AECU-3160

Subject Category: CHEMISTRY

UNITED STATES ATOMIC ENERGY COMMISSION

STUDY OF THE FEASIBILITY OF AQUEOUS RECOVERY OF SPENT FUELS. PART I. DISSOLUTION EXPERIMENTS ON ALLOY SAMPLES

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June 1954

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Technical Information Extension, Oak Ridge, Tennessee

Other issues of this report may bear the number ERI-2240-1-F.

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Printed in USA, Price 25 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

AEC, Oak Ridge, Tenn.

ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
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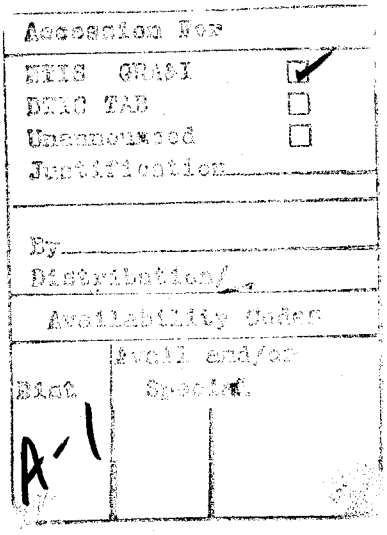
PART I. DISSOLUTION EXPERIMENTS ON ALLOY SAMPLES



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Work done for Dow Chemical-Detroit Edison and Associates, Atomic-Power Development Project at request of Consumers Power Company (Jackson County).

Project 2240

CONSUMERS POWER COMPANY (JACKSON COUNTY)
FOR THE DOW CHEMICAL—DETROIT EDISON AND ASSOCIATES
ATOMIC-POWER DEVELOPMENT PROJECT

June, 1954

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DISSOLUTION EXPERIMENTS ON ALLOY SAMPLES

OBJECTIVES

The investigation to be described was undertaken at the request of Professor Harold A. Ohlgren as part of Engineering Research Institute Project 2240. The specific purposes of the investigation were to evaluate the following aspects of the dissolution of two-component alloy samples:

(1) Effect of nitric acid concentration on the rate of dissolution of alloy samples.

(2) Effect of hydrofluoric acid as a catalyst on the nitric acid dissolution process.

(3) Dissolution kinetics at optimum nitric acid concentrations.

(4) Effect of dissolved iron on the dissolution kinetics.

(5) Extent of the acid-insoluble material produced in the dissolution experiments.

SUMMARY OF RESULTS

The following statements are an attempt to answer in specific fashion the questions raised in the previous section. It will be apparent from the more detailed subsequent discussion of the work that the generalizations given must be evaluated cautiously when extrapolating to sample sizes and experimental conditions other than those actually used.

(1) and (2): Nitric acid solutions, originally 4.5 or 6.0 M, which are also 0.05 M in hydrofluoric acid, will dissolve the two-component alloy to

an effective concentration of 100 grams of major component per liter within a reasonable period of time.

(3) and (4): The rates of dissolution at various stages in the alloy dissolution process have been measured. These rates seem not to be affected by the presence of dissolved ferric iron if the effective nitric acid concentration is kept constant.

(5): The amount of nitric acid-insoluble material in the alloy seems to be remarkably constant in the range of $4 \pm 1\%$.

EXPERIMENTAL PROCEDURES

Alloy Samples

The samples used for the dissolution tests were pie-shaped pieces, formed by cutting into eighths the 3-mm-thick discs obtained from a massive sample. These wedge-shaped pieces were furnished by Dr. J. Lewis; they varied in weight from 8 to 12 grams each. For the kinetic runs, pieces weighing approximately 2, 4, 6, 8, and 10 grams each were prepared by Dr. Lewis and by the authors as needed.

Chemicals

The acids used (nitric acid, sulfuric acid, and hydrofluoric acid) were of C.P. or reagent-grade quality. Suitable dilutions were made using the label composition data in the case of the nitric and sulfuric acids and the results of titration in the case of the hydrofluoric acid. The concentrations of the 3 M and 4.5 M stock nitric acid solutions were checked by titration with standard sodium hydroxide solution; the values found were 3.12 and 4.77 M, respectively.

The uranyl nitrate used was Mallinckrodt analytical reagent-grade uranyl nitrate hexahydrate. The ferric nitrate was Baker and Adamson A.C.S. reagent-grade ferric nitrate nonahydrate.

Apparatus

All dissolution experiments were carried out in pyrex 250-ml round-bottomed flasks connected to water-cooled condensers by glass-to-glass standard-taper joints. The flasks were heated by Meker burners. Ignition

of the filter papers containing the residual sludges was carried out in porcelain crucibles, using standard analytical techniques.

Procedures

In the preliminary dissolution tests the samples were cleaned by rinsing with acetone, weighed to the nearest hundredth of a gram, and transferred to the flasks. The calculated quantity of nitric acid or sulfuric acid was then added and observations were made of the behavior of the sample in contact with the acid at room temperature. Then the temperature was increased slowly and any changes in color of the solution or appearance of precipitate were noted. The solutions were all refluxed at a rate of about one drop every two seconds. After a predetermined period of time such as 0.5 hour, 1 hour, or complete disintegration, the heating was discontinued and the flasks were disconnected from the condensers and cooled under running water. The remaining sample, if any, was washed free of solution, rinsed with acetone, dried, and weighed. In cases where the sample was completely disintegrated, the residue was filtered off on paper, ignited, and weighed.

In the kinetic experiments, a set of five cleaned samples (approximately 2, 4, 6, 8, and 10 grams) was weighed. The test solutions were then prepared by mixing the appropriate amounts of nitrate salts, nitric acid, hydrofluoric acid, and water. The calculations on the basis of which these solutions were prepared are given in Tables I and II; these calculations are an attempt to depict the composition of a solution at various stages in the dissolution process as discussed in the next section. The samples were added to the appropriate solutions, which were then refluxed for 4 hours or some other selected period at the rate of one drop of returning condensate per two seconds. After completion of the heating period, the undisintegrated sample was separated from the solution, dried, and weighed. The disintegrated residue, composed of finely divided silver-gray particles, was filtered off, washed with water, and ignited. The product of this ignition had a bluish irridescent color; the solution was orange. The ignited residue was weighed and the percentage calculated.

Basis of Calculations in Tables I and II

The figures given in Tables I and II are based on the following assumptions, the validity of which is considered to be adequate for the purpose of the present exploratory study:

(1) The prime salt factor to be considered during the dissolution process is the uranyl nitrate formed; the amount of chromic nitrate formed is assumed to be negligible or of little

TABLE I

CALCULATED INITIAL SOLUTION COMPOSITIONS FOR ALLOY DISSOLUTION IN 4.5 M NITRIC ACID

Solution No.	Composition on Liter Basis				Working Composition on 100-ml Basis*					
	Alloy, g,	U salt, g,	HNO_3, M,	HF, M	Alloy, g, desired	Alloy, g, taken	U salt, g, taken	HNO_3, millimoles, taken	HF, millimoles, taken	H_2O, ml,** taken to make volume of 100 ml
1	105.3	0	4.50	0.05	10	W_1	0	4500 K_1	50 K_1	1000 K_1
2	84.2	42	4.16	0.05	8	W_2	42 K_2	4160 K_2	50 K_2	1000 K_2
3	63.2	84	3.82	0.05	6	W_3	84 K_3	3820 K_3	50 K_3	1000 K_3
4	42.1	127	3.48	0.05	4	W_4	127 K_4	3480 K_4	50 K_4	1000 K_4
5	21.1	169	3.14	0.05	2	W_5	169 K_5	3140 K_5	50 K_5	1000 K_5
6	0	0	2.80	0.05	0					

*Conversion factor, $K_i = W_i$/alloy weight per liter.

**The densities of the uranyl and ferric salts used were taken as 2.81 and 1.68 g/cc, respectively.

TABLE II

CALCULATED INITIAL SOLUTION COMPOSITIONS FOR ALLOY DISSOLUTION IN 4.5 M NITRIC ACID IN PRESENCE OF IRON

Solution No.	Composition on Liter Basis*		Composition on 100-ml Basis*	
	Fe salt, g	HNO_3, M	Fe salt, g, taken	HNO_3, millimoles, taken
1	178	2.74	178 K_1	2740 K_1
2	178	2.40	178 K_2	2400 K_2
3	178	2.06	178 K_3	2060 K_3
4	178	1.72	178 K_4	1720 K_4
5	178	1.38	178 K_5	1380 K_5
6	178	1.04		

*Alloy, U salt, and HF figures are the same as in Table I.

effect. Accordingly, only uranyl nitrate was added to account for the amount formed by the dissolved alloy.

(2) If iron were present, it was assumed that its rate of dissolution would be very much greater than that of the alloy and that consequently all the iron would be dissolved before any sizable fraction of the alloy had dissolved. On this basis, ferric nitrate equivalent to an assumed iron content was added at the start of each test.

(3) The major assumption, i.e., the one in which gross error is most likely, is that made to account for the amount of nitric acid that would be consumed in forming the uranyl and ferric nitrates. The half-cell reactions for nitric acid are usually assumed to be (a) or (b) or a combination of the two processes:

(a) In low, i.e., less than 6 M, acid concentrations

$$NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O \quad .$$

(b) In high acid concentrations

$$NO_3^- + 2H^+ + e \longrightarrow 0.5\ N_2O_4 + H_2O \quad .$$

There is an enormous difference in the amount of acid required to dissolve a given weight of metal by these two processes: reaction (b) would consume three times as much nitric acid as reaction (a). Since this work was carried out in nitric acid concentrations between 3 and 6 M, reaction (a) was assumed for the calculations. Observations were made, especially in the tests involving 6 M nitric acid, to see whether the colorless NO or the dark-brown N_2O_4* was the primary product; such observations must be interpreted with care, however, since a small amount of N_2O_4 would color a large amount of NO and since NO is immediately converted to N_2O_4 on contact with oxygen of the air.

The equations for the reactions in the dissolution of uranium and iron are then assumed to be as follows:

$$(c) \quad U + 4HNO_3 \longrightarrow UO_2(NO_3)_2 + 2NO + 2H_2O$$

and

*N_2O_4 itself is colorless, but its monomer or decomposition product, NO_2, is reddish brown. At 100°C, N_2O_4 is 90% dissociated into NO_2.

(d) $Fe + 4HNO_3 \longrightarrow Fe(NO_3)_3 + NO + 2H_2O$.

If chromium dissolves, the reaction would probably be

(e) $Cr + 4HNO_3 \longrightarrow Cr(NO_3)_3 + NO + 2H_2O$.

On the basis of equations (a), (c), (d), and (e), 100 grams of uranium dissolved per liter would lower the molarity of the nitric acid content by 1.68, 24.6 grams of iron dissolved per liter would lower the nitric acid molarity by 1.76, and 5.1 grams of chromium per liter would lower the nitric acid molarity by 0.40. It is apparent that dissolution of such amounts of uranium and of iron would lower the molarities of nitric acid solutions from 4.50 to 1.06 or from 6.00 to 2.56. Moreover, if reaction (b) occurred to any appreciable extent the residual nitric acid concentration would be even lower.

Tables for the 6 M nitric acid experiments would be similar to Tables I and II except for the nitric acid figures. The selection of the nitric acid concentrations used was determined from the preliminary dissolution experiments subsequently described.

PRELIMINARY EXPERIMENTS ON DISSOLUTION

Variation of Extent of Dissolution

The first experiments were designed to examine the effects of nitric acid and hydrofluoric acid concentrations. The samples, data for which appear in Table III, were refluxed for 0.5 or 1 hour. Although none of the samples disintegrated completely, every one reacted to some extent with the nitric acid. Refluxing for a period of 10 minutes caused all the solutions to turn green; some, of course, required less time. After the predetermined reflux time had elapsed, the flasks were disconnected from the condensers and cooled under running water. The remaining alloy sample was washed free of solution and loose particles, dried after rinsing, and weighed. The percent loss in weight was then calculated.

Sulfuric acid solutions were also examined, but the results were very poor. The two samples treated with sulfuric acid did not disintegrate completely in 24 hours of refluxing. There is, however, a possibility that they would react faster if tested in the presence of hydrofluoric acid. Their behavior under this condition has not yet been investigated.

TABLE III

VARIATION OF ALLOY DISSOLUTION WITH

ACID CONCENTRATION, CATALYST, AND TIME

Experiment No.	Weight of Sample, g	HNO_3 Concentration, M	HF Concentration, M	Time of Experiment, hours	Weight of Solid Residue, g	Loss in Weight, %
1	9.51	3.1		0.5	9.20	3.38
2	8.33	3.1	0.003	0.5	8.06	3.35
3	9.02	6.0		0.5	8.20	9.20
4	9.20	6.0		1.0	6.82	25.9
5	11.57	6.0		1.0	8.06	33.2
6	10.78	6.0	0.002	1.0	8.23	23.7
9	9.17	3.1	0.05	1.0	7.27	20.7
11	7.95	3.1		1.0	7.27	8.55
15	11.67	(1.73)*		24.2	10.10	13.5
16	11.55	(3.45)*		24.2	9.53	17.6

*H_2SO_4 concentration, M.

The solution obtained from the samples treated with sulfuric acid was dark green. The residue was dark brown, almost black, and the remaining undisintegrated sample was black.

Time Required for Complete Disintegration and Completion of Dissolution

The samples, data for which appear in Table IV, were treated with nitric acid or a mixture of nitric and hydrofluoric acids and were refluxed to complete disintegration.

The difference between complete disintegration and complete dissolution should be noted. The sample is considered completely disintegrated but not completely dissolved when there is a residue of finely divided silver-gray particles present. Complete dissolution, i.e., no solid residue of any kind present, was never obtained.

The solution in all cases was yellow after separation from the residue. The residue was silver-gray; after ignition, however, it assumed a bluish irridescent color. The latter color may be due to surface oxidation, producing very thin layers of chromic oxide.

The residue was weighed and its percentage calculated for all the samples. It is highly significant that the data for the percentage of material insoluble in nitric acid approximate the expected content of material nonreactive with nitric acid. It was planned to check the residues by emission spectroscopy for their content of major alloy constituent which may be present due to entrainment, but the time factor prevented this study. Similarly, it would have been desirable to check the amount of minor constituent present in the solutions obtained.

The data in Tables III and IV indicate that hydrofluoric acid, present in 0.05 M concentration, seems to be an effective catalyst.

The data in Table IV indicate that 4.5 and 6.0 M nitric acid solutions containing a low concentration of hydrofluoric acid are capable of dissolving the reactive constituent of the alloy within a reasonable period of time. Accordingly, it was decided to investigate the relative rates of dissolution at various stages of dissolution in these two concentrations of acid. It is again pertinent to recall, as previously indicated, that the presence of iron of a postulated amount would probably decrease the effective acid concentration to react with the alloy from 4.5 and 6.0 M to 2.7 and 4.2 M, respectively.

TABLE IV

TIME REQUIRED FOR COMPLETE DISINTEGRATION

AND COMPLETION OF DISSOLUTION OF ALLOY

Experiment No.	Weight of Sample, g	HNO_3 Concentration, M	HF Concentration, M	Time for Complete Disintegration, hours	Insoluble Residue	
					g	%
12	8.13	3.1		16	0.55	6.8
8	8.84	6.0		6.5	0.59	6.6
10	9.77	3.1	0.05	19.3	0.46	4.7
13	9.20	4.5	0.05	6.8	0.49	5.2
14	9.16	6.0	0.05	4.5	0.52	5.6

KINETIC EXPERIMENTS ON DISSOLUTION

As previously discussed and as outlined in Tables I and II, a series of experiments was run to determine the relative rates of disintegration and dissolution of the alloy in media originally 4.5 or 6.0 M in nitric acid at various stages in the dissolution process. Interpretation of the results obtained must be made with a great deal of care, since the studies to be described involve all the uncertainties inherent in determining the rate of dissolution of a more or less irregularly shaped solid of varying surface area in a medium of varying composition. Assumptions peculiar to the specific problem concerned have been detailed in the subsection on the Basis of Calculations in Tables I and II. In spite of these difficulties in interpretation, it is believed that the results described below may serve as a cautious guide to the tentative evaluation of certain factors involved in the dissolution of the two-component alloy under consideration.

Duplicate sets of runs in originally 4.5 M nitric acid solutions were made by two different investigators; the data for these tests are summarized in Tables V and VI. Runs in (a) originally 4.5 M nitric acid containing dissolved iron, (b) originally 6.0 M nitric acid, and (c) originally 6 M nitric acid containing dissolved iron are detailed in Tables VII, VIII and X, and IX respectively. The 4.5 M acid solutions were heated for 4 hours, and the 6.0 M solutions for either 4 or 2.5 hours; the shorter time was used in the latter case to permit evaluation of the relative change in rate of dissolution, since dissolution was complete for three of the five samples used in the 4-hour experiments of Table VIII.

The behavior of the solutions during the dissolution process is described in the following sections.

Behavior of the "4 M Acid" Solutions

The "4 M Acid" solutions (Table VI) behaved differently when heated. During the initial 30 minutes of heating, the following phenomena were noted:

Solutions 1a and 2a gave off rather large quantities of NO_2 when brought to refluxing temperature. The appearance of the solutions changed from the initial color (colorless for 1a, yellow for 2a) to a greenish gray within the first minute. As heating was continued, this darkened to a grayish green, opagued with some suspended solid. After about 25 minutes, the evolution of NO_2 from solution 2a had abated and only a faint brown color was noticed over the solution. The brown color of NO_2 did not abate in the flask of solution 1a until an hour had passed.

TABLE V

EXTENT OF ALLOY DISSOLUTION IN VARIOUS SOLUTION COMPOSITIONS BASED ON ORIGINALLY 4.5 M NITRIC ACID

Sample No.	Alloy Weight, g	U salt, g	HNO_3, ml of 4.77 M	HF, ml of 0.9 M	H_2O, ml	Undisintegrated Sample, g *	Undisintegrated Sample, % **	Ignited Residue, g	Ignited Residue, %	Ignited Residue, % **	Ignited Residue, % ***
1	10.34	0	93	5.5	0	1.57	15	0.40	3.9	3.9	4.6
2	8.76	4.37	91	5.8	5.7	1.65	15	0.34	3.9	3.1	4.8
3	5.48	7.3	69.6	4.9	14	0.76	8	0.24	4.1	2.6	5.1
4	4.26	12.9	74	5.6	17	0.55	5	0.18	4.2	1.7	4.9
5	2.22	17.8	69.5	6.0	24	0.44	4	0.085	3.9	0.8	4.8

*Time of heating, 4 hours.

**These percentage figures are based on the hypothetical requirement of 105.3 g of alloy per liter of solution.

***These percentages are based on the weight of alloy actually disintegrated in the experiment.

TABLE VI

EXTENT OF ALLOY DISSOLUTION IN VARIOUS SOLUTION COMPOSITIONS BASED ON ORIGINALLY 4.5 M NITRIC ACID

Sample No.	Alloy Weight, g	U salt, g	HNO_3, ml of 4.77 M	HF, ml of 0.9 M	H_2O, ml	Undisintegrated Sample, g *	Undisintegrated Sample, % **	Ignited Residue, g	Ignited Residue, %	Ignited Residue, % **	Ignited Residue, % ***
1a	10.92	0	98.2	5.8	0	1.97	18.0	0.39	3.6	3.6	4.4
2a	8.09	4.03	83.7	5.3	4.5	1.04	10.3	0.34	4.2	3.4	4.8
3a	6.69	8.90	84.9	5.9	12.0	1.23	11.0	0.24	3.6	2.2	4.4
4a	4.24	12.83	73.7	5.6	17.1	0.22	2.1	0.19	4.5	1.8	4.7
5a	2.35	18.93	73.7	6.2	25.4	0.02	0.2	0.10	4.3	0.9	4.3

*Time of heating, 4 hours.

**These percentage figures are based on the hypothetical requirement of 105.3 g of alloy per liter of solution.

***These percentages are based on the weight of alloy actually disintegrated in the experiment.

TABLE VII

EXTENT OF ALLOY DISSOLUTION IN VARIOUS SOLUTION COMPOSITIONS

BASED ON ORIGINALLY 4.5 M NITRIC ACID PLUS DISSOLVED IRON

Sample No.	Alloy Weight, g	U salt, g	Fe salt, g	HNO_3, ml of 4.77 M	HF, ml of 0.9 M	H_2O, ml	Undisintegrated Sample, g *	Undisintegrated Sample, % **	Ignited Residue, g	Ignited Residue, %	Ignited Residue, % **
I	10.07	0	17.10	55.2	5.3	25.5	4.53	45.0	0.23	2.3	2.3
II	7.60	3.78	16.00	45.3	5.0	28.8	3.31	34.8	0.18	2.4	1.9
III	5.71	7.56	16.00	39.0	5.0	33.8	2.44	25.6	0.16	2.8	1.7
IV	3.83	11.56	16.20	33.0	5.0	39.4	1.51	14.4	0.09	2.4	0.9
V	1.84	14.70	15.50	25.2	4.8	42.5	0.56	5.2	0.05	2.7	0.5

*Time of heating, 4 hours.

**These percentage figures are based on the hypothetical requirement of 105.3 g of alloy per liter of solution.

TABLE VIII

EXTENT OF ALLOY DISSOLUTION IN VARIOUS SOLUTION COMPOSITIONS BASED ON ORIGINALLY 6 M NITRIC ACID

Sample No.	Alloy Weight, g	U salt, g	HNO_3, ml of 7.9 M	HF, ml of 0.9 M	H_2O, ml	Undisintegrated Sample, g *	Undisintegrated Sample, % **	Ignited Residue, g	Ignited Residue, %	Ignited Residue, % **
1b	9.96	0	72.4	5.3	17.3	0.15	1.5	0.45	4.5	4.5
2b	8.50	4.25	72.6	5.6	21.3	0.02	0.2	0.34	4.0	3.2
3b***	6.04	8.82	71.0	5.8	25.1	0	0	0.28	4.6	2.8
4b	4.24	12.84	64.0	5.6	26.8	0	0	0.23	5.4	2.2
5b	2.08	16.73	58.2	5.5	31.3	0	0	0.10	4.8	1.0

*Time of heating, 4 hours.

**These percentage figures are based on the hypothetical requirement of 105.3 g of alloy per liter of solution.

***Solution composition for this sample was miscalculated as being based on a 6.64-g sample; the error was not detected until the experiment had been performed.

TABLE IX

EXTENT OF ALLOY DISSOLUTION IN VARIOUS SOLUTION COMPOSITIONS

BASED ON ORIGINALLY 6 M NITRIC ACID PLUS DISSOLVED IRON

Sample No.	Alloy Weight, g	U salt, g	Fe salt, g	HNO_3, ml of 7.9 M	HF, ml of 0.9 M	H_2O, ml	Undisintegrated Sample, g *	Undisintegrated Sample, % **	Ignited Residue, g	Ignited Residue, %	Ignited Residue, % **
Ia	11.66	0	19.70	59.7	6.2	33.5	4.16	35.7	0.32	2.7	2.7
IIa	8.59	4.29	18.15	50.5	5.7	33.6	2.49	23.2	0.24	2.8	2.2
IIIa	6.20	8.23	17.43	44.3	5.4	35.2	2.23	21.6	0.12	1.9	1.2
IVa	4.22	12.70	17.80	40.9	5.6	38.5	1.50	14.2	0.10	2.4	0.9
Va	1.98	15.90	16.72	34.4	5.2	38.8	0.58	5.9	0.05	2.5	0.5

*Time of heating, 2.5 hours.

**These percentage figures are based on the hypothetical requirement of 105.3 g of alloy per liter of solution.

TABLE X

EXTENT OF ALLOY DISSOLUTION IN VARIOUS SOLUTION COMPOSITIONS BASED ON ORIGINALLY 6.0 M NITRIC ACID

Sample No.	Alloy Weight, g	U salt, g	HNO_3, ml of 7.9 M	HF, ml of 0.9 M	H_2O, ml	Undisintegrated Sample, g *	Undisintegrated Sample, % **	Ignited Residue, g	Ignited Residue, %	Ignited Residue, % **	Ignited Residue, % ***
1c	10.77	0	77.6	5.7	18.7	1.37	12.6	0.41	3.8	3.8	4.3
2c	7.72	3.86	66.0	5.1	19.5	1.27	13.2	0.32	4.1	3.3	5.0
3c	6.76	8.98	72.2	6.0	25.6	1.50	13.3	0.25	3.7	2.2	4.8
4c	4.28	12.96	64.4	5.7	27.3	0.66	6.2	0.19	4.4	1.8	5.2
5c	2.03	16.25	55.5	5.3	29.4	0.19	1.9	0.09	4.4	0.9	4.9

*Time of heating, 2.5 hours.

**These percentage figures are based on the hypothetical requirement of 105.3 g of alloy per liter of solution.

***These percentages are based on the weight of alloy actually disintegrated in the experiment.

Solution 3a changed from yellow to greenish yellow about 5 minutes after heating was started. The solution remained clear for 15 minutes; then the suspended solid appeared. The amount of this suspended solid increased, but never became as great as for 1a and 2a. Only a faint brown color was noted in the gases evolved from the solution.

Sample 4a behaved much the same as sample 3a, except that the greenish coloration after 5 minutes of heating was somewhat lighter. Opacity due to the suspended solid material appeared after 10-15 minutes of heating. As with solution 3a, only a faint brown color due to NO_2 was ever noticed above the solution.

Sample 5a developed a slight greenish coloration after 5 minutes of heating. Slight opacity, due to a suspended solid, appeared about 15 minutes after heating was started. The amount of the suspended solid was noticeably less than that present in 4a. Any quantity of NO_2 evolved was so slight that its color was not apparent over solution 5a.

The following conditions, noted after 90 minutes of refluxing, remained essentially the same for the rest of the refluxing period:

Solution 1a: dark gray-green color, opaque, large quantity of suspended solid, trace of NO_2 in gas evolved.

Solution 2a: same as 1a.

Solution 3a: yellowish gray-green, opaque, large quantity of suspended solid, faint trace of NO_2 in gas evolved.

Solution 4a: yellowish gray-green (slightly lighter than 3a), large quantity of suspended solid, faint trace of NO_2.

Solution 5a: light yellowish gray-green, some suspended material (not as much as in 4a), no NO_2 visible in gas evolved.

Behavior of "6 M Acid" Solutions

The "6 M Acid" solutions (Table VIII) behaved somewhat differently from the "4 M Acid" solutions.

Solutions 1c and 2c gave off rather large quantities of NO_2 when brought to refluxing temperature. The initial appearance of these solutions (colorless for 1c, yellow for 2c) changed to a greenish gray within the first minute. As heating continued, the solutions darkened to a grayish green.

The suspended solid material appeared within the first few minutes, as before. The evolution of NO_2 decreased throughout the refluxing period. Appreciable quantities, judged by color, were still being evolved from solutions 1c and 2c when they were removed from the heat, however, in contrast to the behavior of 1a and 2a, which evolved only traces of NO_2 after the first hour of refluxing.

Solution 3c also gave off quantities of NO_2, but not quite as much as 1c and 2c. The solution changed from an initial yellow color to a greenish gray in the first minute and darkened to a grayish green as heating was continued. The solution presented essentially the same appearance as 1c and 2c, except that the color of 3c never became as dark as that of 1c or 2c. Evolution of NO_2 continued throughout the heating period for 3c, in marked contrast to the behavior of solution 3a. The final appearance of the 3c solution was judged somewhat darker than that of the 3a solution.

Solution 4c behaved similarly to solution 3c. The initial yellow color changed to a greenish gray in the first 2 minutes. The appearance of the suspended solid material was somewhat slower than in solution 3c, taking about 2-3 minutes. Solution appearance paralleled that of solution 3c, except that the color was lighter.

Solution 5c behaved quite differently from 5a. NO_2 was evolved by the reaction and the initial yellow color darkened to a yellowish green-gray in about 5 minutes. The appearance of the suspended solid is usually coincident with the gray appearance. The evolution of NO_2 persisted from solution 5c for about 1 hour, by which time it had diminished until only a faint brown color was visible. This brown tint never disappeared from the gases evolved from solution 5c.

The following conditions, noted after 90 minutes of refluxing, remained essentially the same for the rest of the refluxing period:

Solution 1c: quantities of NO_2 still evolved, but not as much as during the first 30 minutes of heating; dark gray-green color, opaque, large quantity of suspended solid material.

Solution 2c: same as 1c.

Solution 3c: same as 1c, except that solution color was somewhat lighter.

Solution 4c: NO_2 evolution decreased, but the brown color was still evident in the evolved gases; yellowish gray-green, opaque, fairly large amount of suspended solid.

Solution 5c: trace of NO_2 visible in evolved gases; color somewhat lighter than that of solution 4c, fairly large amount of the suspended solid.

In general, NO_2 evolution for the "6 M Acid" solutions was dependent on the rate of heating. At low rates of boiling, just sufficient to boil the solution with a very low reflux, NO_2 was given off copiously from all the solutions. On the other hand, if the temperature increased so that the reflux rate doubled or tripled, the quantity of NO_2 evolved reduced to just a trace of brown color. The above observations on the individual solutions were made at the specified reflux rate of one drop per two seconds.

Summary of Kinetic Experiments

In the following paragraphs an attempt is made to summarize certain deductions which are readily apparent from the data of Tables V-X or which appear rather likely on the basis of that data. Due to the time and other limitations imposed, no attempt was made to plot the data or to see if the data would fit any particular rate expressions; all the data are expressed, however, in such form as to facilitate any attempt at curve fitting.

One impressive result is the relative constancy of the undissolved alloy residue or sludge (not to be confused with undisintegrated residue) at about 4-5% of the weight of alloy actually disintegrated (see Tables V, VI, VIII, and X. For iron-containing solutions, where considerable percentages of the alloy were not disintegrated, the percentages of ignited residues based on the weight of disintegrated sample were 3.5, 4.2, 4.9, 3.9, and 3.8% in Table VII and 4.3, 3.9, 3.0, 3.7, and 3.6% in Table IX. It may then be safely concluded that the presence of iron dissolved in the solution does not cause appreciable additional dissolution of the alloy component which does not react with nitric acid.

The slower rates of dissolution in the presence of iron (Table VII compared to Table VI, and Table IX compared to Table X) are probably due to the decreased effective nitric acid concentrations in the iron-containing solutions. Comparing the data in Table IX (effective nitric acid concentration of 4.25 M and 2.5 hours' heating) with the data in Table VI (effective nitric acid concentration of 4.5 M and 4 hours of heating) gives additional evidence for this viewpoint. The differences in extent of dissolution in the latter case can reasonably be ascribed to the difference in exposure time. Accordingly it would be safe to say, at least as a first approximation, that the presence of iron does not affect the rate of dissolution of the alloy if the effective nitric acid concentration is kept unchanged. It would have been desirable to repeat the experiments of Table IX using an effective nitric acid concentration of 4.5 M and 4 hours of heating.