GALVANOSTATIC STUDIES ON THE ELECTROCHEMICAL

BEHAVIOUR OF MOLYBDENUM IN VARIOUS OXY AND

HALOGEN ACIDS

N.S.Hassan, R.Abu-Shahba, S.A.Soliman[*]

and S.M.Abd El-Motaal

Al-Azhar University, Faculty of science (Girls).

Nasr city, Cairo, Egypt.

[*] Al-Azhar University, Faculty of science,
Nasr city, Cairo, Egypt.

ABSTRACT

The anodic behaviour of mechanically polished and acid pickled molybdenum electrode has been examined at constant low c.d. in unstirred, N_2-de-aerated and aerated 1 N solutions of $H PO$, $HClO$, $H SO$, HNO , HCl, HBr and HI acids. The results show a marked dependence on c.d., nature of the prevailing anion and on surface treatment. The potential time curves are characterized by two main segments with different slopes preceded by a less pronounced rapid rise in potential due to the oxide film building and thickening both of which leads to passivation, in areated solutions the potentials are generally less negative than those obtained in de-aerated solutions. Based on the magnitude of the surfae charging capacity (C) one can arrange the different anions according to their effectiveness in producing passivation as follows : HNO > $HClO$ > $H SO$ > $H PO$. while as with halogen acids it was in the following order : HI > HCl > HBr. the magnitude of C and q for acid pickled eletrode in oxyacid, is much less than the corresponding values for the mechanically polished electrode.

INTRODUCTION

Many investigations have been made on the electrochemical behaviour of pure molybdenum. The resistance of Mo to corrosion in most aqueous media has been recognised for many years. reports concerning its corrosion characteristics and anodic dissolution have appeared in the literature (1960, 1966 and 1969). Various Workers (1958) showed that in acid solutions at potentials 0.2-0.5 V, molybdenum is active and passes into solution in the form of MoO ions at a rate depending on Tafel slope. Nakamural et al. (1980) and daly & Keil (1975) were studied the anoidc oxidation of active molybdenum in acetic acid solution under potentiostatic and galvanostatic techniques, they revealed that the passive region extends from -0.2 to -0.1 V vs. S.C.E. and transpassive dissolution occurs above -0.1 V and it dissolved as MoO via the formation of MoO (OH) or Mo(OH) film. The kinetics of the anodic dissolution of Mo in NaOH, other alkaline and acidic solutions were also studied (1952, 1966, 1968, 1970 and 1977). We have investigated the galvanostatic polarization curves for oxidation of molybdenum in oxy and halogenacid solutions, and compared themagnitude of the surface charging capacity $C_S = (dq/dE)$ uF/cm^2 and the quantity of

electricity q_s consumed before the stabilized potential is reached.

EXPERIMENTAL

The test cell was a conventional one and was made from pyrex glass with a nominal capacity of 250 ml. Prior to the introduction of spectroscopically-pure molybdenum electrode (2.5 cm^2 rods) normal solutions of oxyacids (H_2SO_4, $HClO_4$, HNO_3, H_3PO_4) and of halogen acids (HCl, HBr, HI) were either aerated or dearated.

a) Mechanical polishing : The electrodes were; abraded by 0.00 and 000 emery paper, degreased with ethanol, washed with running bidistilled water and, dried between two filter papers.

b) Acid pickling : The electrode was dipped for few seconds in a mixutre of 5% H_2SO_4 and 15% HCl at room temperture, then washed by bidistilled water and dried with filter paper. Electrode receiving such a treatment possessed a dark grey metallic surface and were designed as "pickled" surfaces.

Galvanostatic technique was used to determine the potential-time curve at low and moderate current densities.

Measurement values were re-calculated with respect to the

standard hydrogen electrode, using S.C.E. The molybdenum

electrode was polarized with a cathodic current, sufficient

for eliminating spontaneous corrosion, and, then the current

was switched to the anodic direction.

RESULTS AND DISCUSSION

The potential-time curves obtained upon anodic

polarization of molybdenum at various constant current

densities in 1 N solutions of H_2SO_4, $HClO_4$, H_3PO_4, HNO_3,

HCl, HBr and HI in aerated and deaerated solutions were

studied. The results showed a marked dependence of the

anodic behaviour on the nature of prevailing anion and on

current density. In all acid media studied the general

behaviour was almost the same at low, moderate and high

current densities. The potential increased regularly with

time to reach a stabilized, more positive values. Thus the

potential time curves of molybdenum electrode showed two

linear segments with different slopes, the first with

higher slope and the second runs parallel to the time-axis,

this picture agrees with the reusls observed by previous

investigators. Thus Wikstrom and Nobe (1969) reported

that, the potential time responses exhibited two linear

regions. the initial linear region was attributed to the

charging of the metal-metal oxide interface. At open circuit and during polarization, this capacitance remained constant at 3.75 uF/cm^2 . The second linear region was attributed to the charging of the metal oxide solution interface and showed marked changes with potential. consideration the potential-time curves (Fig. 1), revealed that :

1- In almost all acids there was always a general tendency for the corrosion potential to drift with time to more noble values where it tends to be stabilized.

2- In any particular acid; potential recorded in aerated solution were on the whole less negative than those obtained in dearated solution. Therefore, the effect of nitrogen is clear.

3- Under the two sets of conditions examined (aeratd and nitrogen deaerated solutions), the stabilized potential values vary with the current density over the whole range (Fig. 2).

From the data obtained one can conclude that the immersion potential value of Mo-electrode was greatly affected by lower current densities, but at higher values-

Table (1); Surface Charge Capacity of Mo-Electrode in 1N Oxy, Acids and Halogen Acids

c.d., $\mu A/cm^2$	Aerated IN Acid Solution				Deaerated IN Acid Solutions				Aerated IN Acid Solutions		Deaerated IN Acid Solutions	
	HNO_3	$HClO_4$	H_2SO_4	H_3PO_4	NHO_3	$HClO_4$	H_2SO_4	H_3PO_4	HBr	HCl	HBr	HCl
	$C_s \times 10^3 \; \mu F/cm^2$								$C_s \times 10^3 \; \mu F/cm^2$			
6	0.88	0.98	1.04	1.06	0.77	0.88	0.91	0.98	0.50	0.61	0.45	0.54
12	0.86	0.92	1.02	1.04	0.74	0.86	0.87	0.89	0.48	0.56	0.43	0.51
18	0.81	0.91	1.00	1.03	0.74	0.80	0.82	0.85	0.46	0.53	0.41	0.50
29	0.80	0.89	0.98	1.02	0.73	0.80	0.81	0.84	0.46	0.52	0.40	0.50

starting from 90 uA/cm^2 the potential was more or less constant figs. (3 and 4). This may be due to the formation of oxide film at the beginning of the experiment,then after few seconds the potential did not change even at higher c.d.'s due to the thickening of the surface film formed, the rate of growth of the oxide film depended on the electrolyte composition. These results were in agreement with the results of other investigators (1867 and 1969).

Critical consideration of the potential-time curves (Fig. 1) would reveal that in all cases a steep initial rise in potential as was illustrated in case of aerated H_2SO_4 when the potential abruptly increased from 0.065 to 0.305 V in a matter of few seconds was observed. This S-fold rise in potential could not be attributed solely to charging up of the electrical double layer across the metal/solution interface, but rather to an electrochemical reaction the so-called condenser leakage.

Along the second main sloping portion of potential-time curve (Fig. 1), film, repair took place through blocking of the pores or cracks in the pre-immersion film, with the formed oxide. At this stage the role of the prevailing anion should not be ignord. The higher the degree of incorporation of the anion within the oxide film, and the

Table (2). Comparison between C_s and q_s for mechanically polised and acid pickled electrode.

Current Density $\mu A/cm^2$	6 $\mu A/cm^2$				29 $\mu A/cm^2$			
	Mechanically polished electrode		Pickled electrode		Mechanically polished electrode		Picked electrode	
	$C_s \times 10^3$	$q_s \times 10^2$	$C_s \times 10^3$	$q_s \times 10^2$	$C_s \times 10^3$	$q_s \times 10^2$	$C_s \times 10^3$	$q_s \times 10^2$
HNO_3	0.77	4.26	0.72	4.02	0.73	4.35	0.69	4.15
$HClO_4$	0.88	4.80	0.81	4.50	0.80	4.64	0.74	4.35
H_2SO_4	0.91	4.62	0.84	4.38	0.81	4.62	0.76	4.35
H_3PO_4	0.98	4.20	0.92	3.90	0.84	4.21	0.80	4.00

greater the inhibition character as anoidc inhibitor, the greater will be its effectiveness in the process of film repair, resulting in a higher degree of- passivation. It should be noted that along this linear portion of the potential-time curve the anodic current passing is utilized, for both processes, building of the oxide film and thickening, both of which leads to passivation. This, however, doesn't exclude that, along this portion of the curve, opposing processes, e.g. those due to chemical dissolution of the freshly formed oxide film-leading to surface uncoverage may take place. It appears that the rate of surface repair or film perfection comes to a limit· when this portion of the curve merges to the stabilized potential limit, the quantity of electricity passing is mainly devoted to oxide thckening. Along this stabilized potential limit a state of equilibrium is reached at which the two opposing rates (rate of thickening and dissolution), are equal, and the potential does not change with time. In all media examined the stabilized potential value were found to increase regularly with the applied curent till it reached a specific current density value (viz) 60 uA/cm2. then the potential nearly doesn't change with increasing current density even at 206 uA/cm . These results are obtained- in case of aerated and deaerted solutions except
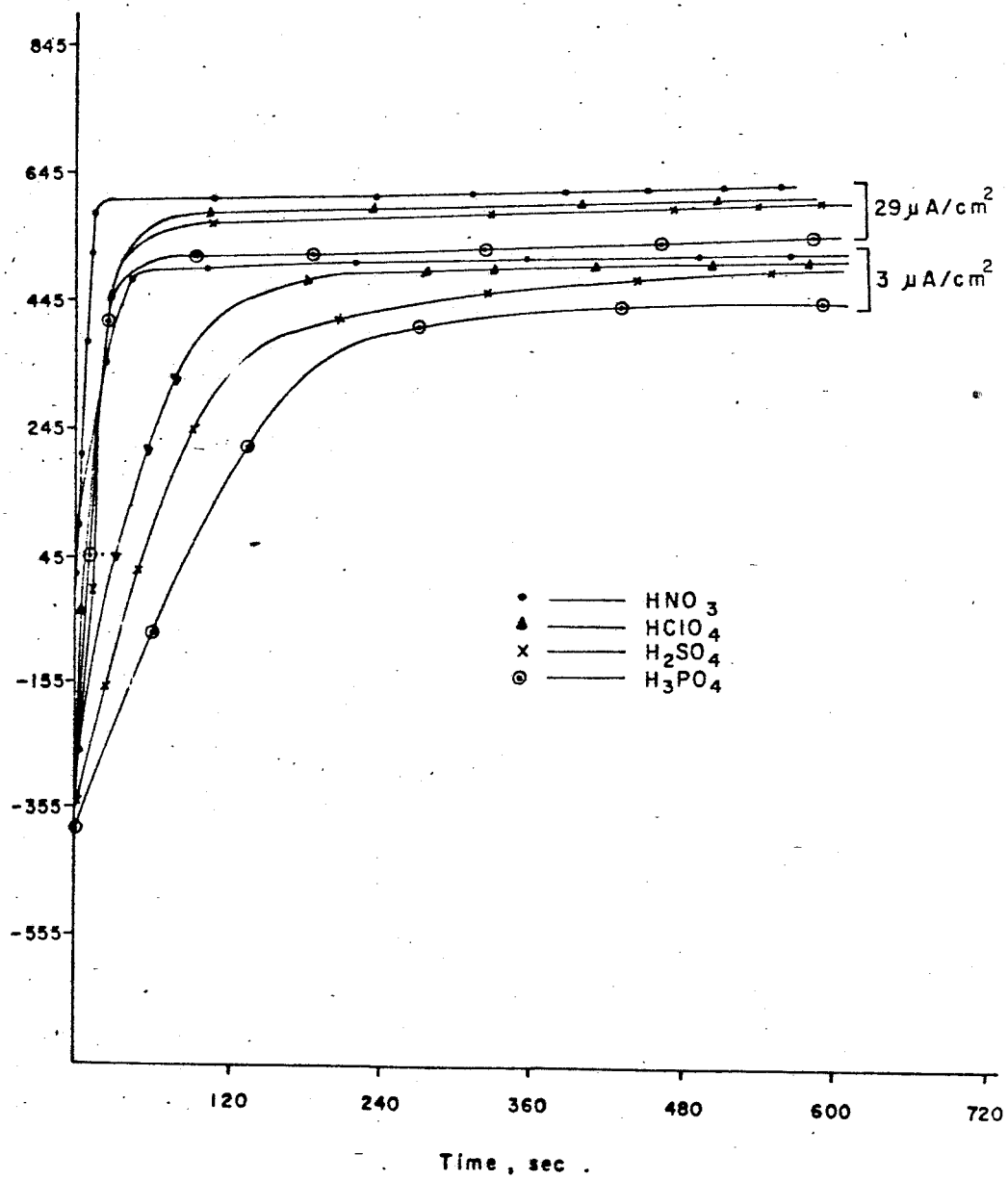
Fig.(1)Anodic Polarization Curves of Mo_Electrode at Constant
Current Densities In Different Anions .

table (1). The position of perchlorate ion in the series as found in the present work, appears to be strange since it is known that this anion possesses low inhibition character. Most probably $HClO_4$ exerts its action through oxidation rather than through its inhibition character. Being a strong oxidizing agents $HClO_4$ accelerates the onset of passivation and leads to more perfect surface oxide films. That is why the surface charging capcity, C_S along the first linear segment of the potential-time curves are smaller than the corresponding value in other acid media examined.

Evidences for incorporation of anions and the dependence of properties of the surface oxide film on the nature of electrolyte during formation were previously given by Randal et al. (1965) and Makrides, A.C. (1962).

For hlogen acids studied at the same comparable current densities, one can arrange the difference anions based on C_S values (table 1) obtained according to their effectiveness in producing passivation, in the following order in case of aerated and deaerted solutions.
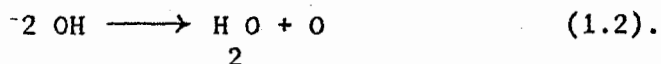
$$HI > HCl > HBr$$

In spite of the known fact that Cl^- has an aggressive

electrolyte there is a general tendency for the capacity values to decrease with current density, hence the onset of passivation. Such large surface charging capacity may be ascribed to an electrochemical reaction involving water, and. leading to progressive oxidation of the surface according to·:
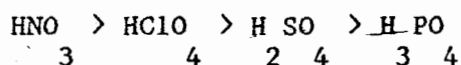
$$H_2O = H_+ + OH_- + e \qquad (1.1).$$

The formation of hydroxyl radicals contributes to the filmbuilding process prior to liberation of oxygen which could then occur only partially through combination.

$$^-2\ OH \longrightarrow H_2O + O \qquad (1.2).$$

These results are in agreement with those obtained by previous investigators (1952-1980).

Based on the magnitude of surface capacity at comparable current densities, one can arrange the different anions according to their effectiveness in producing passivation according to :

$$HNO_3 > HClO_4 > H_2SO_4 > H_3PO_4$$

in aeated solutions and also the same order is realized in case of deaerated solutions, for oxy acids as shown in

N.S. Hassan et al.

table (1). The position of perchlorate ion in the series as found in the present work, appears to be strange since it is known that this anion possesses low inhibition character. Most probably $HClO_4$ exerts its action through oxidation rather than through its inhibition character. Being a strong oxidizing agents $HClO_4$ accelerates the onset of passivation and leads to more perfect surface oxide films. That is why the surface charging capcity, C_S along the first linear segment of the potential-time curves are smaller than the corresponding value in other acid media examined.
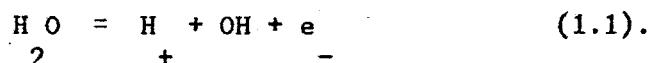
Evidences for incorporation of anions and the dependence of properties of the surface oxide film on the nature of electrolyte during formation were previously given by Randal et al. (1965) and Makrides, A.C. (1962).

For hlogen acids studied at the same comparable current densities, one can arrange the difference anions based on C_S values (table 1) obtained according to their effectiveness in producing passivation, in the following order in case of aerated and deaerted solutions.
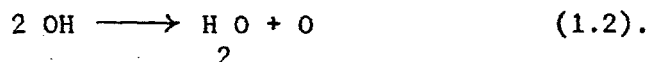
$$HI > HCl > HBr$$

In spite of the known fact that Cl^- has an aggressive

electrolyte there is a general tendency for the capacity values to decrease with current density, hence the onset of passivation. Such large surface charging capacity may be ascribed to an electrochemical reaction involving water, and leading to progressive oxidation of the surface according to :
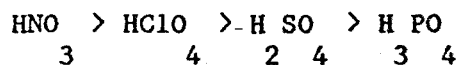
$$H_2O = H_+ + OH + e_- \qquad (1.1).$$

The formation of hydroxyl radicals contributes to the filmbuilding process prior to liberation of oxygen which could then occur only partially through combination.

$$2 OH \longrightarrow H_2O + O \qquad (1.2).$$

These results are in agreement with those obtained by previous investigators (1952-1980).

Based on the magnitude of surface capacity at comparable current densities, one can arrange the different anions according to their effectiveness in producing passivation according to :

$$HNO_3 > HClO_4 > H_2SO_4 > H_3PO_4$$

in aeated solutions and also the same order is realized in case of deaerated solutions, for oxy acids as shown in

Fig.(3) Variation of Immersion Potential with Current Density of Mo-Electrode in Aerated Oxy Acids.
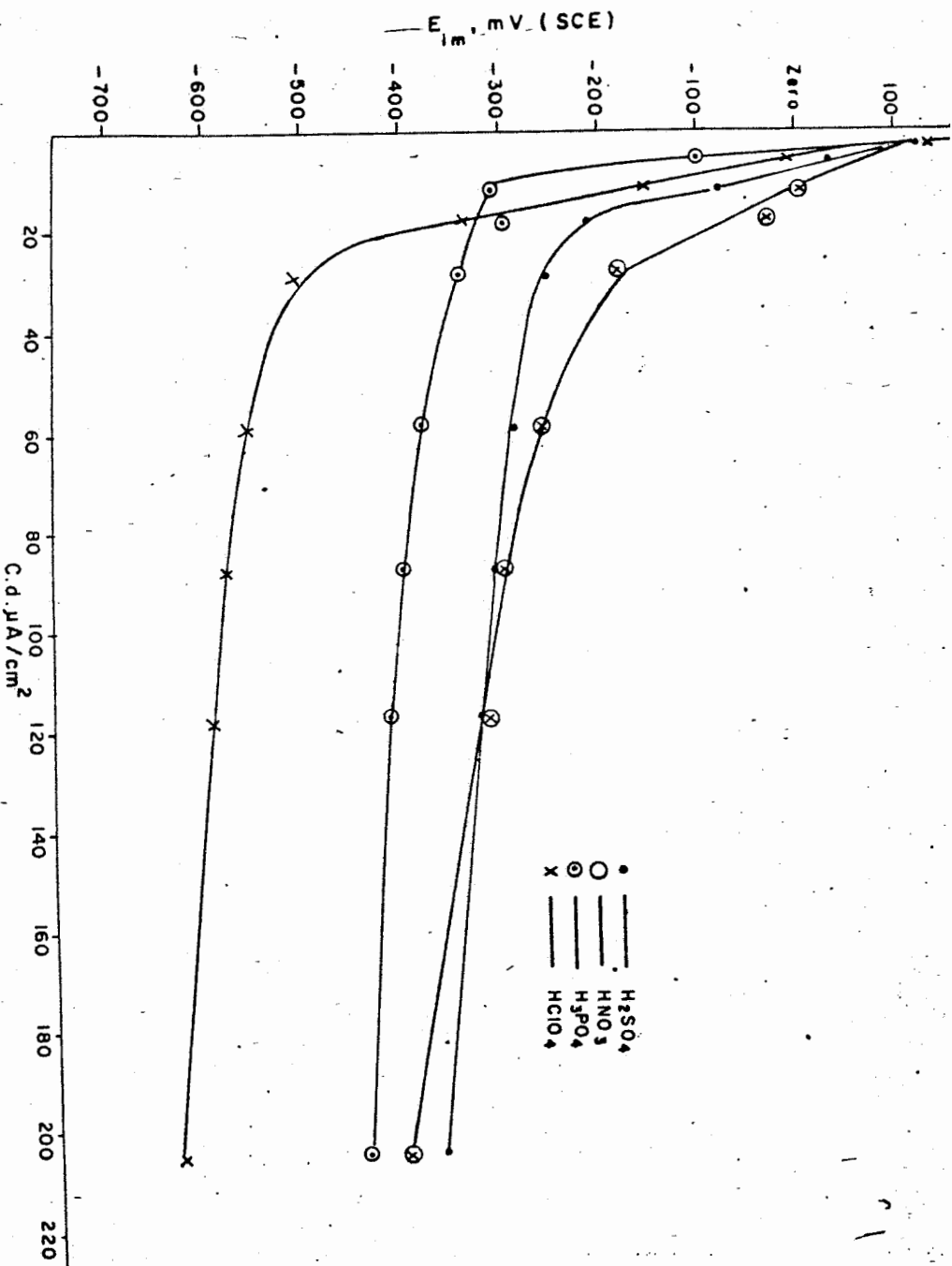
character, the surface charging capacity C_S for Mo in acid chloride solution lie in the middle of the series, this may be due to higher passivation character of molybdenum which prevent Cl to play its expecting role of aggressiveness. The results are in conformity with those obtained previously by Johnson and Lee (1970).

The above order for oxy acids can be arrived at by consideration of the magnitude of the stabilized potentials at comparable current densites. Plotting the stabilized potential values obtained in the various acid media against the constant c.d.'s applied, curves are shown in Fig. (2) was obtained, in all cases the curves obtained consist of two linear segments, with higher. and lower slopes respectively. The two segments interest together at nearly the same c.d. range (viz. 20-30 uF/cm^2. Below this c.d. range. the slopes (slope E/L = R resistance of the film) were found to depend on the nature of anion, and hence distinction between the effectiveness of the anions is possible. The higher slope was obtained in HNO_3 and the lower one in H_3PO_4. Above c.d.'s (higher than 30 uA/cm^2) the slopes of the curves are nearly identical and distinction between the various anions from this respect is rather impossible. It appears therefore that this c.d. is
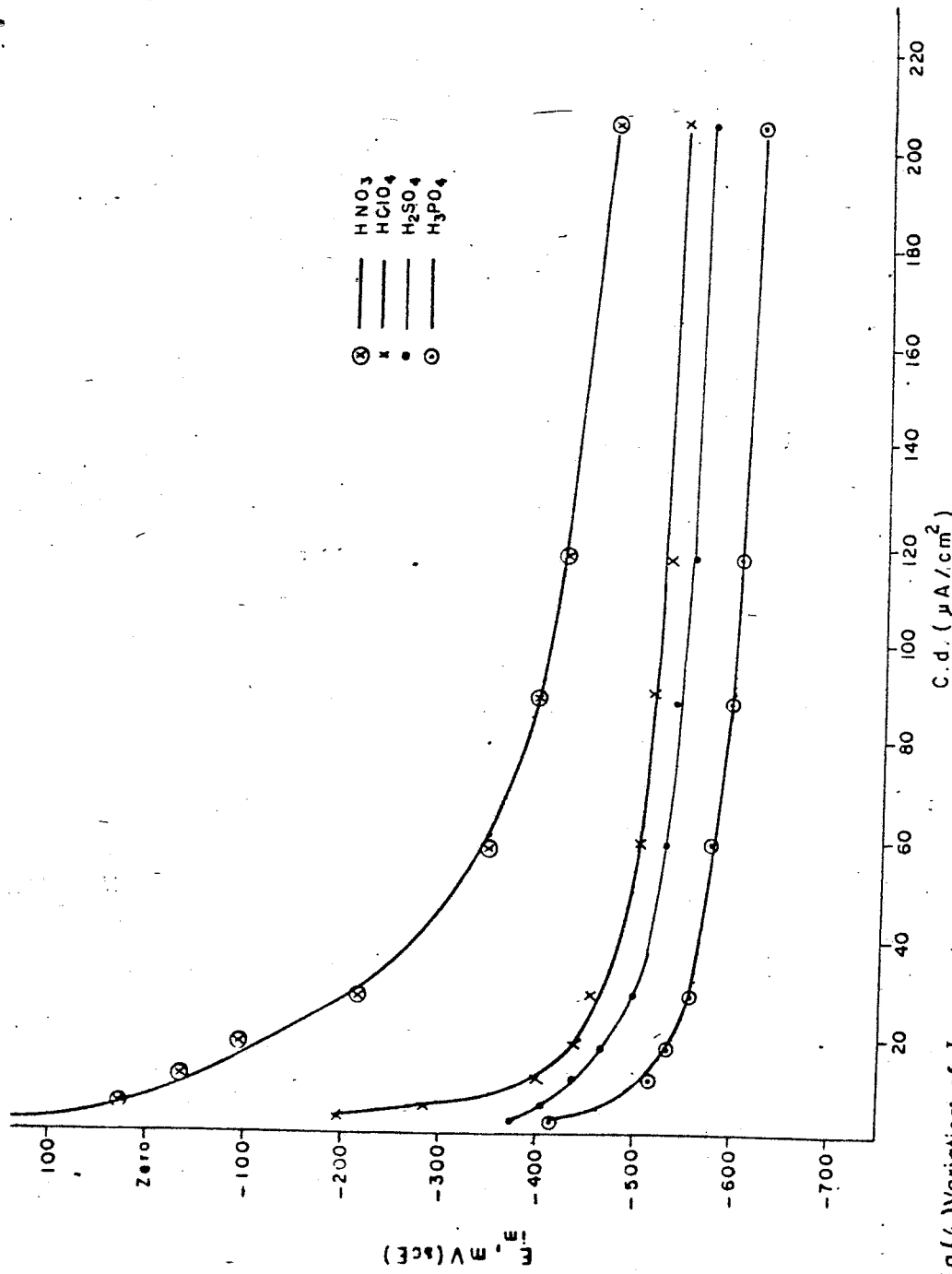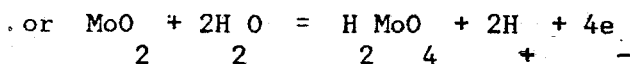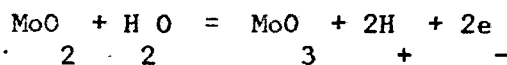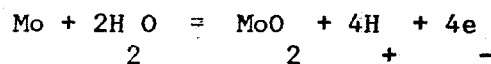
Fig(4)Variation of Immersion Potential with Current Density of Mo-Electrode in Deaerated Oxy Acids.

critical, and that it corresponds to a certain oxide thickness below which the oxide film is rather imperfect and hence the diffeent anions can display their inhibiting role, and distinction between them becomes possible. Above this thickenss the oxide has acquired sufficient degree of perfectin to the extent that distinction between the anions is not clear. The anions reflect their influence on such anodic process in an indirect manner by incorporation through the surface film or through surface oxidation as in case of oxidizing anion.

Based on the magnitude of the quantity of electricity passed at the intercept and as assuming surface oxidation of the metal to MoO_3 with a 100% efficeincy in accordance with the reaction.

$$Mo + 2H_2O = MoO_2 + 4H^+ + 4e^-$$

$$MoO_2 + H_2O = MoO_3 + 2H^+ + 2e^-$$

or $$MoO_2 + 2H_2O = H_2MoO_4 + 2H^+ + 4e^-$$

One can calculate the thickness of the surface oxide formed on Mo under these conditions according to

$$Q = i \cdot t$$
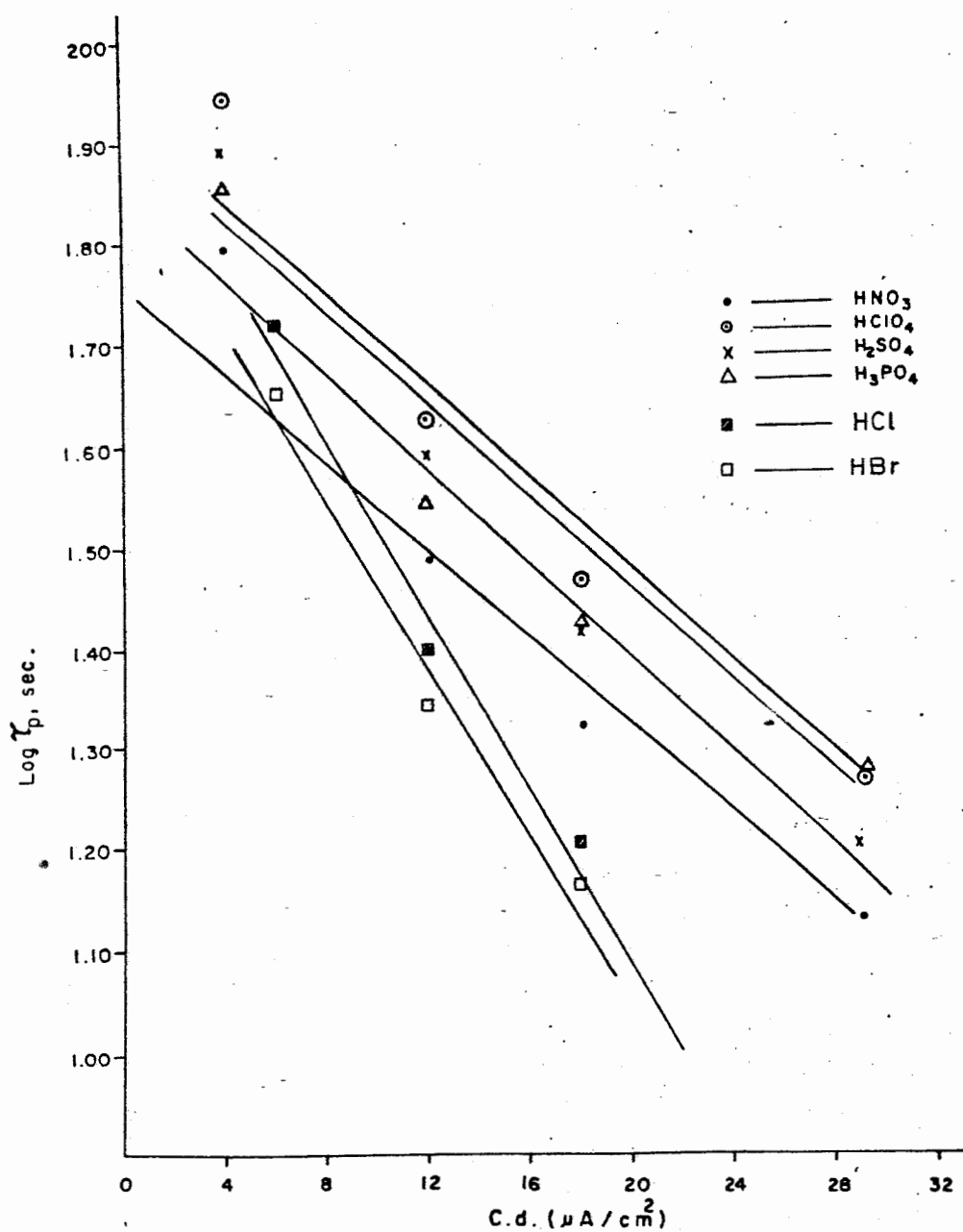
in couloms   c.d.(in Amp.)   Time (in Sec.)

Fig.(5) Variation of Log τ_p with Current Density of Mo – Electrode in Aerated Oxy Acids and Halogen Acids.

$$20 \times 10_{-6} \times 100 = 0.002 \text{ Coul.}$$

Molecular wt of MoO_3 = 143.94

∴ weight of MoO_3 deposited in grams

$$w = \frac{143.94 \times 0.002}{6 \times 96500} = 4.97 \times 10^{-7} \text{ gm/cm2 apparant surface area.}$$

$$\text{Volume} = \frac{w}{d} = \frac{4.97 \times 10_{-7}}{4.69} = 1.06 \times 10^{-7} \text{ cm3/cm2 of true area}$$

Volume = area X thickness

$$\therefore \text{thickness} = \frac{1.06 \times 10_{-7}}{2.54} = 108 = 4.17 \text{ A}$$

The variation of the passivation time τ_p and current density for oxy acids in aerrated and deaerated solutions, and also in halogen acids are represented graphically in Fig. (5). It is clear from these curves that, the relation between the passivation time τ_p (the time required for Mo electrode to reach the stabilized potential) and the current density was found to follow the following relation:

$$\log \tau_p = a - b \log i$$

where a and b are constants. As is seen from the curves of Fig. (5) a straight lines with constant slope 0.030 and
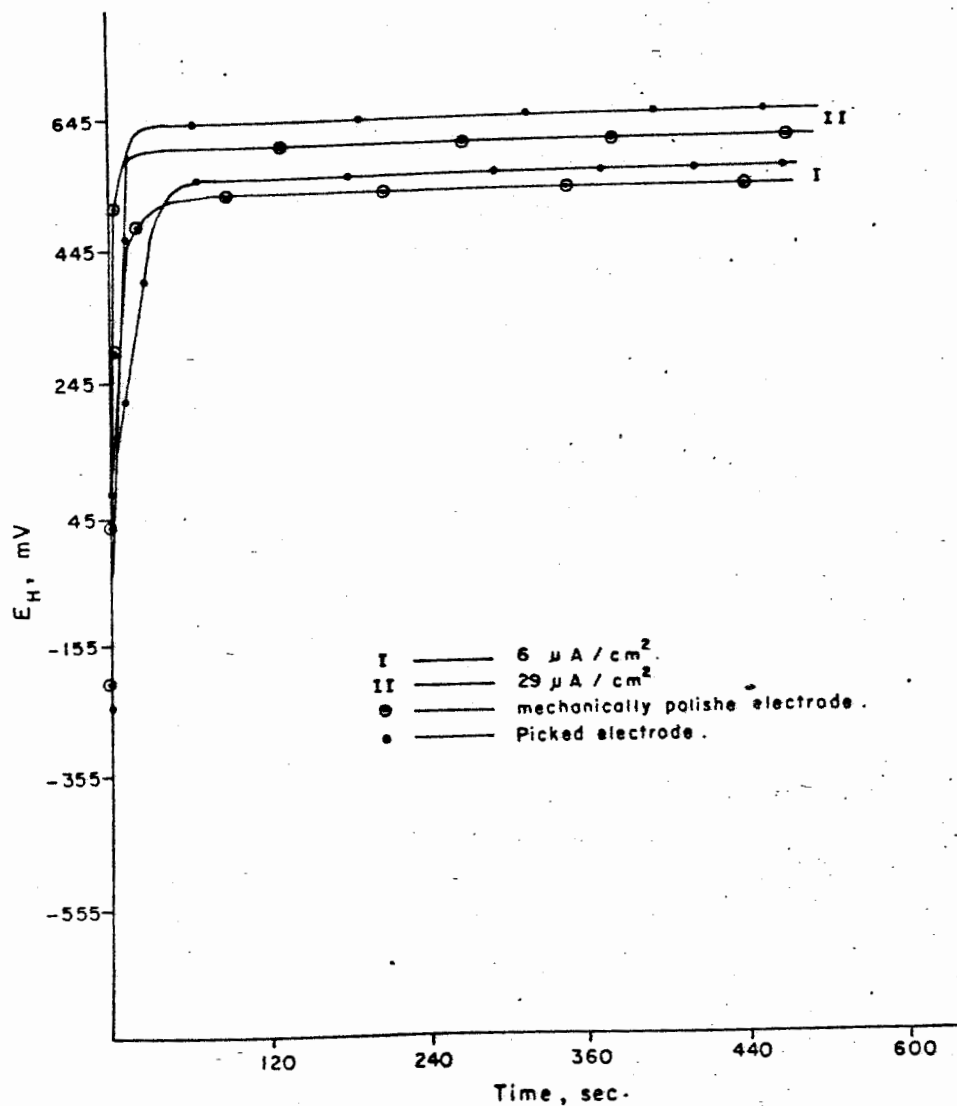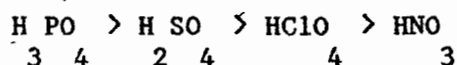
Fig.(6) Anodic Polarization Curves of Mo-Electrode in Deaerated
1.0 N HNO$_3$.

0.040 for oxy and halogen acids respectively in both aerated and deaerated solutions. The time required for passivation in the same c.d.'s in case of oxy acids was found to obey the following order :

$$H_3PO_4 > H_2SO_4 > HClO_4 > HNO_3$$

These results confirm the previous results obtained from C_S measurements i.e. enhancement of passivation.

ACID PICKLED ELECTRODE

As previously inferred, the characteristics of the anodic polarization of molybdenum depend also on the mode of preparation of surface prior to anodization. Fig.(6) show comparative results obtained with mechanically polished as well as acid pickled eletrode at two specified current densities in 1.0 N HNO_3. The results show clearly that, though the general features of the potential-time curves are not materially changed, distinction between the anodic behaviour of the two differntly treated molybdenum surface becomes possible if we consider the data shown in table(2).

These data indicate clearly that acid pickling leads to increased passivation of molybdenum. Enhancement of passivation induced by acid pickling is reflected in :

i- Decreased capacity along the first linear segment of the potential time curve.

ii- Decrease in the quantity of electricity, q_s, consumed before stabilized potential is reached. These reuslts gave simple evidence in support of the view of existence of a layer of molybdenum hydride on the surface of the acid pickled electrodes; further, the hydride film is more inhibitive in character than the oxide. Such hydride films can be formed on the metal surfae by acid-pickling in the variuous media.

REFERNCES

Acherman, W.L., Carter, J.P. and David Schlain (1966) :

Corrosion Properties of Mo, W.V. and Some V-alloys. Bur. Mines, Rept. Invest., 6715 (1), 59.

Andrew, P. Povey and Adrienne, A. Metcalfe (1977) : Andoic

Dissolution of Mo in Alkaline Solution, X-Ray Photoelectron Spectroscopic Studies. J. Electroanal. Chem., 84, 73.

Armstrong, R.D., Bell, M.F. and Adrienne A. Metcalfe

(1977): Anodic Dissolution of Mo in Alkaline Solution & Electrochemical Measurements. J. Electroanal. Chem., 84, 61.

A. Ya. Shatalov and I.A. Marshakov (1954) : Electrode

Potentials and Corrosion of Mo and W.Zh. Fiz. Khim. 28, 42.

Beson, T. and Drautzburg, G. (1960) : Anodic Behaviour of Mo and tungeston. Electrochemica Acta, 3, 158.

Daly, C.M. and Keil, R.G. (1975) : Anodic Oxidation of Molybdenum, J. Electrochem. soc., 122 (3), 350.

George Masing and Gunther Roth (1952) : The Behaviour of Mo and Ni and some Mo-Ni Alloys in Acid Electrolytes. Werkstoffe Korros, 3, 176.

Johnson, J.W., Lee, M.S. and Janes, W.J. (1970) : Electrochemical Behaviour of Molybdenum. Corrosion-NACE, 26 (11).

Kozlova, M.v., Lashko, N.F., Shumilian, N.A. and Burmistrova, A.A. (1968) : Anodic Polarization of Mo, Alloy BM-3P and some Carbide Phases. Zavod Lab., 34 (7), 79.

Makrides, A.C. (1962) : Electrochemistry of surface Oxides. Corrosion, 18, 338 t.

Nakamura, Toyohisa, Haruyama and Shiro (1980) : Anodic Behaviour of Mo in Acetic acid solution Under Potentiostatic and galvanostatic Conditons. Denki Kagaka, 48(7), 406.

Pozdeeva, A.A., antonovskaya, E.T. and sukhotin, A.M. (1966) : Passivity of Molybdenum. Corros. Sci., 6, 149.

Randall, J.J., Bernard, W.J. and wilkinso, R.R. (1965) : A Radiotracer study of the Composition and Properties of Anodic Oxide Films on Tantalum and Niobium.

Wikstrom, L.L. and Ken Nobe (1969) ;: electrochemical Behaviour of Molybdenum. J. Electrochem. Soc., 116, 525.