

## PITTING CORROSION OF STAINLESS STEELS IN CHLORIDE CONTAINING MEDIA

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Pitting corrosion has always posed a serious problem to the corrosion scientists and technologists to encounter. Much knowledge has accumulated over the years on the subject of pitting corrosion through continued research work carried out on pitting (Osozawa *et al.*, 1975; Heusler & Fischer, 1976; Shibata & Takeyama, 1977; and Galvele, 1976) and its related phenomena, in particular the structure and properties of the passive film (Okamoto, 1973; and Bulman & Tseung, 1973). Yet there is no clear understanding of its nature or mechanism, and it has been found difficult to even evaluate it in a comprehensive manner.

Presently, the most widely practised methods for studying pitting corrosion are those involving potentiostat, e.g., chronopotentiostatic, potentiodynamic, etc. More recently another very useful technique, the scratch technique has also been introduced.

In the present work, investigations have been carried out on pitting corrosion of stainless steels of two types, AISI 304L and 316L in various chloride-containing media. Both potentiodynamic and scratch technique were employed to determine the resistance of a given material to pitting in a given environment (Herbsleb & Schwenk, 1973). The experiments were conducted in a two-compartment, H-shaped glass cell, using a potentiostat which was designed and fabricated indigenously.

The chloride-containing media used in the present work were mainly of two types, e.g., (1) Sodium chloride solutions of different concentrations, the *pH* being varied between 2 and 10 for each concentration of solution and (2) phosphoric acid of 60 per cent (wt) containing varying amounts of chlorides with various additives such as ferric oxide and fluosilicic acid. This latter type of solution is generated during acidulation of rock phosphates for producing phosphoric acid slurries as is done in fertilizer plants.

Some interesting observations were made during the determination of the breakdown potentials in sodium chloride solutions using the scratch-technique. When a fresh specimen was to determine the breakdown potential by this method and the specimen was re-passivated without removing it from the system and then the breakdown potential was determined a second time by the same method, the value of the breakdown potential obtained at the second time was higher than that obtained at the first time. On repeating the procedure, a still higher breakdown potential could be obtained at the third time.

The results could be correlated on the basis of a model proposed to explain pit initiation process. Some other commonly observed phenomena, e.g., enhancement of breakdown potential at higher *pH* of solution could also be explained.

The model proposed for pit initiation is the dissolution of metal species in chloride ion containing solutions through anodically disrupted passive metal oxide film, the latter process being influenced by the oxygen partial pressure existing at the metal/metal oxide/solution interface. The pit however propagates through anodic dissolution of metallic species in the pit-environment which progressively gets for more and more acidic and poses problem for easy repassivation.

The effects of some inhibitors on the breakdown potential obtained in phosphoric acid solution with various additives were also investigated.

**Keywords :** Pitting Corrosion; Stainless Steels; Passive Film & Pits

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#### INTRODUCTION

PITTING is a type of corrosion occurring in an extremely localized form on a metal or alloy. This type of corrosion proceeds with the formation of holes or pits which puncture across the passive layer on the metal surface and grow in depth penetrating the section of the material without any appreciable widening of the attacked area. Generally, a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth. It may be considered as the intermediate stage between general overall corrosion and complete corrosion resistance as shown in Fig. 1. Pitting corrosion is dangerous because only a small percentage of metal is lost while rendering the entire structure unusable (e.g., a few perforations in a storage tank). Also, a pitgrowth can proceed without being noticed, until total failure occurs, because of the small size of pits and because pits frequently remain covered with corrosion products. Even when a pit does not cause complete perforation, it can nevertheless weaken the material by producing stress-concentration sites, and causing stress-corrosion failure. Pitting corrosion occurs usually on metals and alloys that exhibit an active-passive transition characteristic, e.g., stainless steels, aluminium, titanium. Pitting has also been reported to occur on noble metals like copper (Cornwell *et al.*, 1973).

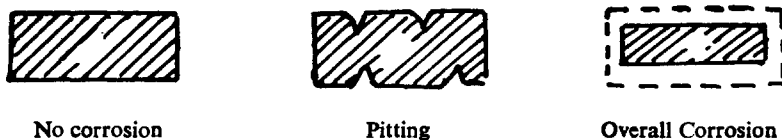


FIG. 1. Diagrammatic representation of pitting corrosion as an intermediate state.

It has now been established that the occurrence of pitting requires the presence in the environment of aggressive anions like chloride, bromide, iodide or oxyhalides.

Some interesting observations regarding pitting are :

- (a) Stagnant media cause more severe corrosion than the flowing ones (Fontana & Greene, 1967); and increased velocities often decrease pitting attack, e.g., in stainless steel pumps handling seawater, pitting is found to occur only during shut-down period, but no damage occurs when it is in continuous operation.
- (b) Pits usually tend to grow in the direction of gravity, e.g., downward from the bottom of a tank.
- (c) Pitting usually require an extended initiation period, sometimes months or years, before visible pits appear (Fontana & Greene, 1967).
- (d) Effect of surface finish: pitting is less likely to occur on polished surface than on etched or ground surfaces.

#### COMBATING PITTING CORROSION

There are several methods available for the control of pitting corrosion:

- (a) Selection of proper material — its chemical composition. This is very important for controlling pitting corrosion. One should try to avoid using a material in an environment showing pitting tendency. Alloying elements can markedly improve the resistance properties e.g., addition of 2-3 per cent Mo to type 304 (18Cr-8Ni) stainless steel. The molybdenum steel shows much greater resistance to pitting than the straight Ni-Cr alloy.
- (b) Control of heat and mechanical treatment. Sensitized stainless steels are more susceptible to pitting corrosion than the corresponding solution-treated steels (Greene & Fontana, 1959).
- (c) Cleanliness and homogeneity of the alloy. The presence of sulphide inclusions in stainless steels has been blamed by several authors for the initiation of pitting (Smialowska, 1971; and Smialowska & Szklarska-Smialowska, 1969). The free machining stainless steels containing upto 0.75 per cent S and/or 0.06 per cent Se are much more susceptible to pitting than stainless steels without these addition (Payer & Staehle, 1971).
- (d) Proper design and maintenance. This can minimize the chances of pit initiation considerably, by avoiding possible zones of stagnation and making arrangement for complete drainage and water rinsing of the equipment during shut-down periods.

#### EVALUATION OF PITTING CORROSION AND METHODS OF STUDY

The classical method of testing for pitting corrosion is to immerse specimens of the material in the environment where it is to be used, and then observe for the damage occurring. This often being time consuming, a more aggressive environment is

sometimes used, e.g., solution of NaCl and K-cyanoferrate is used for accelerated testing (Wranglen, 1972).

Interpretation of test results should be done carefully. Weight loss methods are practically useless here since the percentage metal loss is very small even for deep penetrations. Similarly, number of pits per unit area does not give any clue to the depth of penetration. A better way is to measure the depth of the deepest pit (and again, not the average depth) because the 'first puncture' will cause the failure. This will be clear from Fig. 2. Moreover, such measurements should not be used to predict equipment life, because, pit depth is also a function of specimen area immersed (Fig. 3). However, for laboratory comparisons of pitting resistance, maximum pit-depth measurements (on a given specimen area) are quite acceptable.

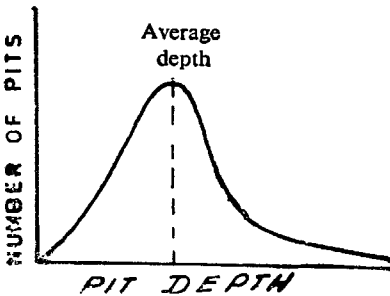


FIG. 2. Relationship between pit depth and the number of pits appearing on a corroded surface.

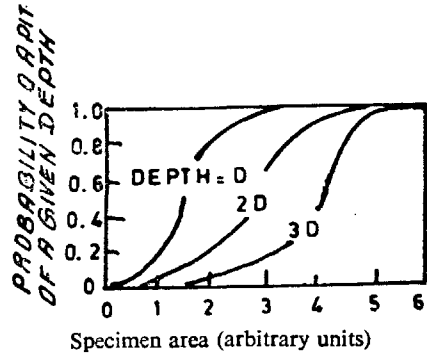


FIG. 3. Pit depth as a function of exposed area.

A common procedure, as cited by Wranglen is to measure the depth of 10 per cent deepest pits on a given surface area, e.g., 1dm<sup>2</sup> and report the maximum and average depths (Wranglen, 1972).

Apart from the classical method of immersion testing described above, there are a series of electrochemical tests for determining the relative pitting tendencies of various metals and alloys. Most often the breakdown potential is measured.

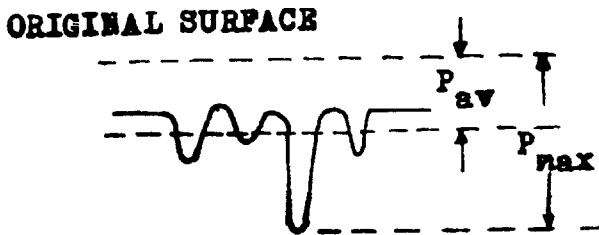


FIG. 4. Pitting factor is the ratio of the deepest penetration,  $P_{max}$  and average penetration,  $P_{av}$ , pitting factor,  $P_{max}/P_{av}$ .

Another method is to determine the lowest concentration of chloride ions to cause pitting.

Electrochemical studies have shown that there exists a critical potential value which characterizes the onset of pitting on a given metal in a given solution. The importance of this potential, known as the critical pitting potential or breakdown potential, was first emphasized by Brenner (1935). This breakdown potential,  $E_b$ , illustrated schematically in Fig. 5, may be determined by either potentiostatic or galvanostatic methods; or their modified forms like potentiodynamic or galvanokinetic methods, where a continuous potential or current sweep respectively, is applied.

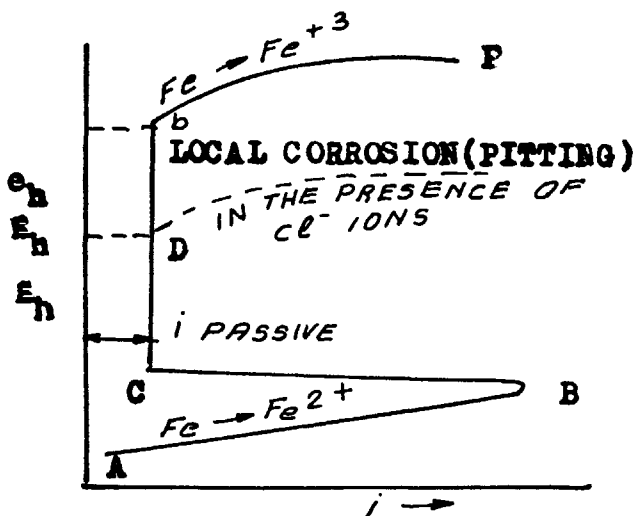


FIG. 5.

The minimum concentration of chloride (or other aggressive) ions required to cause pitting, can be determined from a measurement of the induction time for pit formation. The induction time is the time required for the first pits to appear at a given constant potential of polarisation. (The choice of this potential is somewhat arbitrary but should be sufficient to cause pitting at several  $\text{Cl}^-$  concentrations). The specimen is directly polarized at the chosen potential, and maintained at this potential. The current remains constant ( $i_{\text{passive}}$ ) till a time after which it starts increasing, showing the onset of pitting. This time  $t$  is the induction time as shown in Fig. 6. The induction time is determined at several chloride ion concentrations. Schwenk and Stolica have shown that reciprocal of induction time  $t$  is a linear function of  $\text{Cl}^-$  ion concentration :

$$1/t = K [\text{Cl}^-]$$

Hence, by plotting  $1/t$  versus  $\text{Cl}^-$  concentration, a straight line is obtained which, when extrapolated intersects the X-axis (representing  $\text{Cl}^-$  concentration) at a point at

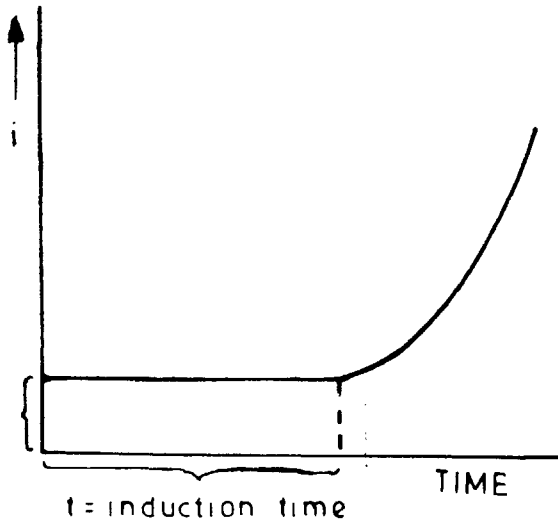


FIG. 6.

which  $1/t = 0$ , or  $t = \infty$  (see Fig. 7). This means that the  $\text{Cl}^-$  ion concentration corresponding to this point of intersection is the highest level of  $\text{Cl}^-$  ion concentration which the material will be able to withstand for an indefinite time without any damage occurring to it.

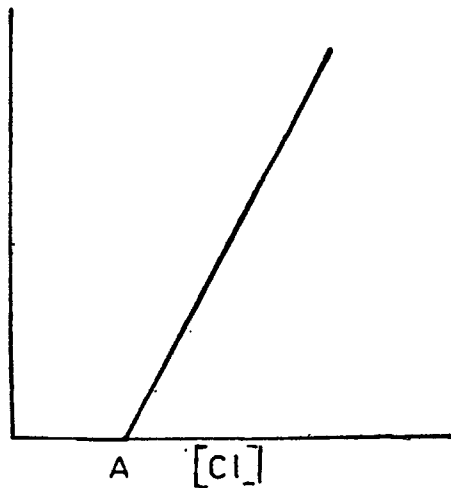


FIG. 7.

Broli *et al.* (1973) have shown that the induction time is strongly dependent on the applied potential. Their result is shown in Fig. 9. Herbsleb and Engell found that the number of pits on iron specimens held at constant potential

increases linearly with time. Their results for three chloride concentrations are shown in Fig. 8. Stolice, during studies on pitting corrosion of Fe-Cr and Fe-Cr-Ni alloys, observed the formation of hemispherical pits. The number of pits were directly proportional to the time, and the c.d. in the pits was approximately that for dissolution of metal in the active region. Current density-time curves (at constant potential) showed an induction period during which the c.d. remained constant, followed by a reaction period in which the c.d. increased according to the equation :

$$i = Kt^3$$

where  $K$  is a constant.

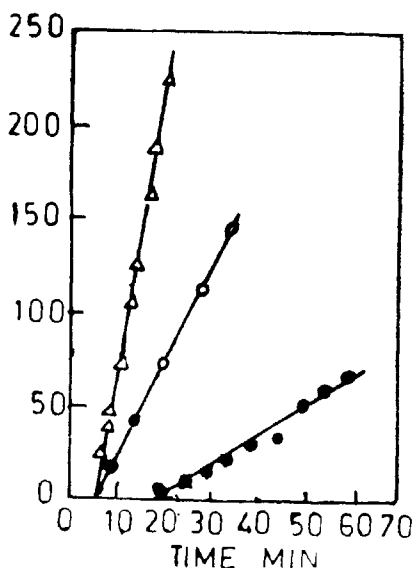


FIG. 8.

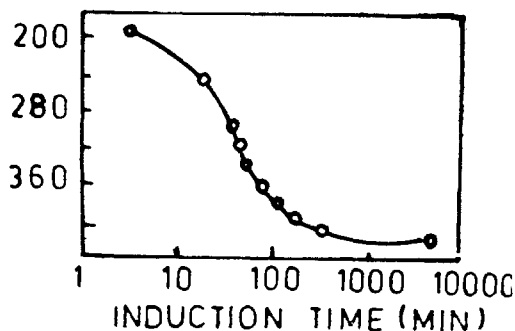


FIG. 9. Applied potential vs. induction time.

#### BREAKDOWN OF PASSIVE FILM AND GROWTH OF PITS

The pits grow by an autocatalytic process as shown schematically in Fig. 10, which shows a growing pit on a metal  $M$  in aerated  $\text{NaCl}$  solution. It is called autocatalytic process because the corrosion processes going on in a pit produce conditions which are both stimulating and necessary for continuing activity of the pit (Fontana & Greene, 1967; and Wranglen, 1972). The reactions are as follows: Rapid dissolution of  $M$  occurs at the bottom of the pit:  $M \rightarrow M^+ + e$ . The released electrons are consumed on surfaces adjacent to the pit in oxygen-reduction reaction:  $\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^-$ . The rapid dissolution of metal inside the pit produces an excess positive charge in this region resulting in the migration of chloride ions into the pit to maintain electro-neutrality. Thus there is a high concentration of  $\text{MCl}$  inside the pit. Hydrolysis of  $\text{MCl}$ :  $\text{M}^+\text{Cl}^- + \text{H}_2\text{O} = \text{MOH} \downarrow + \text{H}^+\text{Cl}^-$  produces high  $\text{H}^+$  ion concentration inside the pit. Both hydrogen and chloride ions stimulate the

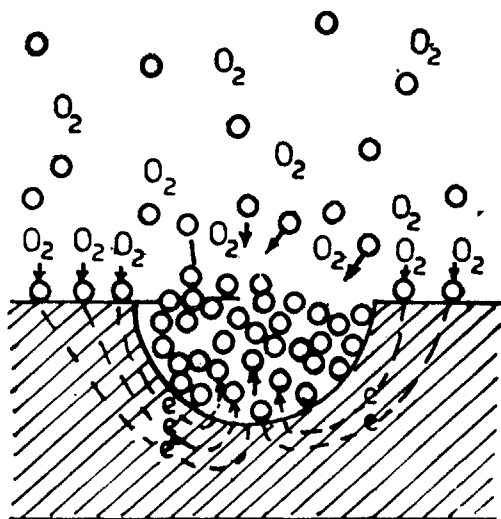


FIG. 10. Autocatalytic processes occurring in a corrosion PIT.

dissolution of most metals and alloys, by locally raising the passivation potential of the metal (Wranglen, 1972). The entire process therefore, accelerates with time.

As already mentioned, the breakdown or rupture of the passive film is associated with a characteristic potential—the breakdown potential. The first to mention the existence of such a potential was Brennert.

The existence of a critical or breakdown potential above which passive alloys are liable to pitting corrosion in halide solutions but below which they resist pitting, probably for an indefinite period of exposure, has also been described by Kolotyrkin and by Leckie and Uhlig.

From discussions by Leckie and Uhlig, Schwenk and Kolotyrkin concerning the measurement of breakdown potential ( $E_b$ ), it can be said that the potentiostatic method for determination of  $E_b$  is practicable only when the induction time for pit nucleation is not too long. The  $E_b$  value can also be obtained by applying the galvanostatic conditions, pitting occurring at a steady anodic potential equal to  $E_b$  (Schwenk, 1964; and Szklarska-Smialowska, 1971). However, in some cases, where during galvanostatic polarization, the potential of the anode reveals periodic oscillations with an amplitude of several hundred millivolts (Szklarska-Smialowska, 1971; and Rosenfeld & Danilov, 1967), it becomes difficult and often impossible to measure the correct value of  $E_b$ .

Many authors have compared the  $E_b$  values determined by using potentiostatic, potentiokinetic or galvanostatic methods. Some of them have found a good agreement among the  $E_b$  values determined by these methods. Others, on the contrary, have concluded that  $E_b$  values determined by the different methods do not agree among themselves (Lizlovs & Bond, 1968). Pourbaix has shown that these differences occur mainly due to the fact that one should distinguish between two



critical potential values for pitting. The critical pitting potential ( $E_{cp}$ ) corresponds to a state below which the metal or alloy is just completely resistant to pitting, i.e., no new pits can form and if any earlier pits were present, they undergo repassivation and do not develop any further. The pit nucleation potential, ( $E_{np}$ ), on the other hand is a value higher than  $E_{cp}$  and is such that below  $E_{np}$  (and above  $E_{cp}$ ) no new pits can form, but already existing pits can grow. New pits can form only at potentials above  $E_{np}$ . Under certain conditions, e.g., at high chloride ion concentrations,  $E_{np}$  tends to fall towards  $E_{cp}$ . Fig. 11 schematically shows the positions of  $E_{cp}$  and  $E_{np}$ .

Szklarska-Smialowska and Janik-Czachor have also determined two critical potential values. From their studies it appears that for practical applications, determination of  $E_{cp}$  is more useful than the determination of  $E_{np}$ , since  $E_{cp}$  indicates the range of potentials lower than  $E_{np}$  such that below  $E_{cp}$  pitting can not continue.

Leckie, Uhlig and Horvath (cf Leckie & Uhlig, 1966) have shown that the value of the critical potential ( $V_c$ ) obtained by potentiostatic measurements show a variation depending upon the potentiostatic conditions applied. The values obtained under non-steady state conditions ( $V'_c$ ) (i.e., without allowing sufficient time for the current to attain a steady value at a fixed potential) were lower than the values obtained under steady-state condition ( $V_c$ ).

In a more recent communication, Herbsleb and Schwenk have described three different critical potential values for pitting. Two critical potentials for pit formation i.e., stable ( $U_f$ ) and repassivating ( $U_r$ ) pitting and a critical value for pit passivation ( $U_p$ ).

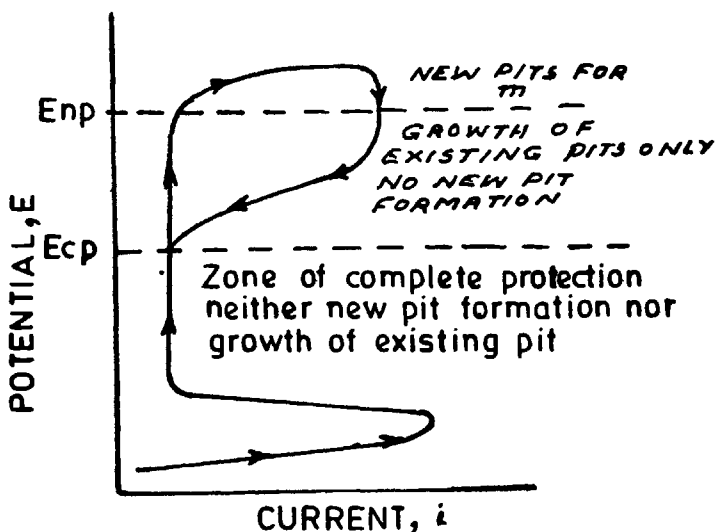


FIG. 11. Position of  $E_{cp}$  &  $E_{np}$ .

The effects of some environmental factors on critical potential for pitting can be discussed here. Leckie and Uhlig observed a marked increase in  $E_{crit}$  of 18-8 stainless steel as the temperature decreases from room temperature (Fig. 12). On the basis of  $E_{crit}$  values determined at 0 °C (+0.84V) and 25 °C (+0.35V) and redox potential for the reaction  $Fe^{++} \rightarrow Fe^{+++} + e$  (+0.77V) containing  $Fe^{+++}$ , 18-8 steel would pit at 25 °C but would not pit at 0 °C. The prediction was confirmed in a 0.5M  $FeCl_3$ —0.5M NaCl solution.

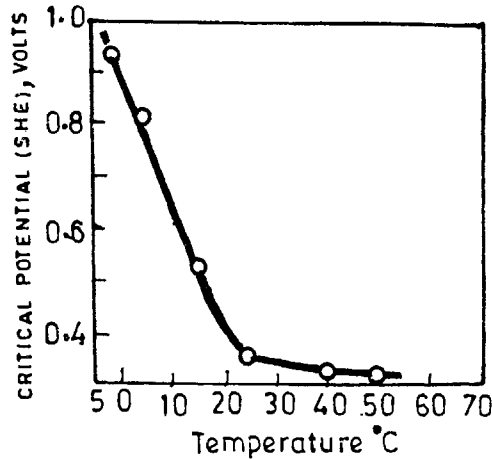


FIG. 12. Effect of temperature on critical potential for pitting of type 304 stainless steel in 0.1N NaCl.

Tatsuya Koizumi and Shuichi Furuya studied pitting corrosion of titanium in high temperature halide solutions. In chloride solution, the pitting potential drastically shifts towards active values upto 130 °C but not so steeply above 130 °C. In bromide solution the critical potential does not change so drastically upto 250 °C from room temperature. Their results are shown in Fig. 13.

Leckie and Uhlig observed the effect of pH on critical potential of 18-8 stainless steel. The critical potential is unaffected by pH changes from 1 to 7 pH but then rise sharply from pH 7 to 10 (Fig. 14). The critical potential in neutral NaCl solutions was found to decrease with increasing  $Cl^-$  concentration (Fig. 15). The values of  $E_{crit}$  in volts are linear with the logarithm of activity as shown in the following equation :

$$E_{crit} = 0.088 \log (Cl^-) + 0.168$$

The critical potentials for pitting of Ti in 0.53N NaCl solution were measured in pH range from 1 to 7 by Koizumi and Furuya, at 200 °C. The effect of increasing acidity in 0.53N NaCl solution is to shift the critical potential in the active direction by about 0.2V from pH 7 to pH 1. The same authors have observed the effect of halide ion concentration and effect of additive anions. They have given

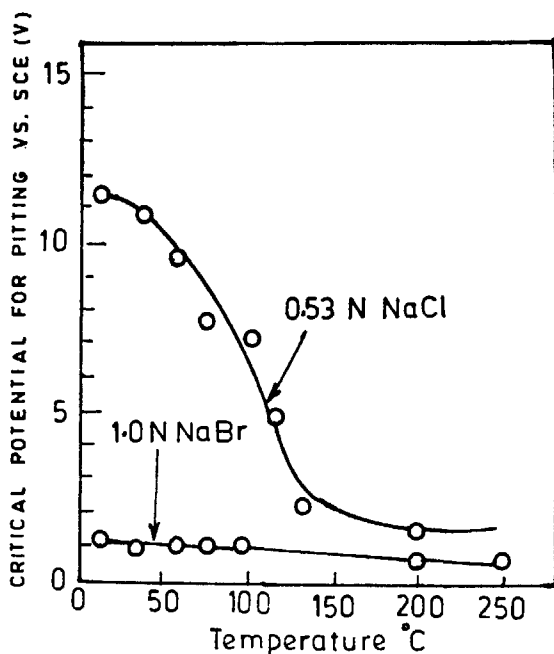


FIG. 13. Effect of temperature on critical potential for pitting in 0.53N NaCl and 1.0N NaBr.

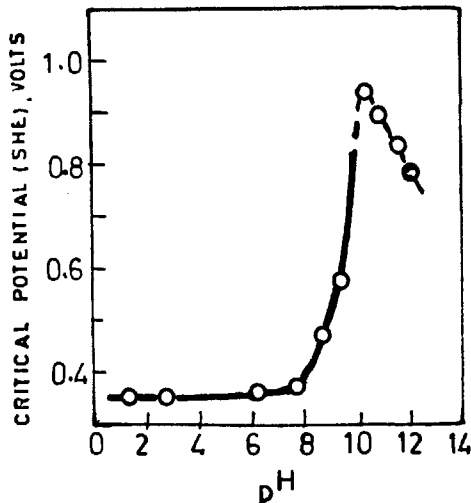


FIG. 14. Effect of pH on critical potential for pitting of type 304 stainless steel in 0.1N NaCl at 25 °C.

the following equations representing the relations between critical potentials vs. S.C.E. in volts and concentration of halide ions :

$$V_0 = 1.4 - 0.10 \log [\text{Cl}^-] \quad (\text{at } 200^\circ \text{C})$$

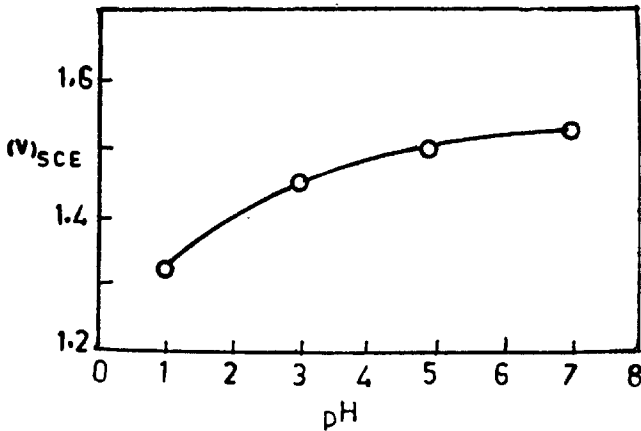


FIG. 15. Effect of pH on critical potential for pitting in 0.53N NaCl at 200 °C.

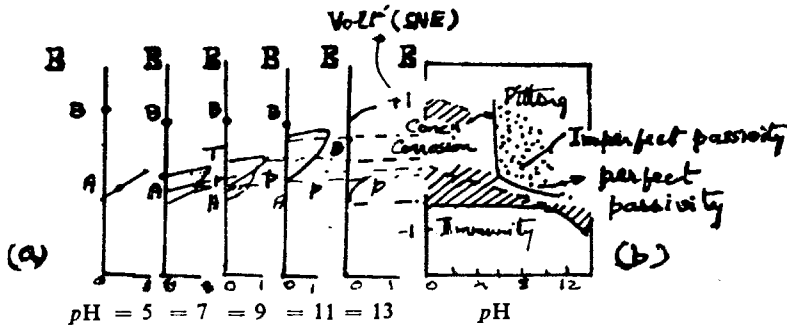


FIG. 16. Behaviour of iron solutions containing chloride ( $10^2$  gm lit i.e., 355 PPM  $Cl^-$ ) (a) Polarization curves in the presence of solutions pH 5 to 13 and (b) Experimental circumstances of immunity, general corrosion imperfect and perfect passivity and pitting.

$$V_c = 1.1 - 0.43 \log [Br^-] \quad (\text{at room temperature})$$

The effects of various oxyanions such as  $SO_4^{2-}$ ,  $MO_3^-$ ,  $CrO_4^{2-}$ ,  $PO_4^{3-}$  and  $CO_3^{2-}$  in NaBr solutions at room temperature and 200 °C were investigated by them.

Hoar presented a diagram illustrating anodic behaviour at various potentials in solutions of various anion/water concentration ratios.

Pourbaix studied the influence of pH in the range from 5 to 13, on the behaviour of iron in solution containing chloride at various potential. The schematic potential—pH diagram showing zones of immunity, general corrosion, pitting and passivity is presented in Fig. 16. Figs. 17 and 18 show the pitting and protection of AISI 410 and AISI 304 respectively for  $Cl^-$  conc. of  $10^{-1}M$ .

#### INVESTIGATIONS CARRIED OUT BY ECRI, KARAIKUDI

Some investigations have been carried out in our laboratory on the pitting corrosion of AISI 316 stainless steel in phosphoric acid. Such problems are encountered at

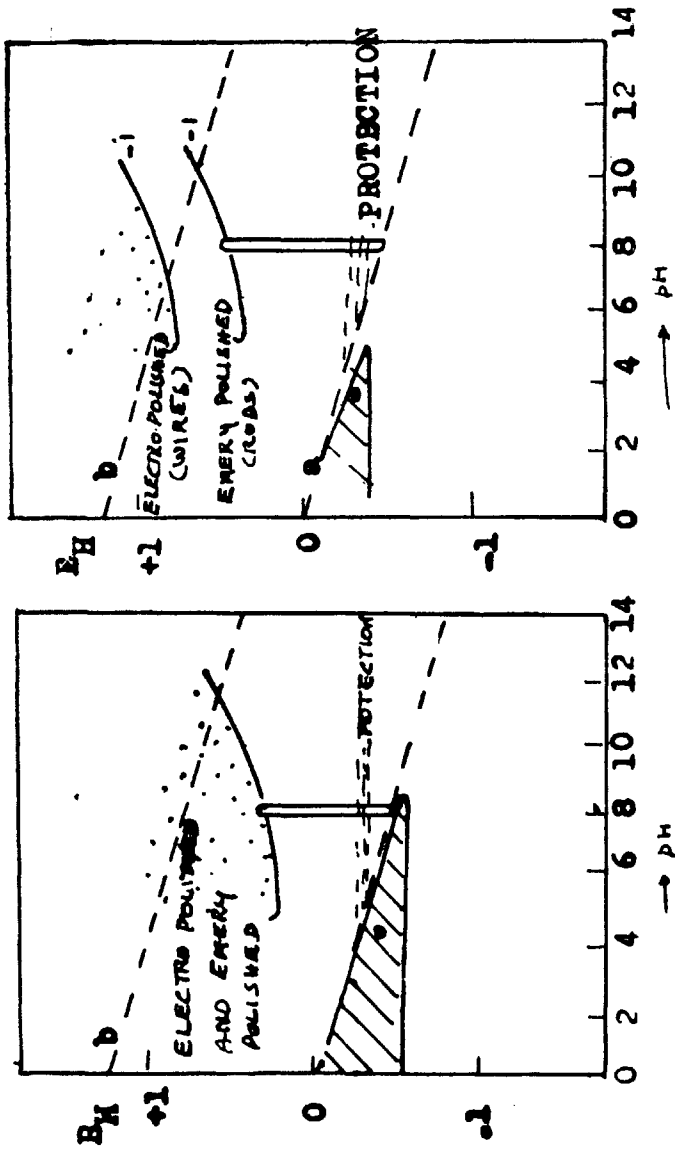


FIG. 17. Pitting and protection of chromium steel AISI 410 ( $\text{Cl}^- 10^{-1}$  molar).

FIG. 18. Pitting and protection of chromium nickel steel AISI (304  $\text{Cl}^- 10^{-1}$  molar).

fertilizer plants in nitrophosphate reactors made of AISI 316L stainless steel. In the nitrophosphate reactors, rock phosphate is reacted with  $H_2SO_4$  and  $HNO_3$  to produce phosphoric acid which is subsequently neutralized with ammonia to produce the nitrophosphate. Pure phosphoric acid is harmless to AISI 316 (and 316L) stainless steel. But the phosphoric acid generated in these reactors contain impurities like chloride, fluosilicic acid,  $Fe_2O_3$ , etc. coming from the original phosphate rock. These contaminants in the acid give rise to severe corrosion of the reactors and agitators—pitting, weld-decay and vapour-phase corrosion are observed to occur. Investigations were first carried out by anodic polarization measurements. Then immersion tests in solutions of various compositions were conducted to compare the relative corrosion behaviour predicted by the anodic polarization measurements.

A classical potentiostat (Greene & Pontana, 1959) was used for polarizing the test electrode. It consisted of a stabilized d.c. power supply (0–30V, 0–10Amp continuously variable) across which a manganin-wire potential divider of 1ohm resistance was connected. The output from the potential divider was connected across the cell. The electrolyte consisted of 60 per cent solution of analar grade phosphoric acid and various impurities were added to it. The experimental sequence was as follows :

- i. Determination of  $E_b$  values from polarization studies with increasing chloride concentration,  $Fe_2O_3$  addition and addition of  $H_2SiF_6$ .
- ii. Induction time measurement and determination of the lower  $Cl^-$  ion concentration required to initiate pitting.

### Results

The induction times were measured in two solutions : (i) 60 per cent  $H_3PO_4$ , 2.5 per cent  $Fe_2O_3$  (results are shown in Fig. 19) and (ii) 60 per cent  $H_3PO_4$ , 2.5 per cent  $Fe_2O_3$ , 9 per cent  $H_2SiF_6$  (results are shown in Fig. 20). Variable quantities of chloride ions were added in each of the above solutions. A constant polarizing

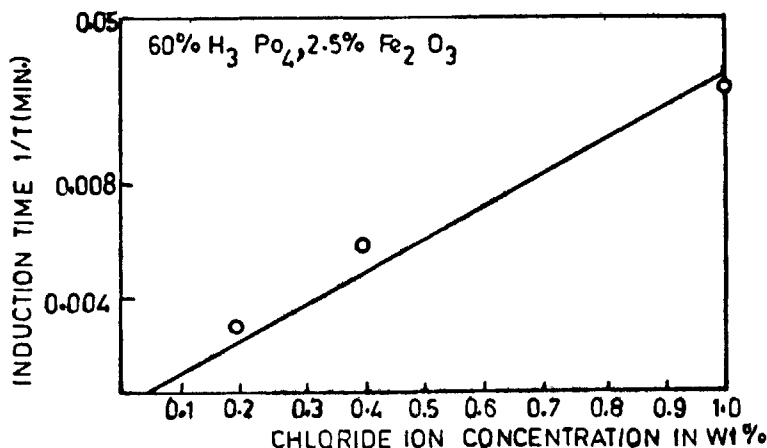


FIG. 19. Reciprocal of Induction time vs. chloride ion concentration curve

potential of +500mV was used for determining induction time  $t$ . Then the minimum chloride ion concentration, required to initiate pitting, was determined from graphs of  $1/t$  versus chloride ion concentration. It was observed that 9 per cent  $H_2SiF_6$  decreased considerably the minimum chloride ion concentration requirements for the initiation of pitting.

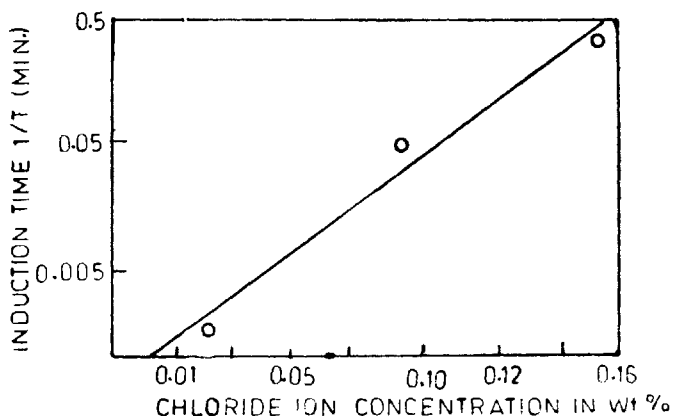


FIG. 20. Effect of hydrofluorosilic acid on minimum 10N chloride ion concentration for pitting.

The following conclusions could be drawn on the basis of these experiments :

The nucleation of pits is a function of the electrode potential and chloride ion concentration.

The induction time for pit nucleation is substantially affected by 9 per cent  $H_2SiF_6$  in phosphoric acid containing chloride ions.

Less than 0.05 per cent  $Cl^-$  ions do not initiate pitting in solution containing 60 per cent  $H_3PO_4$ , 2.5 per cent  $Fe_2O_3$ . In a solution containing 60 per cent  $H_3PO_4$ , 2.5 per cent  $Fe_2O_3$ , 9 per cent  $H_2SiF_6$ , less than 0.006 per cent  $Cl^-$  ions do not initiate pitting (these results are valid for electrode potential of +500mV).

Sulphate ions increase the resistance of AISI 316 stainless steel to pitting.

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