# Reproducible Pitting Corrosion of Mild Steel in Sodium Chloride/Sodium Nitrite Environments

Iqbal Hussain[1], J.D. Scantlebury[1] and D. Fairhurst[2]

[1]*Corrosion & Protection Centre, UMIST, Manchester, M60 1QD, UK.*
david.scantlebury@umist.ac.uk
[2]*BP Exploration Co. Ltd, UK*

## Abstract

The corrosion of mild steel on exposure to solutions of varying molar ratios of sodium chloride (NaCl) to sodium nitrite ($NaNO_2$) has been studied and as a result reproducible pitting corrosion on mild steel surfaces can be produced in 24 hours through galvanostatic polarisation of mild steel in a solution of 3.5% sodium chloride with the addition of sodium nitrite at a molar (M) ratio of 15:1. Other molar ratios of sodium chloride to sodium nitrite were also studied and are reported.

## Introduction

### Pitting corrosion

Pitting is one of the most destructive and insidious forms of corrosion. Pitting corrosion frequently arises from a failure of the passive or protective surface film. Thus, metals in the passive state may be susceptible to pitting attack when the surface film ruptures and does not reform [1]. Generally the service environment must be sufficiently oxidising to favour and maintain passivity while species, such as chloride, that are able to break down the passive film and initiate pitting should be absent or at low concentration [2]. Pitting also may occur over a range of pH and potentials, however, in all situations the potential of the metal must be within the passive region so that passivity is maintained on the major part of the surface [1]. Finally, pitting is unpredictable and its rates are variable, depending on the migration of corrosive species into and out of the pit. Once initiated the corrosion processes within a pit produce conditions that are conducive to the continuation of activity of the pit [3].

## Sodium nitrite

Sodium nitrite ($NaNO_2$) is a passivating anodic inhibitor that is generally considered to enhance the formation of an insoluble tightly adherent (passive) oxide film [4]. The efficiency of inhibitors in solution is influenced by a number of factors: e.g. the concentration of aggressive ions in the solution, the pH of the solution, the concentration of dissolved oxygen in the solution, the temperature of the solution, the state and condition (i.e. surface preparation) of the metal in the solution and the concentration of the inhibitor itself [4–7]. Prevention of pitting corrosion by use of inhibitors is potentially useful, but must be considered with caution. Thus, the quantity (concentration) of an inhibitor is very important because if insufficient inhibitor is present then fewer but deeper pits may result (i.e. more severe localised corrosion than in the complete absence of inhibitor [2,6]).

Generally, below pH 6, sodium nitrite is relatively ineffective as an inhibitor; however, its inhibitive properties increase with increasing pH and reach a maximum in a pH range of between 9 to 10 [8]. Also, sodium nitrite and nitrites in general are rarely used in open systems because of bacterial decomposition leading to the formation of nitrate [9]. An in depth discussion of anodic inhibitors and in particular for sodium nitrite can be found elsewhere [4,6–7,9–10].

For an appropriate combination of sodium chloride and sodium nitrite a reliably pitted surface on mild steel should be achievable [11]. Also, since the cathodic reduction reaction of nitrite produces nitrogen, there is an added advantage of not leaving any residues or contaminants on the surface of the metal. However, the correct combination of sodium chloride and sodium nitrite together with the experimental procedures and parameters needed to generate reliably pitted surfaces are not commonly known. Thus, this paper is investigates the optimum combination of sodium chloride and sodium nitrite together with the optimum experimental procedures and parameters needed in order to generate reliably pitted surfaces on mild steel.

## Experimental procedure

As received, bright non-corroded mild steel coupons, free from mill scale, were used in this study. All coupons were from the same batch and were cut from a single rolled sheet as stated by the suppliers. Each mild steel coupon had an exposed surface area of 60 $cm^2$ with dimensions of 10 cm x 2.5 cm x 0.4 cm (length x width x thickness).

No special procedures were taken to prepare the mild steel coupons (i.e. preparation of edges etc.), except they were thoroughly washed and degreased in hot soapy water

followed by a thorough rinsing in acetone. The mild steel coupons were then allowed to dry in a warm oven for a few hours before being placed in a desiccator.

In order to generate pits on the mild steel, a pitting environment consisting of 3.5% sodium chloride (NaCl) solution mixed with different molar quantities of sodium nitrite (NaNO$_2$) was produced. Starting initially with a solution composition of 3.5% NaCl + NaNO$_2$ at a molar ratio of 10:1, this was varied above and below this range in order to determine the optimum ratio for reliable pit generation.

# Initial experiments

Initial experiments involved the use of deposits of magnetite (Fe$_3$O$_4$) powder. Mild steel coupons with deposits of magnetite on the exposed surface of each coupon were totally immersed in 500 ml of this pitting environment (shown schematically in Figure 1) for a given amount of time, usually 168 hours and then visually inspected for signs of localised corrosion. For this particular system, it has been suggested that sodium nitrite passivates the surface of the mild steel coupon and that chloride species (Cl$^-$) have the ability to permeate through the deposits of magnetite and thereby corrode the surface, whereas nitrite species (NO$^{2-}$) cannot [11].

It was therefore thought possible that localised corrosion (pits/crevices) on mild steel surfaces could be created by selectively positioning the deposits of magnetite and by reducing the thickness of the magnetite deposits, thereby allowing greater transport of chloride species to the metal surface. However, this proved unreliable, so a trial and error procedure was adopted by varying the concentration of sodium nitrite. Solution compositions of 3.5% NaCl + NaNO$_2$ at a molar ratio of 15:1 and at a molar ratio of 20:1 were then used, with the 15:1 molar ratio showing the greatest amount of corrosion beneath the deposits of magnetite. However, this also proved unreliable with respect to the reproducibility of corrosion beneath the deposits of magnetite and as a result an alternative experimental method/technique was sought. Figures 2–4 show three mild steel coupons after being subjected to the above-mentioned test conditions.

## Potentiostatic polarisation

A potential polarisation technique was then adopted where samples were polarised above their pitting potential (found to be –175 mV v. saturated calomel electrode (SCE) using 3.5% NaCl + NaNO$_2$ at 15:1M under natural aeration). Again a trial and error procedure was adopted, where a range of potentials were selected above the pitting potential to

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potentiostatically polarise mild steel coupons in this environment. Polarisation curves were obtained using auto Tafel software (ACM Instruments) at a scan rate of 1 mV/s on an electrode area of 1 cm$^2$. Figure 5 shows a polarisation curve under natural aeration.

Potentiostatic polarisation of mild steel in this environment was conducted in 24 hours and a polarisation potential of –125 mV (SCE) resulted in the maximum number and most reproducible pits. However, the pitting produced was very severe with most of the pits coalescing with adjoining pits. Efforts were made to manipulate the extent and depth of pitting produced from this technique through adjusting the exposure time period and/or the polarisation potential, however, this too proved unreliable and, again an alternative technique/method was sought.

## Galvanostatic polarisation

Finally a galvanostatic polarisation technique was applied to mild steel coupons of the same dimensions as previously. These were immersed individually in separate glass dishes containing 500ml of solution consisting of 3.5% NaCl + NaNO$_2$ at an optimum 15:1M ratio. The measured pH of this solution was found to be 6.7 at room temperature. A wire mesh counter electrode made from mixed metal oxide coated titanium with dimensions of 10 cm x 2.5 cm (the same length and width of the mild steel coupons) was placed directly above (parallel) to each of the mild steel coupons and were also immersed in each of the same solutions. A galvanostat was used to supply the optimum current for pitting, which was found to be 40 mA; i.e. a current density of 0.667 mA cm$^{-2}$. The fixed current was supplied for a period of 24 hours to the mild steel coupons in solution and the corresponding potentials of the mild steel coupons were measured with respect to a saturated calomel reference electrode over the 24-hour period. After the exposure tests, the mild steel coupons were chemically cleaned in accordance with ASTM: G1-90 [12] and the pitted mild steel surfaces were evaluated in accordance with ASTM: G46-94 [13].

## Results and discussion

Figure 6(a) shows a typical photograph of the coupon after exposure with scribed markings to aid pit counting while Figure 6(b) shows a close-up of one of the marked areas after chemical cleaning. Pitting was also observed on the reverse sides and edges of the mild steel coupons but to a much lesser extent. This is most likely due to the positioning of the counter electrode and shielding of the glass plate.

Efforts were made to manipulate the extent and depth of pitting through adjusting the current supplied and/or increasing the exposure times, however, this did not prove to be

reproducible. Supplying a larger constant current to the mild steel coupons in the pitting environment during the 24–hour period produced greater uniform corrosion of the metal and resulted in a surface profile where pits had coalesced with adjoining pits. Increasing the exposure time of the mild steel coupons in the pitting environment at the critical current density had the same effect as supplying a larger constant current. However, supplying a smaller constant current during the standard 24 hour exposure period produced very few pits with much less general corrosion; a similar result was found when supplying a smaller constant current but over a longer exposure period.

The optimum pitted surface profile on mild steel was found to be produced at a current density of 0.667 mA/cm$^2$. While the pits were being generated using this technique, the potential response of the mild steel coupons in this pitting environment with and without the application of the constant current of 40 mA were also monitored and are shown in Figure 7 and are compared with the potential variation in 3.5% NaCl solution with and without the application of the constant current of 40 mA. Thus that for mild steel immersed in 3.5% NaCl + NaNO$_2$ at 15:1M with no imposed constant current (transient 'd'), mild steel settles at a typical passive potential of around –300 mV (SCE). For mild steel immersed in only 3.5% NaCl (transient 'c'), the potential settles at around –680 mV (SCE), which is the characteristic corrosion potential for mild steel in this environment. However, on the application of an anodic current, the electrode (mild steel coupon) immersed in only 3.5% NaCl is anodically polarised and moves in a positive direction, transient 'a'. Finally, for the nitrite containing solution the potential becomes more negative on application of current and is shown by transient 'b'. This is explained by the fact that, as the electrode is anodically polarised, the passive film formed on the surface of the metal by the presence of sodium nitrite is ruptured and the onset of localised corrosion (pitting) commences. As stable pits form and increase in size, the current density within the pits is reduced and thus, the potential moves towards the negative direction.

## Examination and identification of pitting corrosion

The examination and evaluation of the pitted mild steel surfaces were carried out in accordance with ASTM: G46–94 [13] and is described below in detail. However, for the purposes of this investigation only the pits that were produced on the surfaces of the mild steel coupons positioned directly below the counter electrode (i.e. parallel) were examined and evaluated. The pits produced on the reverse sides and on the edges of the mild steel coupons were ignored.

The pits on the mild steel surfaces were identified with respect to their size, shape and density and Figure 8(a,b) shows that the majority of pits are elongated with irregular openings. Sectioning of pits perpendicular and parallel to the rolling direction will give different shapes and therefore different depths, depending on the amount of metal removed through polishing. However, it must be stated that sectioning carried out in either direction will ultimately give the same pit depth but not necessarily the same size (i.e. geometry). Nevertheless, for the purposes of this study, sectioning of the test specimens was carried out in both directions to characterise the shape and depth of pits. The elongated nature of the pits suggested that pitting was occurring parallel to the rolling direction of the mild steel from the manufacture process. To verify this, it was therefore necessary to section a piece of non-corroded (i.e. not pitted) mild steel from the same batch and to visually examine its grain orientation, structure and size and to then ascertain if this had any effect upon the geometry and distribution of pits. Figure 9(a,b) show optical micrographs etched in 2% nital solution and sectioned perpendicular and parallel to the rolling direction respectively.

## Weight loss measurements

After 24 hours of exposure of the corroded/pitted coupons were then chemically cleaned in accordance with ASTM: G 1-90 [12] and an average weight loss for the mild steel coupons were determined, Table 1.

| Mild Steel Coupons, n | Weight Before Exposure (g) | Weight After Exposure (g) | Weight Difference, x (g) |
|---|---|---|---|
| 1 | 77.103 | 76.383 | 0.720 |
| 2 | 77.093 | 76.332 | 0.761 |
| 3 | 78.008 | 77.310 | 0.698 |
| 4 | 77.517 | 76.782 | 0.735 |
| 5 | 76.869 | 76.081 | 0.788 |
| 6 | 77.677 | 76.905 | 0.772 |
| 7 | 78.152 | 77.441 | 0.711 |
| 8 | 76.961 | 76.161 | 0.800 |
| 9 | 77.495 | 76.764 | 0.731 |
| 10 | 78.101 | 77.397 | 0.704 |

Table 1: Mass losses from replicate coupons after pitting test: average mass loss 0.742 g with a standard deviation of 0.034 g.

## Pit size and density

Pit depth, width, length and number were taken from the same samples (mild steel coupons) used for weight loss measurements. After the weight loss measurements were carried out, all mild steel coupons were then sectioned perpendicular to the rolling direction of the metal and pit depth measurements determined from optical micrographs and images obtained from scanning electron microscopy (SEM) were then used to determine the average penetration caused by pitting of the mild steel and these results are presented in Table 2. The average pit depth was calculated to be about $210 \pm 20$ µm. Table 2 also shows data for the number of pits produced per sample. From this a pit density was calculated as about 90 pits $cm^{-2}$.

| Coupon # | Pit depth | Pit width | Pit length | No. of pits |
|----------|-----------|-----------|------------|-------------|
| 1 | 255 | 450 | 450 | 2050 |
| 2 | 218 | 375 | 441 | 2375 |
| 3 | 176 | 400 | 384 | 2250 |
| 4 | 205 | 300 | 375 | 2450 |
| 5 | 223 | 337 | 412 | 2250 |
| 6 | 230 | 485 | 330 | 2047 |
| 7 | 187 | 420 | 487 | 2323 |
| 8 | 190 | 387 | 422 | 2070 |
| 9 | 215 | 445 | 356 | 2328 |
| 10 | 220 | 393 | 470 | 2304 |
| *Average* | *212* | *399* | *412* | *2245* |
| *Standard error* | *18* | *52* | *48* | *135* |

**Table 2**: Pitting characteristics from 10 replicate samples

## General discussion

After evaluating the extent and morphology of pitting no direct correlation could be made between the grain structure, grain orientation and grain size of the mild steel coupons to the distribution and geometry of the pits.

The likelihood of errors in the analysis and evaluation of pitting must also be taken into account as these can have a significant effect on the values reported, especially when used for comparative analysis. Pit depth, width and length measurements were carried out through sectioning of the mild steel coupons and then polishing on a grinding wheel to

obtain a smooth surface profile. The limitations of such technique, especially with respect to pit depth are that the deepest pits may not have been identified and the pits may not have been sectioned at the deepest point of penetration. Even if the pits were selected at their deepest point of penetration, subsequent polishing may have removed more metal than necessary, therefore resulting in an error in pit depth measurement.

All the above methods used in this study to evaluate and examine the extent of pitting corrosion produced from exposing mild steel coupons to the pitting environment (experimental test conditions) have only provided a guide, in which pitting data/results may be reported and/or presented. An in-depth investigation into pitting corrosion should include as much detailed information as possible, including an in depth analysis on the application of statistics, which incidentally may be found in ASTM: G16-95 [15].

Ultimately, this work has therefore reported on a study on how to produce reproducibly pitted surfaces on mild steel within 24 hours and the above examination and evaluation methods used here for a quantitative and qualitative analysis on the pitting corrosion produced are considered to be suitable and adequate.

## Conclusions

1. An accelerated reproducible procedure has been developed for the production of pits on mild steel surfaces with minimum effort and costs. Thus, pitted surfaces on mild steel can be reproduced reliably within 24 hours by galvanostatic polarisation in a solution of 3.5% NaCl + $NaNO_2$ at a 15:1M ratio at a constant current density of 0.667 mA $cm^{-2}$

2. The general extent of corrosion as evaluated from visual examination of mild steel after exposure to test conditions would appear to be very slight but pitting corrosion is severe.

3. The majority of pits appear to have an elongated subsurface and a horizontal geometry. The elongated nature of the pits is thought to be as a result of how the mild steel was produced from the manufacture process.

4. As a result of the exposure of the mild steel coupons to the test conditions, a pitting density of 90 pits/$cm^2$ was calculated in which the average depth, width and length of pits were about 210 μm, 400 μm and 415 μm, respectively.

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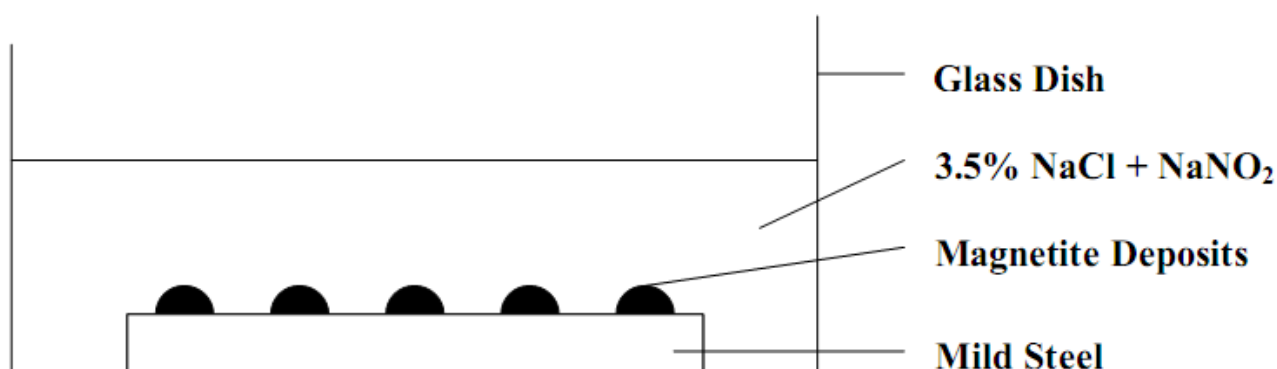
Figure 1: A simplified schematic impression of the initial experimental set-up.



Figure 2: A selectively corroded mild steel coupon upon removal of magnetite deposits and after being exposed to a solution consisting of 3.5% NaCl + $NaNO_2$ at a ratio of 10:1M for a period of 168 hours (magnification x1.6).



Figure 3: A selectively corroded mild steel coupon upon removal of magnetite deposits and after being exposed to a solution consisting of 3.5% NaCl + $NaNO_2$ at a ratio of 15:1M for a period of 168 hours (magnification x1.6).

Figure 4: A selectively corroded mild steel coupon upon removal of magnetite deposits and after being exposed to a solution consisting of 3.5% NaCl + NaNO$_2$ at a ratio of 20:1M for a period of 168 hours (magnification x1.6).
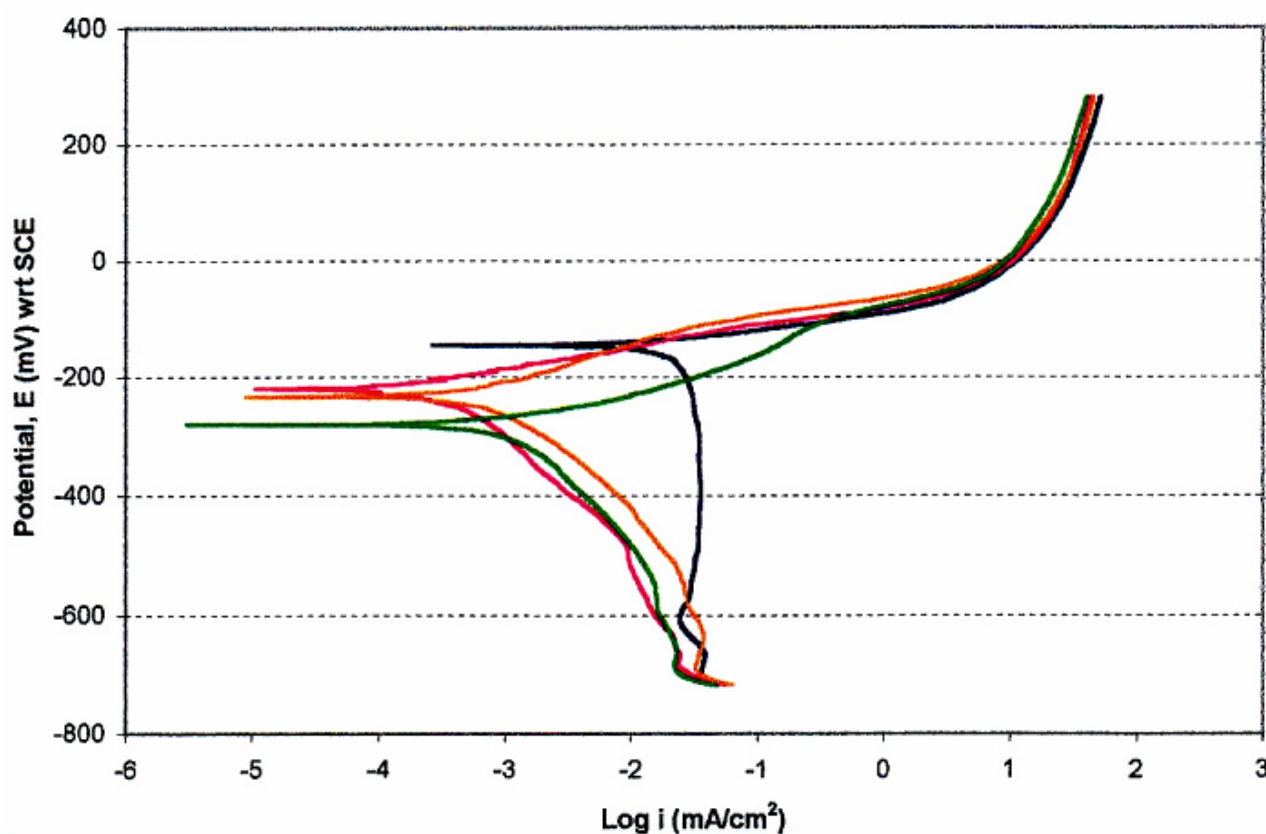


Figure 5: Polarisation curves for mild steel in varying molar ratios of 3.5% NaCl to NaNO$_2$, where the green transient represents 3.5% NaCl + NaNO$_2$ at 20:1M, orange transient represents 3.5% NaCl + NaNO$_2$ at 15:1M and the pink transient represents 3.5% NaCl + NaNO$_2$ at 10:1M.

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(a)                                                            (b)
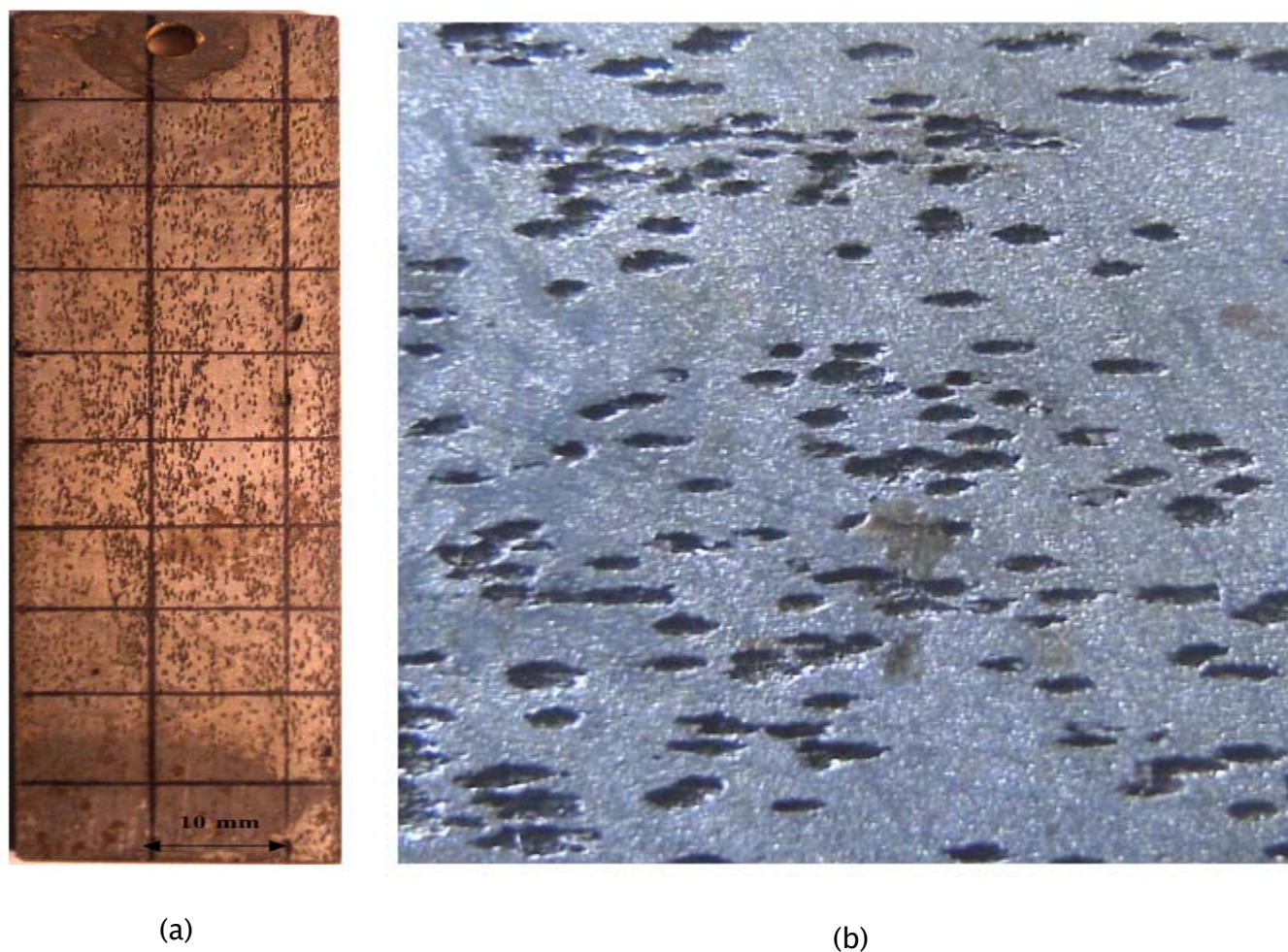
Figure 6: (a) A heavily pitted mild steel coupon (with scribed markings to aid pit counting) after 24 hours of exposure to the test conditions; (b) pitted area after chemical cleaning (magnification x14).
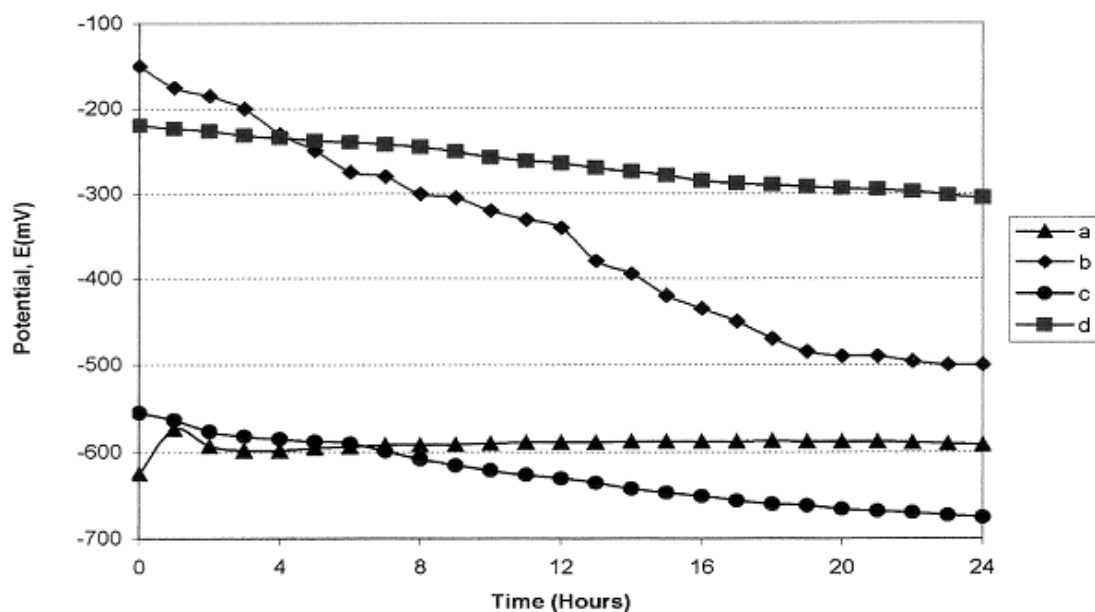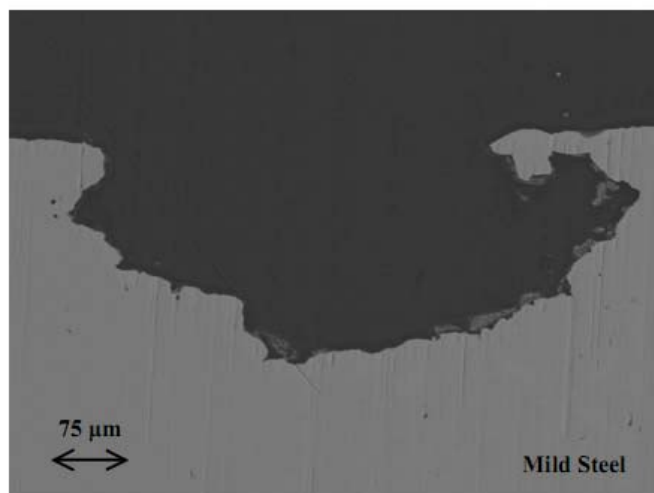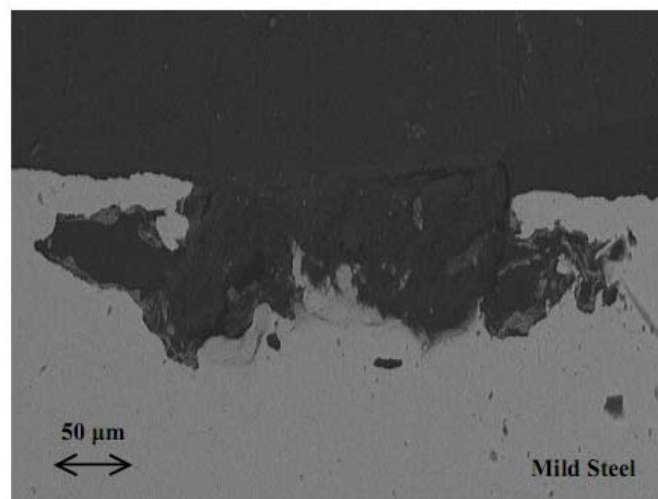
Figure 7: Potential (SCE) transients of mild steel, where 'a' = mild steel in 3.5% NaCl under constant current, 'b' = mild steel in 3.5% NaCl + $NaNO_2$ at 15:1M under constant current, 'c' = mild steel in 3.5% NaCl and 'd' = mild steel in 3.5% NaCl + $NaNO_2$ at 15:1M.



(a)                                             (b)

Figure 8: A SEM micrograph image (BSE x275) of a pit cross-sectioned: (a) perpendicular and, (b) parallel to the rolling direction of the mild steel.
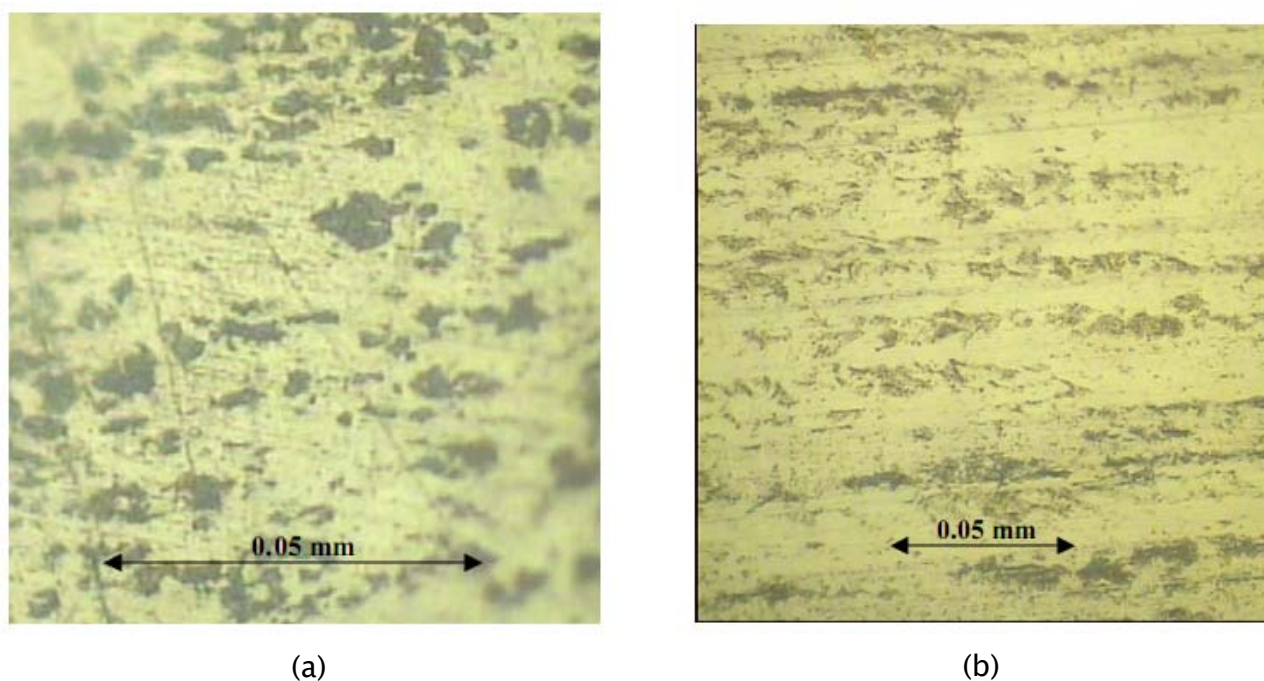
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(a)                                        (b)

Figure 9: Optical micrograph of etched mild steel sectioned: (a) perpendicular and (b) parallel to the rolling direction.