

AEC RESEARCH AND DEVELOPMENT REPORT

ORNL-2239 *cy 4A*
Chemistry-Separation
Processes for Plutonium and Uranium

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LABORATORY DEVELOPMENT OF THE DAREX PROCESS. I. DISSOLUTION OF A NICKEL-CHROMIUM ALLOY

M. L. Hyman

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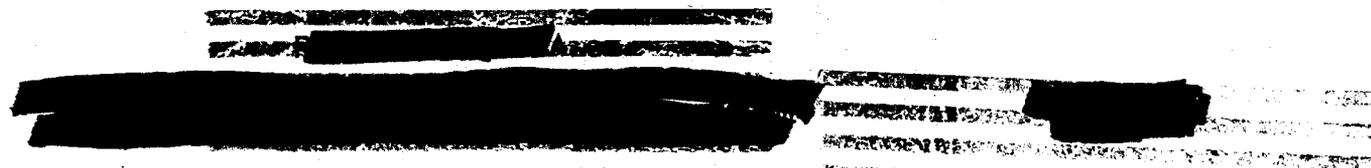


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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

LABORATORY DEVELOPMENT OF THE DAREX PROCESS.

I. DISSOLUTION OF A NICKEL-CHROMIUM ALLOY

Covering work done July 1955-November 1956

M. L. Hyman

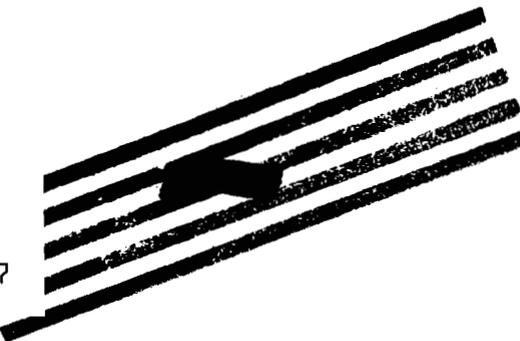
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0.0 ABSTRACT

The laboratory development of the Darex process, a proposed method for the dissolution of oxidation-resistant fuel elements incorporating chromium-containing alloys, is presented. The fuels are dissolved in dilute HCl-HNO₃, the residual chloride is removed, and the solution is adjusted to a Purex type feed for conventional solvent extraction of the uranium.

This report covers studies made on the dissolution of a nickel-chromium alloy.

1.0 INTRODUCTION

This report presents the extensive laboratory-scale experiments on dissolution of Nichrome V that were carried out in development of the Darex process. The Darex process is a proposed method¹ for the dissolution of fuel elements incorporating chromium-containing alloys such as Nichrome V or stainless steel. The dissolvent is a dilute mixture of nitric and hydrochloric acids. In current processing schemes for heterogeneous power reactor fuel elements, uranium and/or thorium are recovered by solvent extraction of a nitrate solution resulting from their dissolution. There are two general categories of power reactor fuel elements—those containing chromium alloys such as stainless steel or Nichrome V and those containing zirconium. These metals do not dissolve in most aqueous reagents, but both stainless steel and Nichrome V dissolve readily in dilute aqua regia.

In the Darex flowsheet,² fuel elements are dissolved in dilute aqua regia, residual chloride ion is removed by distillation or oxidation with nitric acid, and the chloride-free solution is adjusted to concentrations similar to those of the Purex process feed. The uranium is subsequently extracted with tributyl phosphate in stainless steel equipment. Although processing of both Nichrome V and stainless

steel--containing fuel elements by this method is visualized, Nichrome V was selected for the first study because it is more difficult to dissolve than stainless steel. Any process developed for Nichrome is, in general, applicable to stainless steel, but the converse is not true.

If it should be required that a reprocessing plant handle, for example, both Nichrome and stainless steel fuel elements, it is obvious that there is an advantage in employing one process utilizing the same head-end apparatus and flowsheet for both kinds of fuel elements. It appears that the Darex process may be generally applicable to the growing class of oxidation-resistant fuel element alloys whose common constituent is chromium. Iron, nickel, aluminum, cobalt, molybdenum, and other metals may or may not be present also, but it is expected that these alloys will be dissolvable in dilute aqua regia. The major advantage seen for Darex is its application to continuous dissolution of a wide range of fuel elements without the necessity of mechanical handling.

Various schemes have been proposed and studied for the dissolution of stainless steel and Nichrome V fuels preceding solvent extraction (Table 1). In the case of the stainless steel fuels, dissolution of the stainless steel jacket in sulfuric acid followed by nitric acid dissolution of the UO_2 fuel was proposed by KAPL³ for the SIR fuels. This process is now being tested at the Idaho Chemical Processing Plant. Mechanical dejacketing and subsequent leaching of the fuel with nitric acid is applicable, perhaps, to certain specific fuel element configurations. (The APPR fuel element is a notable exception.) The Darex process has been selected for intensive study at ORNL.

For Nichrome V fuels, only dissolution in aqua regia and electrolytic dissolution are applicable. These two techniques are used at Y-12 for recovering highly enriched uranium from nonirradiated prototype Nichrome V-containing fuel elements in glass apparatus. Aqua regia is used at Y-12 for dissolution of both whole fuel element

Table 1. Objectionable Aspects of Proposed Dissolution Processes for Fuel Elements Containing Nichrome V and Stainless Steel

Process	Ref.	Disadvantages* for Stainless Steel	Disadvantages* for Nichrome V
Dissolution in HCl; conversion to nitrate solution	4	3,4,6	Ineffective
Dissolution in HBr; conversion to nitrate solution	4	3,4,6	Ineffective
Dissolution in H ₂ SO ₄ (dissolve fuel in HNO ₃)	3	3,6,7	Ineffective
Dissolution in chromic acid catalyzed HNO ₃	5	Ineffective	Ineffective
Dissolution in molten metal followed by HNO ₃ dissolution	1,3	1,2,6,8	2,6,8,10
Electrolytic dissolution into HNO ₃	6	6,8	6,8
Carburization and HNO ₃ leach	7,8	1,2,5,8	2,8,10
Mechanical dejacketing and HNO ₃ leach	2	8,9	Ineffective
Darex	2	6	6

*Key to disadvantages:

1. Incomplete dissolution and subsequent loss of uranium.
2. High processing temperature (> 200°C).
3. Hydrogen in dissolution off-gas (safety hazard).
4. Slow dissolution rate.
5. Unreliability of process with various alloys.
6. Premium materials of construction required.
7. Lowered solvent extraction plant capacity.
8. Lack of suitable mechanical equipment.
9. Process not applicable to all fuel configurations.
10. Insufficient laboratory data for evaluation.

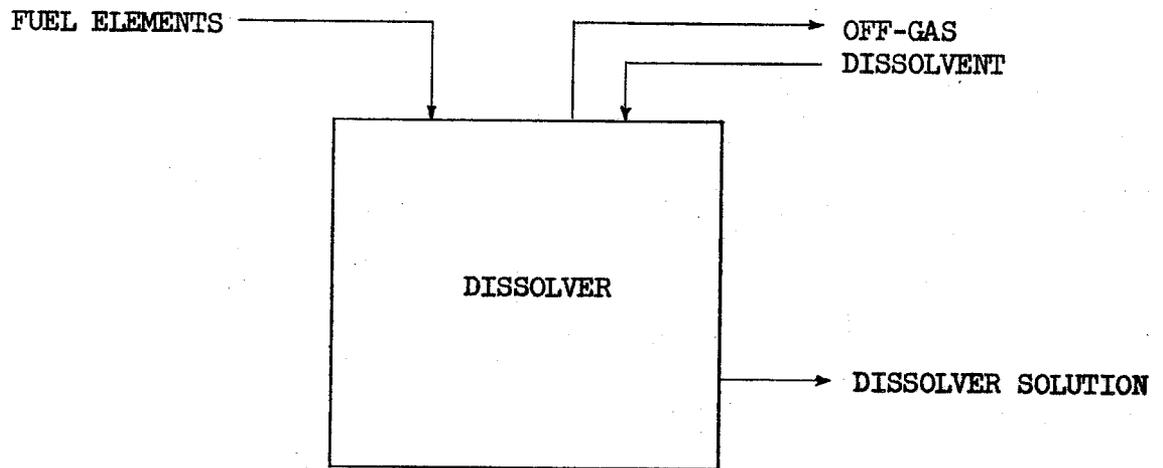
sections and of "tails" remaining in the electrode clamps after electrolytic dissolution. The necessity for processing "tails" and other mechanical difficulties militate against use of electrolytic dissolution for irradiated fuel elements.

Application of the Darex process to zirconium- or aluminum-containing fuel elements is not recommended. Zirconium and its alloys are essentially inert to aqua regia. Aluminum dissolves readily in nitric acid containing mercuric nitrate as a catalyst, and the more drastic aqua regia treatment is therefore not required unless the rapid dissolution rates that may be achieved in aqua regia are of particular interest.

Grateful acknowledgment to J. E. Savolainen of this Division is made for his helpful suggestions, and to W. R. Laing and his associates of the Analytical Chemistry Division for their analytical services.

2.0 FLOWSHEET FOR AQUA REGIA DISSOLUTION OF NICHROME V--CONTAINING FUEL ELEMENTS

The flowsheet for batch dissolution of Nichrome V--containing fuel elements (Fig. 1) in aqua regia uses 6.0 M HNO_3 and 1-2 M HCl as the dissolvent. Based on maximum dissolution rates and minimum solution volumes to be processed, 6.0 M HNO_3 and 2 M HCl are optimum. However, the corrosive action of chloride ion on stainless steel makes removal of the chloride necessary before further processing to protect both the stainless steel solvent extraction apparatus and aqueous waste tanks. Chloride removal by distillation with nitric acid vapor stripping is now visualized. Preliminary data² have shown that the chloride concentration in the feed to the distillation column as well as the concentration of the nitric acid in the stripping vapor have a critical effect on chloride oxidation. That is, in order to recover the chloride values as HCl rather than lose them in the off-gas as Cl_2



Fuel element			
1.0 kg (assumed)		850 g Nichrome V, 150 g UO ₂ (assumed)	
Dissolvent			
HCl, <u>M</u>	1.0	1.5	2.0
HNO ₃ , <u>M</u>	6.0	6.0	6.0
Volume, liters	18.4	9.7	7.5
Dissolver solution			
Ni, g/liter	37	70	91.5
Cr, g/liter	9.3	17.6	22.5
U, g/liter	7.2	13.7	17.7
H ⁺ , <u>N</u>	4.0	2.4	1.4
NO ₃ ⁻ , <u>M</u>	5.4	5.2	5.1
Cl ⁻ , <u>M</u>	0.6	0.9	1.2
Volume, liters	18.1	8.9	6.9
Dissolution temperature, °C	~103	~103	~103
Average dissolution rate, mg/cm ² ·min	13	30	37
Chloride economy (see text)	4.2	6.1	6.0

Fig. 1. Tentative Schematic Flowsheet for Batch Dissolution of Nichrome V-containing Fuel Elements in Aqua Regia

and NOCl , it may be necessary to adjust the HCl concentration in the dissolvent to a lower concentration than would be desirable from consideration of dissolution rates alone. Consequently, a compromise between dissolution and distillation conditions may be required.

The presence of uranium in an actual fuel element, in contrast to the pure Nichrome V used in this study, should have essentially no effect on the dissolution conditions. In the flowsheet shown, only about 5% of the nitric acid specified is required for oxidation of the UO_2 in the fuel element to UO_2^{++} . The anticipated final dissolver composition was calculated from the Nichrome V dissolution data with allowance for the assumed UO_2 content of the fuel element.

The flowsheet data are based on batch dissolution to a small metal heel. The average dissolution rate for complete metal dissolution would, of course, be lower.

Vigorous reaction can be expected to start in the neighborhood of 90°C and to continue readily at about 103°C . The boiling points of the various dissolvents given will never exceed 115°C at 1 atm pressure. Foaming is not serious, but a batch dissolver should be provided with at least 100% freeboard to provide for too rapid reaction.

Materials for construction of the head-end system have been suggested and are being tested.⁹ These include tantalum, titanium, and glass-lined steel. Crystal-bar zirconium may also be suitable for use in the process.

3.0 GENERAL CONSIDERATIONS

3.1 Theories of the Behavior of Aqua Regia

Despite the fact that aqua regia has been known since the time of the alchemists, when it was used for dissolving the noble metals, there have been no attempts to study at length the unique behavior

of this combination of hydrochloric and nitric acids. The preponderance of literature is concerned with describing optimum proportions of the two acids for rapid dissolution of the noble metals or, more recently, some of the base metals such as iron and nickel.

Mellor¹⁰ discusses the theories of the nineteenth century. He reviews Gay-Lussac's inference that the peculiar action of aqua regia on metals is due to the chlorine liberated by its decomposition, the nitrosyl chlorides passing off as they do when the liquid alone is heated. However, Moore,¹¹ writing in a preliminary paper on aqua regia, questioned whether the efficacy of aqua regia is due to chlorine liberated via the now accepted reaction



He suggested the possibility that the chloride ion acts as a catalytic agent in oxidation reactions. The preliminary nature of the work precluded any definitive description of the reaction mechanism.

Briner¹² confined the reactants to a sealed tube and showed that the above equation is reversible. At equilibrium, a stabilized aqua regia is formed, consisting of the aqueous acid phase and a red liquid phase containing liquid NOCl and chlorine.

A current view on the action of aqua regia on noble metals has been summarized¹³ by the explanation that the presence of chloride ion increases the value of the reduction potential of the metal. This has been shown, for example, by comparison of the E° values for the reduction of gold and silver with and without chloride present. Although this theory may be applicable also to the action of aqua regia on base metals and alloys, it is probably only one of many reaction mechanisms involved in a dissolution.

3.2 Previous Open-literature Studies

Most investigators^{14,15} suggest that for dissolving the noble

metals, i.e., gold and platinum alone or alloyed, a volume ratio of about 4 parts of concentrated (38%) hydrochloric acid to 1 part of concentrated (70%) nitric acid is best. Dilution of this mixture with as little as 14% to as much as an equal volume of water has been advised.

Bonilla¹⁶ recognized in 1932 that no work had been done with aqua regia of low hydrochloric acid content and that a study of the dissolving of base metals in this reagent had not been made. He determined that for nickel the maximum dissolution rate occurred with aqua regia consisting of 1 ml of 38% HCl and 13 ml of 70% HNO₃ (0.88 M HCl and 14.7 M HNO₃). The acid was aged 30 min and maintained at 15-20°C during dissolution. The maximum dissolution rate of 7.0 mg/cm².min was obtained in an immersion time of about 30 sec. This extremely short immersion time, which measures only the initial dissolution rate, makes the data valueless for comparison to the work reported here. Using a similar procedure for low carbon steel (0.2 to 0.3% C), Bonilla found a maximum dissolution rate of 117 mg/cm².min with aqua regia made from 7 ml of 38% HCl and 20 ml of 70% HNO₃ (3.2 M HCl and 11.7 M HNO₃). The acid was aged 10 min, which was the optimum time for this aqua regia composition to achieve maximum corrosiveness, and allowed to boil during its short action on the metal. For its action on iron, Bonilla found that, up to about 9.4 M HCl in concentrated aqua regia, the corrosiveness increased with aging time after the two component acids had been mixed. For example, for an acid composition 4.5 M HCl and 10.2 M HNO₃, the optimum aging time was about 20 min, while for acid 9.4 M HCl and 3.8 M HNO₃ the optimum aging time was about 90 min. The acids were aged at room temperature.

3.3 Previous Project Studies

A study of dissolution of Nichrome V--containing fuels was made at the Idaho Chemical Processing Plant in late 1954.¹⁷ Using thin Nichrome V wire, preliminary experiments were performed on the dissolution of the metal in various acids. Dissolution rates at

boiling temperatures in various sulfuric acid concentrations and in nitric acid were too low to be of use. In 85% phosphoric acid the metal was penetrated at a rate of about 3 mils/hr. A large excess of acid was used. Dissolution rates were reported for aqua regia mixtures made up with concentrated acids for the range 5 to 75 vol % hydrochloric acid, the balance being nitric acid. The maximum dissolution rate of 261 mils/hr ($92.5 \text{ mg/cm}^2 \cdot \text{min}$) was reported to occur with boiling 60 vol % HCl--40 vol% HNO_3 (7.38 M HCl--6.33 M HNO_3). It was recognized, as it had been earlier with stainless steel dissolutions,⁴ that chloride removal is imperative if the feed solution is to be extracted in stainless steel equipment; evaporation of the dissolvent with excess nitric acid gave a chloride-free solution.

Later,¹⁸ a Nichrome V-uranium fuel alloy was dissolved in both boiling concentrated phosphoric acid and aqua regia. For the former, the dissolving time was much longer and a large fraction of the uranium remained as an insoluble residue. A residue also resulted from the aqua regia dissolution: 3 wt % for unoxidized fuel and as much as 13 wt % for oxidized metal. In both cases silica was about 1.5 wt % of the initial specimen weight. Little, if any, uranium remained in the insoluble fraction, which, except for the highly hydrated silica, was reduced by prolonged digestion in the dissolvent. These insoluble nickel and chromium oxides were easily filterable.

3.4 Composition of Nichrome V Metal

Nichrome V is a proprietary alloy whose nominal composition is 80% nickel and 20% chromium. It is manufactured by Driver-Harris Company, Harrison, New Jersey. (The designation "V" distinguishes this particular alloy from earlier, and now discontinued, compositions, although Nichrome III, 85% nickel--15% chromium, is still available.) The metal finds wide use in electrical heating elements

because of its resistance to oxidation at elevated temperatures.

The metal used in these dissolution studies was obtained from the stock of the ORNL Metallurgy Division (Table 2). The metal was analyzed by ORNL Special Analysis Laboratory. Included in Table 2 for comparison are the compositions of two samples of Nichrome V submitted by General Electric Company to the U. S. Bureau of Standards for its work in developing coatings for this alloy. These analyses were performed by Driver-Harris Company; the metal is probably representative of material that would be used in certain fuel elements.

3.5 Corrosion Resistance of Nichrome V

In general, Nichrome V shows fair to good corrosion resistance to all aqueous environments except aqua regia. In corrosion studies,²⁰ the metal has demonstrated fair to excellent resistance to sulfuric, sulfurous, and organic acids, alkalies, salt solutions, and dry gases. At 25°C 37 wt % hydrochloric acid barely attacked Nichrome V, but at 96°C the dissolution rate was 0.53 mg/cm².min. The effect of hydrofluoric acid at room temperature was negligible, but at elevated temperatures attack was severe. Phosphoric acid had no effect except at elevated temperatures. In terms of dissolution rates, nitric acid of all concentrations and at all reasonable temperatures had little effect on Nichrome V. The most rapid dissolution with this acid occurred with red fuming nitric acid containing 13 to 18% dissolved NO₂ for which a corrosion rate of 35.4 in./year (1.46 mg/cm².min) at 108 to 170°C was reported for a 6-hr test.

4.0 DISSOLUTION EXPERIMENTS

The laboratory-scale dissolution experiments were designed to

Table 2. Composition of Nichrome V^a

Constituent	Amount, %			
	I ^b	II ^b	III ^c	IV ^c
Ni	77.84	78.69	76.89	78.51
Cr	19.18	19.80	19.13	19.11
C	0.18	0.18	0.03	0.04
Mn	0.31	0.05	1.80	0.46
Si	1.19	0.52	1.28	1.32
Cu	0.021	0.098	0.03	0.03
Fe	0.32	0.25	0.61	0.25
Zr	0.15	0.04	0.09	0.12
Al	0.14	0.01	0.10	0.11
Ca	Not deter- mined	Not deter- mined	0.038	0.050

^aSample sources: (I) 5/16-in. hexagonal rod used in this study; (II) 0.058-in.-thick sheet used in this study; (III) sample A of reference 19; (IV) sample B of reference 19.

^bAnalyzed by ORNL.

^cAnalyzed by Driver-Harris Company.

determine optimum dissolvent compositions and temperatures of dissolution, dissolution rates possible under these conditions, the metal concentrations of the final solutions, changes in dissolvent composition as the reaction proceeded, and the efficiency of utilization of the reagents. Since the present flowsheet calls for removal of the chloride before the solvent extraction step, minimization of chloride in the dissolvent is desirable. For this reason, dissolution in hot dilute aqua regia was most extensively studied, although some experiments were made with cold concentrated aqua regia. Dissolution was satisfactory in both reagents. Dissolution of Nichrome V in hot concentrated aqua regia was not practicable. Above 25°C the reaction is vigorous, with considerable foaming and gas evolution.

4.1 Dissolution in Hot Dilute Aqua Regia

With total acid concentrations of about 10 N and lower the dissolution reaction is relatively quiet. There is little initial foaming and any foam that does form can be readily dispersed by cold water on the top of the flask. Once the initial reaction is over, the acid can be gently refluxed with mild applications of heat to increase the reaction rate.

a. Dissolution Rate

Optimum Acid Concentration. At all constant HCl concentrations except 0.5 M HCl, the maximum dissolution rate of Nichrome V in boiling dilute aqua regia occurs at 6 M HNO₃ (Fig. 2). At constant HNO₃ concentration the dissolution rate increases rapidly with increasing HCl concentrations up to a maximum value of 2-4 M HCl depending on the HNO₃ concentration (Fig. 3).

Variation with Time. The reaction rates decreased exponentially with time (Fig. 4), but were erratic. The irregularity of the data is not surprising since the reaction rate depends on factors other

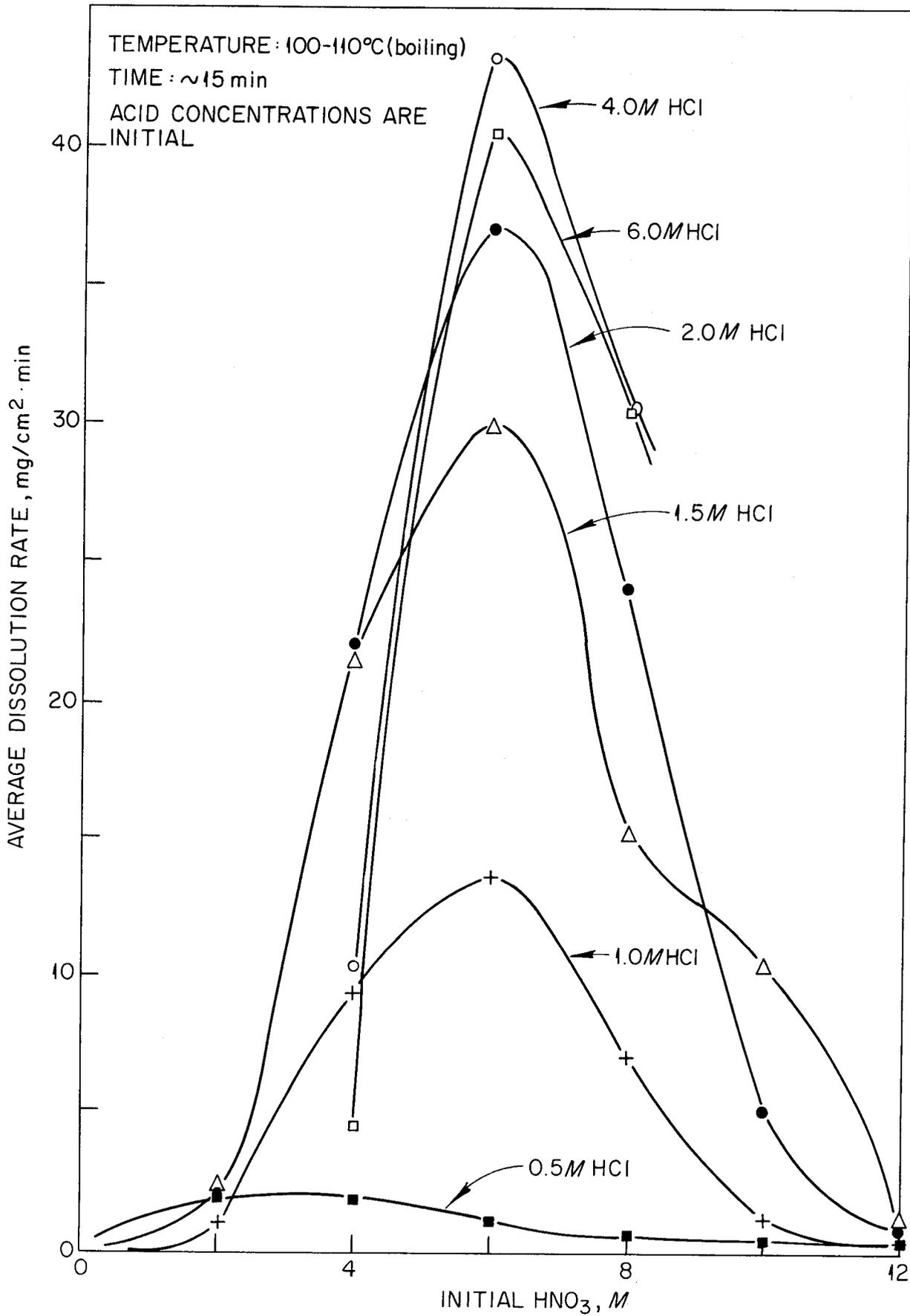


Fig. 2. Effect of Nitric Acid Concentration on Rate of Dissolution of a Chromium-containing Alloy in Hot Dilute Aqua Regia.

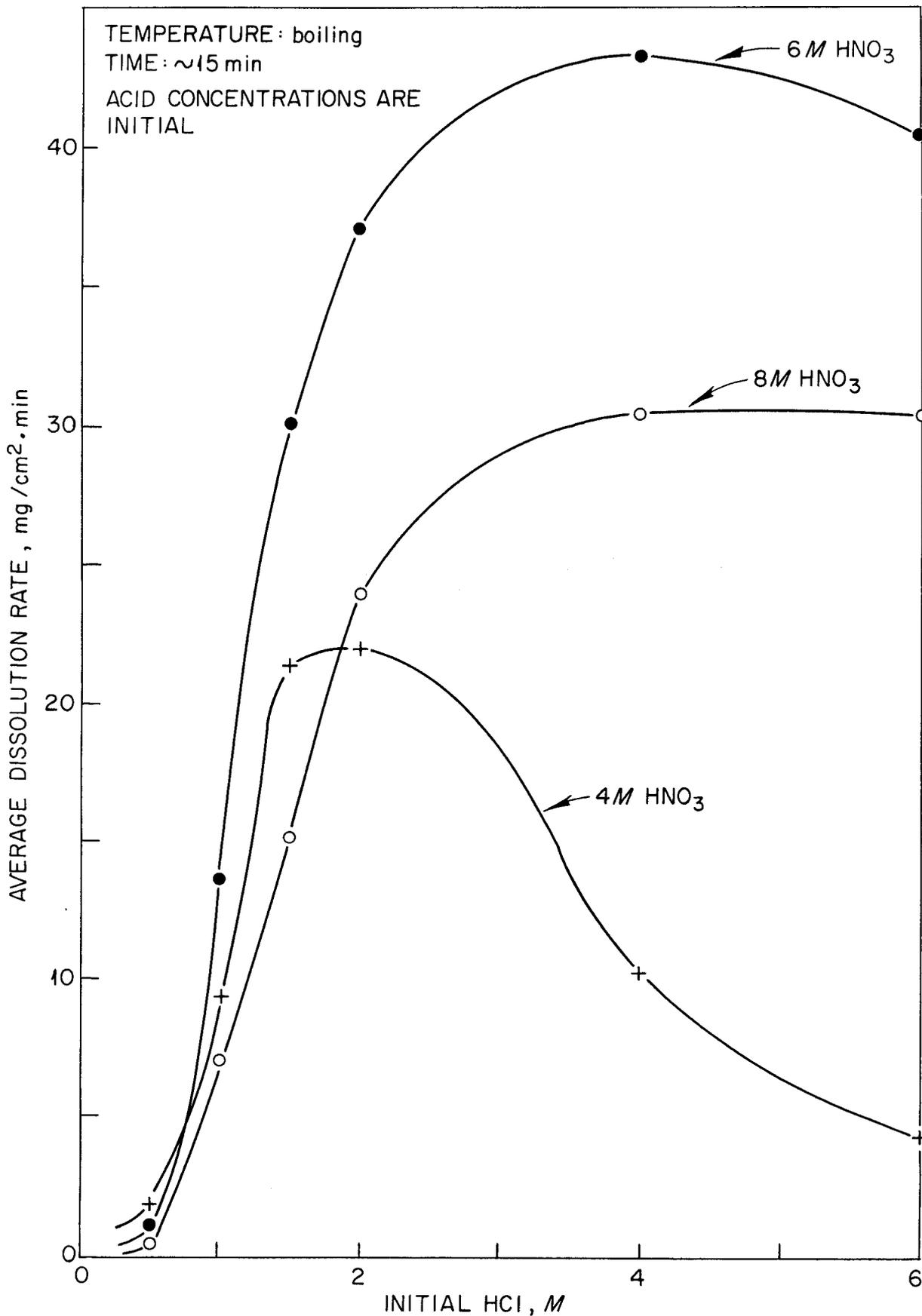


Fig. 3. Effect of Hydrochloric Acid Concentration on Rate of Dissolution of a Chromium-containing Alloy in Hot Dilute Aqua Regia.

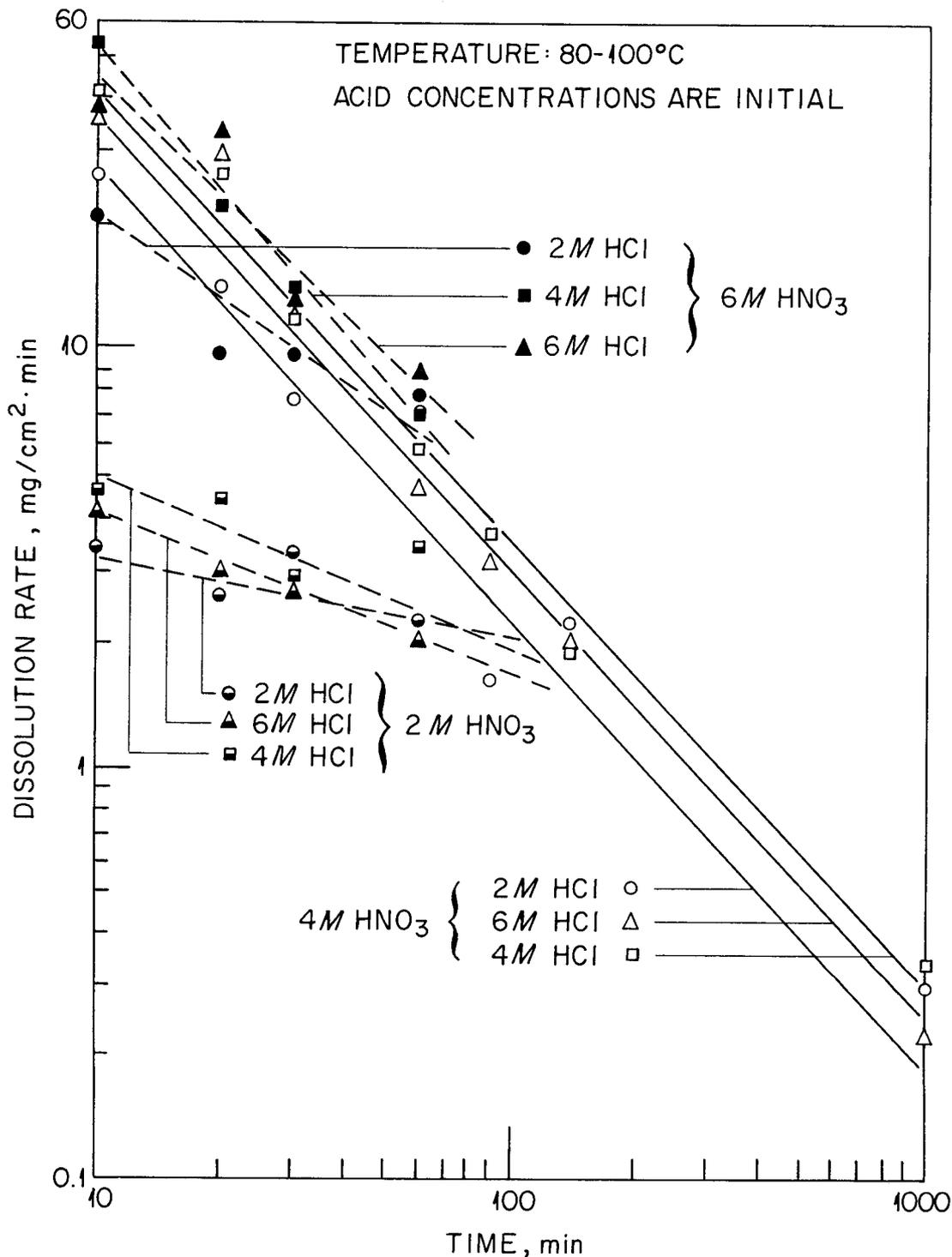


Fig. 4. Progressive Dissolution Rate of a Chromium-containing Alloy in Hot Dilute Aqua Regia. Data obtained in 10-min dissolutions of ~11-g specimens of ~8 cm² area in 60 ml of acid.

than dissolvent composition, e.g., temperature, metal concentration, acid aging time, heat flux, acid-metal ratio, specimen condition, etc. For a given nitric acid concentration, varying the HCl concentration in the range 2-6 M did not significantly affect the rate of change of the reaction rate. The empirical equation for the dissolutions shown in Fig. 4 is of the form

$$R = kt^n$$

where R is the dissolution rate,* $\text{mg}/\text{cm}^2 \cdot \text{min}$; t is the time, min; and n and k are empirical constants. The curves in Fig. 4 are specific for the experimental conditions used. The form of the curve for the longest series studied, 4 M HNO_3 , is uncertain beyond about 200 min, although the departure from a straight line at 1000 min is not great. Data are less reliable for the 2 and 6 M HNO_3 series because of scatter.

For at least the first 100 min of the dissolution the rates of reaction increase in the order 2, 4, 6 M HNO_3 . The rates of decrease of the reaction rate for 6 and 4 M HNO_3 appear to be of the same magnitude, but for 2 M HNO_3 the rate is much steadier. The observations are augmented by a plot (Fig. 5) of the average dissolution rate calculated from the weight loss and average surface area after 1 hr dissolution. The rate increases markedly as the HNO_3 concentration approaches 4 M, but the change in rate is small beyond this concentration. The closeness of the curves for 4 and 6 M HCl confirms that there is little difference between the rates for these two acid concentrations.

There is a variation of 30-150%, and even 500% in one case, for dissolution rates determined from data obtained by direct dissolution of a specimen for 15 min (Fig. 2) and those determined from data obtained in 10-min dissolution increments (Fig. 4). The main reason for the discrepancy lies in the temperature of the acid, which was

*The penetration rate, mils/hr, for Nichrome V of specific gravity 8.4 is found by multiplying the dissolution rate in $\text{mg}/\text{cm}^2 \cdot \text{min}$ by 2.82.

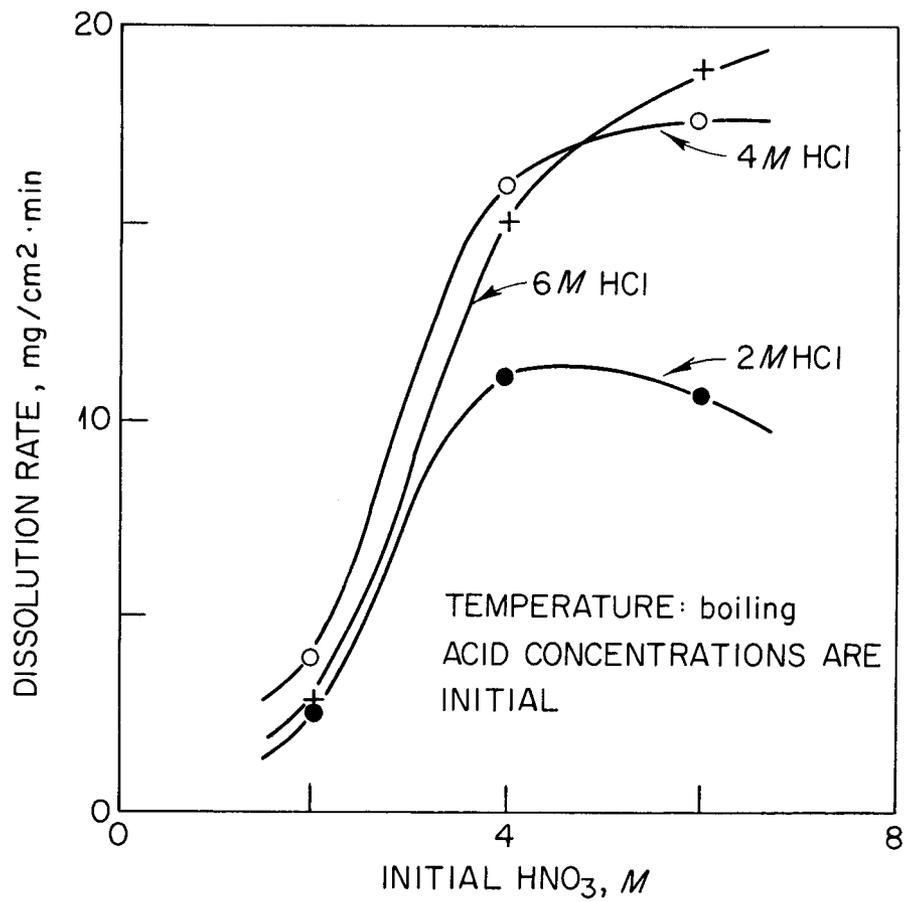


Fig. 5. Average 4-hr Dissolution Rate of a Chromium-containing Alloy in Hot Dilute Aqua Regia.

generally 10-20°C lower in the 15-min dissolution. A second reason is the difficulty in reproducing dissolution data. Discrepancies will naturally occur when slightly varying techniques are used. Exact duplication of experimental conditions is difficult without time-consuming effort.

b. Metal Concentrations

The final metal concentrations obtained by "saturating" the dissolvent, i.e., by allowing the reaction to continue until no further reaction was observed, followed very closely the pattern set by the metal dissolution rates. At all constant HCl concentrations except 0.5 M, the maximum metal concentration was obtained with 6 M HNO₃ in the aqua regia (Fig. 6). With 6 M HNO₃ initially, the metal concentration increased rapidly and linearly with increasing hydrochloric acid concentration up to about 2 M HCl and then leveled off (Fig. 7). A metal concentration of about 138 g/liter cannot be exceeded under the dissolution conditions described here.

c. Changes in Dissolvent Composition

Chloride Ion. At all constant initial HCl concentrations, the fractional decrease of initial chloride ion that remained in the dissolver solution became greater as the HNO₃ concentration was increased (Fig. 8). The values on the axis of ordinates of Fig. 8 (and, similarly, of Figs. 9 and 10) were calculated as follows:

$$\text{Percent decrease of Cl}^- \text{ concentration} = \frac{100(C_i - C_f)}{C_i}$$

where C_i is the number of moles of Cl⁻ initially in the solution and C_f is the final number found by analysis. This computation allows for the reduction in dissolvent volume where this occurred. Chloride leaves the system in the vapor phase as Cl₂ and NOCl, which are generated by the nitric acid--hydrochloric acid reaction.

The substantial decrease in chloride concentration at high nitric acid concentrations explains the almost negligible effect of the more concentrated aqua regia, when hot, on Nichrome V. The excess nitrate

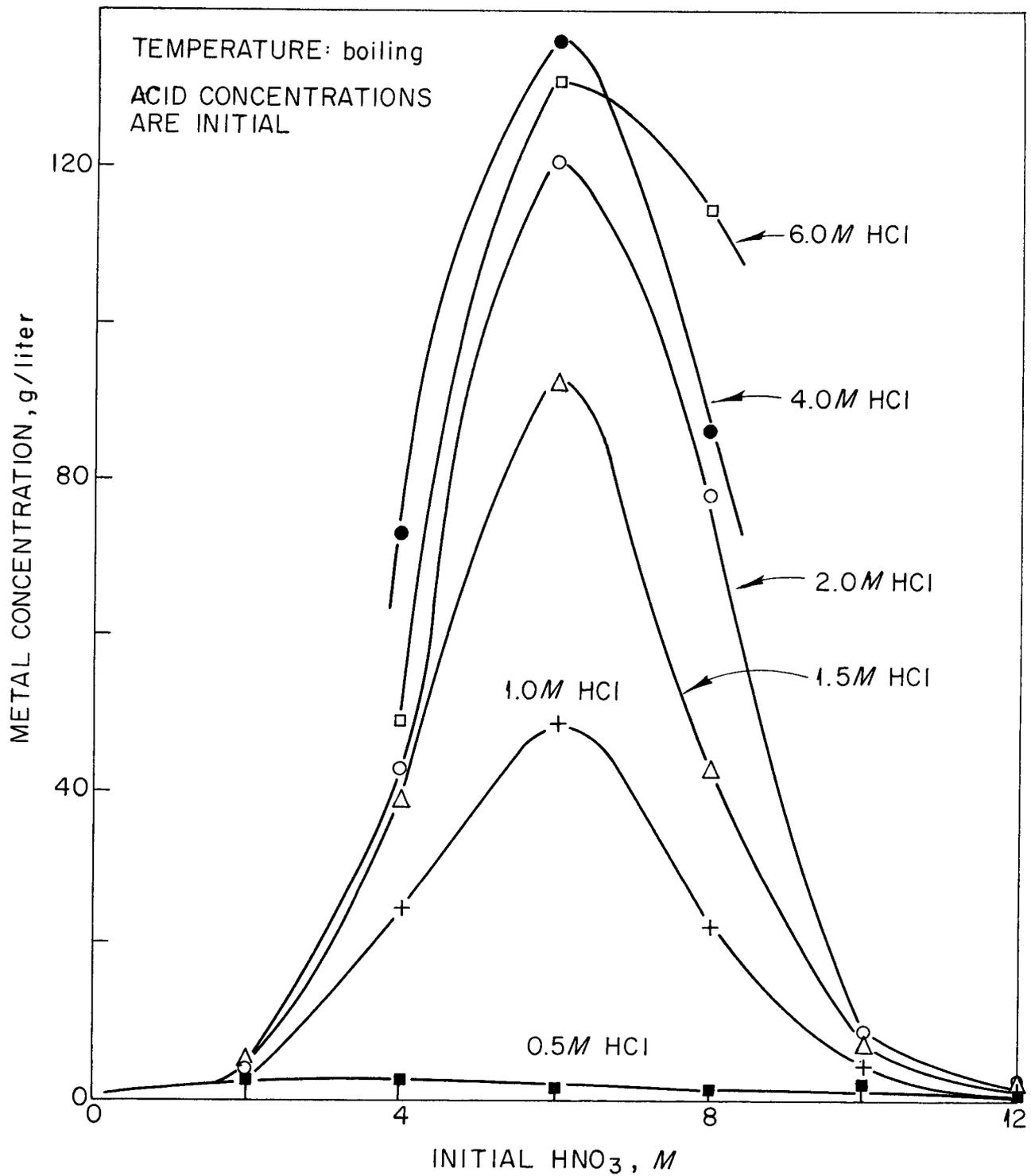


Fig. 6. Effect of Nitric Acid Concentration on Metal Concentration of Solution in Dissolution of a Chromium-containing Alloy in Aqua Regia to Point of No Reaction.

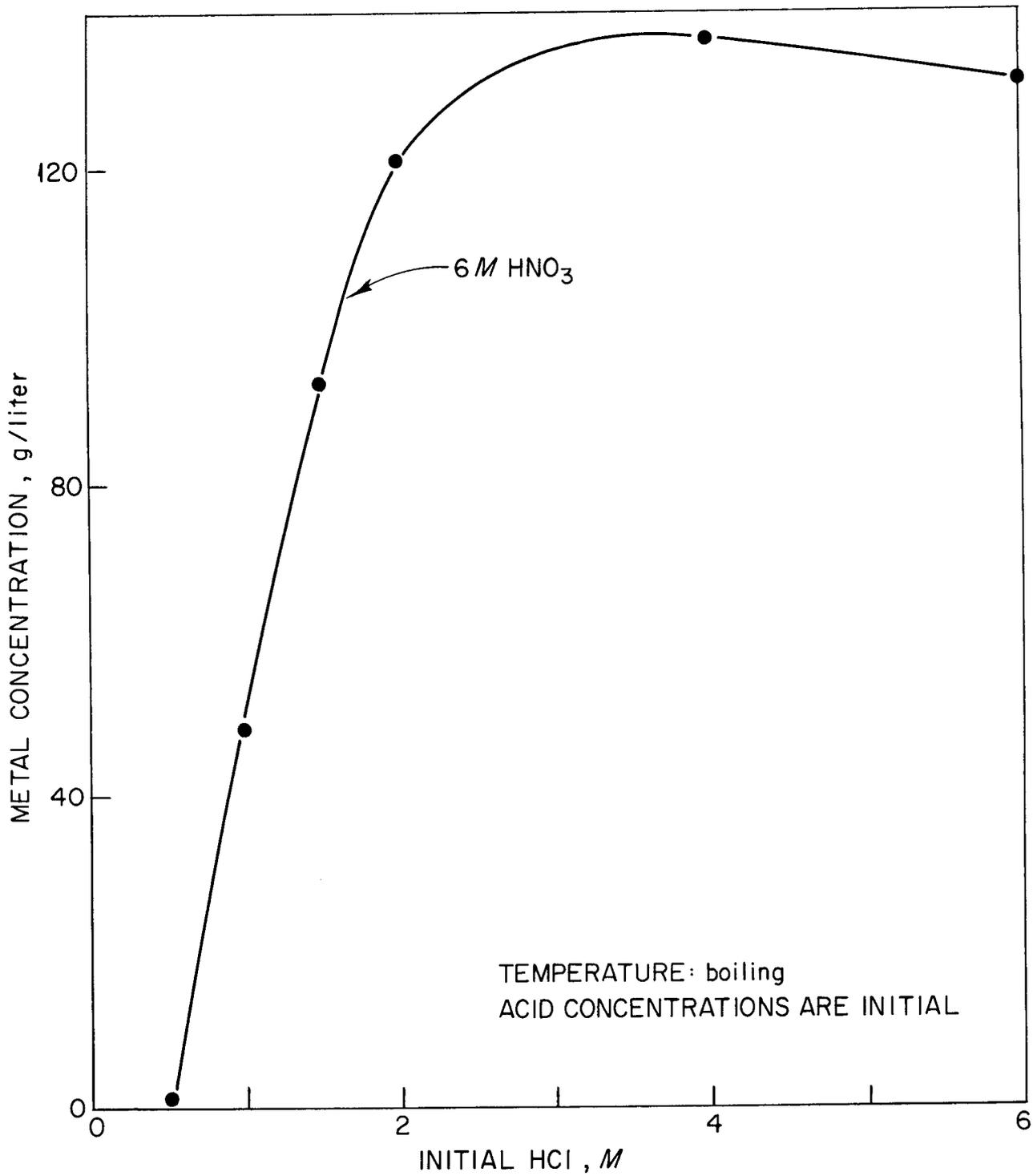


Fig. 7. Effect of Hydrochloric Acid Concentration on Metal Concentration of Solution in Dissolution of a Chromium-containing Alloy in Aqua Regia to Point of No Reaction.

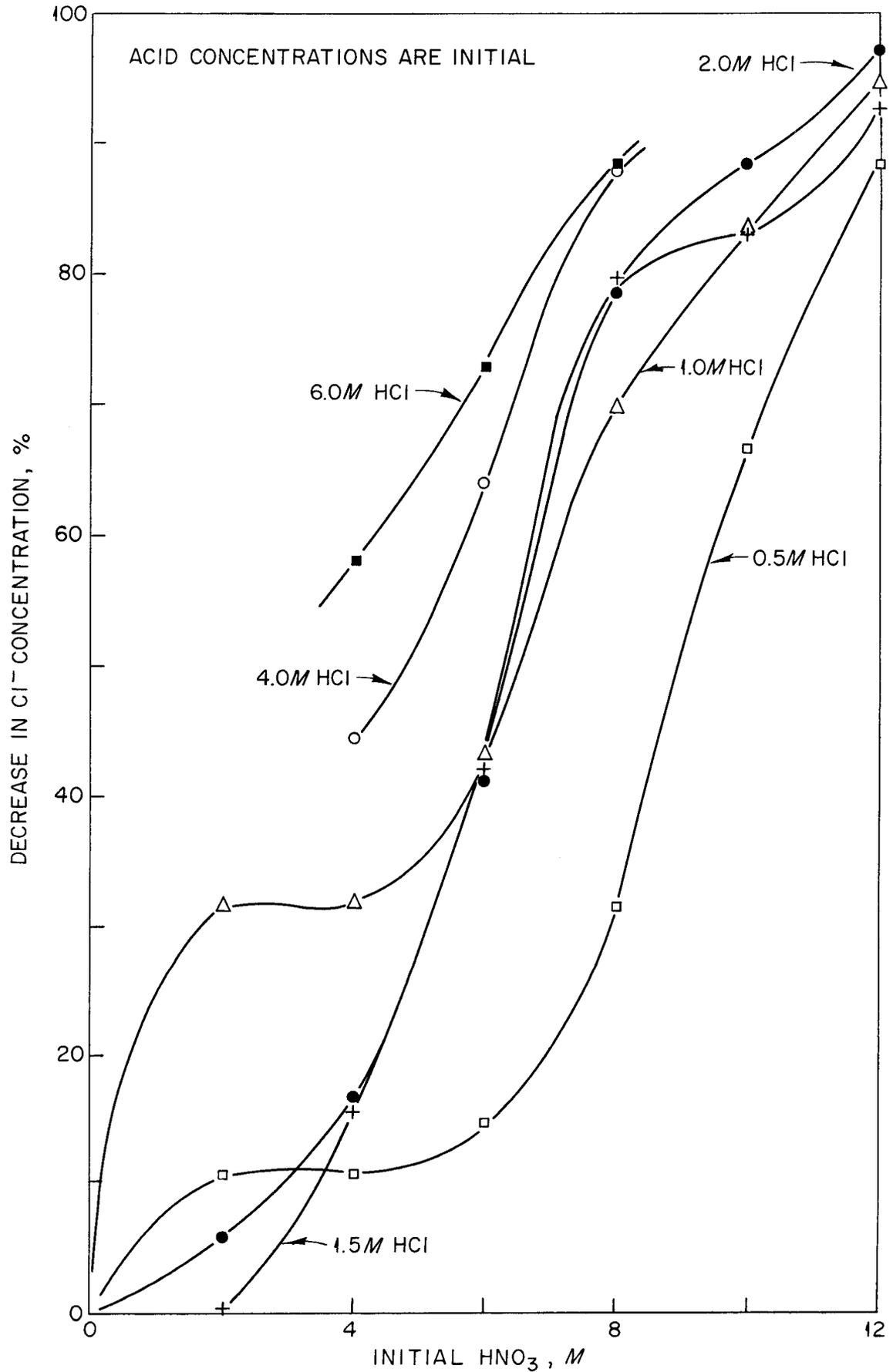


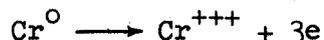
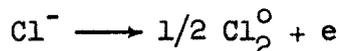
Fig. 8. Decrease in Chloride Concentration during Dissolution of a Chromium-containing Alloy in Aqua Regia.

ion oxidizes the chloride ion to Cl_2 and NOCl rapidly, and these are driven into the vapor phase so quickly by the mass action effect that there is no time for the gross reaction between these products and the metal. Morgan and Bond²¹ showed in their brief work on the mutual decomposition of nitric and hydrochloric acids that chloride ion decomposition is very rapid at first; it can be deduced from their data that the chloride decomposition rate is markedly affected by nitrate ion concentration. They found such a rapid decomposition rate at the highest nitrate concentration studied, 6.27 M, that it is evident that at 8-12 M NO_3^- the decomposition must be immediate and almost quantitative.

It is noteworthy that this mutual acid decomposition takes place even in the presence of Nichrome V metal. The concentrated aqua regia, which has a characteristic orange-brown color, turns darker when heated, evolves copious amounts of brown NO_2 fumes, and continues to do so until the chloride is depleted. The metal specimen remains almost unaffected.

Hydrogen Ion. Hydrogen ion consumption follows closely the metal concentration curves. At constant initial HCl concentration, the fractional decrease of initial hydrogen ion that remained in the dissolver solution was a maximum with 6 M HNO_3 in the aqua regia (Fig. 9). It is apparent that H^+ enters the metal dissolution reaction and is relatively unaffected by its own high concentration in regard to the HCl-HNO_3 reaction.

Nitrate Ion. The role of the nitrate ion in the reaction is to be the sole oxidizing agent for all the oxidizable species in the reaction. The net oxidation reactions, ignoring any internal reaction such as $\text{H}_2 \longrightarrow 2 \text{H}^+ + 2\text{e}$, can be written



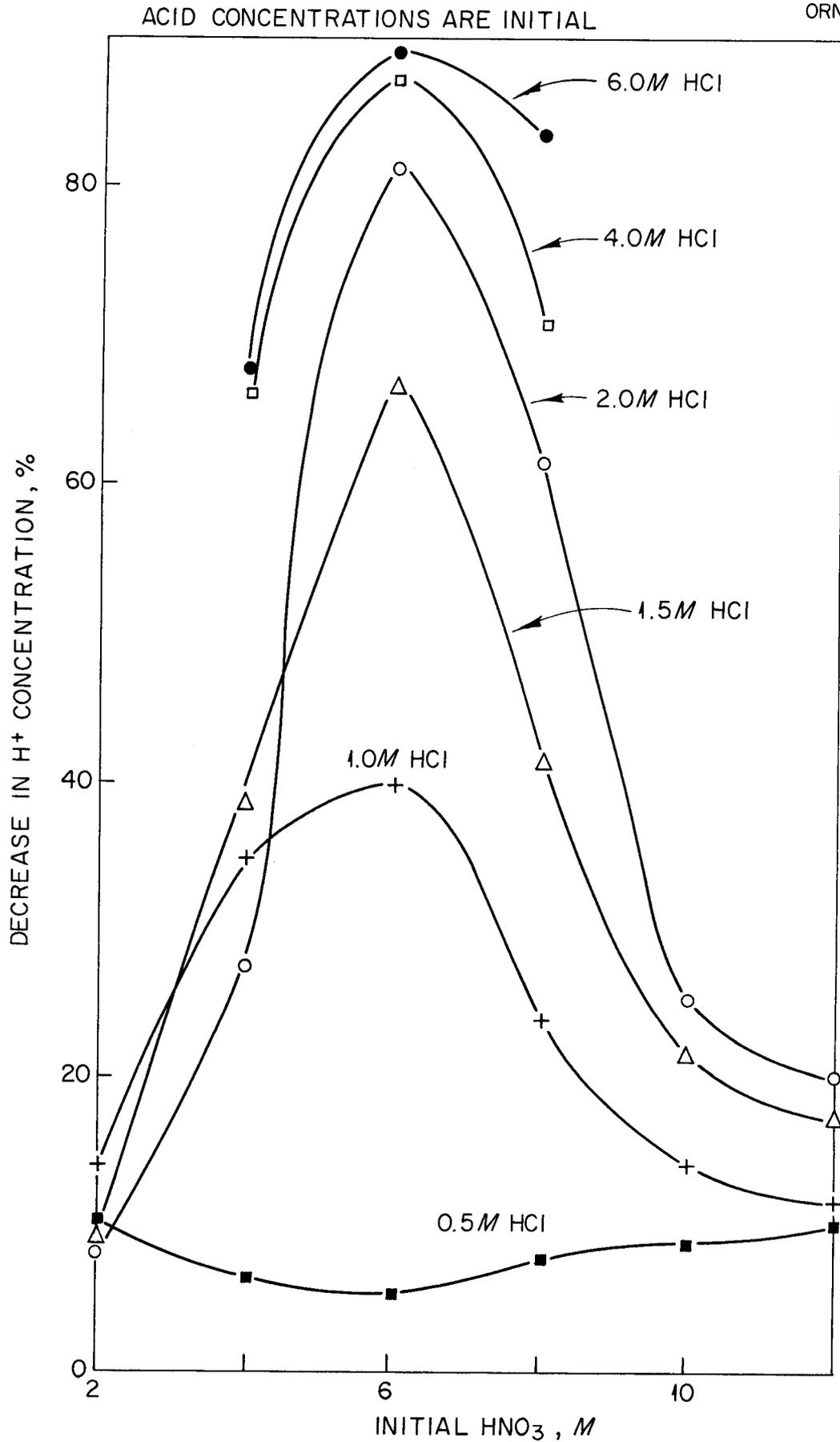
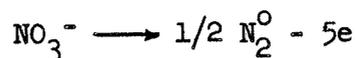
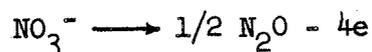
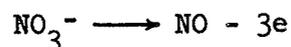


Fig. 9. Decrease in Hydrogen Ion Concentration during Dissolution of a Chromium-containing Alloy in Aqua Regia.

The possible reduction equations* are



A high consumption of NO_3^- would therefore be expected in the runs where considerable metal was dissolved, and also some moderate consumption where Cl^- is oxidized, as in those runs with high nitric acid concentrations. This is found to be the case (Fig. 10). The NO_3^- concentration of the dissolver solution was calculated from the analysis of the solution. In most runs only small amounts of NO_3^- were reduced. The various errors accumulate in this calculation and consequently only the runs with 1.5 and 2.0 M HCl were plotted.

d. Experimental Procedure

Test specimens 1 in. long were cut from 5/16-in. hexagonal Nichrome V rod. The specimens had a mass/area ratio of about 1.4 g/cm². Preliminary runs had indicated that massive pieces of Nichrome, cut from bars, were more convenient to work with than thin flat metal sections with their low mass/area ratio.

The specimens were washed with carbon tetrachloride and acetone and allowed to dry in air. They were then measured and weighed to the nearest decigram. The apparatus set up for the dissolution consisted of a 300-ml round-bottomed flask fitted with a water-cooled reflux condenser and thermometer. The flask was heated directly with a small bunsen burner, which is more convenient than an electric mantle when rapid heating and cooling are necessary.

*Hydrogen is not evolved during dissolution of a metal in aqua regia because of the highly oxidizing nature of the acid. This has been confirmed² for the dissolution of stainless steel, and is certainly true for Nichrome V.

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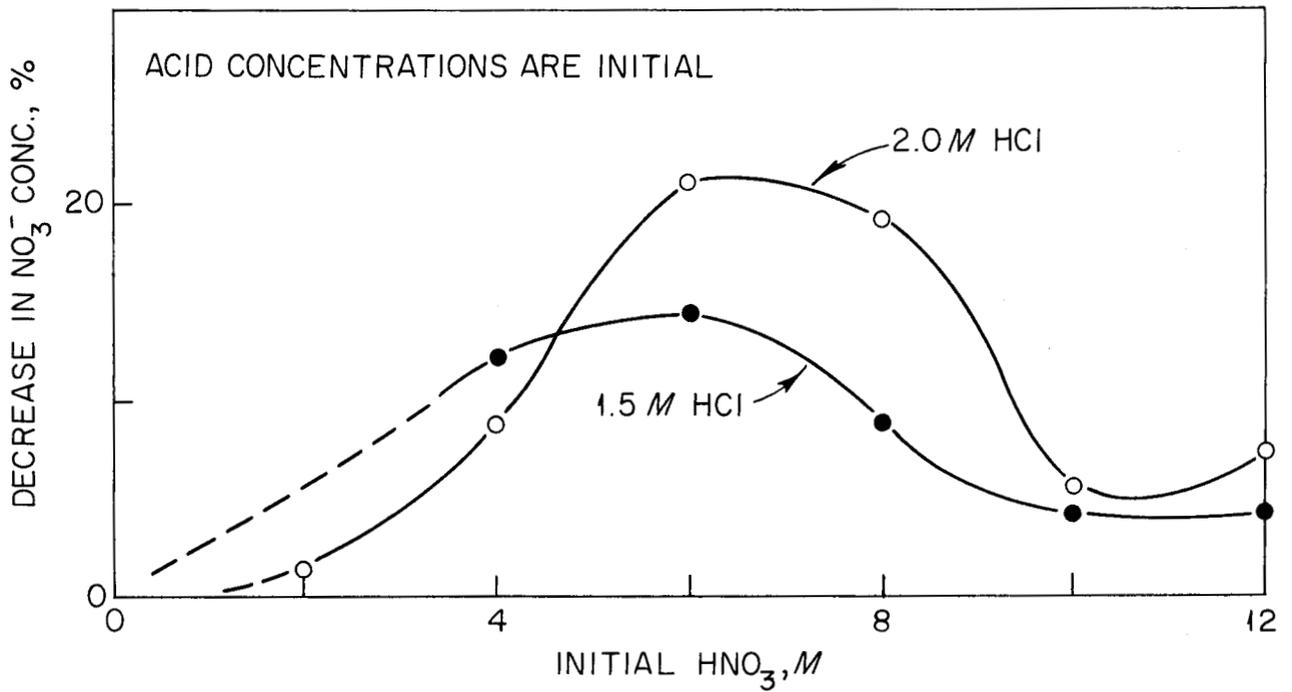


Fig. 10. Decrease in Nitrate Ion Concentration during Dissolution of a Chromium-containing Alloy in Aqua Regia.

The specimens were treated with 60 ml of aqua regia which had been prepared by volume measurement of reagent-grade 38% HCl and 70% HNO₃. The time between mixing the acids and application of heat to the acid to effect dissolution of the Nichrome V specimen never exceeded 2 min. With the metal specimen in place in the flask, the pre-mixed aqua regia was poured into the flask. Except for the runs using the more concentrated acid, there was little or no reaction at this point between the acid and metal (acid temperature about 30°C). Heat was immediately applied to the flask, and the acid was brought to its boiling point as rapidly as possible.

The initiation of the acid-metal reaction was evidenced by vigorous gas evolution at the metal surface accompanied by copious amounts of red-brown nitrogen dioxide fumes in the flask and condenser. In addition, a reaction yielding as little as 1 g of metal per liter in the acid imparts a definite light bluish-green color to the usual yellow or yellow-brown aqua regia. This makes visual recognition of a reaction easy. The reaction was allowed to proceed, in general, for 15 min except in some runs where it was obviously complete much sooner. At the desired time the reaction was quenched by immersion of the flask in cold water and, after cooling, the specimen was removed, washed in water and acetone, dried, measured, and weighed. The average dissolution rate was calculated from the measured weight loss of metal, dissolution time, and average surface area of the specimen.

For those acid compositions where the reaction was incomplete after 15 min, the metal specimen, after being weighed, was returned to the acid in the flask and the solution was again heated to resume the dissolution. In these runs the action was allowed to go to completion—sometimes as much as 1.5 hr—and then the heat source was removed and the solution allowed to cool. The samples were weighed as before and the metal-saturated solution was analyzed. The distinction between "reaction" and "no reaction" when dealing with

metals dissolving in aqua regia is, of course, often a subtle one. Experience has indicated, however, that unless the reaction between the metal and acid is visually observable, then the reaction rate (of the order of $1 \text{ mg/cm}^2 \cdot \text{min}$) is of little practical use for this acid-metal system.

The effect of time on the dissolution rates was determined in a separate study by dissolving Nichrome V specimens in aqua regia prepared from 2, 4, and 6 M HNO_3 and 2, 4, and 6 M HCl . Except for the series using 4 M HNO_3 , specimens were reacted for three 10-min intervals and a final 30-min period. The series with 4 M HNO_3 was reacted for three 10-min, two 30-min, one 50-min, and one 15-hr period. The specimens were 1-in. pieces of rod from the same lot of metal described previously except that a 1/16-in. hole was drilled in one end of the sample. Each specimen was supported with tungsten wire in a 100-ml three-necked round-bottomed flask. The procedure was essentially the same as that described previously except that the specimens were measured and weighed at the end of each reaction period and the new surface area was calculated. In general, the dissolutions were carried out at gently refluxing temperatures, 80-106°C; these varied with acid concentration and time. The specimens were reacted for the desired time, application of heat to the flask was stopped, and the specimen was removed from the flask by means of the tungsten wire. After being weighed and measured, the specimen was replaced in the flask and the next dissolution period was begun.

4.2 Dissolution in Cold Concentrated Aqua Regia

a. Dissolution Rate

Optimum Acid Concentration. The dissolution rate of Nichrome V in concentrated aqua regia at room temperature was a maximum when the acid composition was 3.8 M HCl --10.9 M HNO_3 (Fig. 11), with a sharp drop in rate on either side of this composition. This is quite a

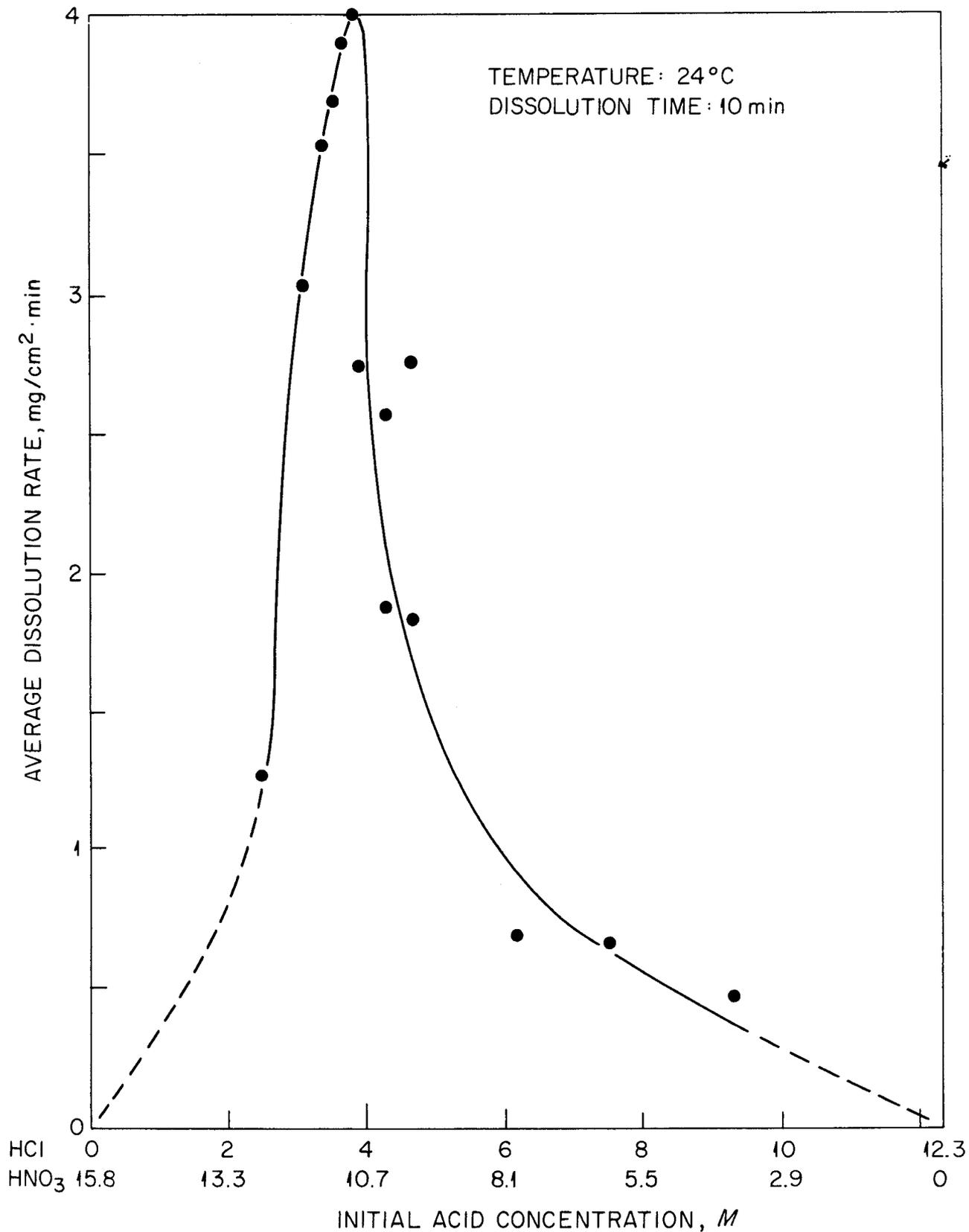


Fig. 11. Rate of Dissolution of a Chromium-containing Alloy in Cold Concentrated Aqua Regia.

different value from the 8.2 M HCl--2.6 M HNO₃ (HCl/HNO₃/H₂O volume ratio of 4/1/1) often recommended (Sec. 3.2) for the most rapid dissolution of the noble metals. The discrepancy between the ORNL work and Bonilla's,¹⁶ who found even less HCl in concentrated aqua regia to be efficacious in dissolving nickel, undoubtedly lies in the extremely short dissolving time that he used and in the 20% chromium content of Nichrome V. The protective action of chromium is substantiated by the work of Schmitz,²² who concluded that the protective agent in alloy steel in the presence of oxidizing agents is chromium while in dilute and concentrated hydrochloric acid it is nickel.

Variation with Time. The dissolution rate for the optimum acid concentration decreased with time (Fig. 12). The slope of the line in Fig. 12 is greater than the steepest lines (4 M HNO₃) in Fig. 4. This indicates that the reaction rate in cold concentrated aqua regia decreases more rapidly with time than in hot dilute acid and, consequently, the reaction is less uniform.

b. Experimental Procedure

Nichrome V sheet rolled from thin-walled tubing was cut into specimens approximately 1.25 cm wide by 4.0 cm long by 0.058 cm thick. The specimens had a mass/area ratio of 0.2 g/cm². Aqua regia of various compositions, prepared from 12.3 M HCl and 15.8 M HNO₃, was aged for 10 min. The specimens were submerged in the aged acid for 10 min, and were then removed, rinsed in water, dried, and weighed. In studying the variation of the rate with time, this procedure was followed repeatedly on the same sample. The temperature was kept near 24°C by immersing the reaction flask in a cold water bath.

4.3 Reaction Stoichiometry

There are too few data to define even approximately the stoichiometry of the Nichrome V--aqua regia reaction. The fact that the

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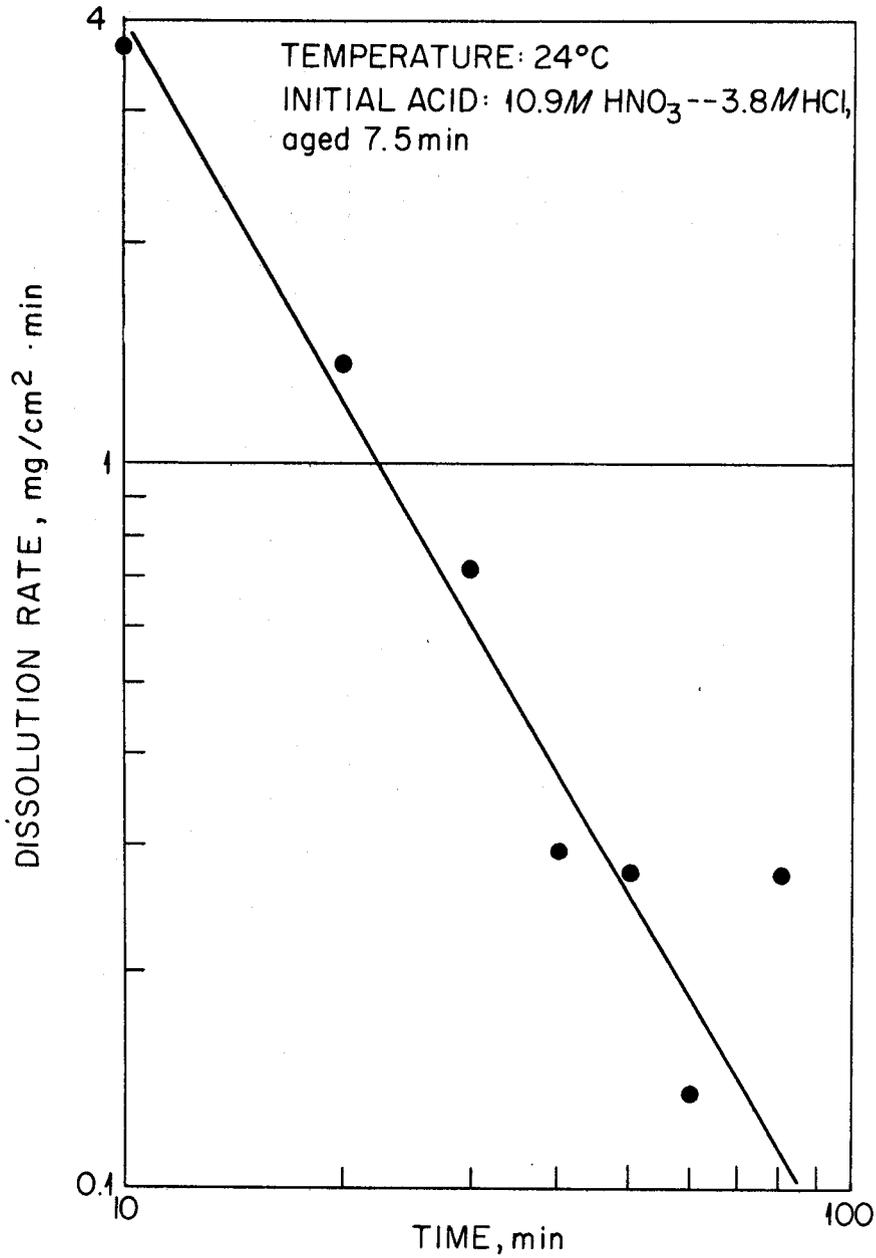


Fig. 12. Progressive Dissolution Rate of a Chromium-containing Alloy in Cold Concentrated Aqua Regia.

reaction is extremely complex is obvious. Morgan and Bond²¹ found that even the $\text{HNO}_3\text{-HCl}$ reaction in some of the dilute solutions used here cannot be defined stoichiometrically. Furthermore, it is well known that the extent of reduction of nitric acid depends on the concentration of the nitric acid as well as on the nature and strength of the reducing agent (here HCl). The presence of a heterogeneous reactant, the metal to be dissolved, complicates the reaction further.

Since in an oxidation-reduction reaction the change in normality of the reductants must equal the change in normality of the oxidants, an attempt was made to determine the average valence change which the nitrogen in the nitrate ion undergoes during the dissolution reaction (Table 3). The number of equivalents of metal ions (Ni^{++} and Cr^{+++}) formed was added to the change in chloride normality, and this sum was divided by the change in nitrate normality. The quotient is the average valence change for nitrogen in the reaction. Only the runs with 2 M HCl could furnish reliable data for this calculation, and even here the results are erratic. It can be seen that the valence change for nitrogen in the reaction appears to be greater than 3.

Confirmation of this is further suggested by examining the off-gas analysis for type 304L stainless steel in 4 M HCl-3 M HNO_3 aqua regia.² The nitrogen valence change calculated from these data appears to be about 3.6 (Table 4).

4.4 Chloride Economy

"Chloride economy" may be defined as the ratio, in equivalents, of dissolved metal (nickel and chromium) to chloride consumed, chloride being consumed when it leaves the dissolution system as a nonrecoverable or nonusable molecular form of chlorine, such as Cl_2 or NOCl . The term is introduced here to distinguish between that chloride involved in some way with the oxidation of the nickel and chromium, and that chloride evolved from the acid-metal system

Table 3. Valence Change of Nitrogen in Dissolution of Nichrome V by Aqua Regia

Initial Concentration (M)		Normality Change		Valence Change of Nitrogen
HNO ₃	HCl	Reductants	Nitrate Ion	
2	2	0.11	0.03	7.2
4	2	0.85	0.35	3.2
6	2	4.34	1.29	3.9
8	2	2.72	1.54	2.8
10	2	0.32	0.54	3.8
12	2	0.06	0.89	2.3

Table 4. Valence Change of Nitrogen in Dissolution of Stainless Steel by 4 M HCl-3 M HNO₃^a

Metal in Dissolvent, g/liter	Nitrogen Valence Change
10.9	3.5
21.8	3.6
32.4	3.5
53.4	3.7

^aFrom Table 7.5 of reference 2.

without affecting the metal. That is, the effect of aqua regia on Nichrome V (or stainless steel) is considered to be due to (a) the formation of Cl_2 (and NOCl) by reaction of HNO_3 and HCl , and (b) the oxidation of nickel and chromium in the Nichrome V by Cl_2 as the one half-reaction, and the reduction of Cl_2 to Cl^- by the metals as the other half-reaction. (The reactions involving NOCl are probably similar, but more complex.)

It is believed that, if reaction (a) proceeds faster than reaction (b), then the excess chlorine generated in (a) goes into the vapor phase, where it is unavailable to the metal and is eventually lost from the system. This is usually the case, since the chloride concentration is always depleted in some measure. If reaction (b) was faster, the chloride ion would be "catalytic" in the sense of being oxidized and reduced continuously. In some aqua regia compositions reaction (a) proceeds so much more rapidly than in others that the metal dissolved per unit of chloride consumed is small.

The evidence for this reasoning is seen in Fig. 13, where chloride economy as the metal/chloride ratio (in equivalents) is plotted against initial hydrochloric acid molarity. The parameter is nitric acid concentration. The maximum utilization of chloride is at about 1.5 M HCl and 6 M HNO_3 . All other concentrations of nitric acid are less efficient. A hydrochloric acid concentration of 2 M is almost as good as 1.5 M for the 6 M HNO_3 curve, but is half as efficient with 4 M HNO_3 . The shape of the 6 M HNO_3 curve in Fig. 13, for example, may be understood by examining Figs. 7 and 8. At low hydrochloric acid concentrations no metal is dissolved, but for 6 M HNO_3 there is still some decrease in chloride concentration due to the HCl-HNO_3 reaction. The net result is a low chloride economy. At high hydrochloric acid concentrations, although the metal concentration is high, the chloride loss is very high. Again, the net result is a low chloride economy. At 1.5-2.0 M HCl the metal concentration and the chloride economy are maximum.

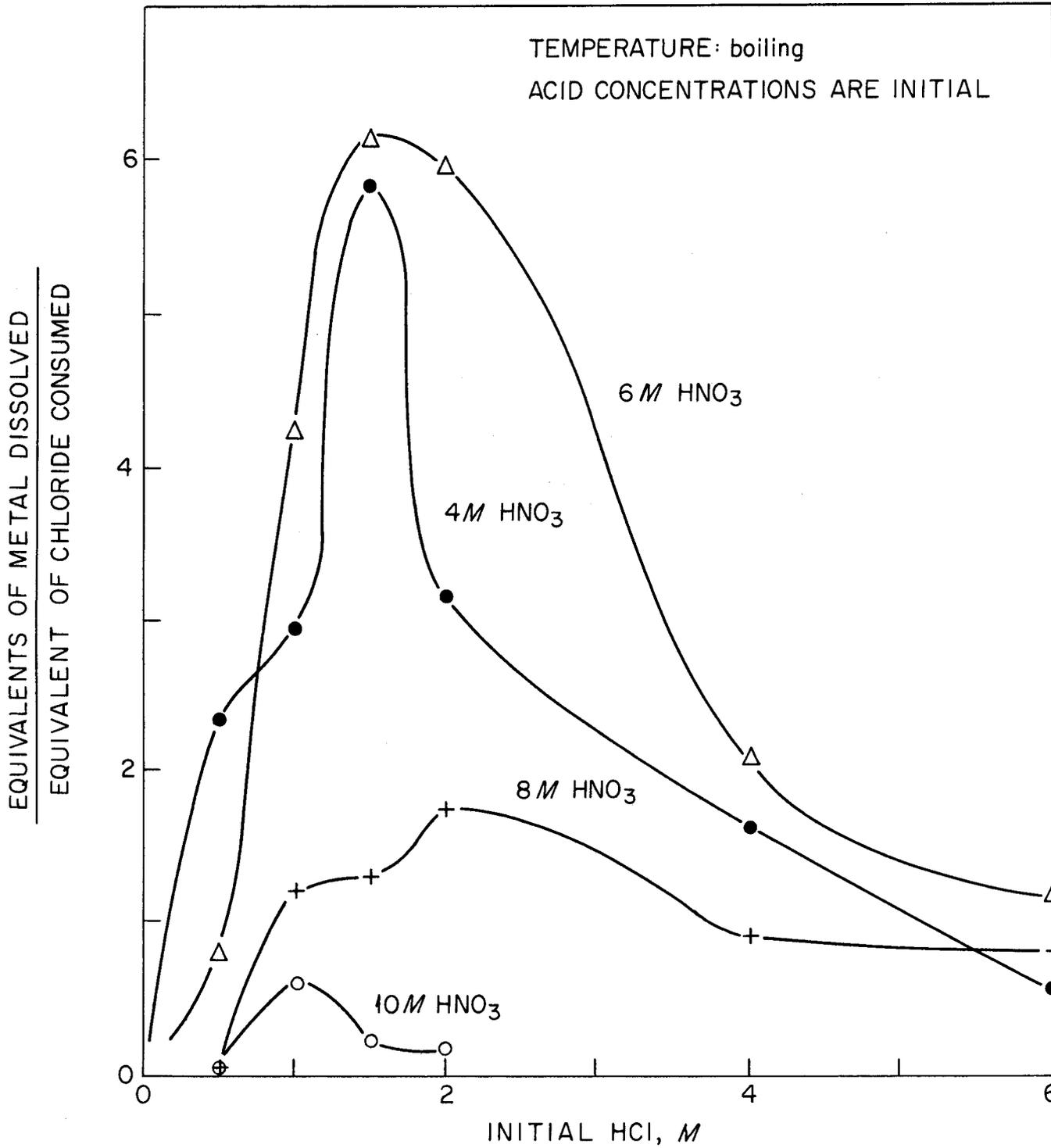


Fig. 13. Chloride Economy in Dissolution of a Chromium-containing Alloy to Point of No Reaction.

4.5 Alteration of Flowsheet Conditions

Considering the various process conditions that determine the flowsheet (Fig. 1), the optimum aqua regia composition for dissolving Nichrome V is 6 M HNO_3 —2 M HCl . However, if later work on chloride removal shows that a concentration of only 1.0 or 1.5 M HCl is desirable in order to limit chloride oxidation, the flowsheet would be altered substantially. For example, with 6 M HNO_3 —1 M HCl , instead of 6 M HNO_3 —2 M HCl , the Nichrome V dissolution rate and metal concentrations are reduced about 60% to 14 $\text{mg}/\text{cm}^2 \cdot \text{min}$, and 49 g/liter respectively. Until more work is done on the removal of chloride from the dissolver solution by a distillation stripping method, the dissolvent composition cannot be established. If a continuous flowsheet²³ was used for stainless steel processing, the actual dissolvent composition at steady state would almost certainly differ from that indicated here as optimum. This would follow from the overall behavior of an integrated dissolver—chloride strip column—rectifier column system when operated continuously.

4.6 Analysis of Solutions

The difficulties encountered in accurately analyzing the dissolver solutions make it worthwhile to outline briefly the successful techniques.

Samples of dissolver solution were submitted to the Special Analysis Laboratory* for determination of chromium, nickel, acidity, and chloride. Chromium was analyzed first by the colorimetric diphenylcarbazide method, but results were erratic. A better method was persulfate oxidation followed by titration of the dichromate with ferrous ammonium sulfate. Nickel was originally determined by the colorimetric dimethylglyoxime method, but results were high. Volumetric cyanide titration was finally used, and with this method

*ORNL Analytical Chemistry Division.

the amount of nickel and chromium in the dissolver solutions agreed within less than 10% with the weight loss of the metal specimens. A few samples were analyzed for Cr(VI), but none was found. Chromium exists in the dissolver solution entirely in the trivalent state.

The acid concentration of samples was determined by complexing the cations with neutral potassium oxalate, followed by potentiometric titration of the free acid. Chloride was determined by a potentiometric silver nitrate titration; sodium pyrophosphate was added first to complex the chromium and release the chloride for titration.

Whenever substantial amounts of Nichrome V were dissolved, gelatinous silica was found in the dissolver solution. Spot checks showed that it absorbed negligibly small amounts of nickel and chromium salts.

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