MASTER

325
7-16-62

ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS
Part III. Stainless Steel (304) in Nitrate Solutions

J. R. Aylward
E. M. Whitener

PHILLIPS
PETROLEUM
COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PRICE \$.50

Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA

IDO-14584
AEC Research and Development Report
Chemical Separations Processes
for Plutonium and Uranium
TID-4500 (17th Ed.)
Issued: June 1, 1962

ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS
Part III. Stainless Steel (304) in Nitrate Solutions

J. R. Aylward
E. M. Whitener

PHILLIPS
PETROLEUM
COMPANY

Atomic Energy Division
Contract AT(10-1)-205
Idaho Operations Office
U. S. ATOMIC ENERGY COMMISSION

ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS
Part III. Stainless Steel (304) in Nitrate Solutions

J. R. Aylward
E. M. Whitener

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	3
I. SUMMARY	5
II. INTRODUCTION	6
III. EXPERIMENTAL	9
IV. RESULTS	10
1. Effect of Solution Composition	11
2. Effect of Temperature	13
V. DISCUSSION	15
1. The Passive State	15
2. The Transpassive Region	15
3. Secondary Passivation	17
4. Limiting Current	18
VI. CONCLUSIONS	18
VII. REFERENCES	21
VIII. APPENDIX	22

LIST OF FIGURES

<u>Number</u>	<u>Figure</u>	<u>Page</u>
1	Schematic Representation of the Rates of Stainless Steel Dissolution (curve 1) and Nitric Acid Reduction (curve 2) as a Function of Potential	8
2	Electrolytic Cell	9
3	Effect of H^+ Concentration on the Anodic Dissolution of 304 Stainless Steel at 25°C with a Constant NO_3^- Concentration of 5.0M	12
4	Effect of NO_3^- Concentration on the Anodic Dissolution of 304 Stainless Steel at 25°C with a Constant H^+ Concentration of 1.0M	12
5	Anodic Dissolution of 304 Stainless Steel in High Concentrations of HNO_3 at 25°C	13
6	Effect of Temperature on the Anodic Dissolution of 304 Stainless Steel in a Solution Containing 1M HNO_3 and 4M NO_3^- from Fe^{+3} , Cr^{+3} , Ni^{+2} Nitrates	14
7	Effect of Temperature on the Anodic Dissolution of 304 Stainless Steel in 10M HNO_3	14
8	Anodic Dissolution of Pure Iron, Nickel, and Chromium in 6M HNO_3 at 25°C	23
9	Effect of Chromium Content on the Anodic Dissolution of Iron-Chromium Alloys at 25°C in a Solution Containing 1M HNO_3 plus 4M NO_3^- from Fe^{+3} and Cr^{+3} Nitrates in the Ratio Corresponding to the Alloy Composition	23

ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS
Part III. Stainless Steel (304) in Nitrate Solutions

J. R. Aylward
E. M. Whitener

A B S T R A C T

The potential-current density relationships for 304 stainless steel dissolution in a nitrate system were studied as a function of solution composition and temperature in order to optimize the conditions for electrolytic dissolution of this material. In the nitrate system, the anodic dissolution of steel takes place in the transpassive region. Under some conditions, deviations from Tafel behavior are observed which depend greatly on the nitrate and hydrogen ion concentration, and on temperature. A discussion of passivity, transpassivity, secondary passivation, the limiting current density, and the effect of alloy composition on the dissolution behavior is given. It was found that at temperatures above 60°C efficient dissolver operation should be possible over a wide range of solution compositions and at current densities up to 2 amp/cm².

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS
Part III. Stainless Steel (304) in Nitrate Solutions

J. R. Aylward
E. M. Whitener

I. SUMMARY

Electrolytic dissolution in nitric acid shows promise as a single headend treatment for processing a variety of fuel element materials, e.g., stainless steel, Nichrome, and aluminum. A nitrate system has the advantage that it may be used directly in well-established subsequent reprocessing steps. At the same time, electrolytic dissolution permits close control of the dissolution rate.

A study of the anodic dissolution of 304 stainless steel in the transpassive region in nitrate solutions was undertaken in order to define the most efficient dissolver operating conditions. The potential-current density relationships were determined as a function of solution composition (hydrogen and nitrate ion dependence) and temperature (25 to 85°C). This study included solutions containing up to 100 g/l of stainless steel with a total nitrate ion concentration of 6M.

The conclusions were: 1. The general characteristics of the polarization curves were found to be quite varied, showing regions of Tafel behavior, secondary passivation, and, in some cases, a limiting current density. It was found that these factors are greatly dependent on solution composition and temperature. The Tafel relationship ($E = a + b \log I$) is obeyed at current densities $< 10^{-3}$ amp/cm². Secondary passivation occurs in the medium current density range at low hydrogen and nitrate ion concentrations, and at low temperatures. A limiting current density (~ 1 amp/cm²) is observed with nitric acid concentrations above 6M. The value of the limiting current density increases with increasing temperature and decreasing nitric acid concentration.

2. Efficient anode operation over a wide range of solution compositions is possible at temperatures above 60°C. At this temperature or higher, secondary passivation, limiting currents, and gas evolution (at anode) are avoided at the current densities (0.1 to 2 amp/cm²) and product

solution compositions that would normally be encountered in dissolver operation.

3. These data, coupled with similar cathodic studies, will permit selection of optimum operating conditions for Idaho Chemical Processing Plant usage.

II. INTRODUCTION

In the recovery of uranium and plutonium from irradiated nuclear fuel elements by aqueous means, there are essentially two main steps: one, the dissolution of the fuel elements in a suitable aqueous inorganic acid, and two, the separation of the fissionable material by liquid-liquid solvent extraction. Fuels composed of different materials have required various headend dissolution systems which must eventually be converted to a nitrate system to be processed in the Idaho Chemical Processing Plant solvent-extraction columns.

The development of a single headend dissolution process for many fuel compositions has long been desired. A simple nitrate system which could be employed for dissolution has several advantages aside from the fact that the resulting solution can be used directly in the solvent-extraction step. First, a minimum of headend facilities would substantially reduce equipment cost and plant investment; second, the process streams would be non-corrosive toward stainless steel plant equipment; and third, the problem of waste storage could be minimized, as nitrates can be readily converted to solids for permanent storage.

Thermodynamically, nitric acid should dissolve many of the metallic fuel element materials, but in most cases the metal surface is different from the bulk metal due to the presence of oxide films, passivation, etc. The problem then becomes one of dissolving or destroying the film and preventing its re-formation. Small amounts of other reagents added to the nitric acid are sometimes successful in altering the nature of the metal surface. For example, aluminum can be dissolved chemically in nitric acid only if its surface oxide film is removed and prevented from re-forming. This is accomplished by the addition of mercuric ions to the nitric acid which results in the amalgamation of the aluminum surface and subsequent destruction of the oxide film barrier. Stainless steel

is normally passive in nitric acid, but the addition of chloride ion destroys this passivity and a reasonable dissolution rate is obtained. However, the addition of these other reagents to nitric acid in order to accomplish dissolution is undesirable in many cases (e.g., chloride ion causes corrosion of stainless steel process equipment).

Dissolution of metal in aqueous solutions involves two separate processes: one, the metal is oxidized and passes into solution as metal ions, and two, a species in solution is reduced. Both reactions take place at the metal/solution interface and occur at the same rate (based on equivalents per unit time per unit area). The reaction rate is determined by the potential across the metal/solution interface as well as the temperature and solution composition. In a "chemical" dissolution, the potential is determined by the kinetics of the oxidation and reduction reactions and can only be varied, over a limited range, by changing the temperature and concentration of the reacting species in solution. If the potential at the metal/solution interface is changed by the application of an external source of electrical energy, passive films may be destroyed. In this way, a number of fuel materials can be dissolved in nitric acid without the addition of other reagents. Also, the reaction rate can be easily controlled.

The effect of potential on the dissolution rate of stainless steel, iron, nickel, chromium, and alloys of these elements in sulfuric acid has been investigated extensively.⁽¹⁻⁷⁾ These studies have been directed mainly toward evaluating the effect of alloy composition on the corrosion resistance. The general shape of the anodic potential-dissolution rate (current density) relationships for stainless steel is shown schematically in curve 1 of Figure 1. In section a, b the steel is active and the dissolution rate increases with increasing potential. From b to c the dissolution rate decreases with increasing potential, and from c to d the metal is passive. Above d is the transpassive region. In some cases secondary passivation is observed (e, f), and from f to g oxygen evolution occurs simultaneously with metal dissolution. Curve 2 of Figure 1 represents the rate of reduction of nitric acid as a function of potential. The current at the point of intersection of the two curves is the corrosion or chemical dissolution rate, and the potential corresponding

Figure 1

Schematic Representation of the Rates of Stainless Steel Dissolution (curve 1) and Nitric Acid Reduction (curve 2) as a Function of Potential

to the point of intersection is the corrosion potential. It is obvious from Figure 1 that electrolytic dissolution of stainless steel in nitric acid will involve the transpassive region. Therefore, it is this region only (from d to g) which will be of concern in this study.

Work reported in the literature deals mainly with the effect of alloy composition on the nature of the potential-current density relationships in 1N sulfuric acid. However, it was expected that the general relationships would be the same in

nitric acid solutions. Prázák, et al., found that the transpassive potential of iron and iron-nickel alloys is above that of oxygen evolution; therefore, the only transpassive region of practical importance is for chromium and its alloys.⁽¹⁾ Pure nickel dissolves to a very limited extent in the transpassive region.^(2,3) Chromium dissolution in the transpassive region obeys the Tafel equation ($E = a + b \log I$) and has a slope (b) of 0.045 volt.⁽⁴⁾ The potential-current density relationships for iron-nickel-chromium alloys are strongly dependent upon the chromium content, as shown in the work of Cihál and Prázák.⁽⁵⁾ As the chromium content of the alloy increases, the dissolution current in the transpassive region increases and the current minimum in the secondary passivation region (e to f of Figure 1) becomes less pronounced. Alloys with up to 16% chromium dissolve to a limited extent in the transpassive region. Secondary passivation is observed for alloys containing 18 to 30% chromium, while alloys containing more than 35% chromium behave like pure chromium. These observations were made in 1N H_2SO_4 solution and are not necessarily valid for other concentrations and/or solutions.* In

* The polarization curves for pure iron, nickel, chromium, and two iron-chromium alloys in nitrate solutions are given in the appendix.

fact, solution composition and temperature have a strong influence on the behavior of these alloys in the transpassive region, as stated by Kolotyркин⁽⁶⁾ and revealed in the present work.

The anodic behavior of stainless steel in nitrate systems has not been studied previously as a function of solution composition and temperature. The present work was undertaken to supply this information in order to optimize the electrolytic dissolution of stainless steel-type fuel elements.

III. EXPERIMENTAL

The electrolysis cell, Figure 2, was essentially the same as used in previous work, and is described in detail elsewhere.⁽⁸⁾ Platinum was

Figure 2
Electrolytic Cell

used for the cathode, and the reference electrode was a saturated calomel electrode (S.C.E.). A solution bridge with a Luggin capillary connected the cell to the reference electrode. The absence of IR drop error and shielding effects with this capillary was confirmed by the use of interrupter techniques. The majority of the anodes were type 304 stainless steel (18-8). Other experiments were performed with steel components either separately or in combination: iron, nickel, chromium, Nichrome⁽¹⁷⁾ (80% nickel - 20%

chromium), a 90% iron - 10% chromium alloy, and an 84% iron - 16% chromium alloy. These metals in rod form were machined to fit into the Teflon holder (see Figure 2) in such a manner that one cm^2 of surface area was exposed to the solution. A screw mechanism facilitated removal of the electrode after each experiment. Prior to each experiment, the exposed surface of the electrode was refaced by machining, and the resulting work-hardened surface was removed by electrolytic dissolution at a high current density in 6M nitric acid.

The anodic polarization curves were first determined in nitric acid over the concentration range $1M$ to $14M$. To study, independently, the effect of hydrogen and nitrate ion concentration on the polarization curves, typical dissolver product solutions containing iron (III), nickel (II), and chromium (III)* nitrates in the ratio found in stainless steel were used. By mixing various amounts of the stainless steel nitrate stock solution and nitric acid, the hydrogen ion concentration could be varied at a constant nitrate ion concentration, and vice versa. The effect of temperature on the polarization curves was also studied over the range 25° to $85^{\circ}C$ in 15° intervals. The majority of the work, however, was carried out at $25^{\circ}C$. Temperatures were controlled to within $\pm 1^{\circ}C$ and the stirring speed maintained at 220 ± 10 rpm.

The potential-current density relationships covered a current range from approximately 10^{-6} amp/cm² to 3 amp/cm² and were obtained with an electronic potentiostat. Automatic plotting of the polarization curves was accomplished with an X-Y recorder which included a log converter for the current axis. A scan rate of 50 mv/min was used. However, since time was required to reach a steady-state current at each potential, the X-Y plots were used only to indicate the shape and characteristics of each curve. For the final curves, current readings were taken after one minute at each potential. Potential intervals of 40 mv were used for both increasing and decreasing values. This procedure was repeated twice for each run. Duplicate experiments were also carried out to check the over-all reliability of the data. Following this procedure, the current at a given potential was found to be reproducible to within $\pm 10\%$.

IV. RESULTS

The general characteristics of the polarization curves for 304 stainless steel are quite varied, showing regions of Tafel behavior, secondary passivation, and, in some cases, a limiting current density.

* Although Cr^{+6} is produced at the anode, the reduction products of nitric acid formed in the cathodic reaction reduce the Cr^{+6} in solution to Cr^{+3} . The predominant chromium species in dissolver product solutions is, therefore, Cr^{+3} .

These factors were found to be greatly dependent on solution composition and temperature. The Tafel relationship is obeyed at low current densities for all the solution compositions and temperatures studied. Secondary passivation occurs in the medium current density range at low hydrogen and nitrate ion concentrations, and at low temperatures. A limiting current density is encountered at high nitric acid concentrations and low temperatures.

1. Effect of Solution Composition

The dissolution rate of 304 stainless steel is shown in Figure 3 as a function of potential at 25°C in solutions containing Fe^{+3} , Cr^{+3} , and Ni^{+2} nitrates with various hydrogen ion concentrations and a constant nitrate ion concentration of 5M. In the low current density region, a Tafel relationship ($E = a + b \log I$) is obtained and the slope (b) is equal to 0.07 volt. It can be seen that the dissolution rate (current density) at constant potential is independent of H^{+} concentration. At higher current densities, secondary passivation is observed, and this is strongly dependent on hydrogen ion concentration. Above the secondary passivation region (~ 1.6 volts versus S.C.E.), the current increases rapidly with increasing potential, and oxygen evolution occurs simultaneously with metal dissolution (current efficiency less than 100%).

Figure 4 shows the effect of nitrate ion concentration on the polarization curves at 25°C. The hydrogen ion concentration was held constant at 1M and the nitrate varied by adding stainless steel nitrates. In the low current density region, the Tafel slope is again 0.07 volt and the dissolution rate at constant potential is inversely dependent on the nitrate ion concentration. The degree of secondary passivation is also a function of the nitrate ion concentration.

The polarization curves obtained in nitric acid solutions at concentrations $\leq 5\text{M}$ without added salts were similar to those shown in Figures 3 and 4, with the exception that appreciable hysteresis was observed in the secondary passivation region.

In more concentrated nitric acid solutions (6 to 14M), secondary passivation is absent as shown in Figure 5. As in the other cases, a Tafel slope of 0.07 volt is observed at low current densities; however, the slope changes at a current density of approximately 10^{-2} amp/cm² in

Figure 3

Effect of H^+ Concentration on the Anodic Dissolution of 304 Stainless Steel at 25°C with a Constant NO_3^- Concentration of 5.0M

Figure 4

Effect of NO_3^- Concentration on the Anodic Dissolution of 304 Stainless Steel at 25°C with a Constant H^+ Concentration of 1.0M

CPP-S-2196

Figure 5
Anodic Dissolution of 304 Stainless Steel
in High Concentrations of HNO_3 at 25°C

such a manner that the dissolution rate in this region at constant potential is nearly independent of nitric acid concentration. At current densities approaching 1 amp/cm^2 , a limiting current density is encountered, the value of which decreases with increasing nitric acid concentration.

2. Effect of Temperature

Two solutions, one containing $1\text{M } \text{HNO}_3 + 4\text{M } \text{NO}_3^-$ from stainless steel nitrates and the other $10\text{M } \text{HNO}_3$, were used for the temperature studies. The results of the studies are shown in Figures 6 and 7, respectively. Increasing the temperature results, as usual, in an increase in the dissolution rate (current density) at constant potential. The activation energy for the anodic reaction in the Tafel region ranges from 14 to 15 Kcal/mole, depending upon the potential. Secondary passivation becomes less pronounced and eventually disappears as the temperature is increased (Figure 6). The value of the limiting current density is increased with increasing temperatures (Figure 7).

CPP-S-2195

Figure 6

Effect of Temperature on the Anodic Dissolution of 304 Stainless Steel in a Solution Containing 1M HNO_3 and 4M NO_3^- from Fe^{+3} , Cr^{+3} , Ni^{+2} Nitrates

CPP-S-2194

Figure 7

Effect of Temperature on the Anodic Dissolution of 304 Stainless Steel in 10M HNO_3

V. DISCUSSION

Basically, nothing is known about the reaction mechanism in the transpassive region. A few general ideas have been put forward^(7,9) regarding the type of over-all reactions, but due to incomplete knowledge of the passive state, a sufficient theoretical foundation upon which to build and extend to the transpassive region is lacking. There are two main schools of thought on the cause of passivity: the oxide film theory, and the adsorption theory.^(10,11,12) The former theory is favored by most authorities, but undoubtedly adsorption plays a part, at least in the beginning stages of passivity. In any case, the composition and structure of the passive layer on stainless steel is not presently known with any certainty.

1. The Passive State

In the passive state, metal dissolution still takes place, but at a very slow rate which is independent of potential. According to the oxide film theory, this slow reaction rate in the passive region is due to a chemical dissolution of the film, and is, therefore, independent of potential. The film is continuously re-formed and maintains a static thickness determined by the potential and its specific electrical properties.⁽¹⁰⁾ It is known that the passive film contains iron and chromium in the trivalent state, and nickel in the divalent condition. The compounds corresponding to these oxidation states in the passive film have been postulated to be $\gamma\text{-Fe}_2\text{O}_3$, CrOOH and NiO .⁽¹⁵⁾ However, there is no a priori reason to assume that the compositions and structure of the passive film would be the same as known compounds in the bulk state. It is just as reasonable to consider the film as having its own unique properties, both chemical and physical, and possibly a nonstoichiometric composition. The anions of the solution may also contribute to the composition of the passive layer, since the dissolution rate in the passive and transpassive regions is generally dependent on the type and concentration of the anion.

2. The Transpassive Region

In the transpassive region, chromium goes into solution as Cr^{+6} . The reaction must therefore be taken as the oxidation of a Cr^{+3} ion in

the passive layer to the hexavalent state, which then passes into solution. At a sufficiently positive potential, then, the metal species in the passive film can be oxidized further to form a readily soluble oxygen complex in which the metallic ion is present in a higher oxidation state. At potentials beyond this point, a continuously increasing rate of dissolution with increasing potential, as observed for chromium in the transpassive region, would be expected.

The reaction sequence described above may be represented as follows:

In the active region, the reaction proceeds by way of path a. Path b results in passivation, in which the metal-oxygen bond becomes stronger with increasing potential until a point is reached at which the passive film is formed (Flade potential)*. Experimentally, an increase in pH lowers the Flade potential, and this is in accord with the above reaction scheme. The transpassive region begins when the potential has become high enough to oxidize the metal ions in the passive layer to higher oxidation states which are, in the case of stainless steel, soluble in the solution.

The relative stability of the higher oxidation states of the major stainless steel components follows the order $Cr^{+6} > Ni^{+4} > Fe^{+6}$, as can be seen from the standard potentials of the following couples in acid solution, (13)

where the initial conditions correspond to the oxidation states of the metals in the passive film. From this, it is to be expected that only chromium will dissolve at appreciable rates below the potential for

* Point c of Figure 1.

oxygen evolution (see appendix). This explains why the transpassive region is prominent only for chromium and its alloys.* Of the three metals, iron should resist dissolution to higher positive potentials, and this is known to be true (see appendix).

Even though the higher oxidation states of iron and nickel are unstable in acid solution, these species can be discharged from the electrode surface at high potentials. This electrochemical reaction would then be followed by a rapid chemical reaction in which the unstable species are reduced to a lower, more stable oxidation state accompanied by oxygen evolution. The existence of a transpassive region for pure iron has been demonstrated by Franck and Weil.⁽¹⁶⁾ The transpassive region in 1N sulfuric acid at 25°C starts just below the potential for oxygen evolution, but because the Tafel slope is steeper than that for oxygen evolution, the latter becomes the predominant reaction at slightly higher potentials.

3. Secondary Passivation

The phenomenon of secondary passivation is much more difficult to explain because investigations in this area have been few, and a sound theoretical foundation for the transpassive region which could be extended to include secondary passivation has not been developed. However, the similarity in the potential-current density relationships for secondary passivation and deviations from Tafel behavior in other systems attributed to double-layer effects⁽¹⁴⁾ makes it tempting for one to postulate that secondary passivation may be accounted for by changes in the structure of the double layer with potential and solution composition. It is known that alloy composition greatly influences the degree of secondary passivation, but this is compatible with the above hypothesis since alloy composition would affect the double-layer structure and the rational potential.**

* In chromium alloys, dissolution of chromium atoms from the surface would leave the other constituents (iron and nickel) in active sites, thus making their dissolution easier. Also, it can be shown that, when the chromium content is above 16 to 18%, continuous paths of chromium atoms into the interior become available.

** The rational potential is the electrode potential measured relative to the zero point of charge (electrocapillary maximum) in the absence of specific adsorption.

Pražák, et al.,⁽¹⁾ have postulated that secondary passivation is caused by the blocking of active sites (chromium atoms) by adsorbed oxygen, but no concrete evidence was offered to support this view. Along the same lines, the saturation of the free valences of the electrode surface by chemisorbed anions (rather than oxygen) could be responsible for secondary passivation. Both of these ideas are in the class of double-layer effects.

Osterwald and Feller⁽¹⁶⁾ have shown in a brief preliminary investigation that pure nickel exhibits secondary passivation in 1N H_2SO_4 at 25°C, so this phenomenon is not uniquely characteristic of alloys. A detailed study of nickel dissolution in the transpassive region is definitely needed, because it appears to be the simplest system in which to study the reactions of this region and the phenomenon of secondary passivation. However, the complete elucidation of the dissolution mechanism will probably have to await further developments in the theory of a discrete double-layer structure and the effect of specific adsorption on electrode kinetics.

4. Limiting Current

The limiting current density observed with high concentrations of nitric acid is due to concentration polarization in which the rate-determining step is the transport of the reaction products (stainless steel salts) away from the electrode surface. The rate is, therefore, independent of potential in this region. Increasing the temperature and/or the stirring rate will result in an increase in the limiting current density, as observed. The decrease in the limiting current density with increasing nitric acid concentration is due to the lower solubility of the stainless steel salts in the more concentrated nitric acid solutions.

VI. CONCLUSIONS

The operational behavior of an electrolytic dissolver is dependent upon the reactions which occur in the dissolver, and a number of undesirable conditions (limiting current density, secondary passivation, high polarization, and competing reactions resulting in a low current efficiency) can be encountered. For efficient and convenient dissolver operation, these effects should be avoided or minimized. At the same time,

acceptable operating temperatures (30°C to 80°C), current densities (0.1 to 2 amp/cm²), and product solution composition (70 to 110 g/l of SS and less than 3M H⁺) must be maintained.

The anodic potential-current density relationships for 304 stainless steel obtained in this study as a function of solution composition and temperature can be used to define the optimum operating conditions for the anodic reactions in electrolytic dissolution.

From an analysis of the data, it is obvious that the dissolver solution should be maintained at a minimum temperature of 60°C. At this temperature (or higher), anode operation is efficient in that secondary passivation, limiting currents, and gas evolution are avoided over a wide range of solution compositions (1 to 10M acid and up to 110 g/l of stainless steel with 6M total nitrate) and at current densities up to 2 amp/cm². Also, anodic polarization changes little with solution composition at the higher temperatures.

Normally, the reduction products of nitric acid formed in the cathodic reaction reduce the Cr⁺⁶ in solution to Cr⁺³, so that at low temperatures Cr⁺³ is the predominant chromium species in dissolver solutions. High temperatures (approaching the boiling point) reduce the solubility of NO₂, etc., thereby adversely affecting the above reduction. Also, the higher temperatures favor the oxidation of Cr⁺³ to Cr⁺⁶ by the nitric acid, so that, under these conditions, an appreciable amount of Cr⁺⁶ will be present in the dissolver product solution. This is undesirable because it can result in excessive corrosion of stainless steel process equipment. There is some indication that lower temperatures would be more favorable for the cathodic reaction, from the standpoint of lower polarization and reduced off-gas, because of the higher solubility of NO₂ which autocatalyzes the cathodic reaction. For these reasons, a tentative maximum temperature of 70°C is recommended for dissolver operation.

In regard to solution composition, stoichiometrically, 5.28 moles of nitrate are needed per 100 grams of stainless steel, and the solubility of stainless steel nitrates at room temperature is approximately 120 g/l stainless steel. Since some acid is necessary to prevent hydrolysis, a product solution containing 100 grams per liter of stainless steel with

a total nitrate ion concentration of $6M$ is about the maximum recommended for efficient dissolver operation and stable product solutions. Operation at lower stainless steel concentrations would, of course, also be satisfactory. The ability to operate efficiently over a wide range of solution compositions is advantageous in that it allows flexibility in the flowsheet so that close control of the dissolver product concentration and feed is unnecessary, at least as far as the dissolution is concerned.

It should be realized that the above conditions apply only to the anodic reaction, and that before the over-all optimum dissolver operating conditions can be specified, similar information for the cathodic reaction must be obtained.

VII. REFERENCES

1. M. Prazak^{✓✓}, V. Prazak^{✓✓} and V. Cihal[✓], Z. Elektrochem., 62, 739 (1958).
2. G. Okamoto, et al., Z. Elektrochem., 62, 775 (1958).
3. Ya. M. Kolotyrkin, Z. Elektrochem., 62, 664 (1958).
4. V. M. Knyazheva and Ya. M. Kolotyrkin, Proc. Acad. Sci. USSR (English translation), 114, 429 (1957).
5. V. Cihal[✓] and M. Prazak^{✓✓}, J. Iron and Steel Inst., 360 (1959).
6. Ya. M. Kolotyrkin, Doklady Akad. Nauk USSR, 130, 585 (1960).
7. Ya. M. Kolotyrkin and V. M. Kniazheva, Zhur. Fiz. Khim., 30, 1990 (1956).
8. J. R. Aylward and E. M. Whitener, J. Electrochem. Soc., 109, 87 (1962).
9. Ya. M. Kolotyrkin, ibid., 108, 209 (1961).
10. T. P. Hoar, "Modern Aspects of Electrochemistry," No. 2, Chap. 4, J. O'M. Bockris, Ed., Academic Press Inc., New York (1959).
11. The International Colloquium on Passivity (Sept. 1957) published in Z. Elektrochem., 62, 619-830 (1958).
12. W. A. Mueller, J. Electrochem. Soc., 107, 157 (1960).
13. W. M. Latimer, Oxidation Potentials, 2nd Ed., Prentice-Hall, Inc., N. Y. (1956).
14. R. Parsons, "Advances in Electrochemistry and Electrochemical Engineering," Vol. I, Chap. 1, P. Delahay, Ed., Interscience Publishers (1961).
15. L. Young, Anodic Oxide Films, Academic Press Inc., New York (1961).
16. U. F. Franck and K. G. Weil, Z. Elektrochem., 56, 814 (1952).
17. J. R. Aylward and E. M. Whitener, Electrolytic Dissolution of Nuclear Fuels, Part II. Nichrome in Nitrate Solutions, IDO-14575 (1961).

VIII. APPENDIX

The dissolution rates of the elements iron, nickel, and chromium at high potentials (Figure 8) are as expected on the bases of the potentials necessary to form the higher oxidation states of these elements ($\text{Fe} > \text{Ni} > \text{Cr}$). The high current densities measured for iron above ~ 1.6 volts are due mainly to oxygen evolution. The separate rates for iron dissolution and oxygen evolution are indicated by the broken lines. Franck and Weil⁽¹⁶⁾ have measured the individual rates of oxygen evolution and iron dissolution at these high potentials, thereby definitely proving the existence of a transpassive region for pure iron.

The addition of chromium to iron is known to reduce the corrosion rate in the passive region. The reason for this is evident from the curves in Figure 8, where it can be seen that chromium has the lowest dissolution rate at low potentials. In the transpassive region, chromium readily dissolves, so that iron or nickel alloys containing chromium will dissolve more easily the higher the chromium content. This was known from previous studies conducted in 1N sulfuric acid solution, and it is also found to be true in nitrate systems (Figure 9).

The electrolytic dissolution of Nichrome (80% Ni, 20% Cr) in nitrate solutions carried out in this laboratory was reported earlier.⁽¹⁷⁾

CPP-S-2192

Figure 8

Anodic Dissolution of Pure Iron, Nickel, and Chromium in $6M HNO_3$ at $25^\circ C$

CPP-S-2193

Figure 9

Effect of Chromium Content on the Anodic Dissolution of Iron-Chromium Alloys at $25^\circ C$ in a Solution Containing $1M HNO_3$ plus $4M NO_3^-$ from Fe^{+3} and Cr^{+3} Nitrates in the Ratio Corresponding to the Alloy Composition

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION