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DEPASSIVATION OF 304-L STAINLESS STEEL in SULFEX DECLADDING SOLUTIONS

by

E. M. Duke

Development and Corrosion Chemistry Operation
Chemical Research and Development Operation
HANFORD LABORATORIES OPERATION

HANFORD ATOMIC PRODUCTS OPERATION

RICHLAND, WASHINGTON

June 30, 1960

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Work Performed Under Contract AT.(45-1)-1350
between the Atomic Energy Commission and
General Electric Company.

DEPASSIVATION OF 304-L STAINLESS STEEL IN SULFEX DECLADDING SOLUTIONS

I. INTRODUCTION

In the Sulfex process, stainless steel cladding, generally 304-L, is removed from fuel elements by dissolution in boiling four to six molar sulfuric acid(4). When cladding removal is complete, the decladding solution is removed to waste. The exposed fuel cores are rinsed and dissolved in nitric acid.

Instances have been noted, particularly in laboratory studies, in which stainless steel has been passive to boiling dilute sulfuric acid solutions(1,2,3). The passive condition may be produced in a number of ways such as treatment with oxidizing media, exposure to high temperature water in a nuclear reactor, coupling to a noble metal, or simply long term exposure to air.

It is desirable that the Sulfex decladding procedure be such that the stainless steel is not made passive to the decladding solution or that activation can be assured for cladding already passive. Chemical and electrochemical means of activating passive stainless steel surfaces in boiling dilute sulfuric acid were studied. Chemical methods included reducing agents and penetrating ions; electrochemical methods included galvanic and electrolytic coupling.

Since nitrate may be present in Sulfex solutions due to entrapment of some previous nitric acid dissolver solution, the effect of nitrate on depassivation was investigated. Destruction of nitrates in Sulfex decladding solution was also studied.

II. SUMMARY

Chemical depassivation of passive 304-L was accomplished by penetrating ions. Fluoride concentrations of 0.02 - 0.10 M in 4 M H_2SO_4, at 106 C produced depassivation. However, attack on uranium core metal was increased excessively by the presence of fluoride ions in Sulfex decladding solutions. Reducing agents evaluated did not depassivate passive 304-L stainless steel in boiling Sulfex solutions.

Electrochemical depassivation of passive 304-L stainless steel in boiling Sulfex decladding solutions was accomplished by both galvanic and electrolytic processes. The ability to produce galvanic depassivation was controlled by the magnitude and polarity of the contact potential developed between passive 304-L steel and a dissimilar metal. Electrolytic depassivation was dependent on the magnitude and polarity of the impressed potential.

Nitrate ions in excess of 0.1 M in boiling 4 M H_2SO_4 suppressed electrochemical depassivation of passive 304-L stainless steel. Nitrate contaminants were effectively destroyed with formaldehyde.

III. DISCUSSION AND EXPERIMENTAL RESULTS

A. General

Since no method is presently known for measuring the degree of passivity or activity of metal surfaces, it was necessary to arbitrarily define "passive" and "active" surfaces before the variables influencing passivation and depassivation could be measured. In this work, surfaces not attacked by the chemical environment for a period of twenty or more minutes were called passive. Those attacked within twenty minutes were called active. "Chemical attack" was defined as continued gas evolution immediately adjacent to the metal surfaces.

Specimens of 304-L stainless steel used were obtained from "cut-off" material — heat and manufacturer unknown. Coupons used were two inches by two inches by 1/8-inch.

Active surfaces were prepared on 304-L stainless steel by heat treating the coupons for thirty to sixty minutes at 2000 F and then cooling rapidly to room temperature. Such surfaces were more reactive to dilute sulfuric acid than "mill-condition" surfaces.

Active surfaces on 304-L stainless steel were made passive by immersing the coupons for one hour in boiling 4 $\underline{M}$ H_2SO_4 - 0.5 $\underline{M}$ HNO_3. The surfaces produced, in all cases, resisted attack by boiling 2-14 $\underline{M}$ H_2SO_4 for sixty minutes, indicating a high degree of passivity on the surfaces.

B. Chemical Depassivation

Reducing agents and penetrating ions were tried as chemical agents for depassivating passive 304-L stainless steel surfaces in boiling 4 $\underline{M}$ H_2SO_4. None of the reductants tried was effective. These were hydrazine and sodium bisulfite at concentrations up to 0.1 M, formic acid and formaldehyde at concentrations up to 0.025 $\underline{M}$, and hydrogen gas flowed over the 304-L surfaces.

Ions, such as chloride and fluoride, which can penetrate oxide layers, are known to promote attack on passive stainless steel surfaces(5). As shown in Figure 1, low concentrations of fluoride ion in boiling 4 $\underline{M}$ H_2SO_4 promoted attack on passive 304-L surfaces. Increasing the fluoride content decreased the time required for depassivation. The effect of added fluoride on uranium metal attack is shown also in Figure 1. The advantages of fluoride as a depassivating agent in Sulfex decladding would have to be balanced against increased attack on fuel cores and, possibly more important, on the container.

C. Electrochemical Depassivation

1. Galvanic Depassivation

The polarity and magnitude of the contact potential developed, when passive 304-L is in contact with a dissimilar metal, determine whether or not depassivation of the stainless steel will occur. Platinum and carbon, which are more noble than passive 304-L stainless steel, did not produce depassivation when contacted with passive 304-L in boiling 4 M H_2SO_4. Aluminum and 1020 mild steel, which are less noble than passive 304-L, did produce depassivation when in contact with passive 304-L in boiling 4 M H_2SO_4. The magnitude of the contact potential influenced the time required to produce depassivation. Aluminum promoted depassivation more rapidly than 1020 steel in boiling 4 M H_2SO_4, in the absence of nitrate ion, as shown by comparison of the points for zero nitrate in Figures 2 and 3.

Galvanic depassivation was hindered by the presence of nitrate ions in boiling 4 M H_2SO_4. As shown in Figure 2, aluminum in contact with passive 304-L in boiling (106 C) 4 M H_2SO_4 did not produce depassivation at nitrate concentrations above 0.05 M. Galvanic depassivation by 1020 mild steel in contact with passive 304-L occurred at nitrate concentrations up to 0.5 M in boiling 4 M H_2SO_4, as shown in Figure 3. However, when the 1020 steel was removed from contact with the depassivated 304-L, repassivation occurred at nitrate concentrations above 0.1 M.

2. Electrolytic Depassivation

The polarity and the magnitude of the potential impressed on passive 304-L stainless steel in boiling 4 M H_2SO_4 determine whether or not depassivation occurs. Making the passive 304-L stainless steel positive in potential (anodic) did not, in any case, produce depassivation. Electrolytic depassivation could be induced when passive 304-L stainless steel was made the negative electrode (cathodic). For a given potential, increasing the temperature or decreasing the electrode separation decreased the time required to produce depassivation. This effect is shown in Figure 4. As shown in Figure 5, increasing the electrode separation increased the potential requirements to produce electrolytic depassivation. When the potential was in excess of the minimum voltage required to produce depassivation, the time for depassivation decreased. This effect is shown in Figure 6 for an environment of 4 M H_2SO_4.

Electrolytic depassivation of passive 304-L stainless steel in contact with Hastelloy F or Ni-o-nel, representing conditions where the dissolver vessel is made the cathode terminal, did not increase the rate of corrosion of these dissolver metals. No weight loss was detectable when Hastelloy F or Ni-o-nel was made cathodic and subjected to a potential of four volts, at an electrode separation of two inches, for one hour in boiling 4 M H_2SO_4. Also, using Hastelloy F or Ni-o-nel as an adjacent cathode had no adverse effects on electrolytic depassivation of passive 304-L stainless steel.

$P_{Kw} = .3635 \times F_{gpm} \times \Delta T_{{}^\circ C}$

The presence of nitrate ions in boiling ~~4 M H_2SO_4~~ interferes with electrolytic depassivation of 304-L stainless steel. The minimum potential required for depassivation increased with increasing nitrate concentration as shown in Figure 7. The conditions given in Figure 7 simulate dissolver conditions with respect to the 304-L steel: Ni-o-nel dissolver cathode couple. At nitrate concentrations in excess of 0.1 M, 304-L stainless steel, which was electrolytically activated, repassivated when the applied potential was removed.

D. Destruction of Nitrate Ions in Sulfex Solutions

While formaldehyde is not effective as a depassivating agent, it may be used to destroy nitrate ions present in Sulfex decladding solutions (6-7). Boiling 4 M H_2SO_4 - 0.1 M HNO_3, made 0.1 M with formaldehyde, contained less than 0.0001 M HNO_3 after five minutes. The resulting solutions exhibited the same ease of galvanic and electrolytic depassivation of passive 304-L stainless steel as Sulfex solutions containing no nitrate ions.

IV. CONCLUSION

Electrochemical processes offer the best methods to insure depassivation and dissolution of passive 304-L stainless steels in boiling Sulfex decladding solutions. Where it is impossible to obtain or insure galvanic contact between passive 304-L stainless steel and a less noble metal, electrolytic depassivation should be employed. For best depassivation results, nitrate contamination should first be destroyed with formaldehyde.

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ribution FROM E. M. Duke DATE July 25, 1960

CORRECTION IN DOCUMENT HW-65985

On Figure 1, Page 6, abscissa values should be 0.02, 0.04, 0.06, 0.08 and 0.1 instead of 0.02, 0.04, 0.08, 0.10 and 0.12. Please make this correction in your copy.

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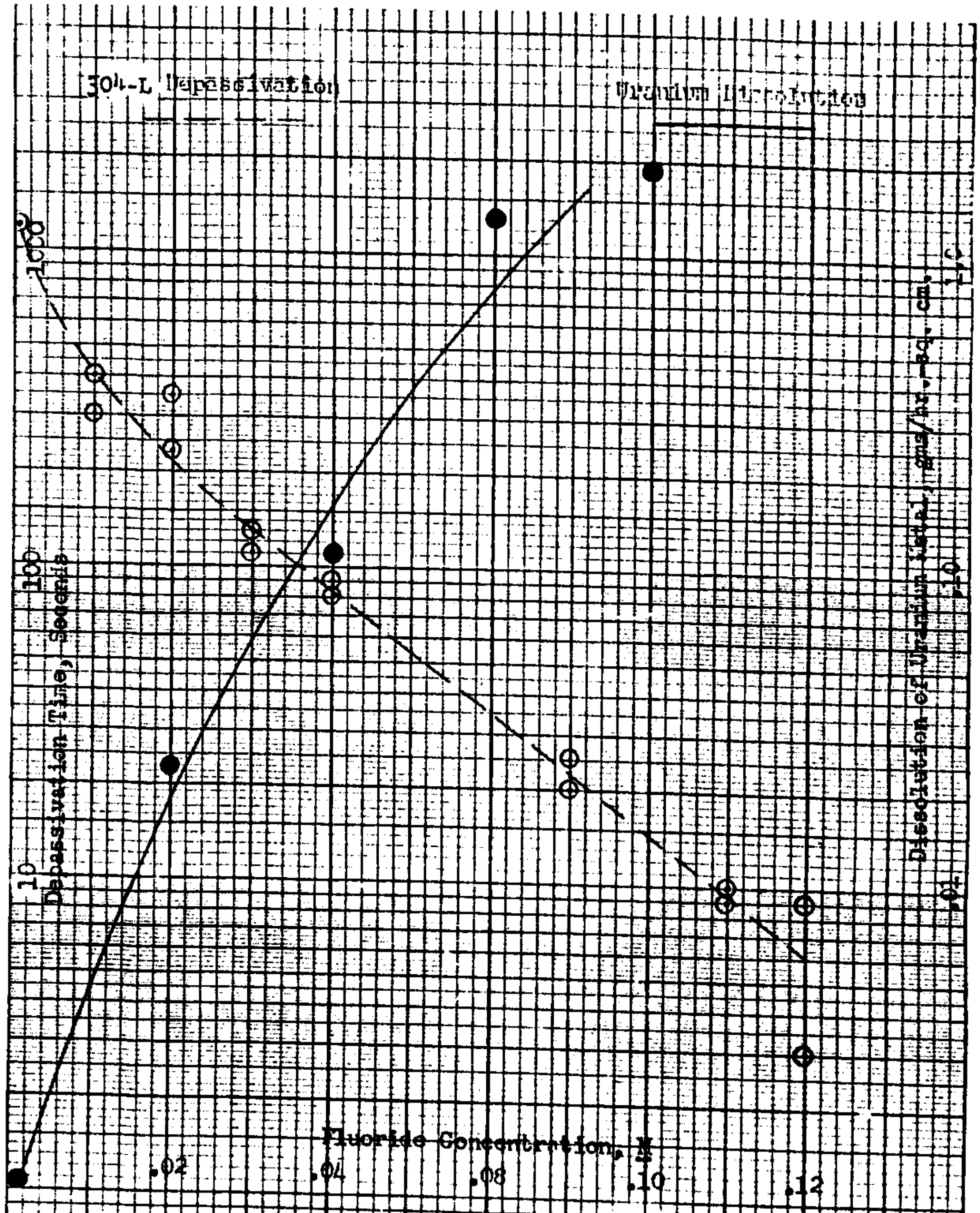

FIGURE 1

CHEMICAL DEPASSIVATION OF 304-L S.S.
IN 4 M H_2SO_4, 105 C

EFFECT OF FLUORIDE CONCENTRATION

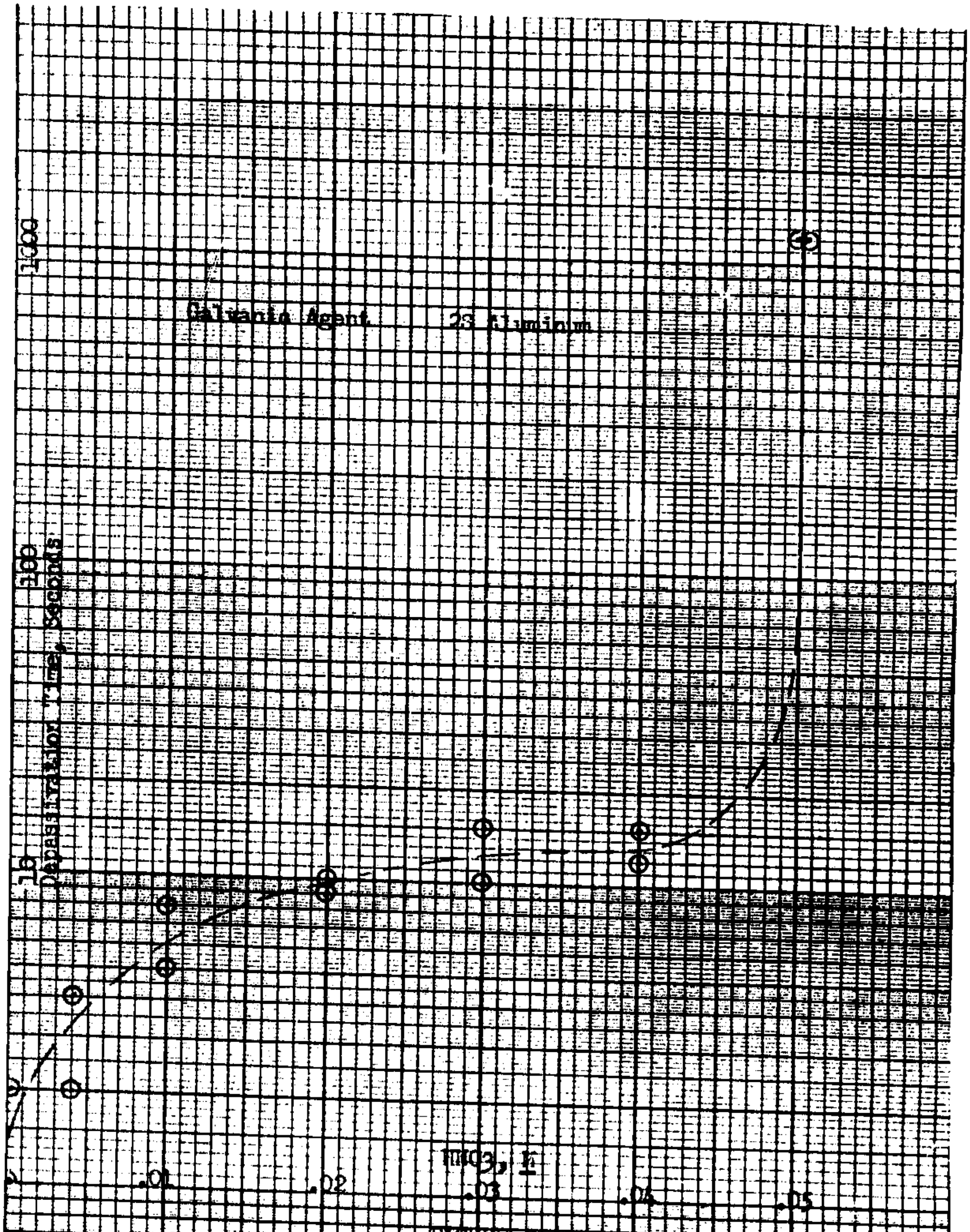

FIGURE 2

GALVANIC DEPASSIVATION OF 304-L S.S.
IN 4 M H_2SO_4, 105 C

DEPASSIVATION TIME AS A FUNCTION OF NITRATE CONCENTRATION

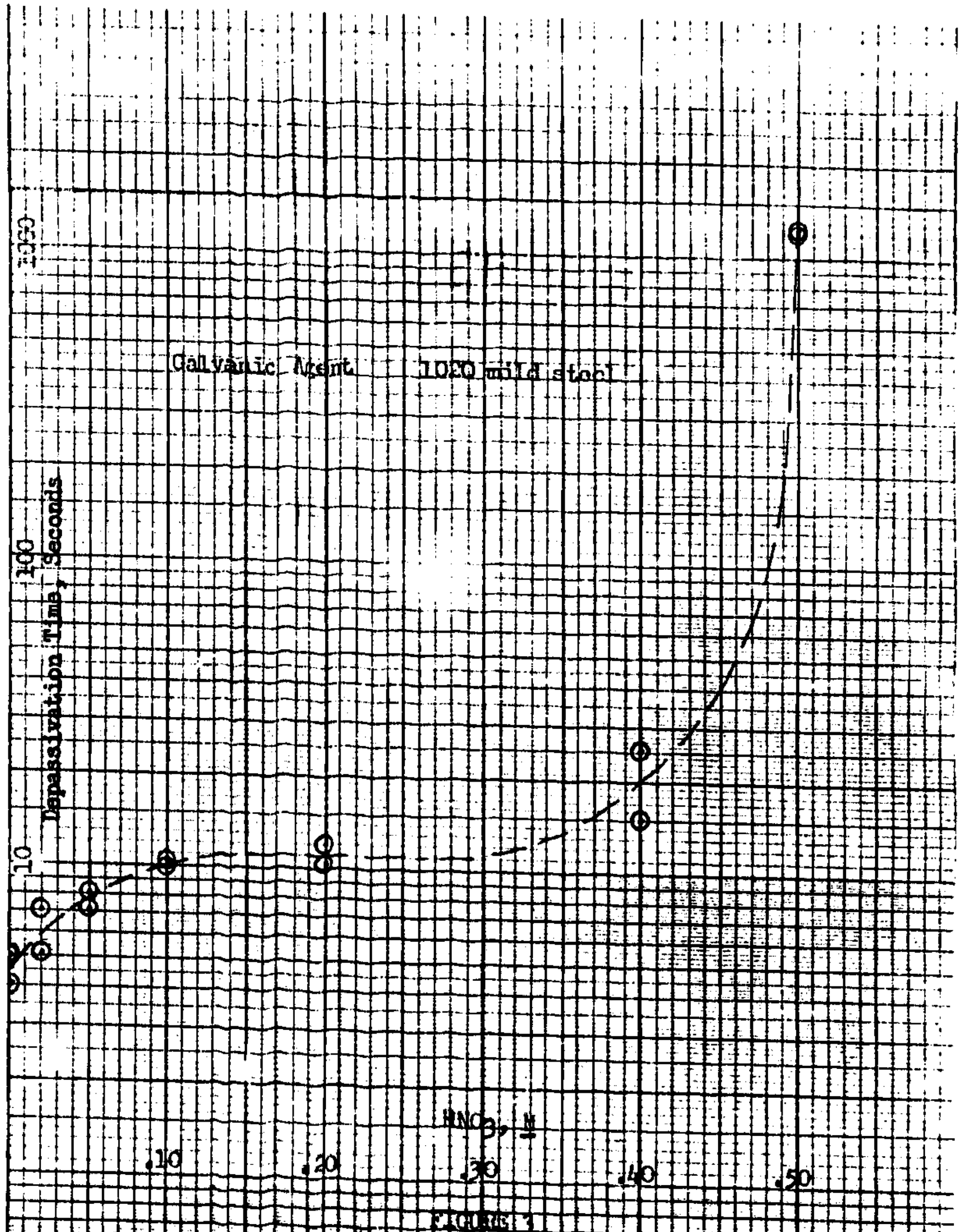

FIGURE 3

GALVANIC DEPASSIVATION OF 304-L S.S.
IN 4 M H_2SO_4, 105 C

DEPASSIVATION TIME AS A FUNCTION OF NITRATE CONCENTRATION

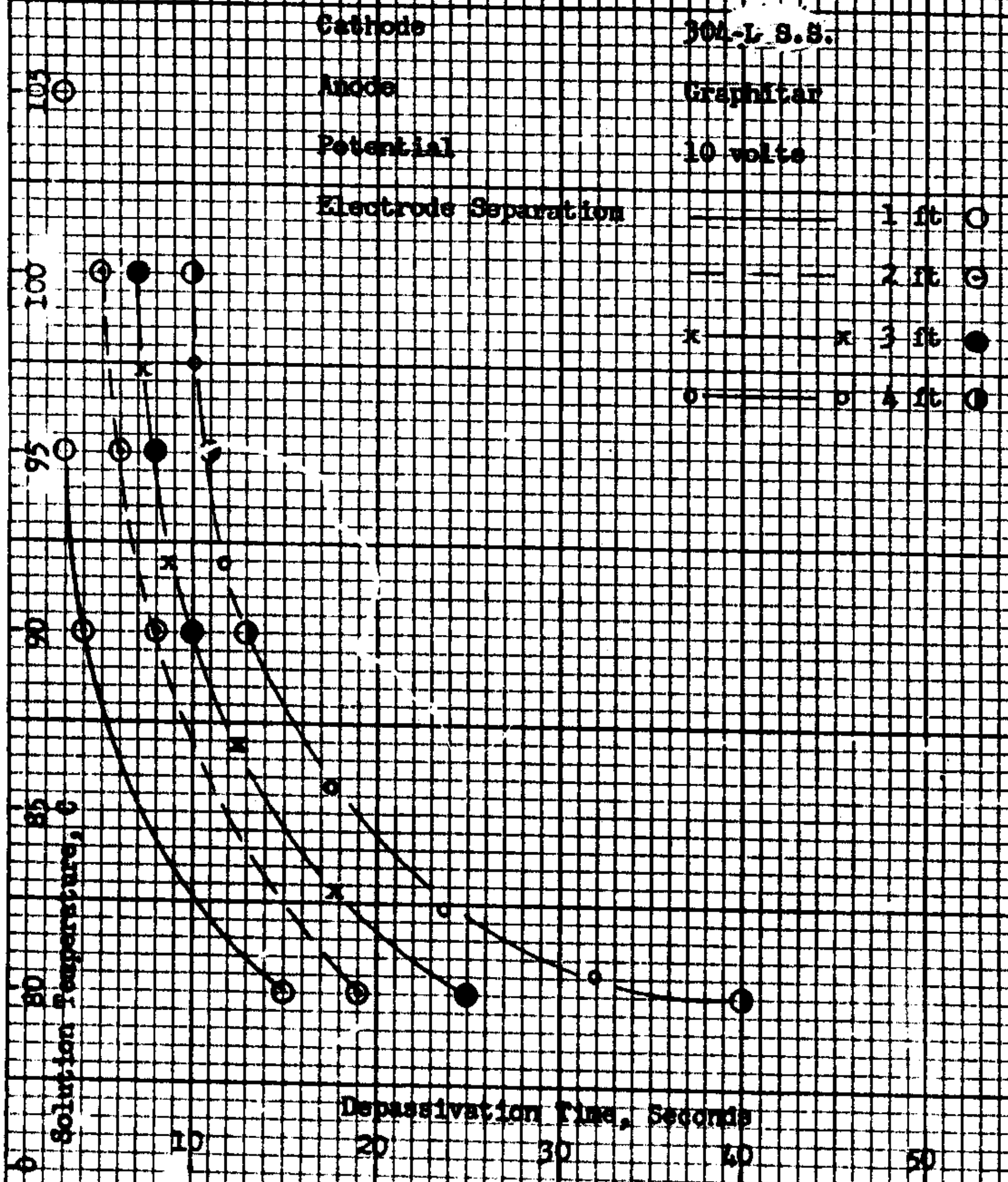

FIGURE 4

ELECTROLYTIC DEPASSIVATION OF 304-L S.S.
IN 4 M H_2SO_4, 105 C

EFFECT OF SOLUTION TEMPERATURE AND ELECTRODE SEPARATION

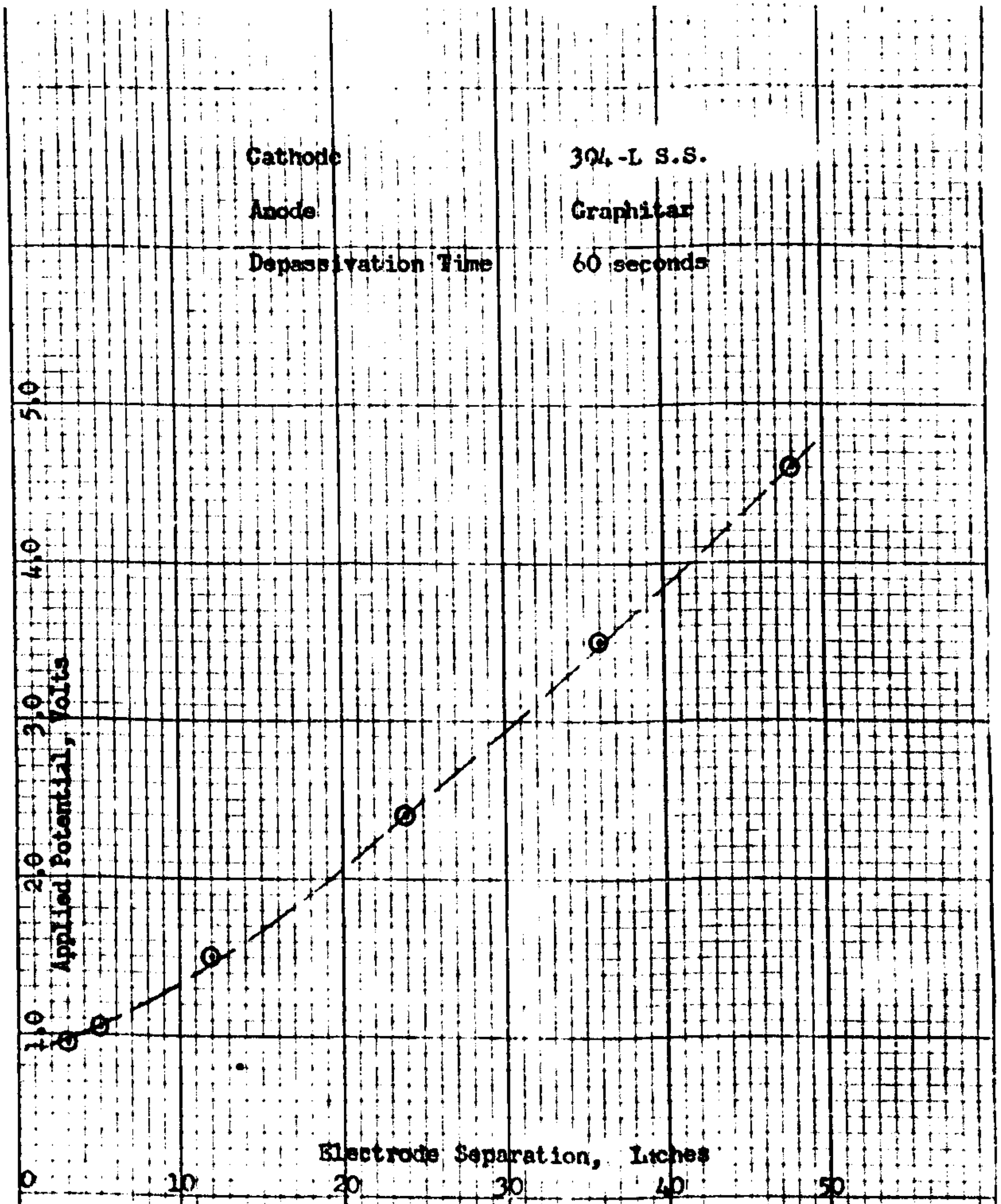

FIGURE 5

ELECTROLYTIC DEPASSIVATION OF 304-L S.S.
IN 4 M H_2SO_4, 105 C

POTENTIAL REQUIREMENTS AS A FUNCTION OF ELECTRODE SEPARATION

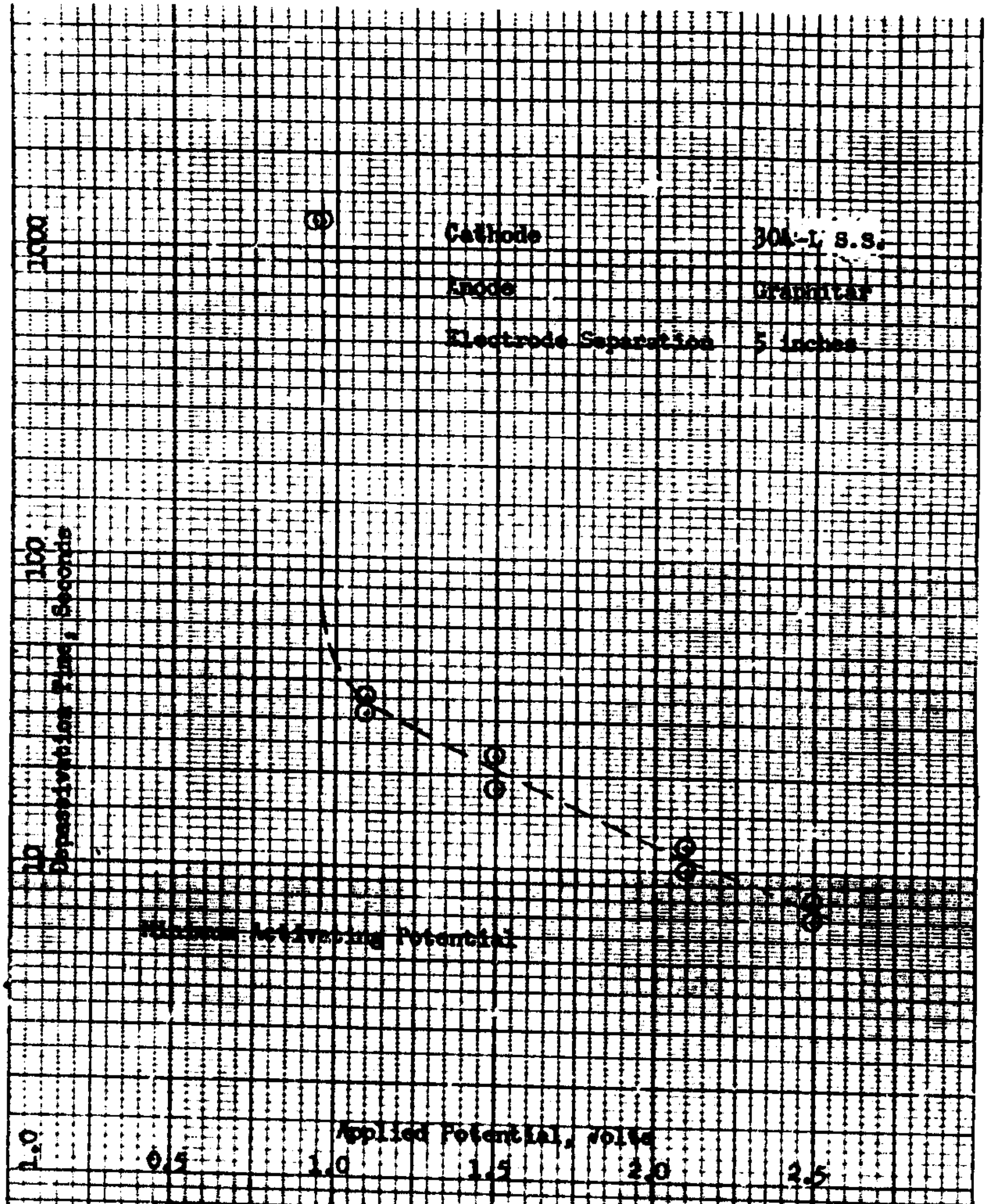

FIGURE 6

ELECTROLYTIC DEPASSIVATION OF 304-L S.S.
IN 4 M H_2SO_4, 105 C

DEPASSIVATION TIME AS A FUNCTION OF APPLIED POTENTIAL

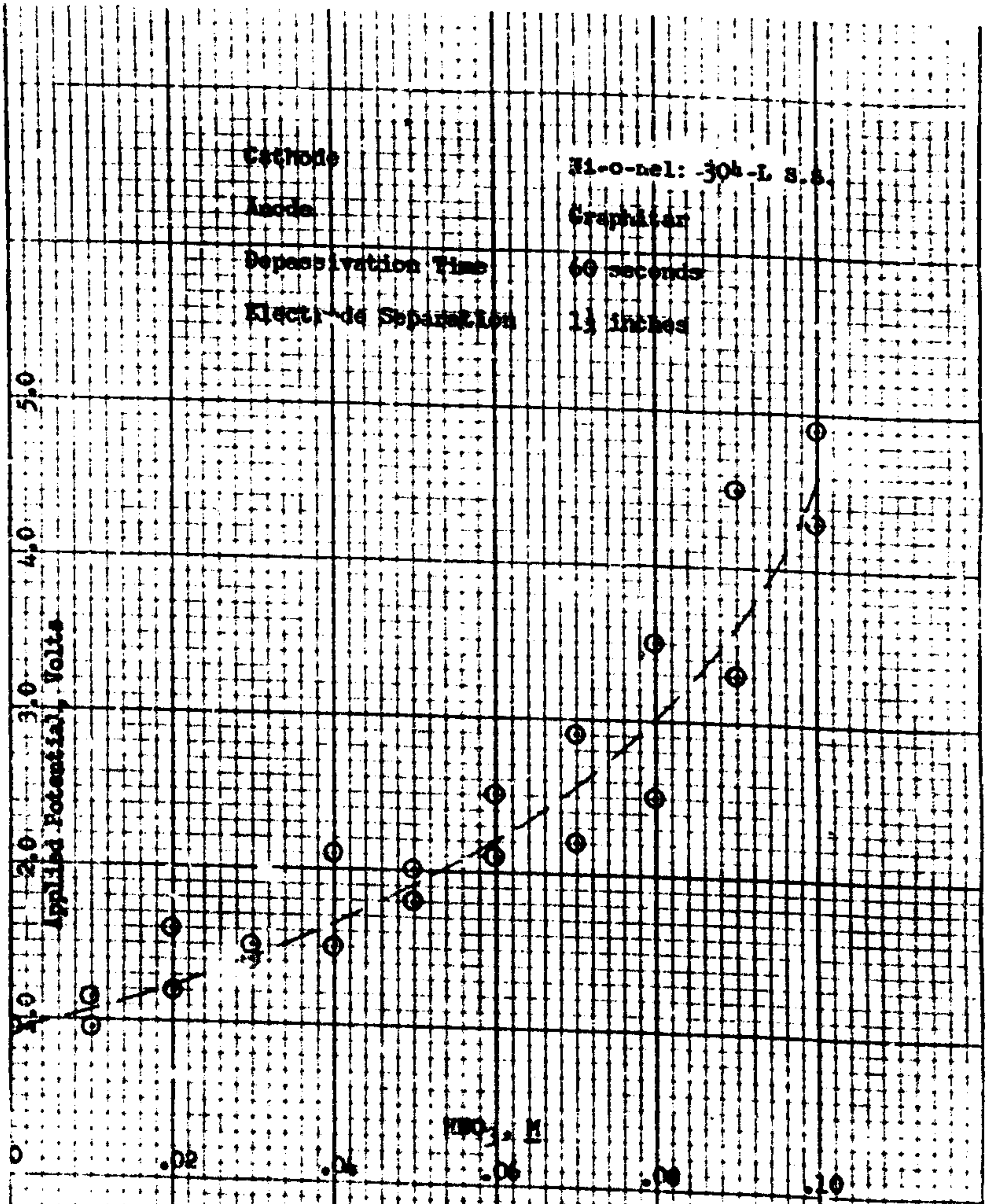

FIGURE 7

ELECTROLYTIC DEPASSIVATION OF 304-L S.S.
IN 6 M H_2SO_4, 105 C

POTENTIAL REQUIREMENTS AS A FUNCTION OF NITRATE CONCENTRATION