Development of a Synergistic Blend of Corrosion Inhibitors for Acid Cleaning

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ABSTRACT

Mineral scale, such as calcite, can build up on the walls of production wells when calcite inhibition is not used or is poorly designed or managed. When this occurs, flow is restricted leading to reduced efficiency or possibly complete loss of production. Scaled wells can be cleaned using acids such as hydrochloric acid. While acids are great for dissolving scale, they are very aggressive to the underlying metal. Corrosion inhibitors are used to prevent damage to the metal during acid cleaning.

A synergistic blend of inhibitors was developed which provide corrosion protection for well rejuvenation with hydrochloric acid. Initial screening began with jar tests at 95 °C and 15% hydrochloric acid. The most promising candidates were blended together and reevaluated. A combination of inhibitors provided superior protection to the individual inhibitors alone. Subsequent tests in 10% HCl at 150 °C showed that a formulation provided excellent protection even at higher temperatures.

1. INTRODUCTION

Geothermal plants are designed to extract energy from subterranean water which has been heated by hot rock. Sometimes the water is hot enough so that steam is produced and used directly. More commonly, high pressure, hot brine is produced, which is then separated into brine and steam through flashing. During this process, the pH and the concentration of dissolved solids are increased. This can lead to supersaturation and the formation of mineral scales in the production well, the flash separator or the production well pumps. The most common scale encountered under these conditions is calcite, $CaCO_3$. Metal sulfides, such as iron sulfide, Fe_xS_y, or stibnite, Sb_2S_3 can also form in wells with high levels of sulfide.

When these scales form, flow becomes restricted leading to loss of efficiency or potentially well closure. Periodic cleaning with acids is necessary to dissolve and remove the scale, thereby rejuvenating the well. Strong acids such as 10-15% hydrochloric acid are commonly used. At high temperatures, 150-200 °C, these acids are very aggressive to the underlying metal. Corrosion inhibitors are used to reduce the corrosion rate and protect the metal. A number of corrosion inhibitors have been used to protect wells against acid-induced corrosion. Common inhibitors include organic compounds such as aldehydes,(Growcock, 1989a, 1989b, Jiancun et al., 2009) acetylenic alcohols,(Singh et al., 1993; Teeschi, 1975) imidazolines,(Quaraishi, 2008) quaternary and filming amines,(Schmitt, 1984; Sastri, 2001) along with inorganic compounds such as antimony(Williams et al., 1992) and bismuth.(Ihara et al., 1992) This report details laboratory work done to evaluate corrosion inhibitors for acid cleaning.

2. EXPERIMENTAL SECTION

2.1 Jar Tests

Two C1010 steel coupons were attached to an alumina screw and separated with alumina nuts and washers. The coupons were submerged in a 200 mL solution of 15% hydrochloric acid and 0.5% inhibitor. This solution was heated in an oil bath to 95 °C. After 3 hours, the coupons were removed and rinsed with deionized water and dried. The corrosion rate was determined by weight loss. The rate was initially calculated in mm per year. This was then converted to mm by multiplying by the time in years. The reported values represent the thickness lost in mm over 3 hours.

2.2 High Temperature Autoclave Tests

Four coupons, two K55 steel and two 316 stainless steel, were placed into an autoclave pressure vessel. 10 grams of $CaCO_3$ were added to simulate the presence of calcite. The inhibitor was added to 200 mL of 10% HCl to make a 1% solution. This solution was then added to the autoclave. The reactor was sealed and heated to 150 °C. The reactor was cooled and the coupons were removed, rinsed with water and dried. Total expose time was 4 hours. The corrosion rate was determined by weight loss. The rate was initially calculated in mm per year, and converted to mm by multiplying by the time in years. The reported values represent the thickness lost in mm over 4 hours.

2.3 Microscope Studies and Film Thickness

Light microscopy work was done using a Keyence VHX 5000 electronic digital microscope. This instrument was used to capture images and develop a surface profile. The depth profile of the surface was calculated by using depth of field and Z stacking analysis of the images.

2.4 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX)

Scanning electron microscopy characterization of corrosion coupons was examined using a Zeiss Auriga 60 Crossbeam field emission SEM in secondary electron (SE) mode. The samples were mounted on a sample stub and then coated with a thin layer of carbon to make the sample surface conductive. Energy dispersive X-ray (EDX) spectrum and mapping were acquired using an X-Max80 Oxford 80mm^2 Silicon Drift Detector (SDD). Characteristic X-rays generated by the interaction of the electron beam and elements in the top layer (~1 µm thick) of the sample surface were detected. The results were recorded in EDX spectra with a series of peaks, whose positions correspond to the energy of the respective X-ray photons (in eV).

3. RESULTS AND DISCUSSION

3.1 Discussion of Jar Tests

Initial screening was done with jar tests at 95 °C. This allowed for the rapid screening of compounds to quickly determine the most promising candidates. Without any added inhibitor there was a significant amount of corrosion. The thickness lost was 0.511 mm over 3 hours. There was also a significant evolution of hydrogen throughout the test. A coupon exposed to HCl without an inhibitor is shown in Figure 1a. The untreated coupon was significantly degraded to the point of being very thin and fragile. The corrosion on the edges and throughout the coupon was quite significant, as shown in Figure 1b. A variety of inhibitors were screened and the results are listed in Table 1. The best individual inhibitor was an Aromatic Aldehyde, which reduced the thickness loss to 0.019 mm over 3 hours under these conditions. The treated coupons had a visible brown, sticky film which formed a physical barrier to corrosion. This film was tenacious and required solvents such as isopropanol to be removed. The underlying coupon was grey and showed only slight evidence of corrosion. During the experiment, the evolution of hydrogen was reduced as the protective layer was formed.

Table 1. Effect of corrosion inhibitors on weight loss in 15% HCl, 95 °C, 3 hours.

Inhibitor	Thickness Lost
No Inhibitor	0.511 mm
Aromatic Aldehyde	0.019 mm
Phosphonate	0.428 mm
Oxime 1	0.198 mm
Oxime 2	0.103 mm
Filming Amine 1	0.082 mm
Filming Amine 2	0.082 mm
Quaternary Amine	0.148 mm
Imidazoline	0.022 mm
Imidazoline Quat	0.032 mm
Carboxylic Acid 1	0.436 mm
Carboxylic Acid 2	0.382 mm
Carboxylic Acid 3	0.196 mm

Filming amines and imidazolines also provided some protection. Two filming amines, Imidazoline and Imidazoline Quat all provided good protection, albeit slightly less than the aldehyde. These coupons did not have a visible protective film, although the coupons were significantly less degraded than the untreated coupons. Presumably, a thin protective film was formed, but that film wasn't large enough to be visible to the naked eye. There were also several marginal inhibitors such as a quaternary amine, and two oximes. While these inhibitors did provide some protection, the coupons experienced significant degradation over 3 hours. Finally, several classes of molecules provided very little protection when compared with the blank. Carboxylic acids and phosphonates were ineffective under these strongly acidic conditions. This contrasts with cooling water conditions, which are often basic and contain higher levels of calcium. Under those conditions, phosphonates and carboxylic acids are known to provide good corrosion protection.(Drew, 1994)

Since the aromatic aldehyde gave the best protection it was decided to investigate it in combination with other inhibitors. These combinations are listed in Table 2. All formulations contain solvent, surfactant, formic acid and the components listed in Table 2. Formic acid was used since it's a known intensifier at high temperatures.(Singh and Quaraishi, 2015) It is thought that formic acid degrades into carbon monoxide which acts as the intensifier. This effect was not specifically studied in the jar tests since the temperature is lower and the jars are open to the atmosphere. Adding an oxime or a filming amine in Formulations 2 and 3 did not significantly change the corrosion rate. Formulation 9, a tertiary combination of aldehyde, filming amine and oxime gave the best results. The thickness loss was reduced to just 0.005 mm over 3 hours. Interestingly, Formulation 6, a combination of filming amine and oxime without the aldehyde, did not provide very good protection.

Table 2. Effect of combinations of corrosion inhibitors on weight loss in 15% HCl, 95 °C, 3 hours.

Formulation #	Components	Thickness Lost
No Inhibitor	Blank	0.511 mm
Formulation 1	10% Aromatic Aldehyde	0.014 mm
Formulation 2	10% Aromatic Aldehyde 2% Filming Amine	0.013 mm
Formulation 3	10% Aromatic Aldehyde 2% Oxime 1	0.015 mm
Formulation 4	2% Oxime 1	0.278 mm
Formulation 5	2% Filming Amine	0.127 mm
Formulation 6	2% Oxime 1 2% Filming Amine	0.154 mm
Formulation 7	10% Aromatic Aldehyde 2% Oxime 1 2% Filming Amine	0.006 mm
Formulation 8	10% Aromatic Aldehyde 1% Oxime 1 1% Filming Amine	0.006 mm
Formulation 9	10% Aromatic Aldehyde 2% Oxime 2 2% Filming Amine	0.005 mm

Reducing the amount of Aromatic Aldehyde increased the corrosion rate. Next jar tests were repeated using 0.5% of the inhibitor formulation. The concentration of the aldehyde was reduced from 10% (Formulation 7) to 6% (Formulation 10), then to 2% (Formulation 11.) Reducing the amount of aldehyde from 10% of the formulation to 2% increased the corrosion rate leading to a 6-fold increase in corrosion over the time period. This aldehyde adsorbs and reacts on the metal surface to form a physical barrier to corrosion. Reduced aldehyde led to increased corrosion.

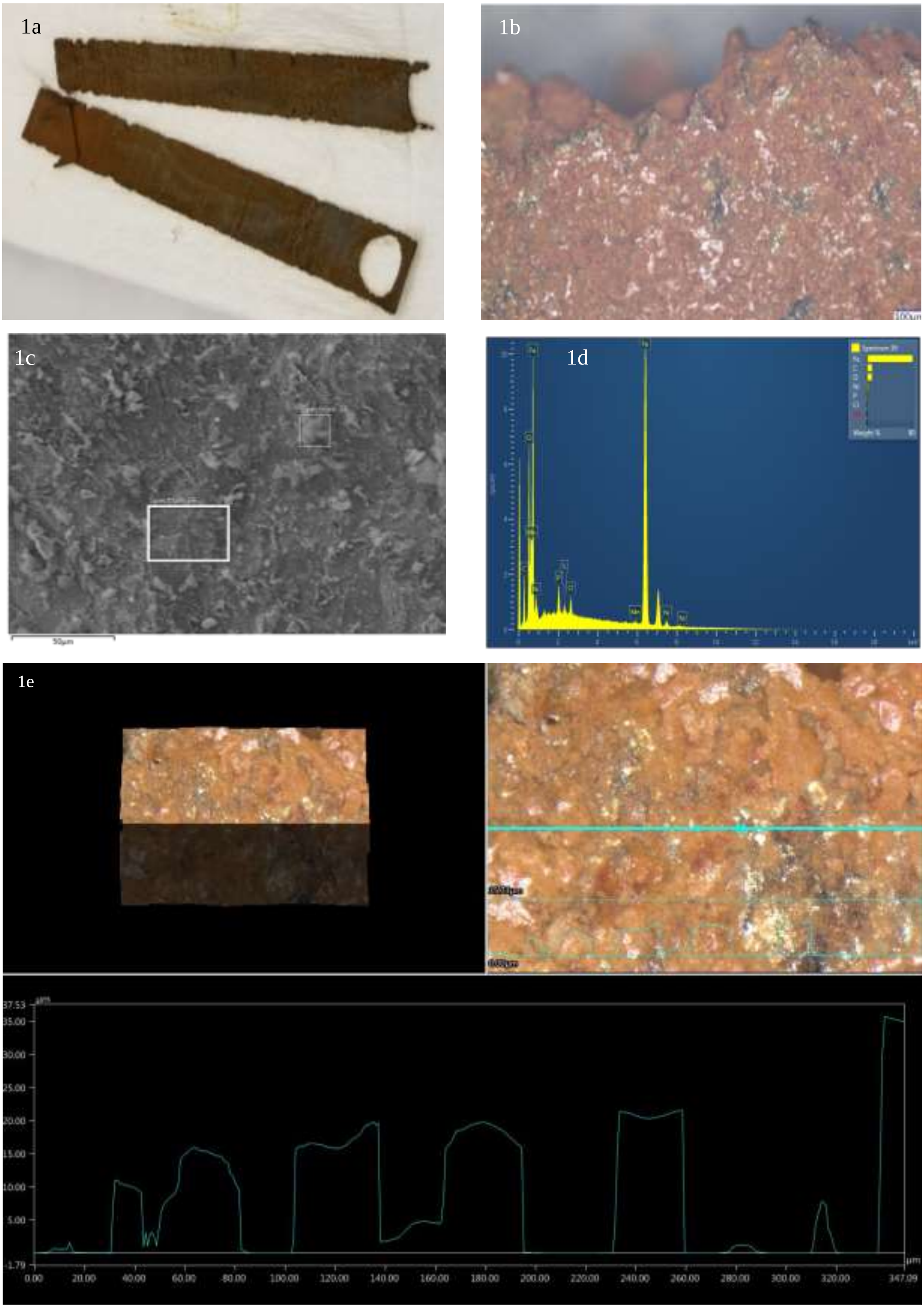

Figure 1. C1010 steel coupons after exposure to 15% HCl at 95 ºC for 3 hours. 1a) Picture of the coupons 1b) Close up of the edge of a coupon. 1c) SEM image of the coupon. 1d) EDX spectrum from the SEM image. 1e) Depth profile of the surface of the coupon.

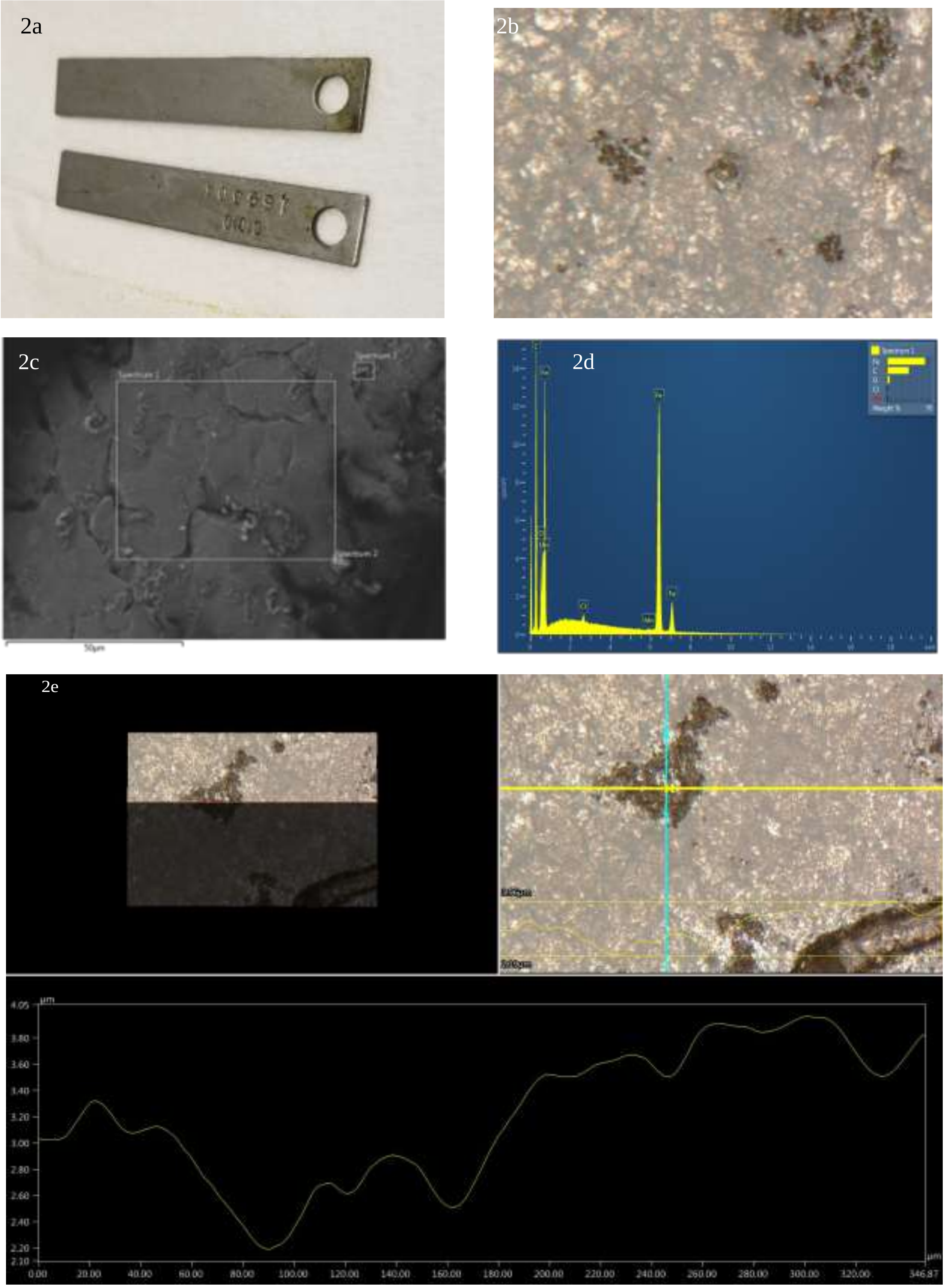

Figure 2. Coupons submerged in 15% HCl at 95 ºC for 3 hours with 0.5% Formulation 1. 2a) Picture of the coupons. 2b) 1000X Magnified picture showing the film formed from Formulation 1. 2c) SEM image of the coupon. 2d) EDX spectrum of the light area of the coupon (Spectrum 1). 2e) Depth profile of the coupon.

Table 3. Effect of reduced aldehyde on weight loss in 15% HCl, 95 °C, 3 hours.

Formulation	Components	Thickness Lost
Formulation 7	10% Aromatic Aldehyde 2% Oxime 1 2% Filming Amine	0.006 mm
Formulation 10	6% Aromatic Aldehyde 2% Oxime 1 2% Filming Amine	0.013 mm
Formulation 11	2% Aromatic Aldehyde 2% Oxime 1 2% Filming Amine	0.040 mm

3.2 Surface Analysis of Coupons

The untreated coupons show significant and visible signs of both general and pitting corrosion. As expected, after the addition of HCl the coupons were significantly corroded as seen in Figure 1a. The coupons were visibly thin and brittle and showed significant signs of edge-based corrosion. A close-up picture of the coupon edge is seen in Figure 1b. The edge was very uneven. The depth profile shows the presence of severe pitting on the interior of the coupon. Pits of 10-15 µm are visible in Figure 1e. There was a large amount of visible rust suggesting a significant amount of general corrosion as well. These results illustrate the severe nature of the conditions and the need for a corrosion inhibitor.

The surface of the untreated coupon was further evaluated using SEM and EDX. The SEM picture, Figure 1c, shows that the surface is very uneven. There are significant deposits of rust throughout the surface. As expected, the EDX spectrum shows the presence of mostly iron, along with traces of other elements, Figure 1d. The small carbon peak is probably due to sample preparation since these samples were coated with a thin layer of carbon prior to analysis.

The coupons treated with these inhibitors have lower amounts of visible corrosion as seen in Figure 2a. The use of Formulation 1 yielded grey coupons with a sticky brown film. An image of this film is shown in Figure 2b. The light, opaque areas are areas with high levels of film coverage and the dark brown areas have low film coverage. The film covered most of the coupon, although there were a few areas of reduced coverage. At the thickest points, the film averaged about 2 µm in height, Figure 2e. This thickness was not uniform and varied throughout the coupon as seen by the depth profile.

The SEM, Figure 2c, showed a relatively smooth surface with a few cracks and deposits. In the EDS spectrum, Figure 2d, a mixture of carbon and iron was present. During the test, it was observed that the bubbling rate was initially high, but then declined throughout the experiment. Presumably, this film formed gradually and provided increasing protection as time went on. The presence of iron in the film suggests that it is a mixture of corrosion inhibitor and the corrosion products.

Coupons treated with Formulation 7, a combination of aldehyde, filming amine and oxime, were grey, and had a lower corrosion rate than coupons treated with the aldehyde alone, Formulation 1. Unlike Formulation 1, which produced a thick sticky film, Formulation 7 did not produce a visible film as seen in Figure 3a. Further analysis with SEM and EDS did show the presence of significant amounts of carbon, suggesting that a thin film was present. The EDS spectrum in Figure 3c was from a region which had high levels of carbon and lower levels of iron indicating the presence of some organic compounds. The EDS spectrum in Figure 3d had higher levels of iron and lower levels of carbon. These results indicate that, while there is a protective film, this film is thin and is mixed with iron in several places.

3.3 High Temperature Autoclave Tests

Next the efficacy of these blends was evaluated at higher temperature. It was decided to test Formulation 2 since it provided good protection in the prior tests. It was also decided to use K55 and 316 stainless steel coupons since these metallurgies are more common in the geothermal industry. 10,000 ppm of formulation 2 was added to a 10% HCl solution. In a typical application, doses are expected to be between 5,000 ppm and 20,000 ppm. Calcium carbonate was added to simulate the presence of calcite scale and carbon dioxide. This procedure both reduced the acidity of the acid solution and generated carbon dioxide. This K55 and 316 stainless steel coupons were added. The reactor was sealed and heated at 150 °C for 4 hours. The coupons were analyzed by weight loss and the results are presented in Table 4.

Table 4. Summary of high temperature corrosion tests using Formulation 2.

Formulation	Metallurgy	Thickness Lost
Blank	K55	0.313 mm
Formulation 2	K55	0.022 mm
Blank	316 SS	0.112 mm
Formulation 2	316 SS	0.022 mm

The coupons had noticeably less corrosion when an inhibitor was added. The untreated coupons were very thin and brittle. General corrosion and pitting were observed throughout the K55 coupons in Figure 4a. Also, there was a significant amount of corrosion on the edge of the coupon as seen in Figure 4b. The K55 coupons treated with Formulation 2 had much less pitting and corrosion as shown in Figure 4c. The brown spots on these coupons were caused by the corrosion inhibitor and were easily removed with isopropanol. There was very little evidence of corrosion at the edge of the coupon in Figure 4d. The edge of the coupon looked relatively smooth with some small pits. The corrosion rate was reduced by over 90% compared with the untreated K55 coupon. The untreated coupons lost 0.313 mm of thickness over the test, while the treated coupons only lost 0.022 mm of thickness.

Similar results were observed with 316 stainless steel. The untreated coupons did not contain a lot of general corrosion, although the coupons did have a beige tint as seen in Figure 4e. There was some evidence of corrosion along the edge of the coupons observed in Figure 4f. As with the K55 coupons, the stainless steel coupons treated with Formulation 2 showed fewer signs of corrosion in Figure 4g. Again, the protective film from the corrosion inhibitor appeared as brown spots on the coupon. The edge of the coupon was noticeably smoother and showed fewer signs of pitting in Figure 4h. The corrosion rate was reduced by about 80% compared with the untreated stainless steel coupon. The untreated coupons lost 0.112 mm of thickness, while the treated coupons lost just 0.022 mm of thickness.

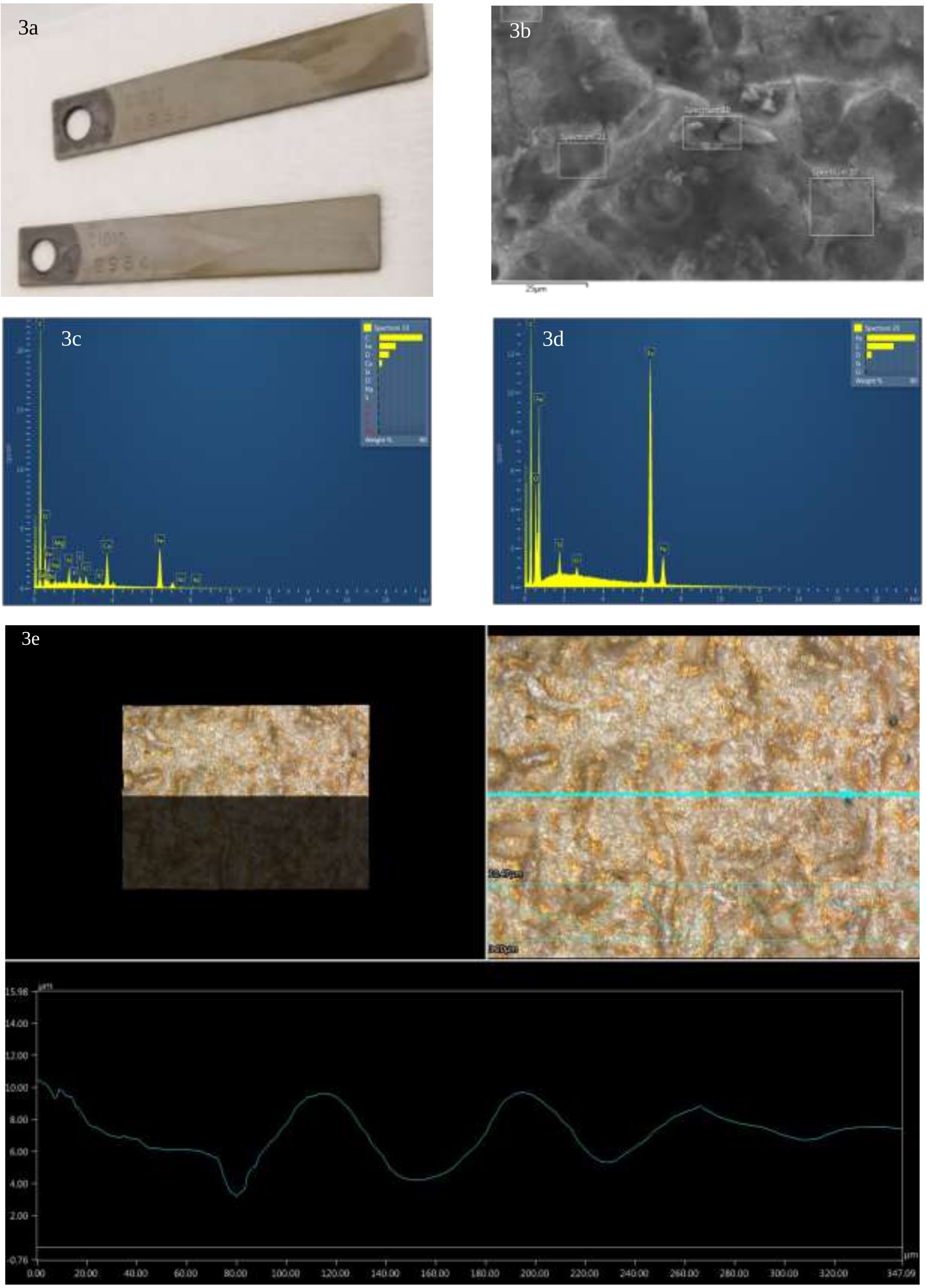

Figure 3. Coupon after exposure to 15% HCl at 95 ºC for 3 hours with 0.5% Formulation 9. 3a) Photograph of the coupons. 3b) SEM picture of the coupon surface. 3c) EDX spectrum from the SEM (Spectrum 19). 3d) EDX spectrum from the SEM (Spectrum 20). 3e) Depth profile of the coupon.

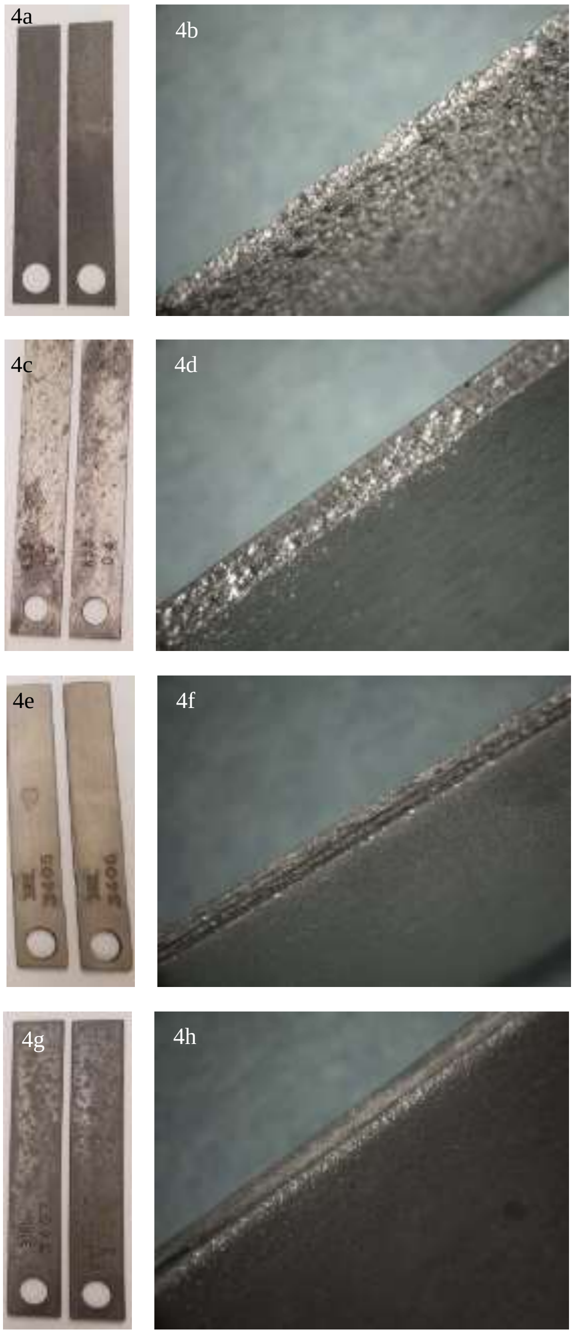

Figure 4. Pictures of K55 and 316 stainless steel coupons after submersion in 10% HCl at 150 °C for 4 hours. 4a) K55 coupons without added inhibitor. 4b) The edge of the coupon from 4a. 4c) K55 coupons protected with Formulation 2. 4d) The edge of the coupon from 4c. 4e) 316 Stainless steel coupons without added inhibitor. 4f) The edge of the coupon from 4e. 4g) 316 Stainless steel coupons protected with Formulation 2. 4h) The edge of the coupon from 4g.

4. Conclusion

A formulation was developed which contains a combination of inhibitors which provided protection for high temperature acid cleaning. This formulation provided good protection at 150 °C on K55 and 316 stainless steel in 10% hydrochloric acid.

Future work will involve the application of these formulations with mud acid (5% HF, 10% HCl). This acid is being used now in New Zealand to remove silica scale and the cost of inhibitors is a significant barrier.

5. Acknowledgements

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