

## **CORROSION RESISTANCE AND SUSCEPTIBILITY OF TYPE 304 AUSTENITIC STAINLESS STEEL IN STRONG ACIDS**

By

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### **ABSTRACT**

The resistance and susceptibility of austenitic stainless steel – Type 304 exposed to strong tetraoxosulphate (VI) and tetraoxophosphate (V) acids contaminated with sodium chloride at ambient temperatures was investigated by the weight-loss method. Scanning Electron Microscope (SEM) was used to examine and characterize the test specimens' surface after immersion in the corrosive media. Surface corrosion deposit composition was analyzed with SEM paired with Energy Dispersive Spectrometer (EDS). This paper reports the observed severe general – and pitting corrosion; and the resistance of the steel to corrosion at different concentrations of the acid chloride media.

**Key Words:** stainless steel, corrosion, acids, anodic dissolution, acid chloride.

### **INTRODUCTION**

The desire to gain more knowledge about corrosion phenomena and their control and hence appropriate and better utilization of austenitic stainless steel – particularly the Type 304 – UNS S304 008, has been of utmost concern and interest to corrosion scientists and engineers world wide. The selection of materials in the fabrication of equipment, components and in the construction of industrial plants for the manufacture of acids, chemicals and their derivatives, is vital in ensuring the long life, dependability, reliability, safety and economic viability of the plants and industrial components. A considerable number of research work has been done in this respect. <sup>(1-6)</sup>

The most common method of preventing corrosion is the selection of the appropriate metal or alloy for a particular corrosion

service. This is the most important method of preventing or reducing corrosion damage. The austenitic stainless steels comprise a large and varied group of iron based alloys containing 18% or more chromium and sufficient nickel to assume fully austenitic metallurgical structure. The most common form is referred to as "18 - 8" stainless steel (18% Cr and 8% Ni) of which the Type 304 stainless steel belongs. These alloys are of major importance in the chemical process industries. They are the alloys of choice for many of the applications which require a higher level of corrosion resistance than carbon steel.

It is widely known that the austenitic stainless steels have a wide spectrum of resistance to corrosion by chemical environments. The stainless steels form a film, which protects the underlying metal from attack in many environments. This film is very thin, essentially transparent, and self-healing; if it is damaged mechanically or chemically, it will reform the protective film very rapidly <sup>(7)</sup>. However, in a situation where the rate of damage is more than the rate of repair, a progressive active corrosion reaction will occur which may cause corrosion degradation of the alloy.

While it is known that stainless steels have wide spread application in resisting corrosion, it should be remembered that they do not resist all corrosives <sup>(7)</sup>. In brief, a large number of corrosion failures can be directly attributed to the indiscriminate selection of stainless steel for construction on the basis that they are the best. Stainless steel represents a class of highly corrosion-resistant materials of relatively low cost, which should be carefully used.

Tetraoxosulphate (VI) (sulphuric) and tetraoxophosphate (V) (phosphoric) acids are the two corrosion media used in this work. Clearly more tetraoxosulphate (VI) acid is produced than any other chemical in the world <sup>(8)</sup>. It is used directly or indirectly in nearly all industries. It is principally used in the production of chemicals and their derivatives, pickling of steel and other metals, manufacture of fertilizers, dyes, drugs, pigments, explosives, synthetic detergents, rayon and other textiles, petroleum refining, and production of rubbers. In making the acid, the problem of corrosion is significant in the production plants. The acid also causes major problem in consumers' plants when it is utilized under a wide variety of conditions. The resistance of austenitic stainless steels to tetraoxosulphate (VI) acid is complex due to

the active-passive nature of the alloys. An excellent summary of this phenomenon has been made <sup>(9)</sup>. In this work, the acids used are further contaminated with sodium chloride (NaCl) to further enhance the breakdown of passivity by the chloride ions.

Tetraoxophosphate (V) acid is the second corrosive environment used in this work. It was chosen, also, because of its industrial applications. Corrosion by tetraoxophosphate (V) acid depends to a large extent on the methods of manufacture and the impurities present in the commercial finished products. Fluorides, chlorides and tetraoxosulphate (VI) acid are the main impurities present in the manufacturing process and in some marketed acids <sup>(10)</sup>. Higher alloys of stainless steels are widely used in tetraoxophosphate (V) acid systems at higher concentrations.

This present investigation looks at the corrosive degradation phenomenon of Type 304 austenitic stainless steels in the two acids used. It aims at evaluating the corrosion resistance of Type 304 austenitic stainless steel at different concentrations of sodium chloride contaminated strong acids to determine its viable usefulness in this type of harsh environments which simulate many industrial applications/conditions. A

further objective of this work is that of making a contribution to the on-going research work in the use of stainless steels in simulated industrial environments such as the very strong acids used in the investigation.

## Experimental Procedure

### Material

The steel used in this work was the Type 304 austenitic stainless steel of average nominal composition: 18.11%Cr, 8.32%Ni, and 68.37%Fe. The energy dispersive spectrometer (EDS) analysis of the steel composition is presented in Fig.1. The material is cylindrical and has a diameter of 0.65 cm (65mm).

### Test media

- i) 9M tetraoxosulphate (VI) acid
- ii) 18M tetraoxosulphate (VI) acid
- iii) 7M tetraoxophosphate (V) acid
- iv) 14M tetraoxophosphate (V) acid

All the acids were of Analar grade. Each of the above test media was contaminated with sodium chloride (NaCl) of 2% concentration.

### Preparation of test specimens

The cylindrical stainless steel (0.65 cm dia.) was cut into a number of test specimens of different dimensions in length ranging between 1.78 and 1.88 cm. The two surface ends of each of the specimens were ground with silicon carbide abrasive papers of 240, 400, 400 and 600 grits. They were then polished with 1.0  $\mu\text{m}$  diamond paste, washed with distilled water, rinsed with methyl alcohol, dried and stored in a desiccator for further weight-loss tests and the scanning electron microscopy surface examination and characterization.

### Energy Dispersive Spectrometer

#### (EDS) analysis

The EDS analysis of the steel composition is presented in Fig.1 as mentioned earlier. A further EDS analyses of the test specimens' surfaces after the immersion tests were performed on the surface film and corrosion products. The representative results obtained are presented in Figs. 2(a) and 2(b).

#### Weight-loss experiments

Weighted test pieces were separately and equally immersed in each of the four different concentrations of the test media contained in separate 100ml beakers for a period of 21 days at ambient temperatures. Each of the specimens was taken out every three

days, washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg) versus exposure time (days); and those of corrosion rate (calculated) versus exposure time (days) were made (Figs. 4 - 15).

### Scanning Electron Microscopy

#### Examination

A polished surface of the steel was etched with oxalic acid and the microstructure examined in the SEM. The obtained micrograph is presented in Fig.3. Micrographs of the surface features of the ground and polished test specimens were made as well (Fig.16). Further SEM characterizations of the corroded surfaces were made after many days of immersion of the test specimens in the different acid media. Micrographs of the representative areas were made (Figs. 17 - 20). All micrographic images were made with JEOL 840 Scanning Electron Microscope (SEM).

## RESULTS AND DISCUSSION

### Energy Dispersive Spectrometer analysis.

The energy dispersive spectrometer analysis of the steel composition, (Fig.1), gave the nominal compositions of the Type - 304 austenitic stainless steel used. Apart from the compositional analysis, the micrographs of the steels' microstructure, Fig.3 made

from the polished and etched specimen surface confirmed the stainless steel used. The analyses of the corrosion deposit on the surface of the specimen after immersion are presented in Figs. 2 (a) and 2(b) for the 9M tetraoxosulphate (VI) acid and 14M tetraoxophosphate (V) acid environments respectively. The elemental sulphur, S, from tetraoxosulphate (VI) acid is indicated as a peak in Fig. 2 (a). Iron, chromium and nickel are also present. In Fig. 2 (b), representing the analysis of the corrosion deposit on the steel specimen surface, immersed in tetraoxophosphate (V) acid, the peak signals include that of sulphur (S) and silicon (Si), in addition to phosphorus, P, from the tetraoxophosphate (V) acid. Depending upon the manufacturing method of the tetraoxophosphate (V) acid, different impurities are usually present including chlorides, silicon and sulphuric acid<sup>(10)</sup> as mentioned earlier.

### Weight-loss method

#### 1. 9M tetraoxosulphate (VI) acid ( $H_2SO_4$ ) environment

The results obtained for the weight-loss method and the corrosion rate in 9M  $H_2SO_4$  are presented in Figs. 4 & 5. In Fig. 4 there was a significant increase in weight-loss of the test specimen with time in the first twelve (12) days of the experiment, which got to 400mg. After

this period, and to the end of the experiment a steady state corrosion reactions phenomenon was maintained and there was no loss of weight of test specimen observed. This observation could be explained to be due mainly to the stifling effect of the corrosive medium by the corrosion deposit, which has weakened the acid chloride test environment. In Fig. 5, which is the corresponding curve of corrosion rate calculated from the data in Fig. 4, the corrosion rate was high, achieving 5.5 mm/yr. within the first three- (3) days of the experiment. From this period, the corrosion rates decrease progressively with time to the end of the experiment. These results are indications that tetraoxosulphate (VI) acid  $H_2SO_4$ , contaminated with 2% sodium chloride at the strength concentration of 9M, is very corrosive to Type 304 stainless steel. While the acid alone could be reactive at that concentration or strength, the addition of sodium chloride further enhanced the corrosion reactions. The chloride ion ( $Cl^-$ ) would have made a contribution in breaking down the steel's passive film for  $Cl^-$  to react with the steel specimen's surface. The result would be that of initiating active corrosive reactions. This environment is indeed very corrosive to Type 304 stainless steel. At this concentration of 9M, the acid had been much diluted with distilled water from the original concentration of 18M. This dilution enhanced not only the solubility of sodium

chloride in the acid, but also the movement of chloride ions to the specimen surface and subsequent corrosion reactions.

## 2. 18M tetraoxosulphate (VI) acid ( $H_2SO_4$ ) environment

In general, weight-loss of test specimen in this test environment was minimal when compared with the 9M  $H_2SO_4$ . The very little weight-loss recorded might be due to the influence of the sodium chloride addition. It was a relatively passive environment. In the first eighteen- (18) days of the experiment, the weight-loss recorded was 6mg; though this jumped to 10mg as at twenty-one (21) days. On the average, the corrosion rate of the steel specimen in this test medium is about 0.045 mm/yr. The test environment -18M  $H_2SO_4$  can therefore be regarded as safe for the use of Type 304 stainless steel.

## 3. Comparing the two different acid ( $H_2SO_4$ ) concentrations

A very good comparison of the weight-loss and corrosion rates for the steel specimens in both the 9M and 18M  $H_2SO_4$  [tetraoxosulphate (VI)] acid concentrations are indicated in Figs. 4 and 5 respectively. It is apparent in Fig.5 that the steel corroded very significantly in the 9M  $H_2SO_4$ , while in the 18M  $H_2SO_4$ , the corrosion can be described as

negligible throughout the experimental period. In Fig.5, the difference in corrosion rate for the steel specimens in the two different acid concentrations is also very significant. In 18M  $H_2SO_4$ , the corrosion rate was very insignificant.

## 4. 7M tetraoxophosphate (V) acid ( $H_3PO_4$ ) environment

The results for the variation of weight loss with exposure time for the stainless steel specimen immersed in 7M  $H_3PO_4$  are presented in Fig.6. Also presented in Fig.7, are the results of the corresponding corrosion rate for the steel specimen immersed in the same acidic environment. Weight loss of the specimen in this acid concentration is low, achieving a maximum of 0.7mg in the last fifteen (15) to twenty-one (21) days of the experiment. The addition of 2% sodium chloride (NaCl) did not indicate any appreciable influence. This environment can therefore be regarded as relatively safe for the Type 304 stainless steel. The corrosion rate, as shown in Fig.6, did not show any increasing trend during the period of the experiment. The overall trend, to the end of the experiment was that of a slow or gradual decreasing corrosion rate to

about 0.0056 mm/yr. This corrosion rate is negligible.

#### 5. 14M tetraoxophosphate (V) acid ( $H_3PO_4$ ) environment

In this environment, weight loss is very significant as shown in Fig.6, achieving a weight loss of 190mg in twenty-one (21) days of the experiment. This result was observed to be in opposite to what was obtained in the tetraoxosulphate (VI) acid environment, in which the higher strength of 18M was just only very slightly corrosive. It is, however, very difficult to explain the differential corrosion behaviour. The reacting species of this acid, the  $PO_4^{=}$  and  $Cl^-$  ions from the added sodium chloride at the strength of 14M has been able to depassivate and penetrate (by film rupture) the stainless steel's chromium protective film and initiate active corrosion reaction by anodic dissolution.

The corresponding corrosion rate to the weight loss, presented in Fig.7 shows initial drastic decreasing corrosion rate with time. It was about 7 mm/yr. as at three days of the experiment. It further decreased to about 3 mm/yr. as at six days of the experiment. The corrosion rate, thereafter, decreased very slowly to 1 mm/yr. at the end of twenty-one (21)

days of the experiment. In general, the decreasing rates of corrosion with exposure time, can be explained to be due to the reduction in the strength of the acid corrosion medium by the contamination of corrosion deposits which came from the corroding metal specimen.

#### 6. Comparing the two different $H_3PO_4$ concentrations

A comparison of weight loss for the two specimens immersed in 7M and 14M  $H_3PO_4$  is given in Fig.6. The 7M  $H_3PO_4$  medium did not give any appreciable corrosion while in 14M  $H_3PO_4$ , the weight loss, which is an indication of the magnitude, is very significant as presented in Fig.6. In Fig.7, the corrosion rates for the steel specimens in the two different concentrations of the sodium chloride contaminated acids are compared. No appreciable corrosion rate was observed in 7M  $H_3PO_4$  medium; this is unlike the 14M  $H_3PO_4$  where the corrosion rate decreases with the time of exposure.

#### Scanning electron microscopy (SEM) examination and characterization

##### 1. Specimen examination before immersion. The representative polished

cross-section surface and the side view (length-wise) of the cylindrical test specimens were examined in the SEM before the immersion test for the weight loss method. Two micrographs were taken Figs.8 (a) and (b) to show the specimens surface appearance before the corrosion test.

**Steel specimen immersed in 9M H<sub>2</sub>SO<sub>4</sub>.** The SEM micrographs made for the steel test specimen immersed in 9M H<sub>2</sub>SO<sub>4</sub> are presented in Figs.9 (a), (b) and (c). Fig.9 (a) shows the cross-section surface after the weight loss immersion test at a low magnification of X15. Fig.9 (b) is a portion of Fig.9 (a) but at a higher magnification of X300. Fig.9 (a) shows the topographic image of the corroded surface. The very severe corrosive degradation of the acid test medium is very apparent. The corrosion mode was that of severe general corrosion which was accompanied with pitting as evidence in Fig.9(c). In this test medium, the corrosion reaction species are sulphate ions (SO<sub>4</sub><sup>2-</sup>) from the tetraoxosulphate (VI) acid and chloride ions (Cl<sup>-</sup>) from the added sodium chloride. Mechanistically, these ions are known to depassivate the chromium protective film on the stainless steel's

surface (film rupture). This is achieved by penetrating through the passive film to begin a process of active interfacial corrosion reactions at the specimen's surface. Pit formation then results from the anodic dissolution of the steel alloy's specimen. The SEM micrographs of the side view of the steel specimen after the immersion test are shown in Fig.10 (a) and (b) respectively. The corrosion damage here was immense. It was a complete corrosive degradation with just very few discernible number of pits. Due to the negligible magnitude of corrosion observed in the 18M H<sub>2</sub>SO<sub>4</sub> as indicated by weight loss method, the SEM examination and characterization were not performed.

**3. Steel specimen immersed in 14M H<sub>3</sub>PO<sub>4</sub>.** Fig.11 (a) and (b) shows SEM micrographs of the steel specimen cross-section surface immersed in 14M H<sub>3</sub>PO<sub>4</sub> at the low (X15) and high (X1000) magnifications respectively. The corrosion damage here was also tense. It was a severe general corrosion damage together with pitting corrosion. The corrosion mechanism here is as discussed above for the H<sub>2</sub>SO<sub>4</sub> test media. The reacting species here are however, phosphate ions and chloride



ions. The impurities like tetraoxo- sulphate (VI) acid in tetraoxophosphate (V) acid medium such as indicated by sulphur peak in Fig.2 (b), could also make a contribution to the adverse corrosion effect.

**CONCLUSION**

Austenitic stainless steel – Type 304, at ambient temperature can resist corrosion in tetraoxosulphate (VI) acid contaminated with sodium chloride (2%) at very high strength concentration (18M H<sub>2</sub>SO<sub>4</sub>). The steel, under the same temperature condition, is also very susceptible to corrosion as it can undergo severe general corrosion and pitting in the same acid-chloride environment but at a lower strength concentration of 9M H<sub>2</sub>SO<sub>4</sub>.

The tetraoxophosphate (V) acid and 2% sodium chloride environment used can also resist corrosion, but at a lower concentration of 7M H<sub>3</sub>PO<sub>4</sub>. At the higher concentration of 14M H<sub>3</sub>PO<sub>4</sub>, austenitic stainless steel Type – 304 is very much susceptible to corrosion.

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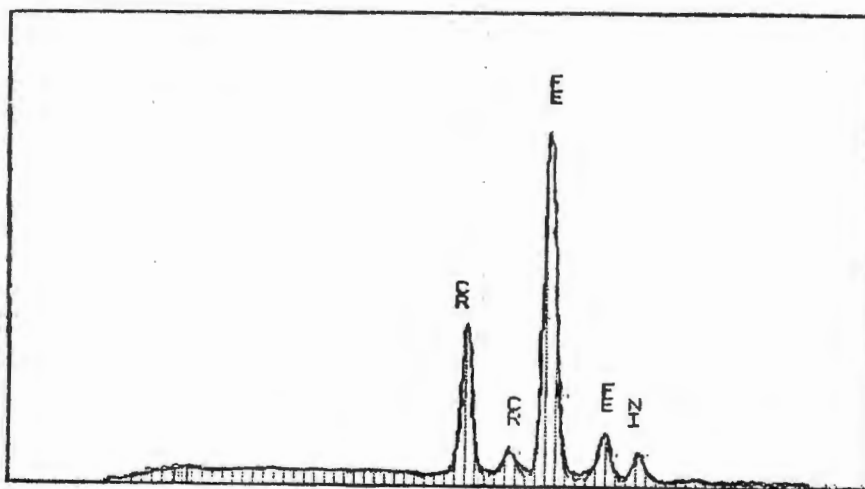


Fig.1 The energy dispersive spectrometer (EDS) analysis of the steel specimen composition.

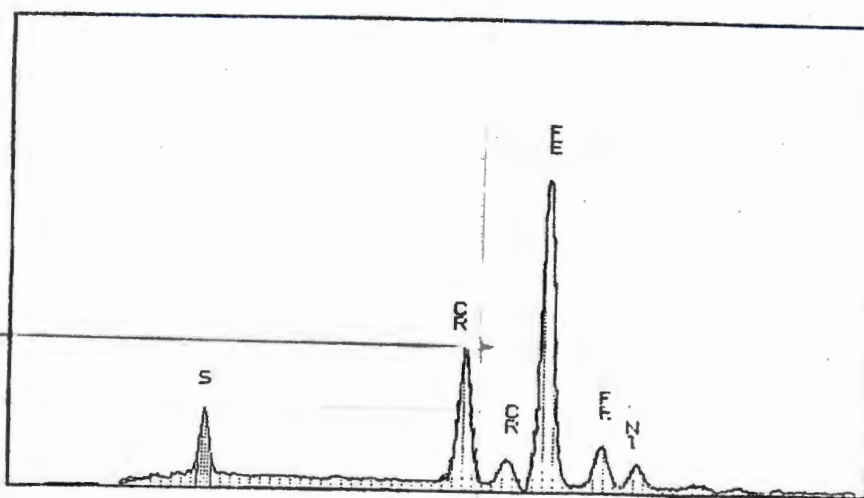


Fig.2 (a) Energy dispersive spectrometer (EDS) analysis of the surface film and corrosion deposit on the steel specimen surface after the immersion test in tetraoxosulphate (VI) acid.

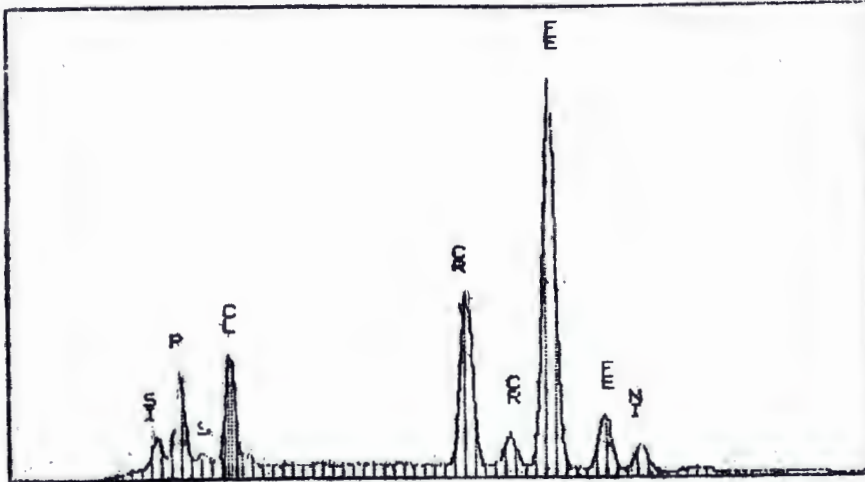


Fig. 2(b) Energy disnersive spectrometer (EDS) analysis of the surface film and corrosion deposit on the steel specimen surface after the immersion test in tetraoxophosphate (V) acid.

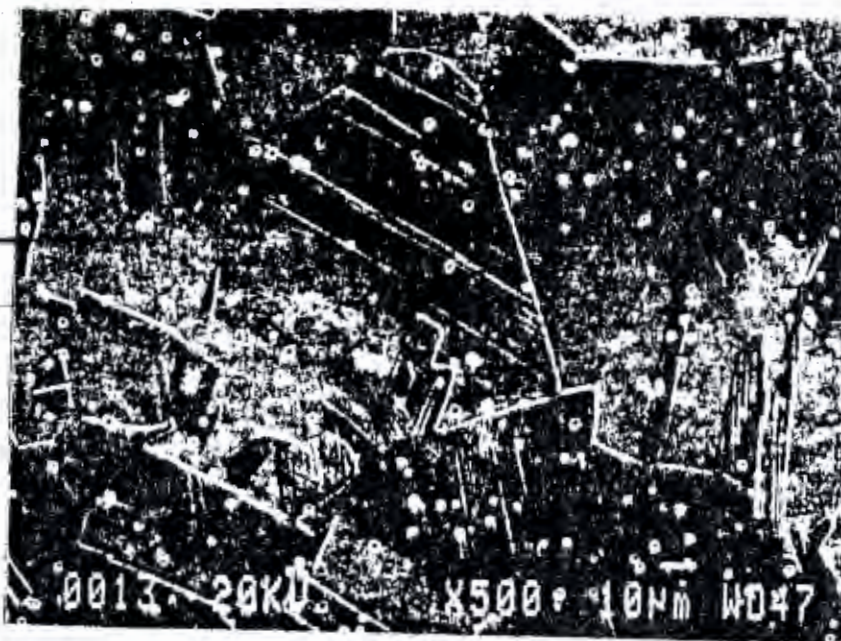


Fig. 3 Micrographs of Type 304 austenitic stainless steel. Etched in oxalic acid.

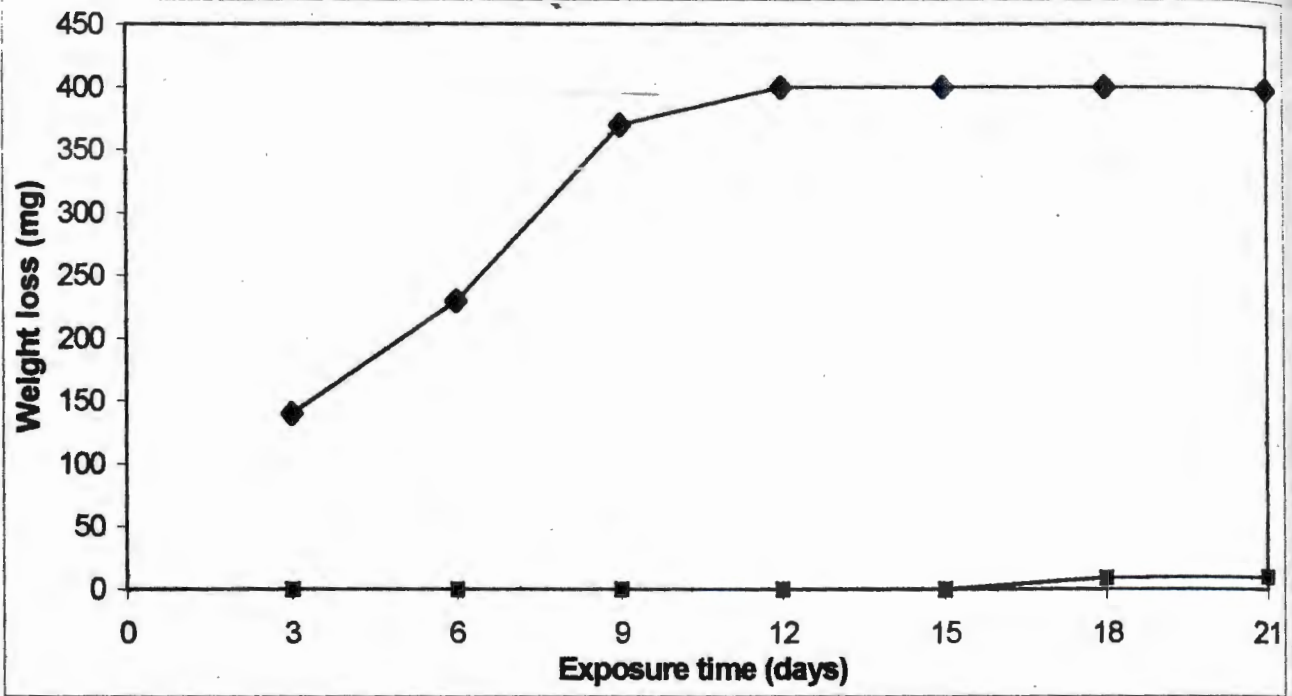


Fig 4: Variation of weight loss with exposure time for stainless steel specimens immersed in 9M and 18M sulphuric acid.

- ◆ = 9M H<sub>2</sub>SO<sub>4</sub>
- = 18M H<sub>2</sub>SO<sub>4</sub>

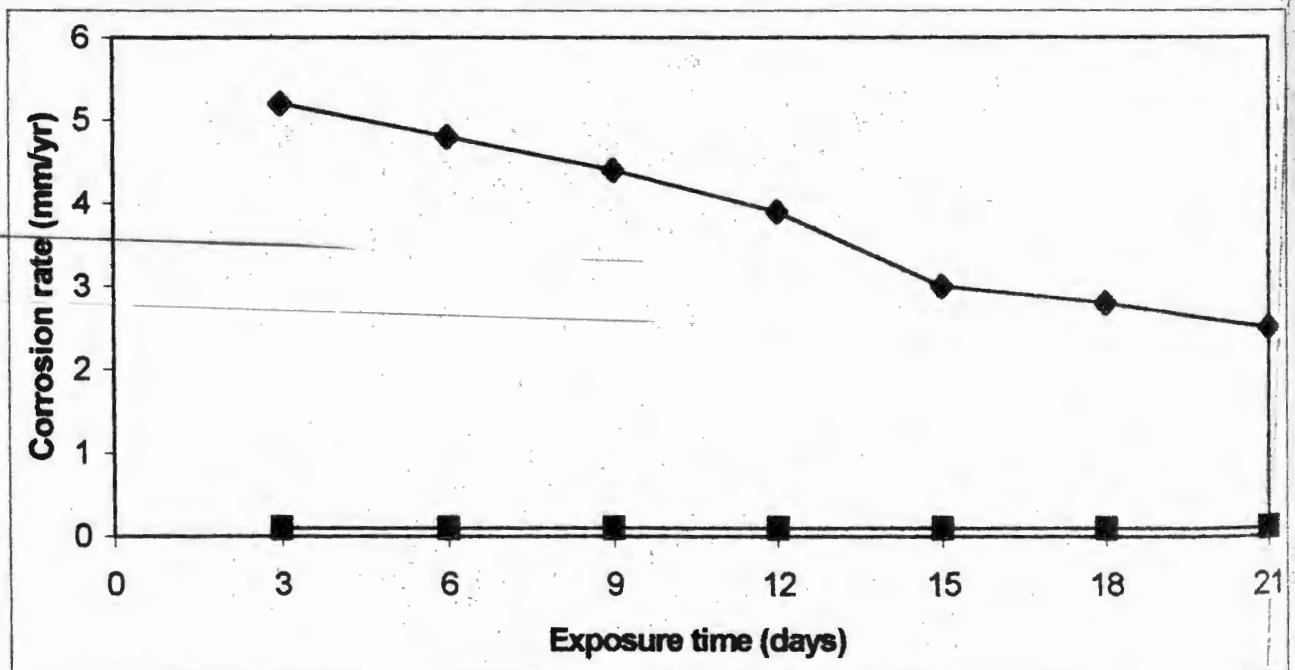


Fig 5: Variation of corrosion rate with exposure time for the stainless steel specimens immersed in 9M and 18M sulphuric acid (tetraoxosulphate (VI) acid)

- ◆ = 9M H<sub>2</sub>SO<sub>4</sub>
- = 18M H<sub>2</sub>SO<sub>4</sub>

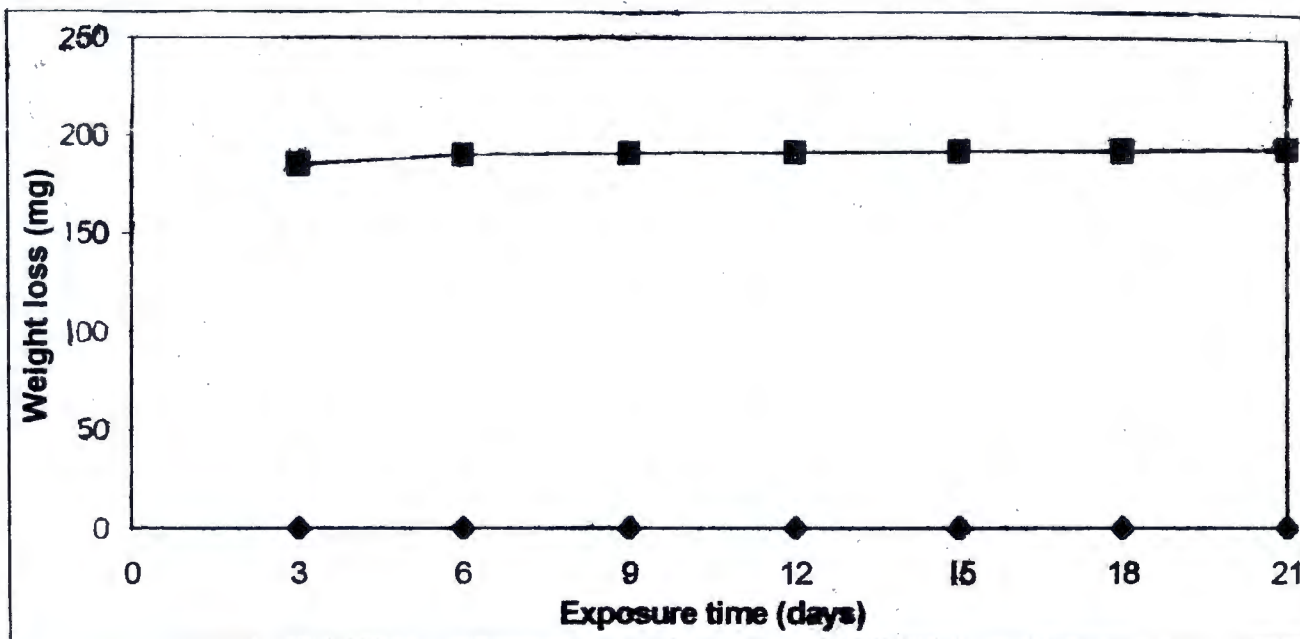


Fig 6: Variation of weight loss with exposure time for stainless steel specimens immersed in 9M and 18M sulphuric acid.

- ◆ = 7M H<sub>3</sub>PO<sub>4</sub>
- = 14M H<sub>3</sub>PO<sub>4</sub>

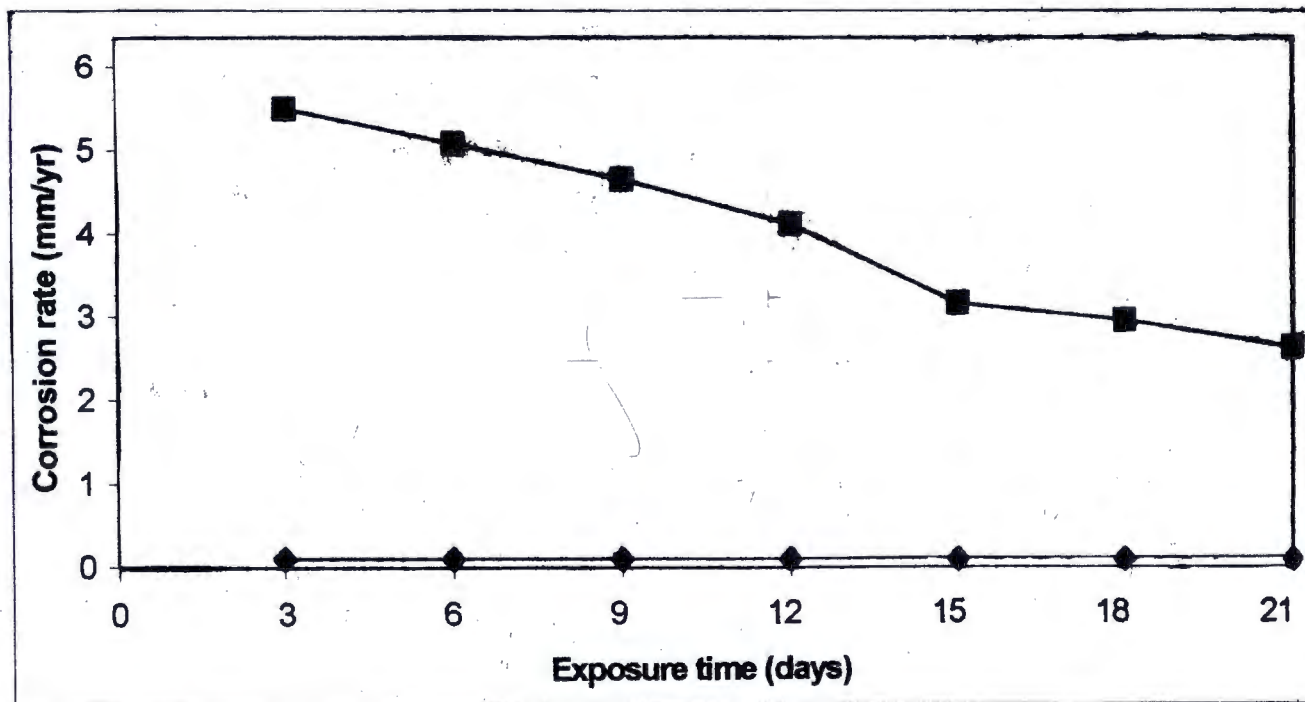
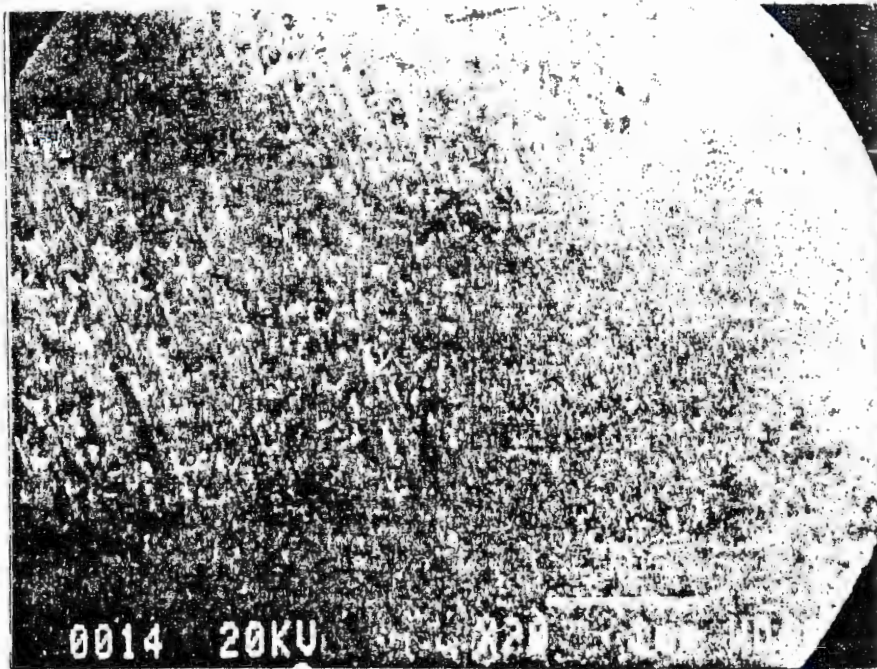
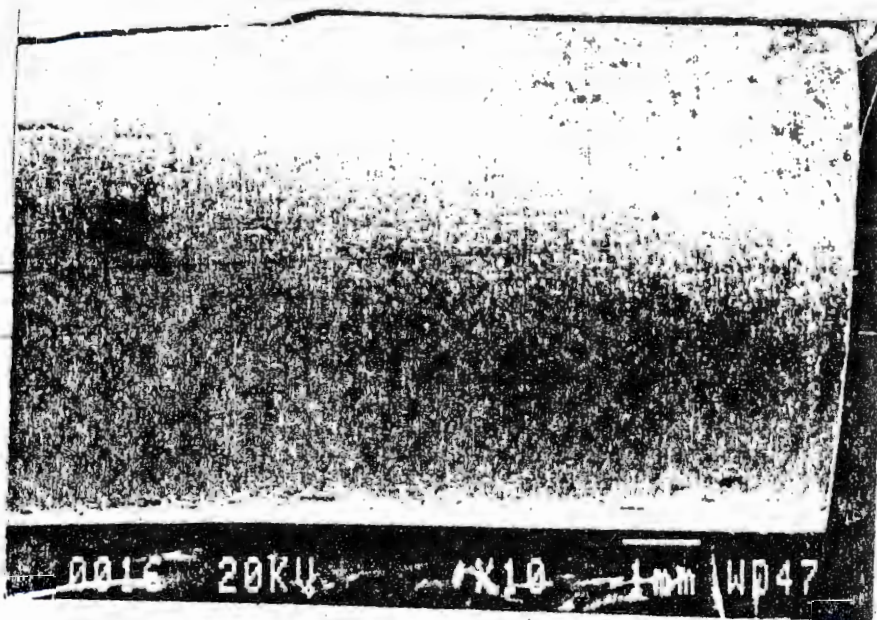


Fig 7: Variation of corrosion rate with exposure time for the stainless steel specimens immersed in 9M and 18M sulphuric acid (tetraoxosulphate (VI) acid)

- ◆ = 7M H<sub>3</sub>PO<sub>4</sub>
- = 14M H<sub>3</sub>PO<sub>4</sub>



(a)



(b)

Fig. 8 SEM micrographs of the steel test specimen before immersion in test media  
(a) Polished cut surface (b) side view of the cylindrical specimen.

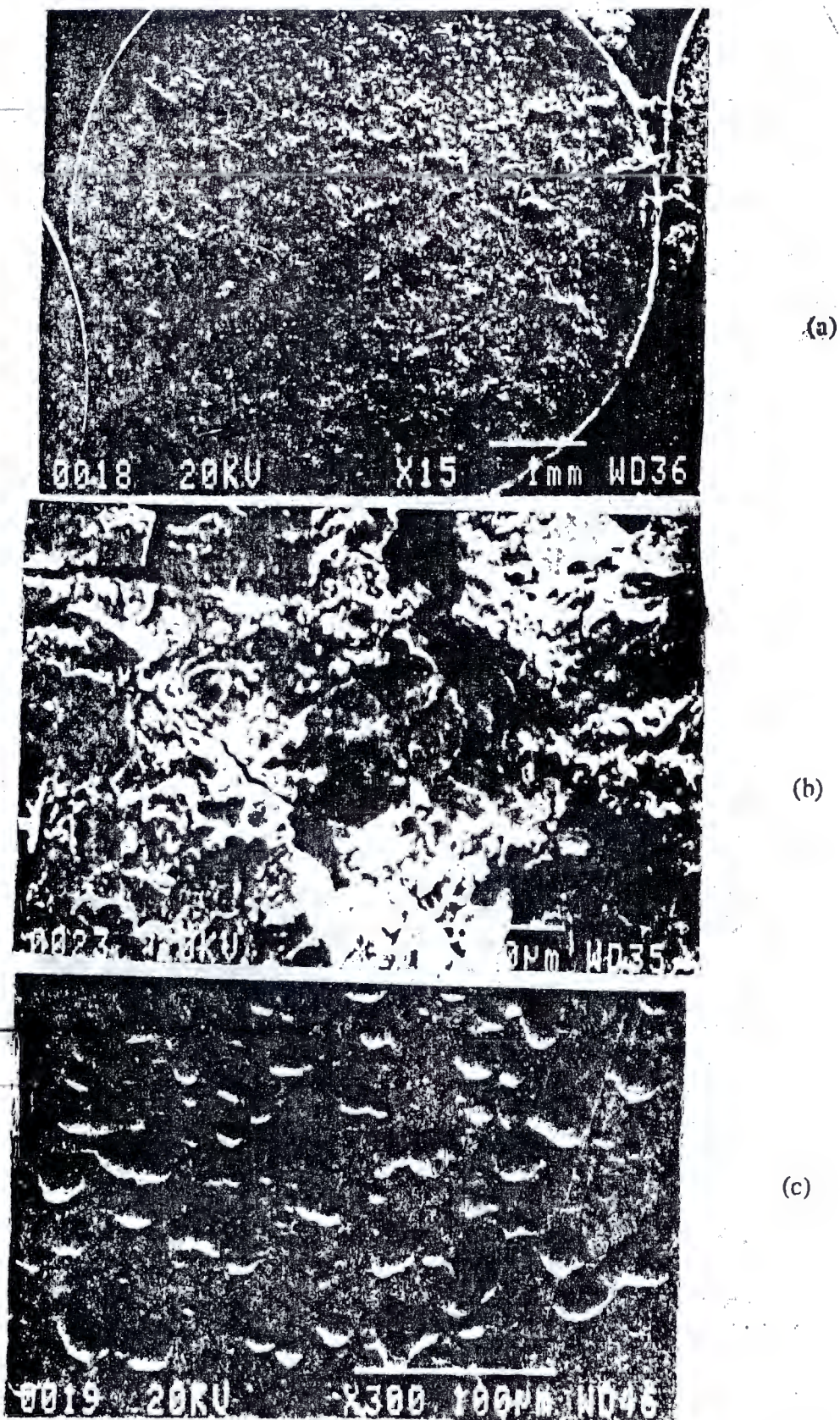
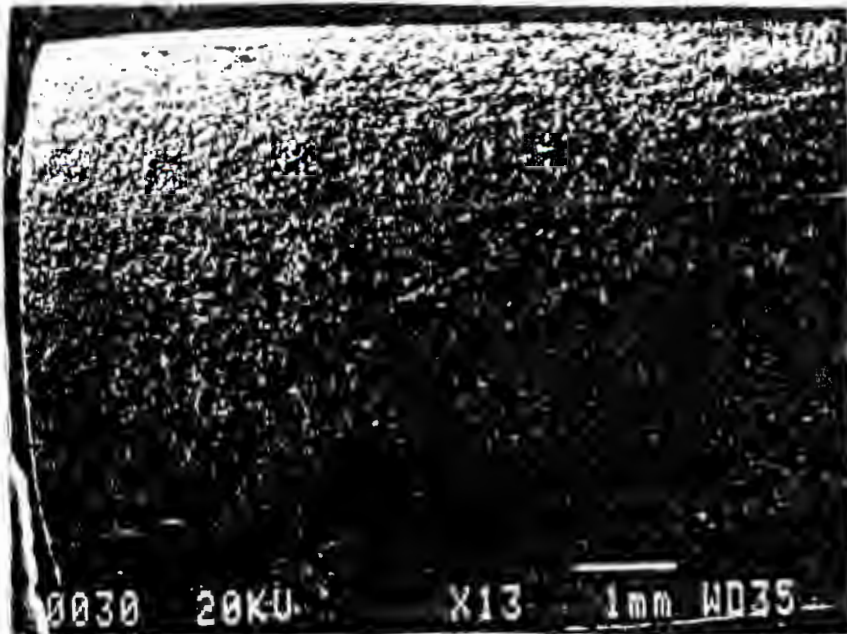


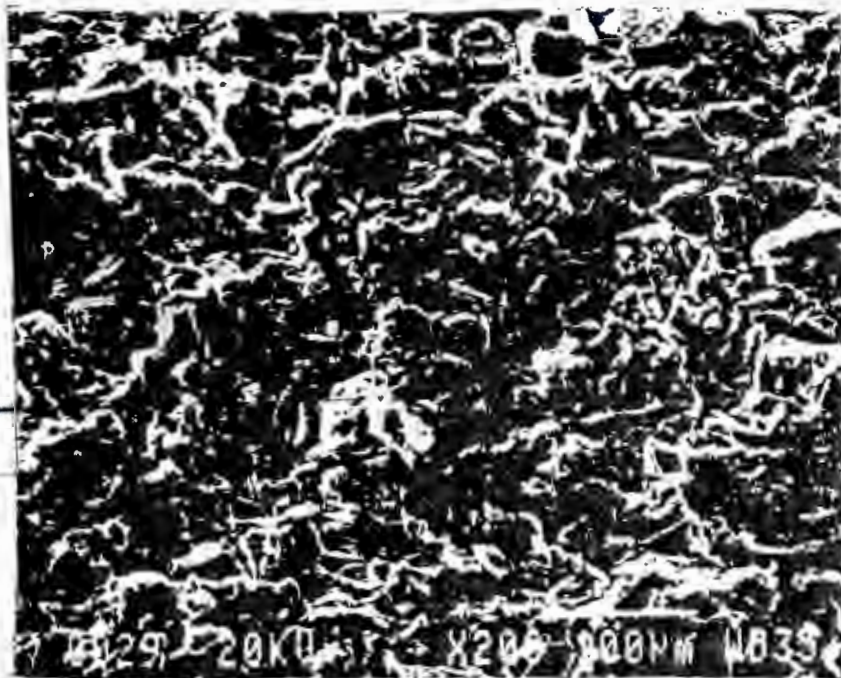
Fig. 9 SEM micrographs of the steel test specimen immersed in 7M tetraoxosulphate (VI) acid.

- (a) Cut surface after immersion
- (b) as in (a) at higher magnification
- (c) topographic image of the pitted surface. (x300)





(a)

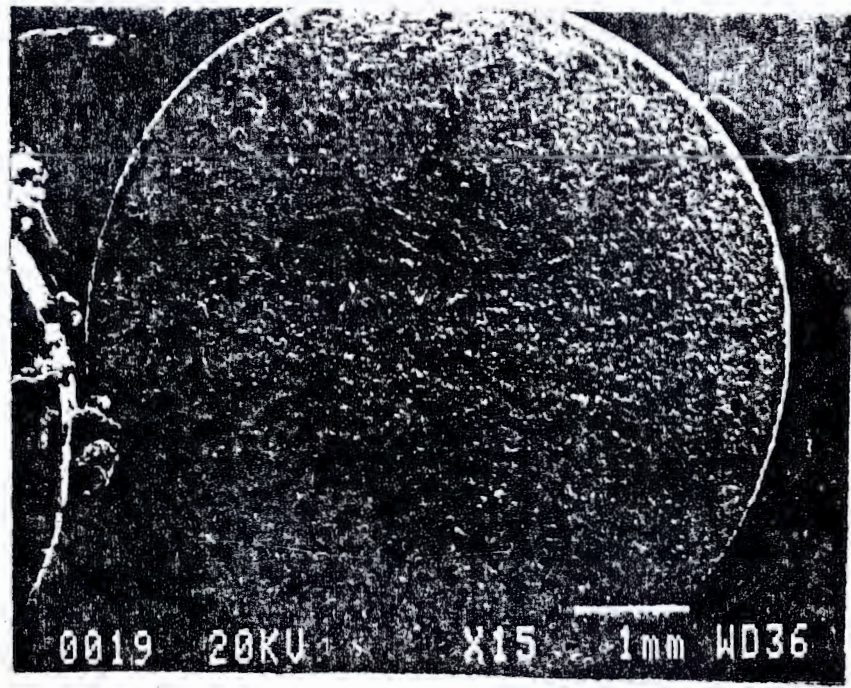


(b)

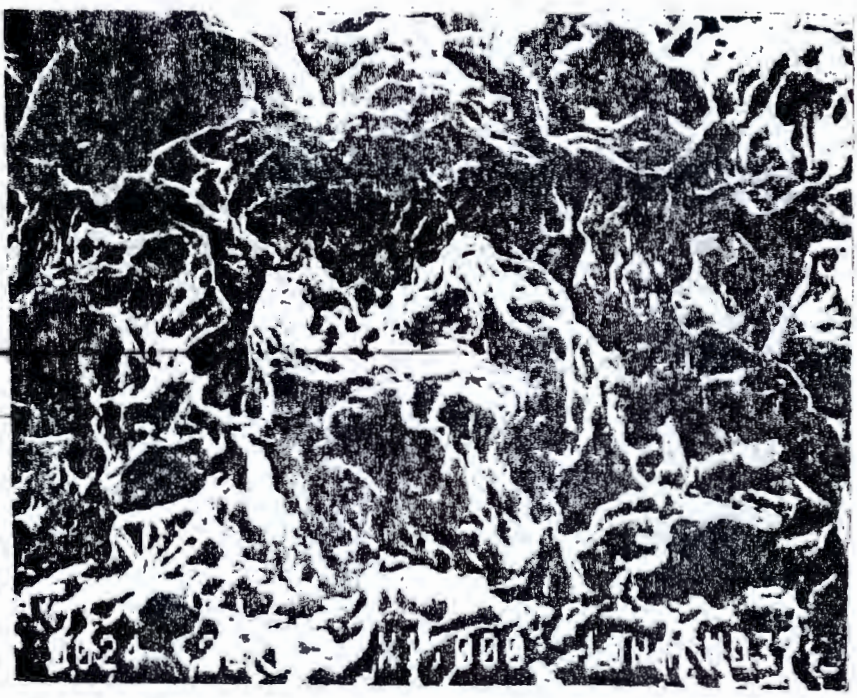
Fig.10 SEM micrographs of the steel test specimen immersed in 9M tetraoxosulphate (VI) acid.

(a) Side view of the cylindrical test specimen. Magnification. (x15)

(b) As in (a) at higher magnification. (x200)

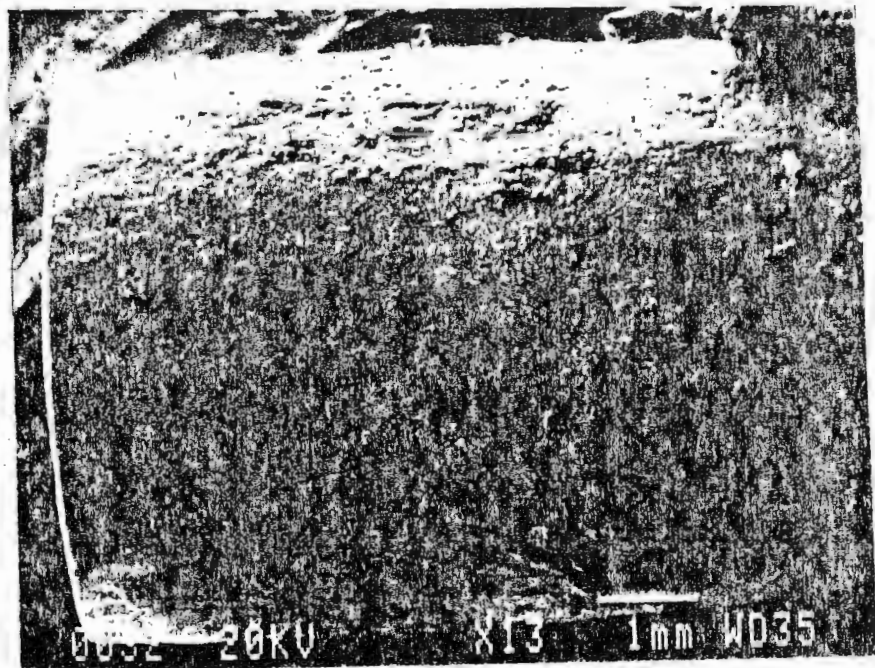


(a)

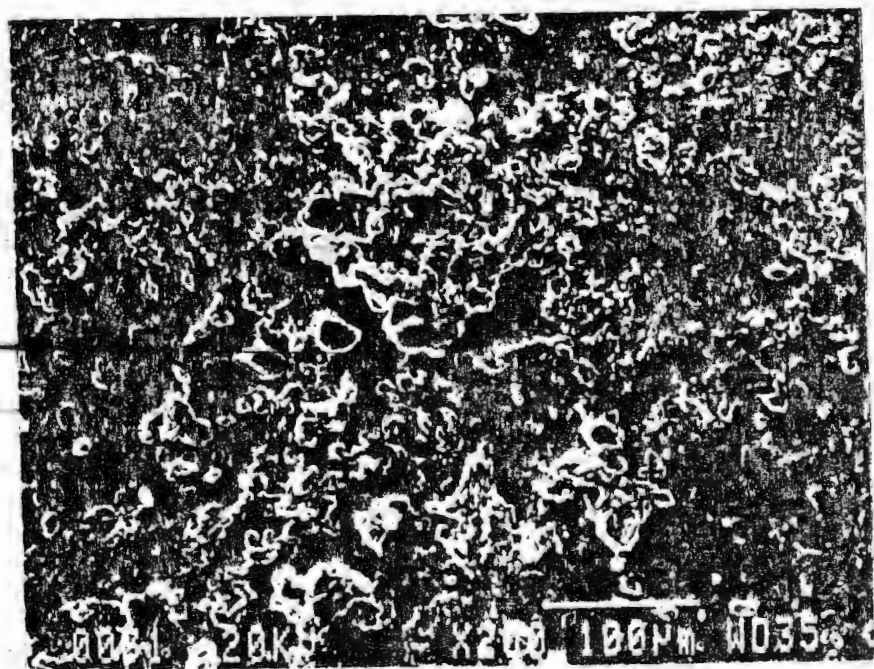


(b)

Fig.11 SEM micrographs of the steel specimen immersed in 14M tetraoxophosphate (V) acid.  
(a) Cut surface after immersion (b) as in (a) at higher magnification. (x1000).



(a)



(b)

Fig.12 SEM micrographs of the steel specimen immersed in 14M tetraoxophosphate (V) acid.

(a) Side view of the cylindrical test specimen (x15).

(b) As in (a) at higher magnification (x200).

