

# Microstructure dependency on Adsorption of imidazoline on 1018 Steel: A PEEM and NEXAFS Study

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## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is found naturally in oil and gas wells. It is primarily dissolved in waters pumped into oil wells to reduce the viscosity of oil to enhance recovery. Carbon dioxide flooding to maintain a higher reservoir pressure is also a common practice. Thus CO<sub>2</sub> corrosion is a great concern in these C-steel pipelines, which leads to the formation of a weak carbonic acid (H<sub>2</sub>CO<sub>3</sub>) during the corrosion reaction.<sup>1</sup> Iron carbonate (FeCO<sub>3</sub>) is the primary corrosion product and it precipitates out of solution because of its low solubility and forms a film on the surface of C-steel further reducing the corrosion.<sup>2</sup> CO<sub>2</sub> corrosion of C-steel is influenced by several factors, such as, flow type, fluid composition, pH, temperature, etc. The flow characteristics have a significant effect on corrosion rates.<sup>4</sup> Previous studies have demonstrated that corrosion rate increases with increase in Froude (Fr) number due to the destruction of the protective iron carbonate film formed on the C-steel.<sup>4,5</sup> Corrosion of C-steel pipelines has prompted the consideration of a corrosion inhibitor program in various oil fields around the world. The importance and usefulness of oleic imidazoline inhibitors in oil and gas pipelines has been studied in detail by several researchers.<sup>6, 7, 8, 9</sup> Most of these commercial inhibitors have organic polar molecules that absorb on to the metal surface and form a protective film barrier. However, change in microstructure of steel may cause difference in adsorption kinetics and can greatly affect the corrosion rates. This communication represents a combined PEEM (Photoemission electron microscopy) and NEXAFS (Near Edge X-ray absorption fine structure) study on the microstructure dependency on adsorption of imidazoline on 1018 steel used for constructing oil and gas lines.

## EXPERIMENTAL

1018 C-steel coupons of 0.437 inch in diameter and 0.126 inch in thickness were rough polished, cleaned in deionized water and used for the experiments. The as-received steels were heated to 910°C for 30 minutes and slowly cooled inside the furnace to obtain ferrite-pearlitic microstructure. Subsequently, the steels were fine polished using 1-micron diamond paste. Other steels were heated in the austenitic region and quenched rapidly in the ice brine solution to obtain a needle like martensitic structure. Usually, carbon content of the steel should be minimum 0.4% to obtain a fully martensitic structure. In the present case, the carbon content is 0.18 – 0.2%. The hardness of this steel is further verified using a hardness tester and the measured hardness was found to be 55R<sub>c</sub>. The hardness of an ideal martensite is 62-64 R<sub>c</sub>.

A drop of imidazoline was smeared in both the steels with a plastic knife and kept for 24 hours. Before inserting the samples in the PEEM chamber, the imidazoline is wiped off thoroughly from the surface with soft paper tissues. The samples were then pumped down for 2 hours before the analysis.

Both NEXAFS and PEEM measurements were carried out in a total electron yield mode at the Advanced Light Source (ALS) on a bend magnet beamline 7.3.1.1. Linearly polarized X-rays delivered from a bending magnet beamline were dispersed by a spherical grating monochromator. The energy range was 250-1200eV. The resolution was  $(E/\Delta E)$  approximately 1500. The spatial resolution is 20nm for NEXAFS. All NEXAFS spectra have been ratioed to the incident photon flux and normalized to the largest spectral feature. Background subtraction was done in all the NEXAFS spectra shown in Figures 1 and 2. Energy calibration of the NEXAFS spectra was achieved by using the Fe L edge at 710 eV (iron oxide) as a reference.

## RESULTS AND DISCUSSION

Figure 1 (a) shows a PEEM topographic image of a ferritic 1018 steel, whereas Figure 1 (b) illustrates a PEEM nitrogen K image of the same steel acquired at 380 eV. Both pits and defects are visible in both the images. Dark and hot spots are prominent in the images. In the center of the dark spots very little nitrogen is found, whereas in the hot spots the nitrogen concentration is high. This nitrogen is from the imidazoline inhibitor. This is a very important observation, because the steels can undergo pitting corrosion in multiphase environments existing in the oil and gas lines. Inhibitors are primarily responsible for corrosion prevention of steels. If there is a poor nitrogen adsorption in the pits, then the corrosion action will start from the pits leading structural destruction. These pipelines suffer varying weather patterns ranging from extreme hot to bitter cold. Temperature difference can change the local steel microstructures, which might also affect the adsorption behavior of the imidazoline on steel.

While ferrite is a BCC structure, martensite has BCT structure and the atomic packing density is different in both the structures, which might lead to varying adsorption kinetics. As seen from the N image, there is a uniform distribution of the imidazoline layer in Figure 1. However, in the pits and the defects, the concentration is very different, and hence they are named hot spots or dark blobs.

Detailed nitrogen K-edge NEXAFS measurements from the hot spots, dark blobs and background are shown in Figure 1(c). X-ray photoabsorption is both elemental and chemical specific since thresholds are observed at core levels which can be identified with particular atoms while the near edge absorption fine structure spectrum can be used to map the density of final states which are sensitive to the local environment. The sharp  $\pi^*$  resonance in Figure 1c and Figure 2c is due to the excitation of the N 1s electron to the non-bonding  $\pi^*$  orbital. The two peaks in the spectrum belong to two different N environments.  $N_1$  corresponds to N in the benzene ring, whereas  $N_2$  belongs to the pendant chain ( $-NH_2$ ). As evident from Figure 1c, the nitrogen intensity is less in the dark blobs as compared to the white spots. The relative difference in the peak intensity signifies the relative presence of the N- environment adsorbed on the steel surface.

Figure 2 (a) shows a PEEM topographic image of a martensitic 1018 steel, whereas Figure 2 (b) illustrates a PEEM nitrogen image of the same steel at 380 eV. It is evident from the PEEM images, that the martensitic transformation is not complete and hence a low hardness compared to a fully martensitic structure. In between the martensite needles, the flat area is primarily ferrite. Again there is a preferential N adsorption in the martensite and ferrite region. The nitrogen is higher in the background region than in the needles. Also in the designated needle area (Figure 2 A'), one observes preferential distribution of nitrogen. Martensite is stressed and will corrode faster than a ferrite structure. Preferential distribution of imidazolines in martensitic steels can be a major concern for corrosion prevention.

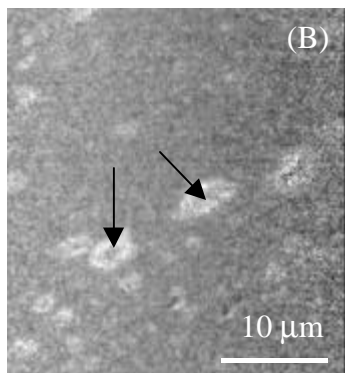
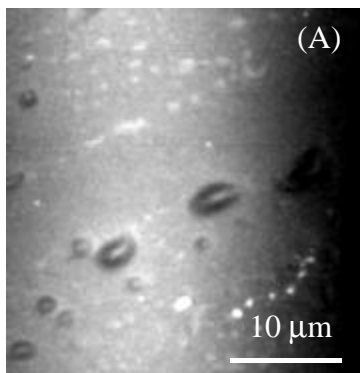
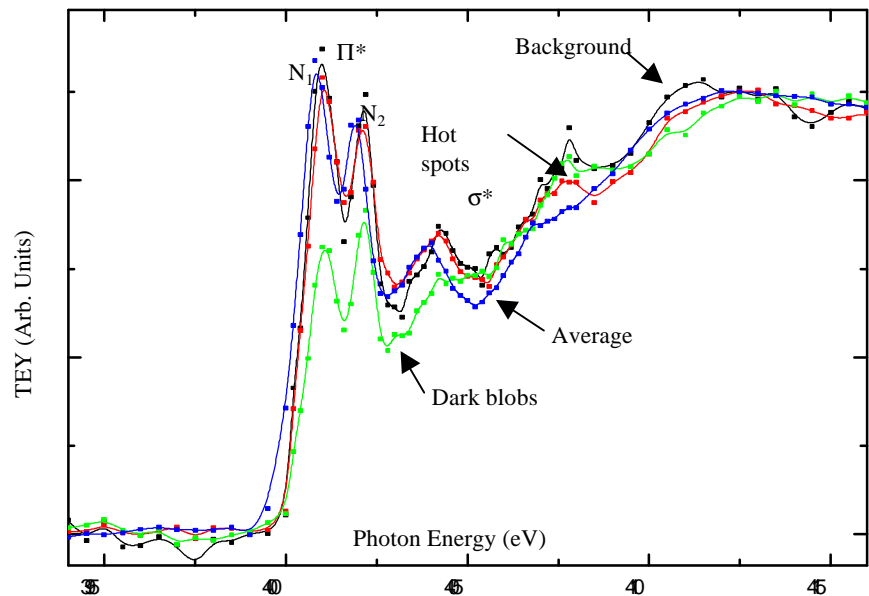


Figure 1 : Local NEXAFS spectra (C) on polished (pearlite) sample with PEEM images of standard image (A) and Nitrogen image(B). Arrows indicating the blobs. Note: Brightness in the image is due to illumination.

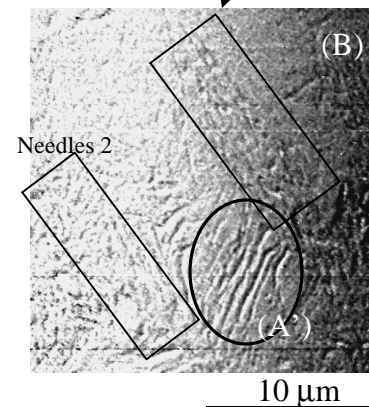
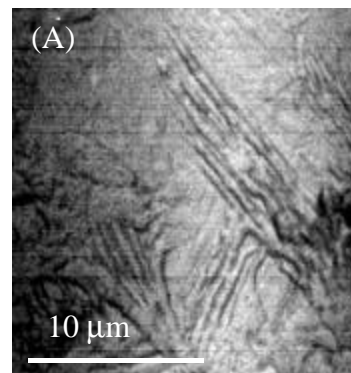
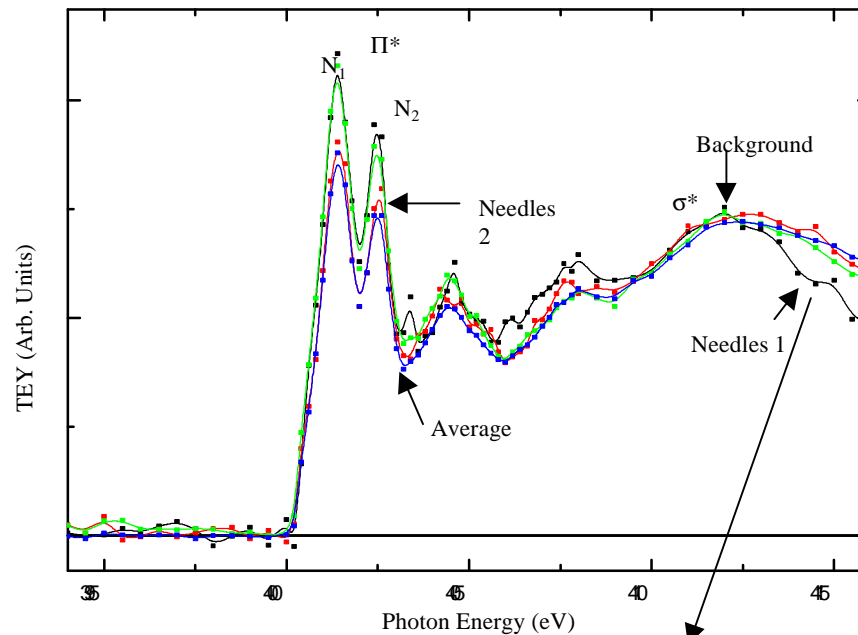


Figure 2 : Local NEXAFS spectra (C) on polished (Martensite) sample with PEEM images of standard image (A) and Nitrogen image(B). Selected area A'. Note: Brightness in the image is due to illumination.

PEEM images are supported by NEXAFS spectra in Figure 2(c). Preferential N distribution is found to be present in the Needles 1 and Needles 2, whereas the background N concentration is relatively higher than the needles. A structure like this will not be beneficial for oil and gas lines, because of nonuniform N adsorption kinetics. Martensite is BCT and hence the nitrogen adsorption is poor than the ferrite structure, which is BCC.

## CONCLUSIONS

Successful PEEM images are acquired in both imidazoline coated ferrite and martensitic 1018 steels. Adsorption kinetics of imidazoline on 1018 steels is microstructure dependent. Pits have a lower concentration of nitrogen as compared to the background and hence the pits will be initiators to the corrosion in oil and gas lines in presence of multiphase environment. Nitrogen adsorption on ferritic structures is higher than the martensitic structure and hence the martensites will be vulnerable to material degradation in oil and gas environment. Preferential adsorption on the martensitic needles is found from both PEEM images and NEXAFS spectra.

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