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Effect of different surface preparations prior to painting on the corrosion behaviour and surface activity of mild steel

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Abstract:

Previous work in our laboratory showed that the type of surface preparation of the steel prior to coating had a dramatic effect on the subsequent corrosion protection afforded in immersion tests and in salt spray testing. Particularly water jetting led to better performance. It is generally accepted that factors such as removal of impurities and introducing surface roughness to steel to obtain better adhesion through the mechanical interlocking of polymeric structure and the metal surface play a part. However it is postulated that the ease of breakdown of the oxide film is also critically important and varies between surface preparations. This was investigated in the present study where 5 different surface preparation methods (abrasive blasting, water-jetting, abrasion, acid pickling and degreasing) were applied to the mild steel surface and each resultant surface was characterised using electrochemical methods. The Scanning vibrating electrode technique (SVET) was performed in dilute saline water to detect anodic and cathodic sites on the surface and also to determine the intensity of electrochemical activity at these sites. Scanning electron microscope (SEM) together with energy dispersive X-ray spectroscopy (EDX) was used to characterise the surface structure and its chemical composition. Changes in open circuit potential have been monitored during the time of exposure to electrolyte in order to investigate the general surface activity. The electrochemical impedance spectroscopy (EIS) was employed to analyse the charge transfer situation on the metal surface. Results using these techniques will be presented and discussed. An anticipated outcome from this work is development of a simple electrochemical method to assess that a metal surface is in a condition suitable for coating. This could also be used as a way of checking that standard pretreatments had been effective and assist in the development of new ones.

Keywords: surface pre-treatment, SVET, surface activity, electrochemical characterisation

Introduction

Surface preparation, together with the related process of removing existing coatings, always ranks as one of the most critical steps in successful coatings application. The objectives of these processes are twofold: to clean and roughen the substrate according to the specified requirements [1]. Any visible oxide layer e.g. mill scale will be unstable and can lead to early delamination of protective coating from the substrate and reduce the performance of paint. So it is quite essential to remove such an oxide layer prior to painting [2]. Also the surface preparation enhances the performance of protective system through increasing the adhesion between organic coating and substrate. Mechanical interlocking of the polymeric structure into the surface profile and electrostatic bonds between coating and substrate are two of the mechanisms involved in adhesion of paint to metal surface [3]. Surface preparation promotes electrostatic bonds through activation of the surface. Also introducing a surface profile increases the chance of entanglement of polymeric chains into the surface profile. A high surface roughness provides more electrical/mechanical sites to improving the coating's bonding with substrate. Most adhesion theories consider a rough surface to be favourable for achieving a high adhesive strength with a given organic coating [4]. In spite of this, some investigations have shown no relationship [5] or inverse relationship [6-7] between corrosion protection properties of the organic coating and the surface roughness. So, study and characterisation of the surfaces produced by different methods of preparation is highly important. In neutral conditions a thin layer of protective oxide layer forms on mild steel's surface. The initial corrodibility of steel when exposed to aqueous solution depends both on the solution and on this oxide layer's structure and its vulnerability to break down [8]. The corrosion resistance of mild steel in neutral NaCl solution has been shown to depend highly on the formation of a passivating iron oxide layer and the extent to which this layer is partially destroyed by pitting [9]. Recent studies of Chen et al [10] have shown that the geometrical depth of the surface irregularities plays a key role in providing potential sites for pit forming and active localized corrosion. They used SVET (Scanning Vibrating Electrode Technique) to investigate different surface irregularities, including scratch, mechanically induced hole and an existing corrosion pit. Their results revealed the fact that anodic sites tend to form at the bottom of valleys where the surface has lowest access to oxygen and gives highest value of local current density. Atmani et al. [11] investigated the effect of surface preparation on corrodibility of mild steel. Their results revealed higher sensitivity to the salt solution of oxide layer on the surface prepared by acid pickling rather than the abraded and as received surfaces. Also they showed that Cl⁻ concentration had a dramatic effect of on break down of the protective oxide layer.

In the present study 5 commonly used surface preparation methods have been applied to steel surface to provide differing extent of removal of the existing oxide layer and/or to introduce surface roughness. The electrochemical characteristics and corrosion behaviour of each have been investigated. This paper gives selective results. The work will be reported more fully subsequently.

Experimental

Surface preparation methods:

As received and degreased: the panel was swabbed with iso-propanol. Abrasive blasted: a naturally occurring mineral (garnet) was entrained in water and blasted at the surface 10K psi.

Water jetted: UHP (ultra high pressure) water was fired at the surface at 40K psi. Acid pickled: the specimen was immersed in 20%w. hydrochloric acid for 100 sec followed by rinsing with distilled water. Abraded: the panel was roughened with 180 grit emery paper. Degreasing, abrasion and acid pickling methods were performed on steel Q-Panels and abrasive blasting and water-jetting were applied on the low carbon steel plates provided by Rentajet Group Ltd. All samples were placed in desiccator immediately away after preparation.

Techniques

- Surface profile

Profilometry for abrasive blasted and water-jetted surface has been done using Taylor Hobson equipment, model Form Talysurf Series 2. This calculates the S_z which is the Ten Point Height over the complete 3D surface and represents the average difference between the 5 highest peaks and 5 lowest valleys.

- Scanning Electron Microscope (SEM)

The images were obtained from 5cm by 5cm specimens using a Hitachi S3000N scanning electron microscope under vacuumed condition and 5KV accelerating voltage

- Scanning Vibrating Electrode Technique (SVET)

Experiments were performed using SVET machine built by Department of material science at the University of Swansea. The test area was approx. 10mm×10mm and the rest of the surface was masked in order to avoid interference. All surfaces were assumed flat and so the 4 points height scan method was employed to adjust the 150 μm distance between vibrating probe and the metal surface. The measurement's resolution was 200 μm between each 2 consecutive measured points. The primary result of the SVET (surface potential data) has been calibrated upon operating functions and used in producing the current density map

- Open Circuit Potential (OCP)

This measurement was performed on 3.1 cm^2 of surface using automated ACM GillAC potentiostat with one second interval in respect to saturated calomel Electrode (SCE)

- Electrochemical Impedance Spectroscopy (EIS)

This was done using ACM GillAC potentiostat with 20 mV voltage perturbation around OCP in frequency range of 10 kHz-10 mHz. The provided software by ACM was employed to fit appropriate equivalent electrical circuit and calculate the charge transfer resistance value.

Note that all the electrochemical experiments were done in the 0.001 M NaCl solution at RT (18-22 °C).

Results and discussion

Surface profile

The S_z for water-jetted surface was 62 μm and for abrasive blasted surface was 119 μm . It is interesting to note that water jetting produces a significant profile although it is only about half that produced by the abrasive blasting. Other surface preparation methods produced relatively smooth surfaces.

SEM images

Figures 1a-1e are SEM images from surfaces after preparation showing the physical structure of surface after treatment. Figure 1e shows some particles embedded into the steel surface. EDX analysis showed these to be a mix aluminium, magnesium and silicon oxides, consistent with them being crushed garnet.

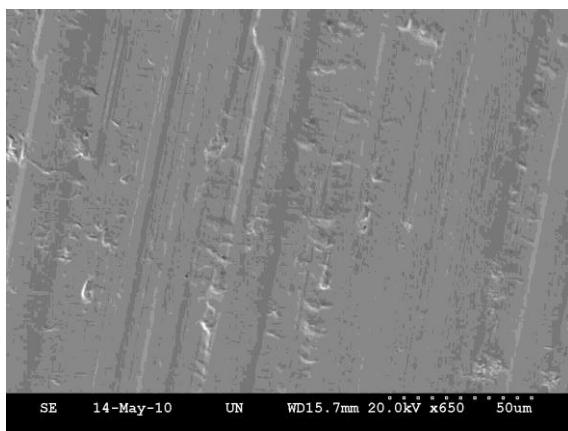


Fig1a: As received surface at X 650 magnification

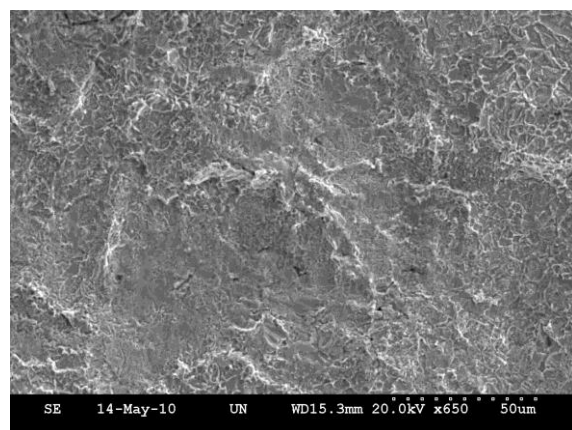
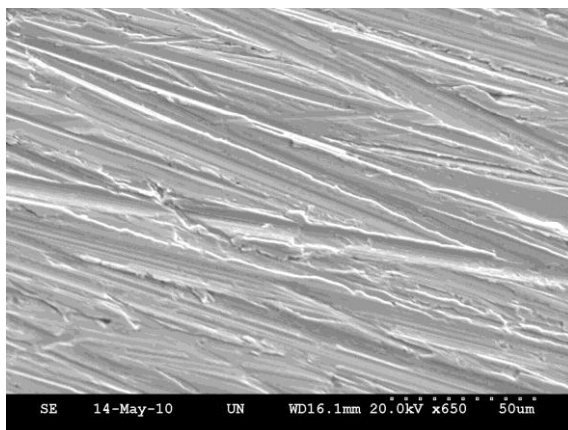


Fig1b: Water-jetted surface at X 650 magnification, Fig1c: Abraded surface at X 650 magnification

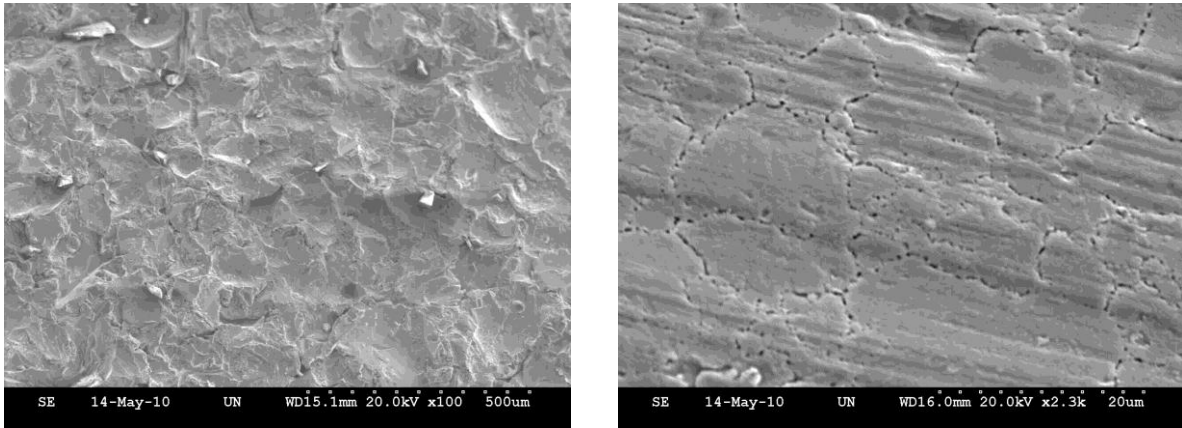


Fig1d: Abrasive blasted surface at X 120 magnification, Fig1e: Acid pickled surface at X2.3K magnification

SVET results

Figures 2-6 show the current density map of surfaces after 5 min and again after 2 hrs immersion in the 0.001 M NaCl solution. In all cases results show an increase in the difference between the extremes of anodic and cathodic current densities over the surface as the immersion time increases. This indicates the generation of bigger driving force for corrosion as a function of time via deposition of corrosion products on the surface and establishment of more anodic sites. The figure 7 explains the anodic sites development while the corrosion process goes on. According to the Nernst equation, areas with less access to oxygen act as anode and cathodic reactions take place in the area with higher access to oxygen. The highest number of anodes can be seen on the abrasive blasted surface and water-jetted samples which indicates higher electrochemical heterogeneity of these surfaces and the lowest number of anodes have been observed on the as received sample with no dramatic change after 2 hr contact with the solution.

According to SVET results the activity of surfaces can be ordered as below:

$$\text{Abrasive blasted} \geq \text{water-jetted} > \text{abraded} \geq \text{acid pickled} > \text{as received}$$

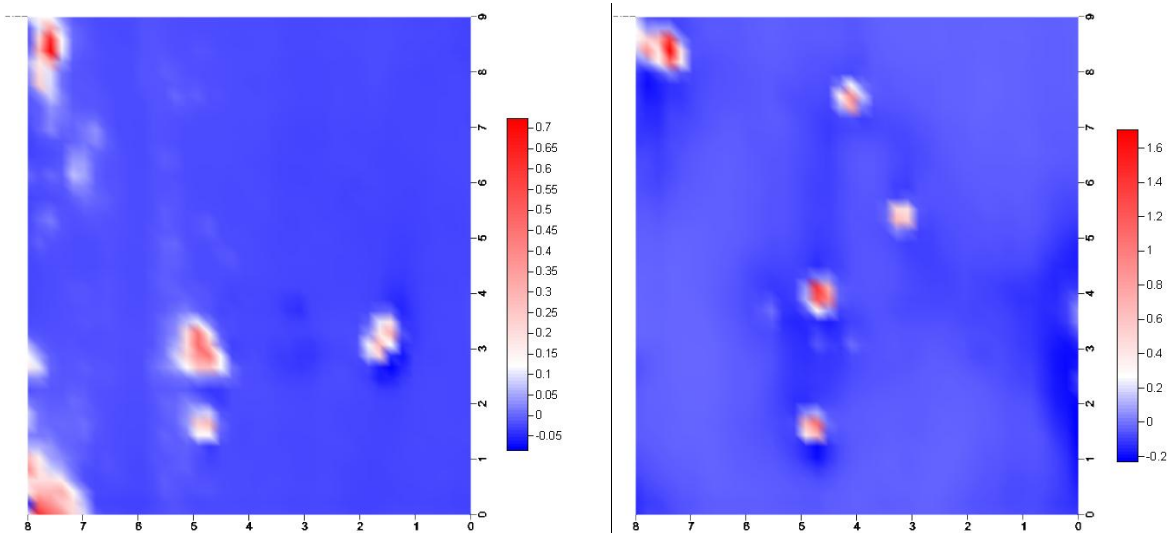


Figure2: Current density map of the As received mild steel surface after 5 min (left) and 2 hrs (right) immersion in 0.001 M NaCl

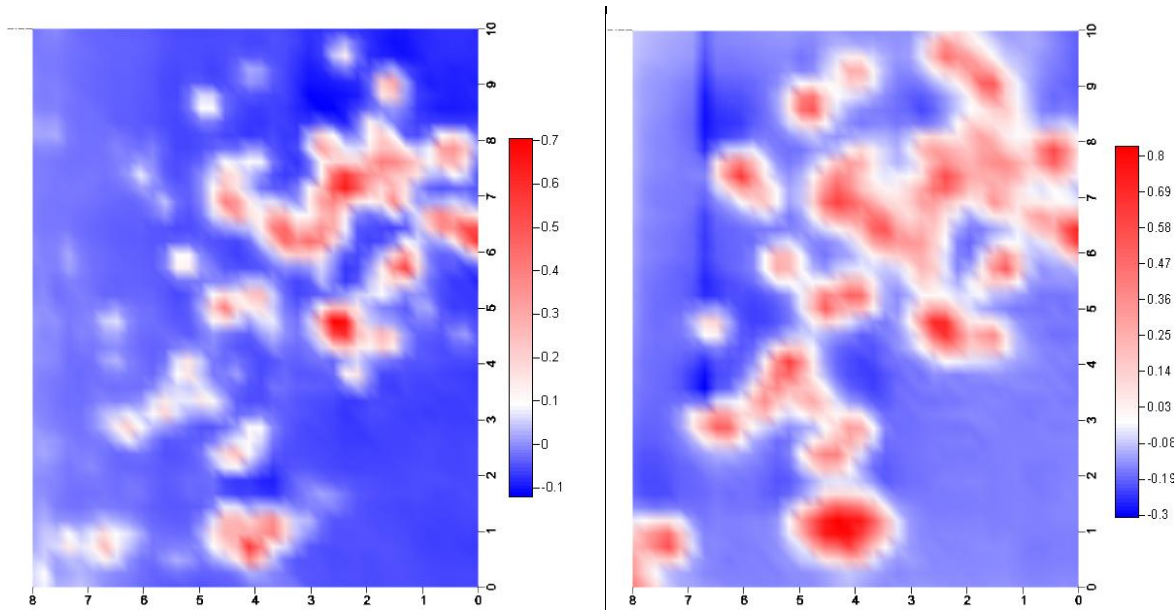


Figure3: Current density map of the water-jetted mild steel surface after 5 min (left) and 2 hrs (right) immersions in 0.001 M NaCl

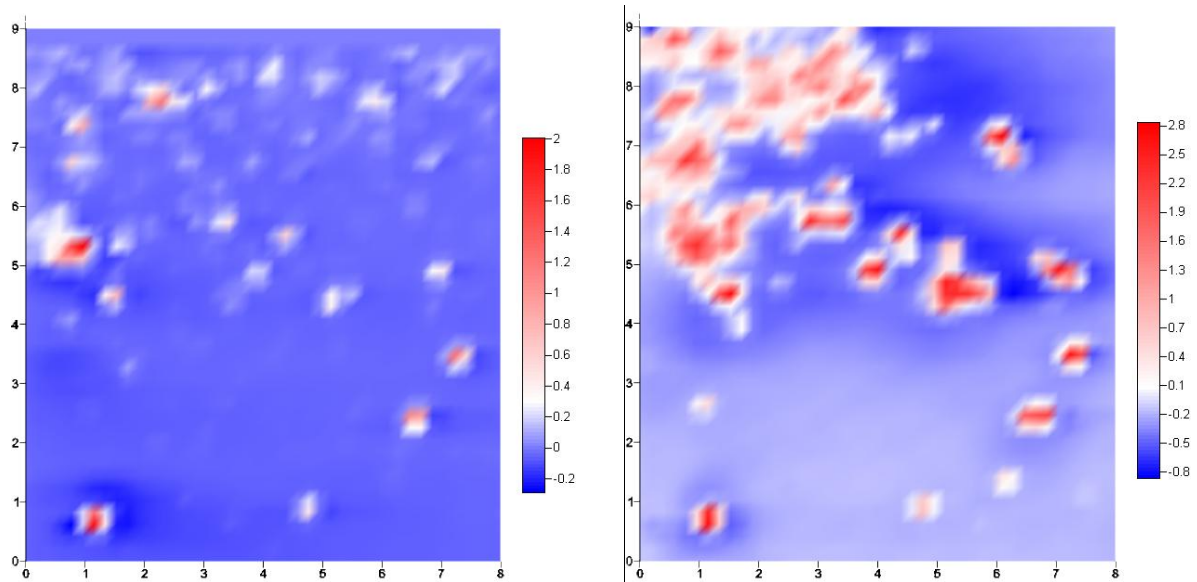


Figure4: Current density map of the abraded mild steel surface after 5 min (left) and 2 hrs (right) immersions in 0.001 M NaCl

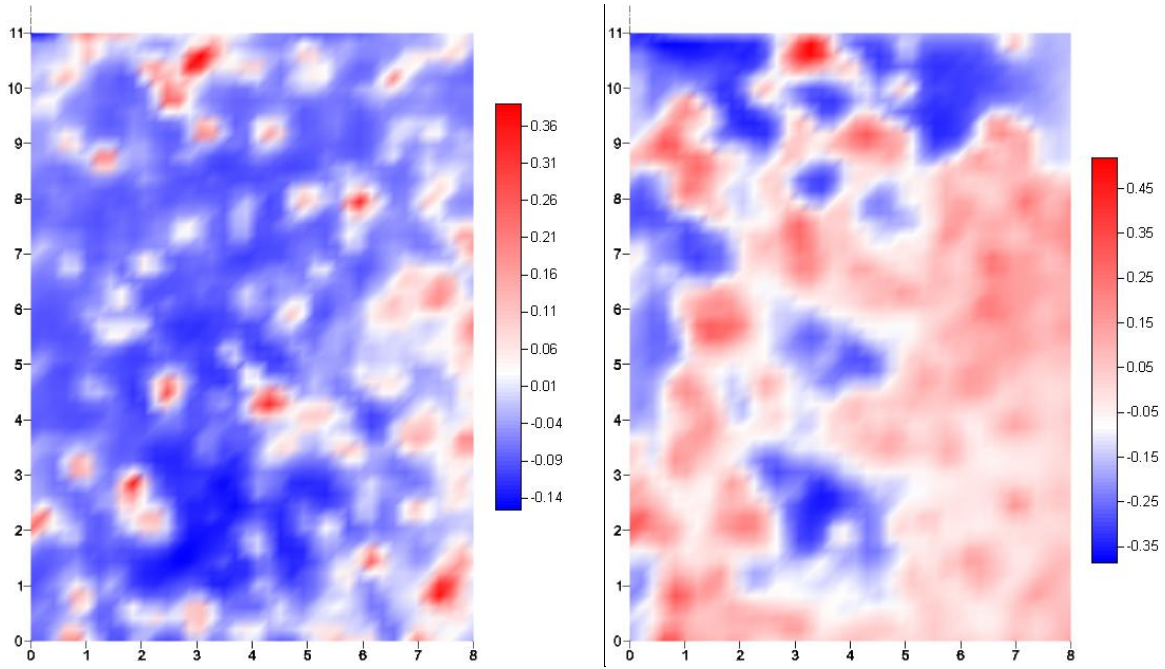


Figure 5: Current density map of the abrasive blasted mild steel surface after 5 min (left) and 2 hrs (right) immersion in 0.001 M NaCl

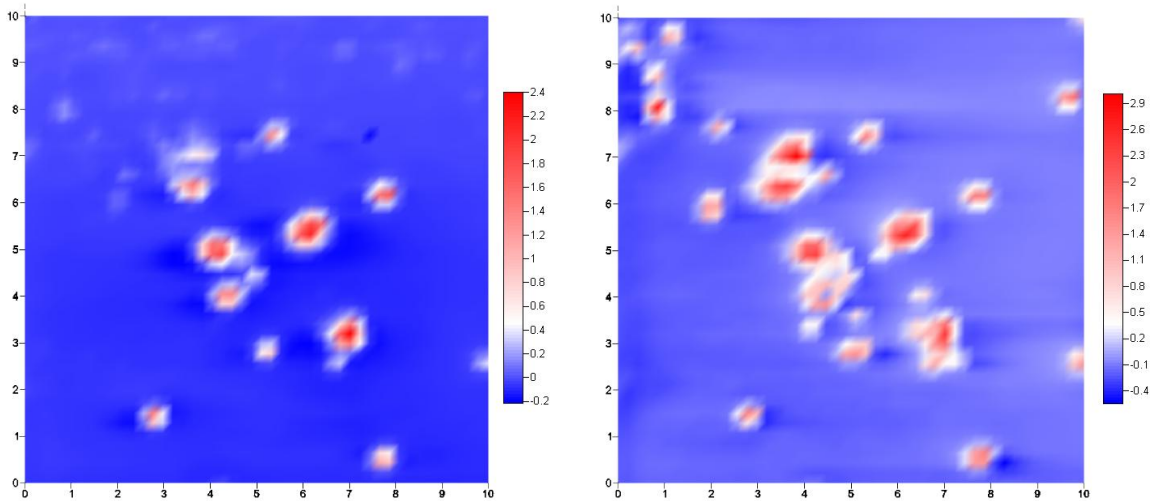


Figure 6: Current density map of the acid pickled mild steel surface after 5 min (left) and 2 hrs (right) immersions in 0.001 M NaCl

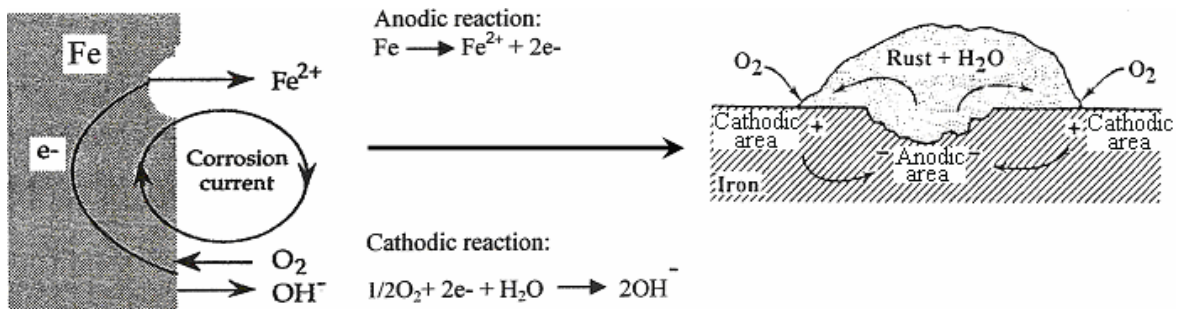


Figure 7: schematic illustration of corrosion process and development of cathodic and anodic sites

OCP analysis

Figure 8 shows the trend of OCP during 135 min contact with 0.001 M NaCl solution. A fast initial drop is either the result of quicker formation of cathodic sites or a more rapidly expanding anodic area. It can be seen that the abrasive blasted falls faster than the water jetted. The finishing level of OCP will be affected by the final ratio of anodic to cathodic area. The abrasive blasted and water-jetted surfaces show more active OCP than other samples during measurement which indicates a higher ratio of anodic area/cathodic area. These results are in line with the anodic-cathodic map of the surfaces obtained from SVET.

In terms of change from the initial value, the acid pickled surface shows the biggest potential drop which indicates higher sensitivity of the oxide layer on the surface to the presence of chloride ion. On the other hand, the lowest rate of change can be seen in case of as received surface which reveals more stability of the oxide layer and lower rate of its break down. With respect to this fact, surfaces can be ordered according to their oxide layer's sensitivity and the rate of its break down as below:

Acid pickled \geq water-jetted > abrasive blasted > abraded \geq as received

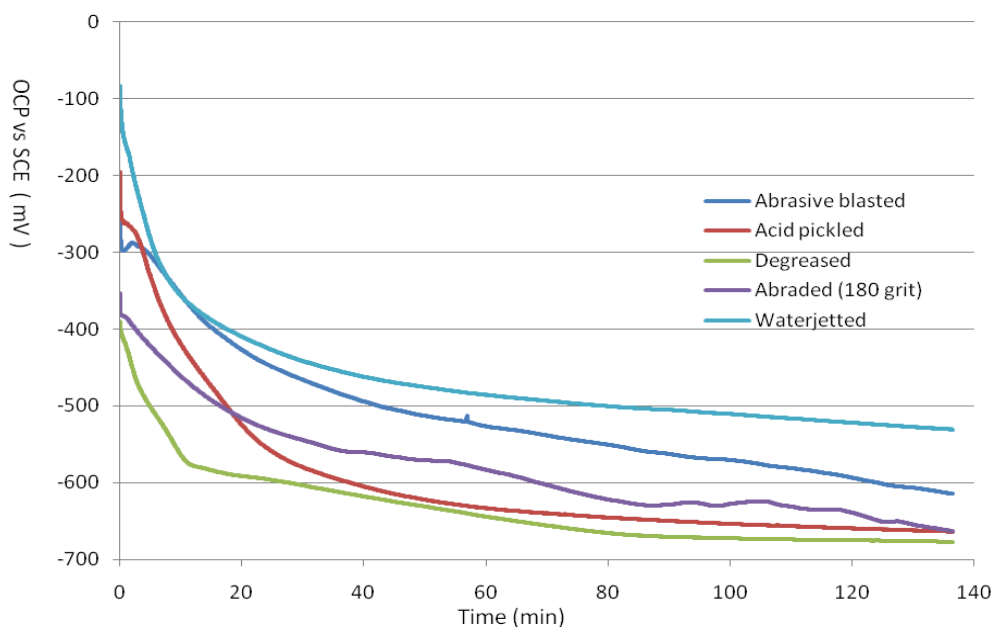


Figure 8: OCP value monitoring during contact with 0.001 M NaCl solution

EIS results

Figure 10 illustrates the change of overall charge transfer resistance (R_{ct}) values over a period of about 11 hours. The as received surface shows highest R_{ct} after 2 hrs contact with electrolyte while it has the lowest R_{ct} at the beginning. It suggests that the oxide layer which forms on as received surface is more stable against corrosive species. On the other hand, the R_{ct} of water-jetted surfaced dropped after 2 hrs immersion which would indicate an initial higher sensitivity of the oxide layer to break down compared with the abrasive blasted. However R_{ct} for the water-jetted sample subsequently (after 250hr) rose. Examined surfaces can be ordered according their R_{ct} values as follows :

As received > Acid pickled \geq abraded > water jetted > abrasive blasted

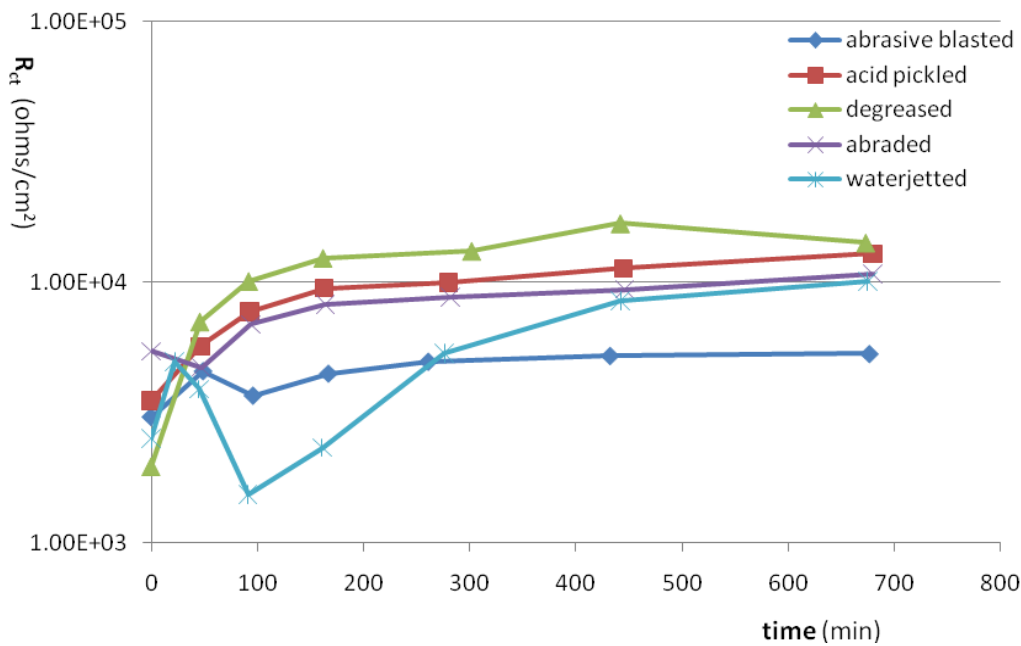


Figure 9: Trend of charge transfer resistance during contact with 0.001 M NaCl

Conclusions and future work

Results have shown that the differently prepared surfaces vary quite considerably in their electrochemical activity. The high level of electrochemical activity associated with the abrasively blasted surface is consistent with previous work (7) where coatings applied to that surface provided poor protection. This is in contrast to coatings applied to water-jetted surfaces which performed well. When the water jetted surfaces used in that work (7) were examined using SVET (experiments not previously reported) they showed very little electrochemical activity. However this current work has indicated that the water jetted surfaces are also quite active. This difference may well be due to the time between preparation and application of paint/examination which was longer in the earlier work than in the work reported here. Future work will involve application of maintenance alkyd coatings onto these five substrates and exposure of the coated samples in immersion tests and accelerated tests. The subsequent performance will be correlated both with the results presented here and with any effect on the structure of the coating itself induced by the different surface finishes.

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