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1.0 ABSTRACT

Batch and continuous aqua-regia dissolution of 304 and 304-L stainless steels, and APFR plate were studied ~~during the 1956 fall as of quarter 4~~. Dissolution techniques are described and preliminary results are presented. A short survey of the known chemistry of aqua-regia is also presented.

2.0 SUMMARY

Preliminary batch dissolution studies were carried out to provide information concerning insoluble particles produced in aqua-regia dissolution of stainless steel. A partial compilation of the published chemistry of aqua-regia has been made so that the known gold and platinum reactions are available for comparison.

A continuous dissolution apparatus was constructed to provide data necessary for the design of a large scale aqua-regia dissolver. Some data were obtained showing the dependence of reaction rate upon acid strength and acid feed rate.

Continuous dissolution rates of 304 stainless steel in 6 M HNO_3 - 2 M HCl and 6 M HNO_3 - 4 M HCl are presented along with product solution concentrations for these runs.

3.0 INTRODUCTION

Power reactors which must operate for extended periods at high temperatures and pressures without fuel reprocessing require fuel elements with very high corrosion resistance. For service with water stainless steel is excellent. It has therefore been selected as the structural and cladding material for several power reactors.

The excellent corrosion resistance of stainless steel presents a severe problem in aqueous chemical reprocessing of a "burnt" fuel element. It is necessary to dissolve the element rapidly enough to make an economical process possible. The answer is being sought through dissolution of the element in aqua-regia.

A process for continuous dissolution of stainless steel alloys and stainless steel clad fuel elements had been proposed but had not been carried out experimentally previous to this report. Some preliminary work was done in the design of a pilot plant scale continuous dissolver. It became apparent, however, that much data could be obtained at relatively little expense on a much smaller scale. Small scale batch dissolutions were made to obtain basic data concerning reaction rates and insoluble residues. A bench scale continuous dissolver was then designed and constructed. Some preliminary data were obtained and are presented in this report, along with results from preliminary batch dissolution studies.

4.0 BATCH DISSOLUTION STUDIES

Batch dissolutions of 304 stainless steel and APFR plate were made to determine the composition size and amount of solid particles which might be produced during continuous dissolution. Four dissolutions were made, two with stainless steel and two with APFR plate.

Production of insoluble particles was much more pronounced in the APFR plate dissolutions. Calculations indicated that the volume of filterable particles produced may be as high as 0.90 cc per liter of product solution.

Particle size determined by microscopic comparison to a 10^{-3} mm scale showed a maximum size of approximately 2.5 microns. The smallest particles were too small to be resolved under a 500 power microscope. A period of one day was sufficient to settle or digest virtually all of the particles.

The composition of the particles was determined by spectroscopic analysis. Chromium constituted the largest portion with nickel and iron also present in measurable quantity. Uranium constituted less than 0.1% of the total material. Measuring the α radiation from a known weight of the particles confirmed the uranium analysis.

5.0 THE BENCH SCALE CONTINUOUS DISSOLVER

A bench scale continuous dissolver was designed and operated to obtain preliminary data which will allow more precise design of a large scale system. Some construction details of the dissolver and the first result obtained are presented in the following sections.

5.1 Necessity of Continuous Dissolution Studies

Numerous batch dissolution data are available for stainless steel in aqua-regia. However, these data are not directly applicable to continuous dissolutions, because reaction rate may be a function of acid feed rate. In addition, the acid concentration within the reaction vessel may be significantly different from the concentration of the acid fed into the vessel.

Because reaction rate is determined critically by both temperature and acid strength, continuous dissolution data are necessary. Therefore, a system capable of obtaining these data was constructed.

5.2 Flow and Components

In the dissolver system as originally constructed, two acids were fed into an acid mixer and combined in the proper preparation with water (Fig. 5.1). The acid mixer was fitted with a heating mantle to allow pre-heating if necessary. A sample was introduced into the dissolver where it was

Fig. 5.1. Bench Scale Aqua-Regia Dissolver Flow

reacted with the aqua-regia. The reaction products were then cooled and collected.

An alternate to the procedure stated above consisted of pre-mixing the aqua-regia and using the acid mixer for a pre-heater only. This method of operation proved more adaptable to obtaining the necessary data with a minimum of error.

The assembly of the experimental apparatus is shown in Fig. 5.2. Heating mantles around both the acid mixer and dissolver were necessary to maintain a constant reaction temperature.

The glass parts of the dissolver are shown in detail in Figs. 5.3, 5.4, and 5.5.

The dissolver was fabricated from 4-in. Pyrex pipe and various standard Pyrex joints (Fig. 5.3). The openings are (left to right) off gas outlet, thermometer hole, top port, outlet, and acid inlet.

Two methods of maintaining an acid level in the dissolver utilized an internal standpipe and an external jack leg (Figs. 5.4 and 5.5). The internal stand pipe assembly was used with success. The external jack leg has not been tried to date.

5.3 Experimental Variables

Several important reaction variables to be studied with the bench scale continuous dissolver are: (1) continuous dissolution rate, (2) off gas production, (3) condensate composition, (4) insoluble precipitate production, and (5) materials of construction.

The most significant of these, continuous dissolution rate, was studied as a function of acid feed composition, acid feed rate, and sample composition. These data should provide information particularly valuable in the design of a larger scale dissolver.

5.4 Dissolution Rate Calculations

The all-glass construction of bench scale continuous dissolver allowed a convenient method of determining reaction rates.

Reaction rates were measured in units of $\text{mg}/\text{cm}^2/\text{min}$. The liquid level in the dissolver was variable and known at all times; therefore, the surface area of sample immersed was known. By measuring the length of sample dissolved per unit time and knowing the weight of the sample per unit length, the reaction rate was calculated without chemical analyses. If data for several feed rates at constant acid composition were to be obtained, an added convenience of this system was that little time to reach steady state was required between feed rate changes. The operator merely changed the feed

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Fig. 5.2 Bench Scale Dissolver Assembly

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Figure 5.3

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Figure 5.4

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Figure 5.5

rate and observed the change of sample length over a given period of time. This measurement was easily accomplished by using a tube or pipe shaped sample and measuring the time required for a 5 cm movement of the top of the sample down the dissolver.

With the exception of the combination of high feed rates, concentrated acids, and thin walled tubing; the pipe movement was perfectly smooth. Figure 5.6 illustrates the reason for this steady behavior. The taper on the pipe was produced in the dissolver and remained constant, independent of actual pipe length.

When the pipe drop was not smooth, the increments of drop (0.5 cm) were not sufficiently large to cause breakage of the dissolver bottom. The reaction rate was still satisfactorily determined by measuring the drop per unit time over a longer distance (~10 cm). Figure 5.7 shows the condition of tubing which was dissolved fast enough to produce uneven pipe drop. The end of the pipe which was not immersed in aqua-regia is shown in Fig. 5.8 for comparison.

5.5 Experimental Results

Only very limited data were obtained by the end of the 1956 fall quarter. Those data which were obtained showed that reaction rate increased with increasing acid feed rate and ranged from 25.4 to 131 mg/(cm²)(min) (Fig. 5.9). Stainless steel loadings in the dissolver exit stream varied from 49.0 to 325 g/liter and passed through a minimum when plotted as a function of acid feed rate (Fig. 5.10). From these plots it may be observed that the reaction rate increased even in the range of acid feed rates where stainless steel loading increased. This anomalous situation may be interpreted as evidence that mass transfer effects were more important than kinetic effects in controlling the rate of reaction. Further studies of this nature may make possible the design of a larger scale dissolver.

6.0 PERSONAL EVALUATION OF CO-OP PROGRAM

Four outstanding features of this quarter's co-operative program in the Unit Operations Section were: (1) the opportunity to apply fundamental engineering and scientific principle, (2) the development of the ability to communicate through written reports and short talks, (3) the freedom allowed in choosing experimental techniques, and (4) the incentive to learn, provided by co-op trips, seminars and classes, and the discussion of problems on an informal basis. This program has amply fulfilled the student's requirements of a co-operative program in every respect.

The author wishes to express his sincere appreciation to Dr. J. J. Perona who made this quarter so highly educational and enjoyable.

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Fig. 5.6 Partially Dissolved Heavy Wall Tubing

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Fig. 5.7 Partially Dissolved Thin Wall Tubing

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Fig. 5.8 Partially Dissolved Thin Wall Tubing

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Reaction Rates for the Dissolution of 304 Stainless Steel in Aqua Regia

Figure 5.9

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Product Stream Concentration for the Dissolution of 304 Stainless Steel in Aqua Regia

Figure 5.10

7.0 APPENDIX

The appendix contains a compilation of aqua-regia chemistry and continuous dissolution data.

7.1 Aqua-Regia

The published chemistry of aqua-regia is almost exclusively devoted to platinum and gold reactions. Because even this information is not readily available, a compilation of the chemistry was made from several source books. Various observations which were made while experimenting with aqua-regia are also presented in this section.

Aqua-Regia Chemistry. The name aqua-regia dates from the days of the alchemists who noted its unusual corrosive characteristics with platinum and gold, the "king of metals".^{1,3} Although the name implies a mixture of any two acids, in recent years aqua-regia has come to mean a mixture of hydrochloric and nitric acids.³ This is the composition of the aqua-regia described here.

Nitric and hydrochloric acids are considered to combine according to the following equation:¹

However, this is undoubtedly an idealization of what actually occurs upon mixing the two acids.¹

Gold reacts with aqua-regia in the following manner:

A similar reaction with platinum produces $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (chloroplatinic acid hexahydrate), which forms deliquescent prisms.² Vigorous boiling of the platinum aqua-regia reaction yields $\text{PtCl}_4 \cdot 2\text{NOCl}$ (nitrosylplatonic chloride). This compound is soluble in water, liberating NO_2 upon dissolving.²

The active agent in dissolving gold or platinum is the free chlorine and not the nitrosyl chloride (NOCl). In fact, nitrosyl chloride will not even attack gold or platinum even though it readily dissociates into chlorine gas and nitric oxide at its boiling point of -50°C .³

A few of the temperature dependent physical characteristics of dilute aqua-regia are the following:¹

<u>Temperature, °C</u>	<u>Characteristic</u>
10	Changes color
30	Evolves gas
90	Vigorous gas evolution
109	Boiling point

Acid Designation. The concentration of hydrochloric or nitric acid in an aqua-regia determine its chemical properties. Therefore, some convention whereby these concentrations could be easily stated was necessary. The one adopted is based on the molarity of the NO_3^- and Cl^- ions. It is written 6-4- for a 6 M NO_3^- concentration, 4 M Cl^- concentration; 5-2 for a 5 M NO_3^- concentration, 2 M Cl^- concentration, etc. Note that a 6-4 aqua-regia does not mean a mixture of 6 M HNO_3 and 4 M HCl . It is 6 M NO_3^- and 4 M Cl^- with respect to the final mixed solution.

7.2 Miscellaneous Observations

While conducting dissolution experiments several general observations were made concerning aqua-regia.

Color. Aqua-regia up to 6 M NO_3^- and 2 M Cl^- is a light yellow. Above this chloride concentration, the color deepens to orange which is quite dark at 4 M chloride concentration.

Effect on Plastics and Rubber. Polyethylene is suitable for containing aqua-regia at temperatures below 90°C and concentrations up to 6-4. Severe discoloration and possible softening resulted from storage of 7-7 aqua-regia in a polyethylene bottle.

Teflon has proven satisfactory for rotameter floats under all concentrations and temperatures up to 109°C.

Tygon tubing may be used for conducting cool aqua-regia if frequent replacement is possible. Tygon is not suitable for hot aqua-regia.

Rubber is unsatisfactory for containing aqua-regia. Decomposition occurs much more slowly than with concentrated HNO_3 , however.

7.3 Summary of Continuous Dissolution Data

In Table 7.1 are presented the complete data for the seven continuous dissolution runs carried out during this program.

Table 7.1 Summary of Continuous Dissolution Data

Acid	Feed Rate	Time	Pipe Movement	Weight Dissolved	Volume Out	Product Production Rate	Reaction Rate	Product Concentration	Product Stream Molarities		
	cc/min	min	cm	g	cc	cc/min	mg/cm ² min	g/liter	H ⁺	NO ₃ ⁻	Cl ⁻
6-4	20	4.03	1.4	13.0	4.0	9.9	25.5	325	1.00	3.74	3.54
6-4	100	7.76	5.0	46.5	-	-	47.5	-	3.78	4.11	3.23
6-4	150	4.47	5.0	46.5	575	129	82.6	80.8	3.95	4.35	3.38
6-4	200	5.6	10.0	93.0	1000	179	131	93.0	4.00	1.9	3.38
6-2	50	5.81	2.0	18.6	285	49.0	25.4	65.3	3.2	5.7	1.88
6-2	100	10.2	5.0	46.5	950	93.0	36.2	49.0	3.1	5.85	1.85
6-2	150	5.83	5.0	46.5	825	142	63.3	56.3	3.9	5.82	1.85

7.4 References

1. J. W. Mellor, Mellor's Modern Inorganic Chemistry, p. 506.
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