.76	+ 3.8	5.7			S
FP-3	2%	20								

* Standard deviation for comparison to pure Al

$$^{**} t = \frac{\Delta}{\sigma} \sqrt{\frac{4x2}{4+2}}$$

*** Significance level in t test with 4 degrees of freedom.

S = Significant

N = Not Significant

Appendix 4

INSTANTANEOUS DISSOLUTION RATES AT 30 GRAMS ALUMINUM PER LITER FOR
PHASE I STUDIES

Test	Composition	Dissolution Rate $\text{g-l}^{-1}\text{-min}^{-1}$	Average Rate $\text{g-l}^{-1}\text{-min}^{-1}$	Variance in Average	σ	Δ $\text{g-l}^{-1}\text{-min}^{-1}$	t	0.05 (2.78)	0.02 (3.75)	0.01 (4.60)
Al 1	99.999% Al	1.35	1.45	0.041						
2	99.999% Al	1.42								
3	99.999% Al	1.62								
5	99.999% Al	1.42								
Cu 1	2%	0.92	0.97	0.005	0.11	- 0.48	5.0			S
2	2%	1.02								
3	1%	1.43	1.50	0.008	0.11	+ 0.05	0.5	N		
4	1%	1.56								
Fe 1	2%	1.68	1.66	0.001	0.10	+ 0.21	2.4	N		
2	2%	1.64								
Fe 3	1%	1.54	1.60	0.004	0.11	+ 0.15	1.6	N		
4	1%	1.65								
Ni 1	2%	1.09	1.11	0.001	0.10	- 0.34	3.9		S	N
2	2%	1.13								
Ni 3	1%	1.09	1.09	< 0.001	0.10	- 0.36	4.1		S	N
4	1%	1.08								
Ni 5	0.1%	1.47	1.45	0.001	0.10	0	0	N		
6	0.1%	1.43								
Mg 1	2%	1.62	1.52	0.02	0.12	+ 0.07	0.7	N		
2	2%	1.42								
Mg 3	1%	1.53	-	-		+ 0.08		N		
Mn 1	2%	1.44	1.41	0.002	0.10	- 0.04	0.05	N		
2	2%	1.38								
Mn 3	1%	1.35	1.35	< 0.001	0.10	- 0.10	1.1	N		
4	1%	1.34								
Zn 1	2%	1.65	1.58	0.010	0.11	+ 0.13	1.4	N		
2	2%	1.51								
Zn 3	1%	1.64	1.53	0.024	0.13	+ 0.08	0.7	N		
4	1%	1.42								
U 1	8%	1.32	1.29	0.002	0.10	- 0.16	1.8	N		
2	8%	1.26								
FP 2	2%	1.21	1.23	0.001	0.10	- 0.22	2.5	N		
3	2%	1.25								

Appendix 5

BATCH DISSOLUTION TIMES FOR ALUMINUM ALLOYS-PHASE II STUDIES
(Minutes)

To Aluminum Concentrations of							
Alloy	Test Number	20 g/l		30 g/l		40 g/l	
		Average		Average		Average	
Unalloyed	A1 1	4	4	9	8.6	18	17.2
	2	4		9		17½	
	3	4		8½		16	
	5	4		8		17½	
1673	1	3	3.2	6½	7.2	14½	14.8
	2	3½		8		15	
1617	1	12½	12	36	36.8	> 85	> 85
	2	11½		37½		> 85	
1022	1	588	660	935	1030	1010	> 1000
	2	5		8		14½	
	3	730		1130		> 1650	
774	1	840	920	1280	1460	> 1425	> 1400
	2	1000		1650		> 1890	
1033	1	446	430	683	700	> 910	> 900
	2	421		715		> 900	
1091	1	174	170	> 235	340	-	> 460
	2	170		338		> 460	
2618	1	96	100	166	170	> 270	> 270
	2	111		173		> 270	
5456	1	5½	5.8	13	13.5	35	> 35
	2	6		14		> 38	
6061	1	277	330	294	500	324	-
	2	360		> 460		-	
	3	350		660		-	
8001	1	933	1000	> 1320	1600	-	> 1800
	2	1070		1598		> 1890	

STATISTICAL ANALYSIS OF DATA FROM APPENDIX 5

	<u>Sample</u>	<u>Time</u>	<u>Average Time</u>	<u>Variance in Average</u>	<u>σ</u>	<u>Δ</u>	<u>t</u>	<u>0.05</u>	<u>0.01</u>
20 g/l	A1 1	4	4	0				(2.78)	(4.60)
	2	4							
	3	4							
	5	4							
	1673 1	3	3.25	0.12	0.17	0.75	5.9		S
	2	3.5							
	5456 1	5.5	5.75	0.12	0.17	1.75	13.7		S
	2	6							
30 g/l	A1 1	9	8.62	0.69					
	2	9							
	3	8.5							
	5	8							
	1673 1	6.5	7.25	1.1	0.67	1.37	2.72	N	
	2	8							
	5456 1	13	13.5	0.50	0.55	4.88	11.8		S
	2	14							
40 g/l	A1 1	18	17.2	1.8					
	2	17.5							
	3	16							
	5	17.5							
	1673 1	14.5	14.75	0.12	0.69	2.45	4.7		S
	2	15							

Appendix 6

RATE CALCULATIONS FOR ALUMINUM ALLOYS

Table I

$$A_1 = a_0 + a_1 (\log t) + a_2 (\log t)^2 + a_3 (\log t)^3$$

Test	a_0	a_1	a_2	a_3	s^2
A1-1	7.64	15.22	10.91	-2.02	0.111
A1-2	5.82	28.80	-14.04	10.56	0.041
A1-3	8.28	19.03	-1.90	6.75	0.135
A1-4	7.0	15.69	7.90	-0.88	0.170
A1-5	4.11	35.18	-16.62	9.34	0.420
2618-1	296.28	480.09	251.28	-40.04	0.0564
2618-2	146.40	-244.82	129.57	-19.39	0.0441
1617-1	7.99	-4.17	19.47	-4.95	0.0827
1617-2	6.52	4.39	10.20	-2.10	0.0914
774-1	39.74	-10.58	-14.55	5.48	1.0493
774-2	28.24	-2.98	-13.84	4.65	0.0321
6061-1	-13.00	28.64	-21.88	6.18	0.0486
6061-2	-0.25	10.85	-14.0682	5.06	0.0173
6061-3	27.82	-32.13	7.68	1.41	0.0756
1091-1	9.66	-22.43	12.69	-0.26	0.108
1091-2	2.45	-7.07	3.62	1.38	0.0669
1673-1	10.14	12.82	20.08	-7.47	0.132
1673-2	15.02	-16.29	55.49	-20.32	1.181
1033-1	17.70	4.85	-18.20	6.34	0.127
1033-2	-0.93	13.07	-14.89	4.92	0.086
5456-1	15.22	-16.74	41.84	-13.22	0.289
5456-2	15.06	-18.06	42.86	-13.45	0.217
1022-1	35.41	-7.80	-15.57	5.92	0.0865
1022-2	2.58	-12.33	80.09	-36.17	0.00017
1022-3	-12.55	29.86	-21.92	5.49	0.0532
8001-1	-46.11	79.66	-45.36	8.75	0.122
8001-2	-54.82	89.51	-48.69	9.05	0.0845

Appendix 6

RATE CALCULATIONS FOR ALUMINUM ALLOYS (Continued)

Table II

$$Al = a_0 + a_1 (\log t) + a_2 (\log t)^2 + a_3 (\log t)^3$$

Al = 15 g/l			Al = 30 g/l	
<u>Test</u>	<u>Time</u>	<u>Rate</u>	<u>Time</u>	<u>Rate</u>
A1-1	2.4	4.1	8.8	1.5
A1-2	2.3	4.3	9.2	1.5
A1-3	2.2	3.9	8.7	1.7
A1-4	2.7	3.6	10	1.2
A1-5	2.3	5.1	8.5	1.5
2618-1	73	0.23	160	0.12
2618-2	75	0.21	170	0.11
1617-1	6.7	1.2	36	0.25
1617-2	5.9	1.2	35	0.26
774-1	580	0.026	1200	0.020
774-2	700	0.019	1600	0.014
6061-1	250	0.053		
6061-2	260	0.053		
6061-3	260	0.049	660	0.029
1091-1	110	0.10		
1091-2	110	0.098	340	0.049
1673-1	1.9	5.1	6.6	2.0
1673-2	2.2	2.8	7.7	1.9
1033-1	310	0.045	690	0.034
1033-2	300	0.043	730	0.029
5456-1	2.8	2.0	13	0.93
5456-2	3.1	2.0	14	0.86
1022-1	430	0.034	930	0.026
1022-2	3.7	5.1	8.0	2.4
1022-3	460	0.028	1100	0.019
8001-1	700	0.021		
8001-1	728	0.020	1600	0.015

Appendix 6

RATE CALCULATIONS FOR ALUMINUM ALLOYS (Continued)

Table III

$$Al = a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$$

<u>Test</u>	<u>a₁</u>	<u>a₂</u>	<u>a₃</u>	<u>a₄</u>	<u>s²</u>
A1-1	7.86999	-0.87448	0.051654	-0.001143	0.2692
A1-2	8.42382	-1.07641	0.071681	-0.001748	0.1668
A1-3	8.65805	-1.13836	0.079810	-0.002060	0.1559
A1-4	7.08747	-0.71573	0.037634	-0.000738	0.4991
A1-5	8.27530	-0.93634	0.054337	-0.001166	0.3354
1673-1	10.16365	-1.43452	0.108136	-0.003076	0.0576
1673-2	9.28544	-1.36543	0.111607	-0.0003396	1.4947
5456-1	5.66344	-0.41236	0.014378	-0.000181	2.4681
5456-2	5.37935	-0.38052	0.013094	-0.000164	2.0840

Table IV

$$Al = a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$$

<u>Al = 15 g/l</u>			<u>Al = 30 g/l</u>	
<u>Test</u>	<u>Time</u>	<u>Rate</u>	<u>Time</u>	<u>Rate</u>
A1-1	2.5	4.4	8.9	1.4
A1-2	2.4	4.4	9.4	1.4
A1-3	2.3	4.5	8.8	1.5
A1-4	2.8	3.9	10	1.1
A1-5	2.4	4.7	8.5	1.3
1673-1	1.9	5.7	6.7	1.8
1673-2	2.2	4.7	7.9	1.9
5456-1	3.4	3.3	12	0.68
5456-2	3.6	3.1	13	0.65