Amine Based Vapor Phase Corrosion Inhibitor Alternatives to Hydrazine for Steam Generation Systems and Power Plants

For:

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Hydrazine is generally used as an oxygen scavenger and corrosion inhibitor for corrosion control in steam generating systems. Although hydrazine is very effective in this application, it is a genotoxic carcinogen. The use of alternative chemicals such as nontoxic corrosion inhibitors, oxygen scavengers or new oxygen scavenger-free water treatment technologies is highly recommended. A new amine based vapor phase corrosion inhibitor has been developed and was investigated as an alternative to hydrazine. Electrochemical and corrosion tests were conducted and results showed that this new inhibitor is very promising to significantly lower corrosion rate in the steam generating boilers and boiling water. Short term corrosion tests (720 hours test duration) in boiling water showed a significant decrease in corrosion rate. Corrosion rates dropped from 5.3 mpy to 1.93 mpy for 50 ppm VCI and 1.32 mpy for 100 ppm VCI addition to the water.

Long term corrosion tests (2,200 hours test duration) in the hot steam generating closed loop system showed that the corrosion rate decreased from 8.2-8.9 mpy for the control sample to 0.72-0.74 mpy when the loop was washed with a 500 ppm VCI solution. The closed loop system was subsequently maintained at ~ 100 ppm inhibitor for the remainder of testing. When inhibitor was added from the beginning of the test, average corrosion rate was measured to be 1.09-1.24 mpy for a test conducted in the presence of 100 ppm S-15 VpCI inhibitor. High resolution XPS analysis showed that the amine based vapor phase corrosion inhibitor promoted and stabilized a very protective Fe_3O_4, magnetite oxide, on internal surfaces of pipes to lower corrosion rate significantly.

This investigation confirmed that the S-15 vapor phase corrosion inhibitor can be an effective replacement for the toxic hydrazine for steel materials exposed to hot steam/hot environments. The major advantage of S-15 VpCI is its very low toxicity that makes it safe and easy to handle in typical application systems. The oral toxicity test measure of LD_{50} for the S-15 VpCI is 2190 ppm, while hydrazine has LD_{50} of ~15-22 ppm, indicating a very high toxicity substance. The S-15 VpCI corrosion inhibitor is very promising and can reduce environmental impact, improve the work environment, reduce deposition that minimizes frequency of chemical cleaning for through-flow boilers, and reduce pipe wall thinning due to flow-accelerated corrosion.

Introduction:

The presence of dissolved oxygen in boiler feedwater and steam generating systems can present serious problems in a steam generating plant by promoting corrosion and thick scale formation in the feedwater system, the boiler, and the steam condensate system. Therefore, it is important to remove oxygen from the feedwater and also from the condensate where in-leakage can occur. The first step in the elimination of oxygen from the boiler feedwater is mechanical deaeration. The second step involves chemical oxygen scavenging to remove the residual oxygen. For many years sodium sulfite and hydrazine were the chemical oxygen scavengers of choice. However, sodium sulfite contributes solids to the boiler water and hydrazine was found to be extremely toxic.

Hydrazine was generally used as an oxygen scavenger and corrosion inhibitor for corrosion control in steam generating systems. Although hydrazine is very effective in this application, it is a genotoxic pollutant. The use of alternative chemicals such as nontoxic corrosion inhibitors, oxygen scavengers or new oxygen scavenger-free water treatment technologies is highly recommended and in most countries required by law. Prohibiting the use of hydrazine requires the availability of nontoxic alternatives for water treatment technology without oxygen scavengers [1-9]. Hydrazine-free water treatment provides the following advantages: reduction in environmental impact and improvement of the work environment; reduction in deposition, which in turn reduces the frequency of chemical cleaning for through-flow boilers; reduction in pipe wall thinning due to flow-accelerated corrosion, and reduction in startup time and water consumption in the drum boilers and heat recovery steam generator boilers.

Corrosion-Control Effects of Hydrazine

Oxygen dissolved in water is the source of the cathodic reaction that eventually causes corrosion to occur. Hydrazine removes the oxygen and also converts ferric oxide to protective magnetite via the following reactions:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O,$$

$$\underset{\text{hydrazine}}{N_2H_4} + \underset{\text{hematite}}{6\,Fe_2O_3} \rightarrow \underset{\text{magnetite}}{4\,Fe_3O_4} + \underset{\text{nitrogen}}{N_2} + \underset{\text{water}}{2H_2O}$$

Therefore corrosion is retarded by formation of a protective magnetite. Hydrazine also decomposes at a temperature of 200°C or more to form ammonia: ($3\,N_2H_4 \rightarrow 4\,NH_3 + N_2$).
The ammonia acts as a pH adjuster or pH neutralizer. Its scavenging reaction proceeds very slowly near room temperature, and the formation of ammonia by decomposition is not very beneficial for corrosion protection of copper alloys[4-7]

Restrictions on the Use of Hydrazine

In recent years, an international framework for the control of chemical substances has been created. In 1992, the United Nations Conference on Environment and Development adopted "Agenda 21" (Chapter 19) [3], a global action plan for sustainable development in the 21st century. In 2002, the World Summit on Sustainable Development adopted the "Johannesburg Plan of Implementation" containing guidelines on the management of chemical substances to minimize major adverse effects on human health and the environment by 2020. The International Conference on Chemicals Management in 2006 adopted the "Strategic Approach to International Chemicals Management" designed to implement the Johannesburg Plan[1]. In 2007, the European Union implemented the Regulation on Registration, Evaluation, Authorization, and Restriction of Chemicals to achieve the World Summit on Sustainable Development goals by 2020.

These factors led to the introduction of alternative oxygen scavengers including amine-based compounds, Diethylhydroxylamine, Helamine **(** polycarboxylates as sodium salt [22-26]), surface-active fatty alkyl polyamines and -mines of different volatility (Cyclohexylamine + aminoethanol + (Z)-N-9-octadecenylpropane-1,3-diamine), and Cyclohexylamine based corrosion inhibitors[8-16, 33]. These amine-based compounds were introduced as an alternative oxygen scavenger to hydrazine, offering the advantages of very low toxicity and the volatility of a neutralizing amine. Like hydrazine, amine-based compounds also promote the formation of a passive magnetite film on low carbon steel surfaces minimizing corrosion in the system [11]. Amine-based water treatment has numerous beneficial properties as an oxygen scavengers in boiler feedwater systems: protects by forming a thin protective magnetite (Fe_3O_4) layer; prevents lime scale or minerals on the surface installations; removes old deposits without causing damage; disperse impurities, inorganic salts and oxides of iron; alkalinizes vapor networks, including the return of condensate and hot water systems; and provides effective heat transfer and energy savings.

The operating parameters of the boiler systems (pressure, temperature) are very important in determining how much inhibitor is required to maintain an acceptable corrosion rate level (less than 1.0 mpy). In low to moderate pressure industrial boiler systems, an initial feedwater inhibitor dosage of 100-500 mg/L (ppm) is recommended [23]. However, during operation an adjusted product feed rate is used until a consistent inhibitor residual of 80-120 mg/L can be established in the condensate.

Steel Pipe Passivation in Boiler and Steam Generating System

The primary objectives of a boiler water treatment program are the prevention of both scale formation and corrosion on internal surfaces in the system. Minimizing corrosion in boiler systems involves removing all traces of oxygen from the boiler feedwater and creating conditions that promote the formation of a passive magnetite film on the internal surfaces. At high temperatures, iron corrodes in water to form magnetite as follows:

$$Fe + H_2O = FeO + H_2$$
$$3FeO + H_2O = Fe_2O_3 \cdot FeO\ (Fe_3O_4) + H_2$$

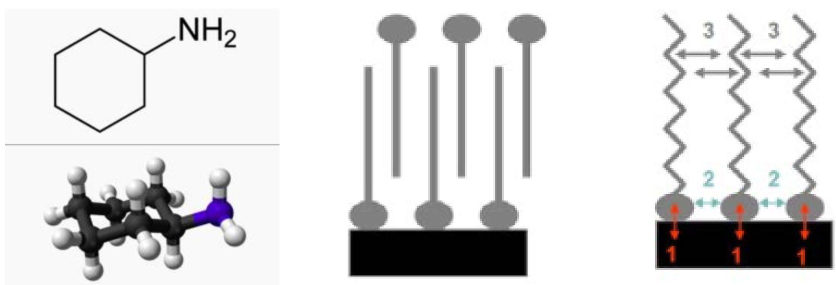
Under normal boiler system conditions magnetite forms a stable tightly bonded surface layer that inhibits further corrosion [30-33]. Therefore, amine-based water treatment is very beneficial to stabilize the magnetite on the internal surfaces.

Sodium sulfite has also been widely used as an oxygen scavenger in boiler systems particularly at lower pressures. It is nontoxic and relatively easy to apply. It can be used in either solid or liquid (sodium bisulfite dissolved in water) form. On a stoichiometric basis 8.0 ppm of sodium sulfite is required to react completely with 1.0 ppm of oxygen. In lower pressure systems it is generally recommended that an excess of 20 - 40 ppm of sodium sulfite be maintained in an operating boiler. Use of sodium sulfite adds considerable solids to the boiler water, which limits its use in systems with high purity boiler feedwater. Sodium sulfite does not promote passivation in boiler feedwater or boiler water systems. The ability of sulfite based products to minimize corrosion stems solely from their capability to remove oxygen from the water. Sodium sulfite is totally non-volatile. It is used exclusively to protect the boiler feedwater system and the boiler system. Sulfite based products cannot be used to protect the steam condensate system. Compared with sulfite, amine-based inhibitors offer many benefits due to its volatility and ability to promote passivation of steel surfaces in the system.

Volatile Corrosion Inhibitors

Volatile Corrosion Inhibitors (VCI) are compounds transported in a closed loop environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH toward less acidic and corrosive values [12-18]. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are generally used. When these inhibitors come in contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds; fast action wanting high volatility while enduring protection requires low volatility and complex compound formation. The common model for surface adsorption and complex compound formation is demonstrated in Figure 1.

In addition to oxygen scavenging and metal passivating capabilities, another key advantage of amine-based inhibitors are their volatility. Not only do they scavenge oxygen and passivate metal in the feedwater and boiler portions of a steam boiler cycle, they also cause evaporation or dispersion by vapor phase (volatilize) with the steam to provide complete system protection [31]. The fact that the amine-based compounds are volatile represents an enormous advantage in condensate system treatment because most of it is transported and absorbed into the condensate system allowing it to: passivate condensate system metallurgy preventing corrosion; scavenge oxygen if it enters the condensate system preventing corrosion; reduce corrosion byproduct transport to the boiler, minimizing the potential for boiler deposition and under deposit corrosion; improve equipment reliability and efficiency; and minimize overall condensate system corrosion reducing the related maintenance costs.



Cyclohexylamine 1. Adsorption, 2. Ionic interaction, 3. Van der waals forces

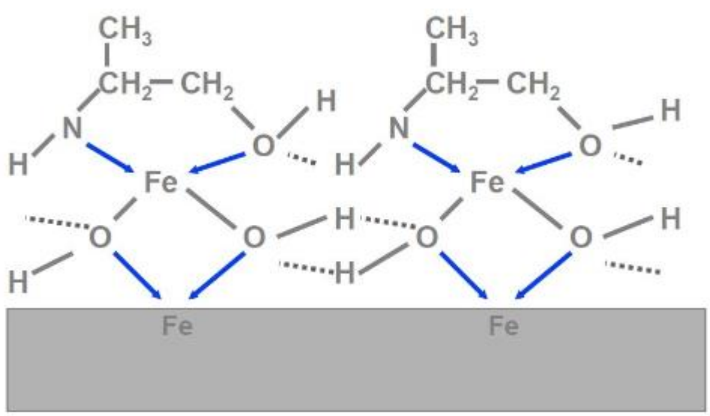


Figure 1: Surface attachment of cyclohexylamine to the oxidized steel pipe surface (complex compound formation)[31-32].

Research Objectives:
Corrosion of the steam/waterside interiors during the various stages of the steam cycle is a major problem for steam generating and power plant operators. The industry standard for corrosion protection in operating systems is the use of hydrazine required to be limited per the European Union implemented regulation on Registration, Evaluation, Authorization, and Restriction of Chemicals to achieve the World Summit on Sustainable Development goals by 2020. Amine-based compounds are considered an alternative to hydrazine. These amines are normally injected into the steam line but may be injected into the boiler water or the condensate system. The purpose of this investigation was to compare the performance of Cortec VpCI S-15 versus the hydrazine capabilities to provide corrosion protection for the boiler steam/water system internal surfaces through the phases of the steam system (water, transition, steam). Prior to investigating VpCI in a closed loop system, some preliminary testing was done on S-15 at high temp (roughly 360F) to determine when it would start to boil; hydrazine boiling point is 237 F. The assumption was that if hydrazine can survive the steam cycle, then S-15 VCI should provide effectiveness and good functionality in those conditions. The auto-ignition temperature for both hydrazine and S-15 is around 550-560 F. However, when the molecules are attached to surface oxides they are more stable and this temperature is not critical.

The research program implemented a closed loop with water/steam circulating through at 90 psi and 245 F. The objectives were to investigate electrochemical behavior of carbon steel pipe material samples (ASME B31.1 pipes):
1) exposed to VpCI S-15 and a control solution;
2) total immersion in boiling water with VpCI S-15 and without inhibitor (control-reference);
3) in steam/water closed loop system with VpCI S-15 and without inhibitor (control-reference);
4) SEM/EDAX and XPS analysis (post-test evaluation) of surface condition for samples with inhibitor.

Experimental Procedure
Corrosion behavior of steel pipe samples in V_pCI S-15 in steam/water loops at elevated temperature was investigated to explore its inhibiting effectiveness as an alternative for hydrazine.
Electrochemical polarization behavior using Gamry was conducted in 50 to 500 ppm inhibitor solutions. These electrochemical tests were conducted using Gamry PC4/750 Potentiostat/Galvanostat/ZRA instrumentation and DC105 corrosion test software. Samples were polished (1.0 μm surface finish), placed in a flat cell and tested in deionized water solutions containing 50 to 500 ppm VCI inhibitor at elevated temperatures. Corrosion behavior of carbon steel pipe material samples in total immersion in boiling water when exposed to VpCI S-15 and without inhibitor (control sample) using similar apparatus recommended in ASTM G123 (Erlenmeyer flask and condenser, hot plate to maintain solution at its boiling point, Figure 3). These tests were conducted in control solution (filtered water, no inhibitor), 50, 100, 200 and 500 ppm VpCI S-15 addition. Test duration was ~700 hours.

Corrosion behavior of carbon steel pipe material samples in steam/water closed loop when exposed to VpCI S-15 and without inhibitor (control). The steam/water loop system included a Chromalox electric boiler and steel pipe loop. Chromalox Packaged Electric Steam and Hot Water Boiler (Figure 2) is a safe and versatile heat sources to produce low or high pressure steam (~100 psi). A closed loop system was assembled that can circulate and maintain a hot steam of 90 psi at 245 ^oF 118 ^oC). Tests were conducted on the control (no inhibitor was used) for a duration of 1,100 hours. Test duration for the 100 ppm VpCI S-15 was 2,200 hours. During these tests, corrosion rate measurements were monitored using electrical resistance (ER) techniques and the Metal Samples MS3500E electrical resistance probe system with a data-logger was used for measuring and storing corrosion data.

Light microscopy, scanning electron microscopy (SEM/EDX analysis) and XPS analysis were performed after corrosion tests to verify extent of corrosion damage on the exposed surfaces after each test, using Buehler image analysis, JEOL JSM-6480LV with Thermo System Seven detector, followed by surface chemistry post-corrosion tests using high resolution XPS analysis using Kratos Ultra system.

Results and Discussions

Electrochemical polarization behavior of the steel pipes in different concentration of corrosion inhibitors at different temperature are shown in Figures 4-7. Results indicated that S-15 VpCI is an anodic corrosion inhibitor. It is capable of lowering corrosion rate and expanding the passivation range for steel pipe in working condition of hot steam/water system. Corrosion rate based on the cyclic polarization test results as follows: for the control 17.2 $\mu A/cm^2$ (7.91 mpy), in presence of 100ppm S-15 VpCI 4.73 $\mu A/cm^2$ (2.18 mpy) and when a 200 ppm S-15 VpCI was added to solution, corrosion rate dropped to 2.86 $\mu A/cm^2$ (1.24 mpy). In general, the boiler industries assumes ~1.0 mpy corrosion rate to be an acceptable range for the open circulating system.

Corrosion behavior of the steel pipe samples in boiling water are shown in Figure 8-15, corrosion rates were monitored for 700 hours of continuous immersion at boiling temperature. Corrosion rate was 5.3 mpy (determined from weight loss measurement) for the steam environment with no inhibitor. When 50 ppm inhibitor S-15 VpCI was added corrosion rate decreased to 1.94 mpy and for 100 ppm S-15 VpCI addition, corrosion rate dropped to 1.36 mpy. Addition of 200 ppm S-15 VpCI decreased the corrosion rate to 0.97 mpy, while addition of 500 ppm resulted in a very low corrosion rate of 0.37 mpy. The corrosion rates for the solutions with different amounts of S-15 VpCI inhibitor had become steady at ~120 hours (corrosion rate showed a logarithmic rate) while the non-protected steel samples showed an increasing trend for the corrosion rate. Figures 9-15 show the corrosion test results. From observation, the non-protect steel samples (control-reference) showed heavy corrosion attack with Fe_2O_3, hematite formation (brown color solution, indication of heavy rust formation). To the contrary, the presence of S-15 VpCI inhibitor in low dosages (50-100 ppm addition) resulted in an oxide formation of Fe_3O_4 (magnetite) and no significant change in solution color was observed. At higher dosages (200-500 ppm), no color change was observed on the steel samples or their solutions which correlates with the (measured) low corrosion rates.

Electrochemical tests on carbon steel pipe material samples in steam/water loop with VpCI S-15 and without inhibitor (control-reference) were conducted using the Chromalox electric boiler steam/water in a closed loop system that could circulate and maintain hot steam at 90 psi, 245 ^oF (118 ^oC). The test setup and ER probes used for corrosion rate minoring are shown in Figures 16-17. The control-reference test (without inhibitor addition) was conducted for 1,100 hours and corrosion rate was monitored using electrical resistance (ER) techniques and a data logger from Metal Samples (MS3500E). Figure 18 shows the corrosion rate over time for the reference sample without using any water treatment or inhibitor. The average corrosion rate was measured to be 8.2-8.9 mpy.

After 1,100 hours, 500 ppm VpCI S-15 inhibitor was injected into closed loop system, Figure 18. This addition resulted in a significant drop in the corrosion rate to 0.72 mpy. This indicates that VpCI S-15 inhibitor had successfully retarded the corrosion reaction and managed to stabilize formation of a protective Fe_3O_4 (magnetite) on the internal surfaces. The corrosion test in steam/water closed loop was continued for 1900 hours in total (800 hours beyond introduction of inhibitor to closed loop system) and the dosage of inhibitor was maintained at 100 ppm. ER probe showed a steady corrosion rate of 1.30 mpy. This is a very impressive result, indicating that a corroding closed loop steam/water system can be successfully recovered by introduction of inhibitor treatment to lower its corrosion rate to an acceptable level. Figure 19 shows the corrosion rate over time for the corrosion test in steam/water closed loop with 100 ppm S-15 VpCI inhibitor addition for 2,200 hours. The average corrosion rate was measured to be 1.09-1.24 mpy. During the boiler drainage (blowout), no sign of any rust formation in the discharged water was observed.

Figures 18-21 show the comparison of the electrical resistance (ER) probes that were used to monitor corrosion rate during these investigations. Figure 20 shows the comparison of corrosion rate measurements for the inhibitor treated loop and control reference after 2,200 hours corrosion in hot steam/water closed loop. The control probe showed heavy rust formation on its surface (Figure 21), while the 100 ppm S-15 VpCI ER probe showed a thin layer of black magnetite and relatively clean surfaces. Figures 22-24 show the section of the closed loop steel pipe after corrosion tests. Comparison of these internal surfaces show that the control pipes internal surfaces are covered by thick Fe_2O_3, hematite (rust formation due to their high corrosion rate) while the test conducted with corrosion inhibitor S-15 VpCI is mainly covered by a thin Fe_3O_4, magnetite oxide (Figure 23). SEM/EDX analyses on these samples are shown in Figures 25-34. Figures 25-29 show the surface morphology of the ER probes after corrosion tests. The control-reference sample showed a very thick oxygen-rich oxide while the inhibitor treated samples showed relatively clean iron rich surfaces (Figures 29-34).

XPS analyses were conducted on the internal surfaces of both control reference sample and inhibitor treated steel pipe. Results are shown in Figure 35. High Resolution XPS analysis was also conducted on both control-reference and inhibitor treated steel pipes, Figure 36. The nature of surface oxide was compared after 2.0 nm of the top surface deposits were etched to remove any ambient changes or accidental surface contamination. XPS data showed that the oxide on internal surface of the reference sample (no inhibitor) pipe is hematite (Fe_2O_3), Fe 2p, with binding energy 710.4 eV, while the oxide on the inhibitor treated pipes were magnetite oxide Fe_3O_4, Fe 2p with a binding energy of 708.2 eV (Figure 36). These observations reaffirmed that S-15 VpCI presence in water promotes formation of a protective thin layer of black magnetite, adheres very well to steel pipe surfaces due to its magnetic properties and provides very suitable corrosion performance.

Conclusions

Corrosion behavior of carbon steel pipe material samples in steam/water loop with and without VpCI S-15 corrosion inhibitor was investigated. Electrochemical polarization behavior showed the S-15 VpCI is an anodic corrosion inhibitor and when present in the environment expands the region of stability of a magnetite Fe_3O_4 passive film. The passive range and film breakdown potential increased and shifted to more anodic voltage, indicating less susceptibility to localized corrosion. Corrosion behavior of the steel pipe samples in boiling water showed corrosion rates for the reference sample to be ~5.3 mpy, while when 50 ppm inhibitor S-15 VpCI was added it decreased to 1.94 mpy and for 100 ppm addition, corrosion rate dropped to 1.36 mpy. Addition of 200 ppm reduced the corrosion rate to 0.97 mpy, while addition of 500 ppm resulted in a very low corrosion rate of 0.37 mpy.

Corrosion behavior of carbon steel pipe material samples in steam/water loop with VpCI S-15 and without inhibitor in a closed loop system of 90 psi at 245 ^oF showed a corrosion rate of 8.2-8.9 mpy. While the corrosion rate in steam/water closed loop with 100 ppm S-15 VpCI inhibitor addition decreased to 1.09-1.24 mpy. In a corroding system (reference sample condition) when 500 ppm VpCI S-15 inhibitor was injected into closed loop system after 1,100 hours, the corrosion rate dropped to 0.72 mpy. This indicates that VpCI S-15 inhibitor successfully retarded corrosion reactions and managed to form stable protective oxide of Fe_3O_4 (magnetite) on the pipe interior surfaces. This is a very impressive result; a corroding closed loop steam/water system can be recovered with the inhibitor treatment and its corrosion rate lowered to an acceptable level.

High resolution XPS analysis confirmed that the dominant oxide on the internal surfaces of the control (no inhibitor) pipe was hematite, Fe_2O_3, while the oxide on the inhibitor treated pipes was magnetite oxide Fe_3O_4. These observations reaffirmed that S-15 VpCI presence in water promotes formation of a protective thin layer of black magnetite that adheres well to the steel pipe surface due to its magnetic properties and provides very satisfactory corrosion performance.

In summary, this investigation confirmed that the S-15 vapor phase corrosion inhibitor can be an effective replacement for the toxic hydrazine for steel materials exposed to hot steam/hot environments. The major advantage of S-15 VpCI is its very low toxicity, making it safe and easy to handle in typical application systems. While the oral toxicity test measure of the LD50 "Lethal Dose" S-15 VpCI is 2190 ppm for rats, hydrazine has LD_{50} of only ~15-22 ppm, indicating a very high toxicity [11].

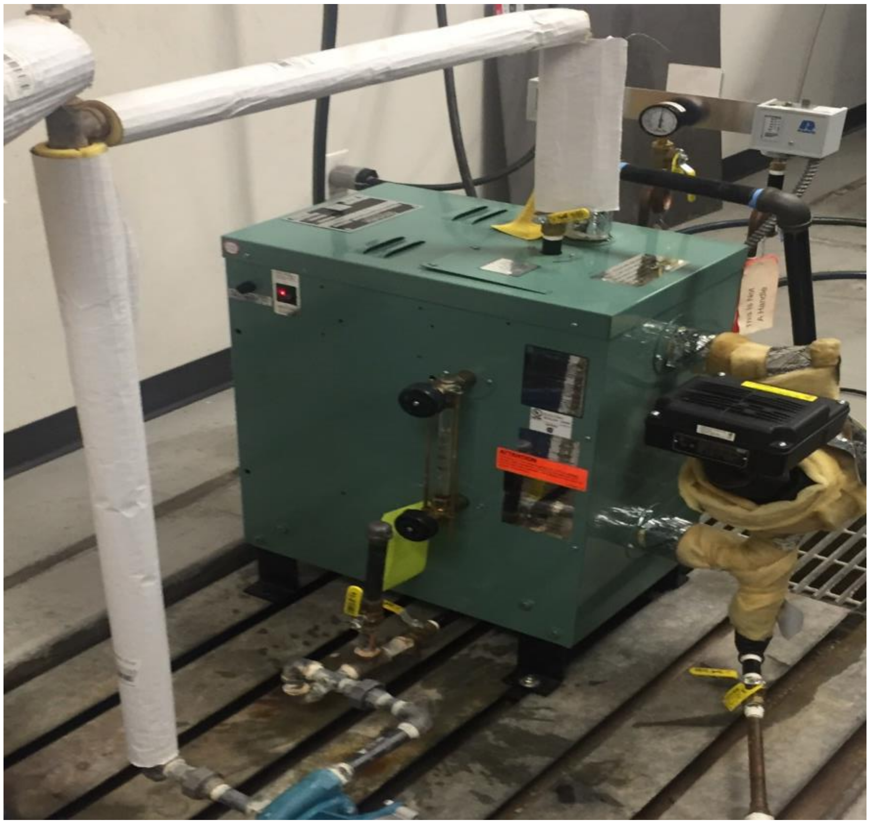


Figure 2: Chromalox Packaged Electric Steam and Hot Water Boiler with its closed loop piping system used for the corrosion tests in the high pressure/hot steam condition.

Figure 3: Corrosion test setup in boiling water solution, similar to the apparatus recommended in ASTM G123.

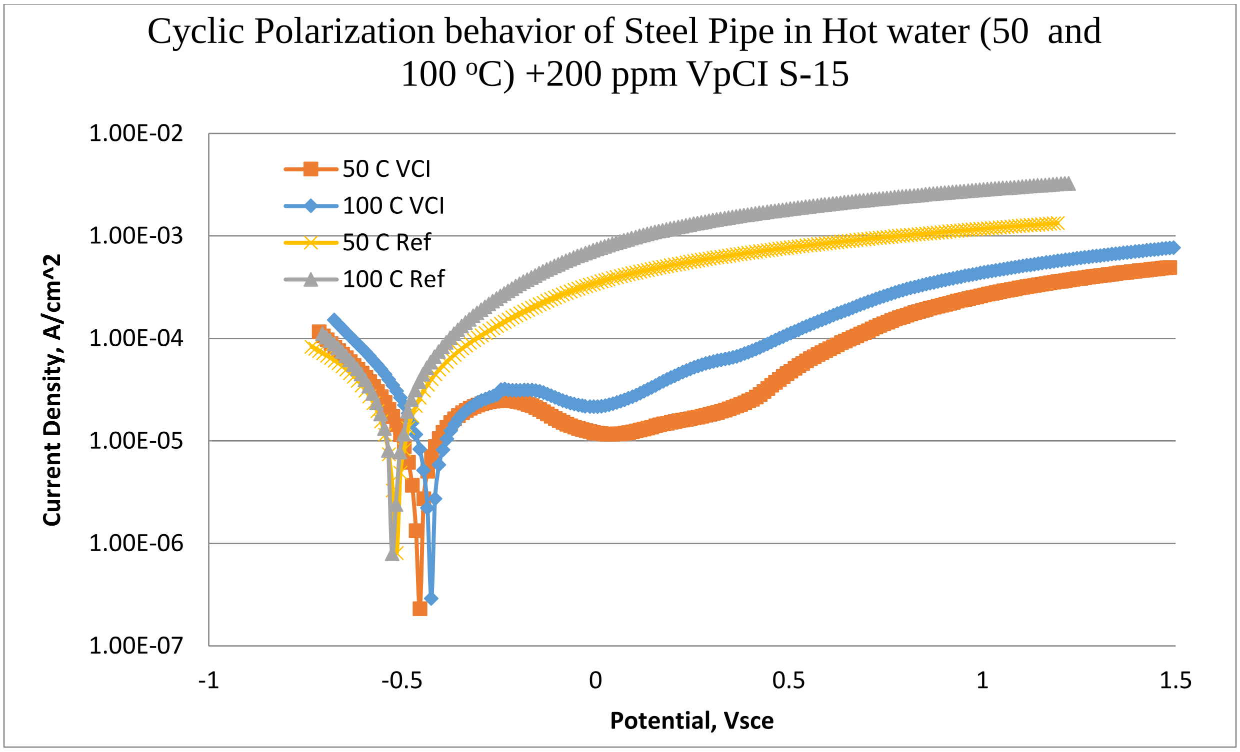


Figure 4: Comparison of cyclic polarization behavior of steel pipe in hot water solution in 50 and 100 C when exposed to control solution and 200 ppm VCI S-15.

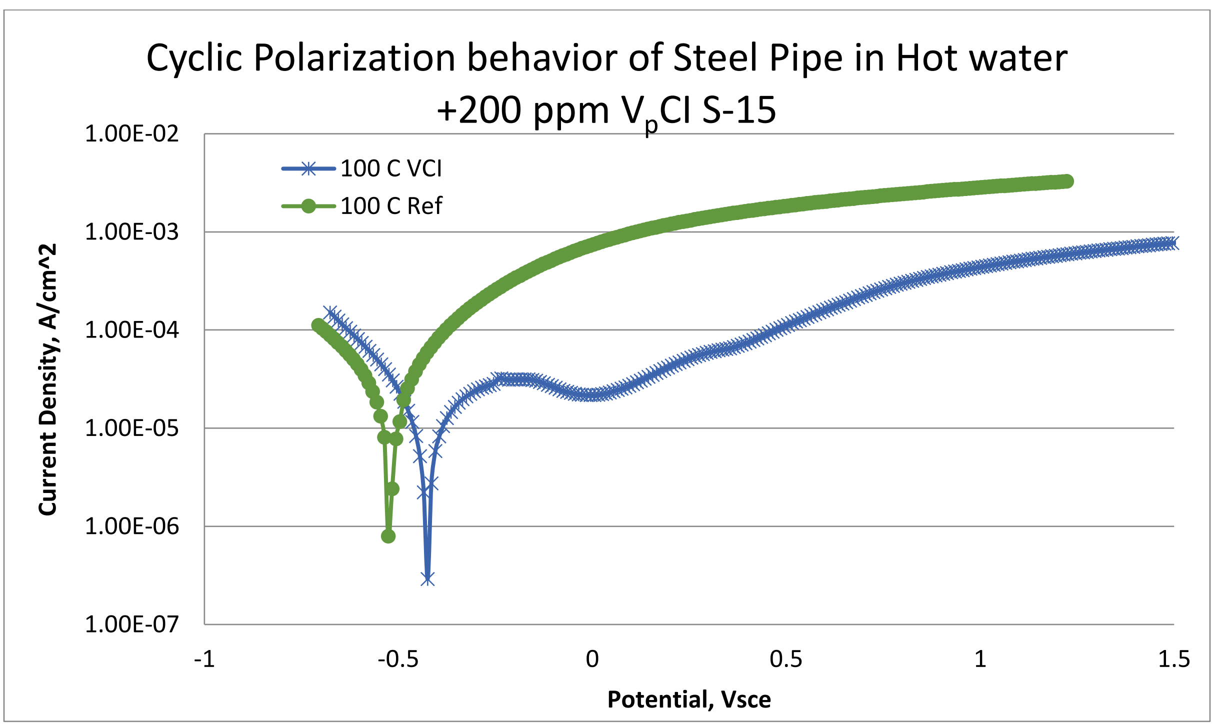


Figure 5: Comparison of cyclic polarization behavior of steel pipe in hot water solution in 100 C when exposed to control solution and 200 ppm VCI S-15.

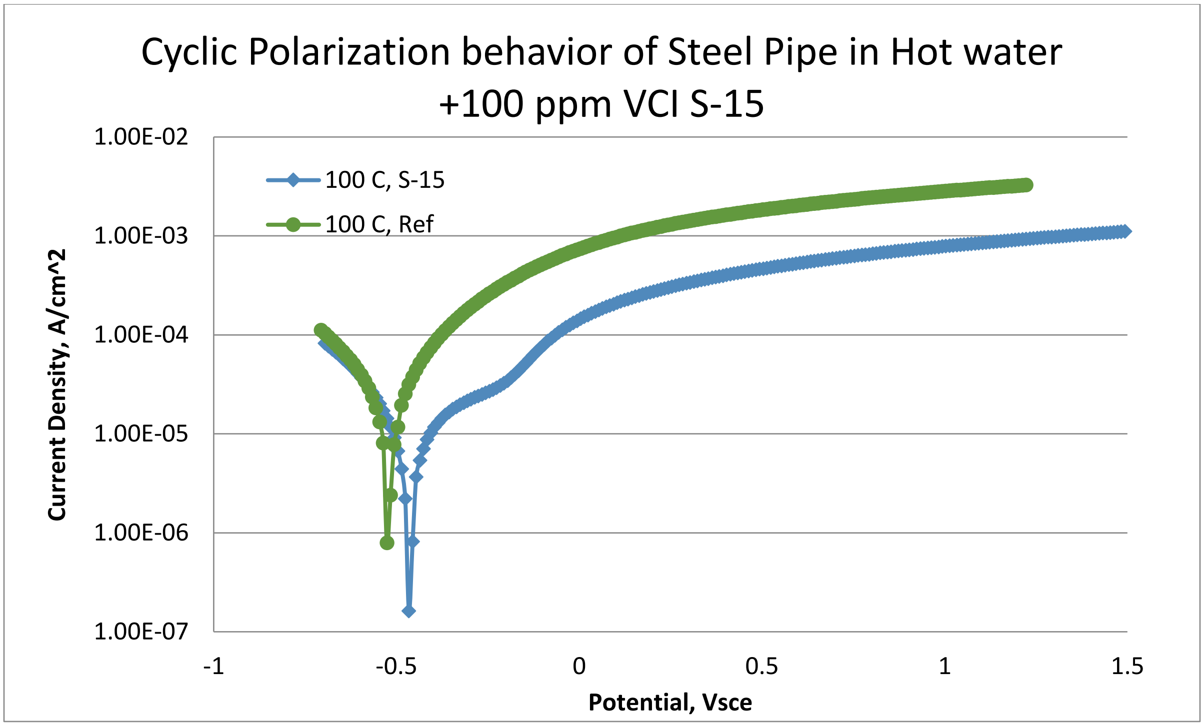


Figure 6: Comparison of cyclic polarization behavior of steel pipe in hot water solution in 100 C when exposed to control solution and 100 ppm VCI S-15.

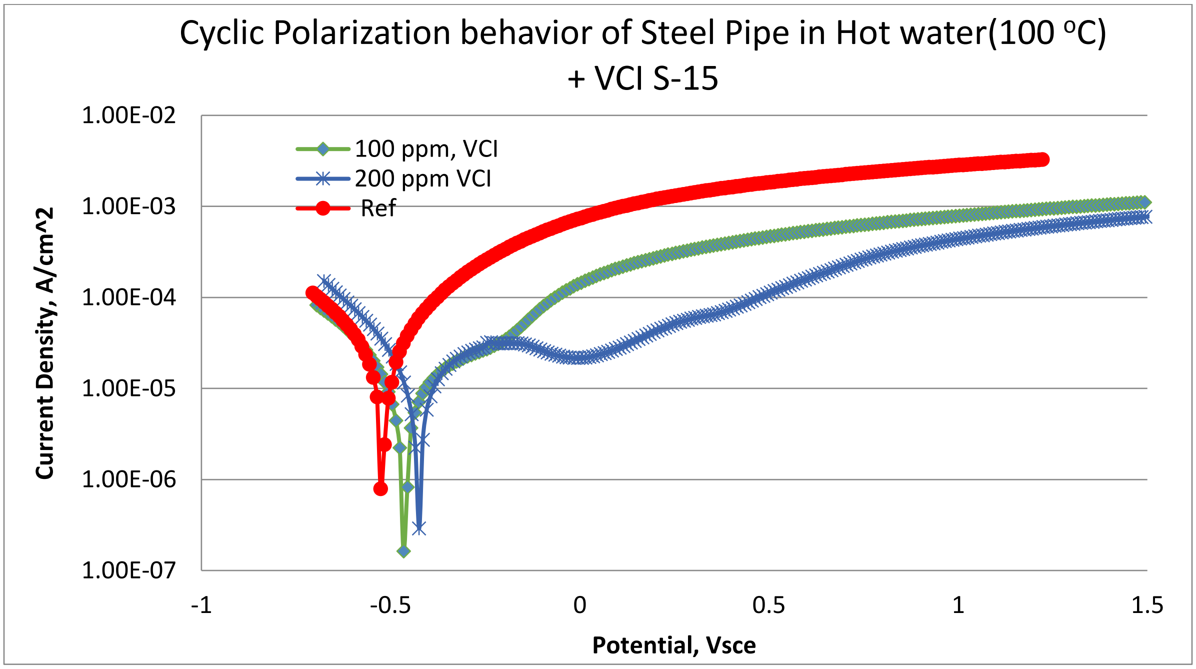


Figure 7: Comparison of cyclic polarization behavior of steel pipe in hot water solution in 100 C when exposed to control solution, 100 and 200 ppm VCI S-15.

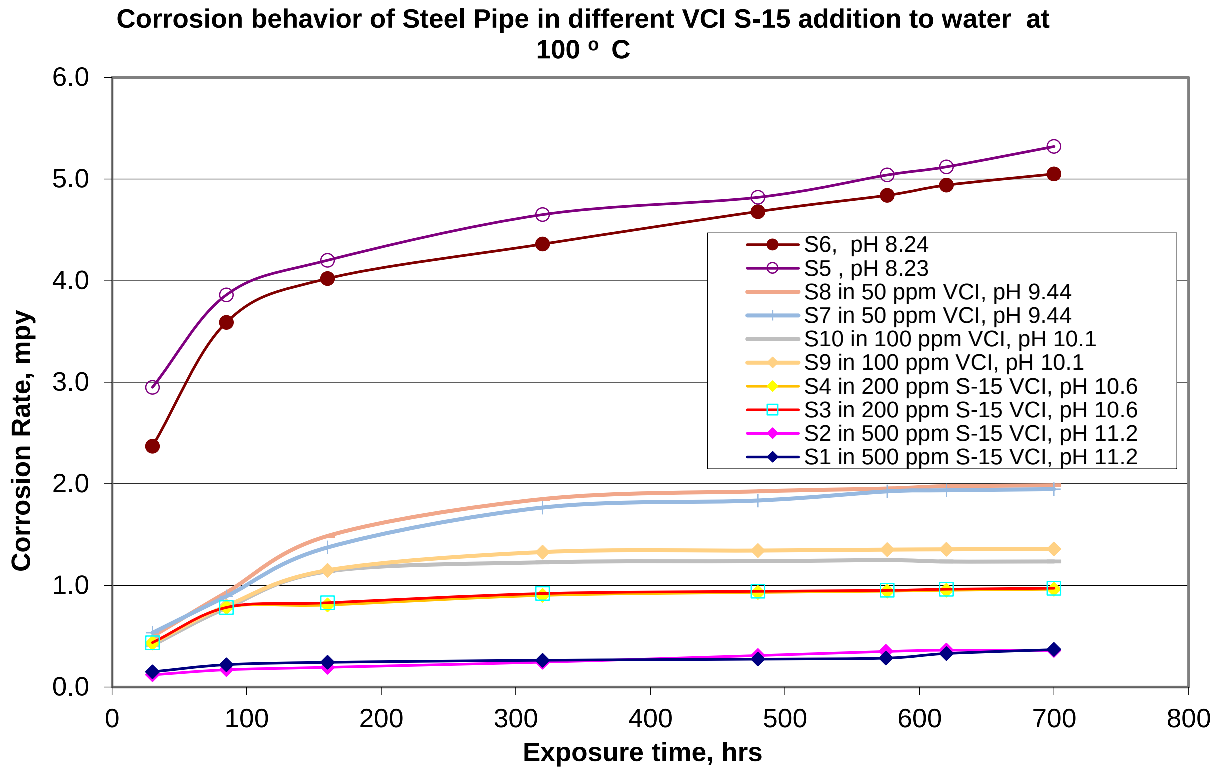
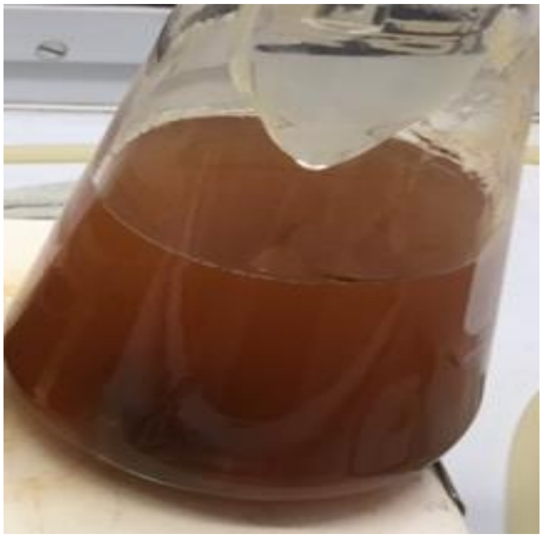
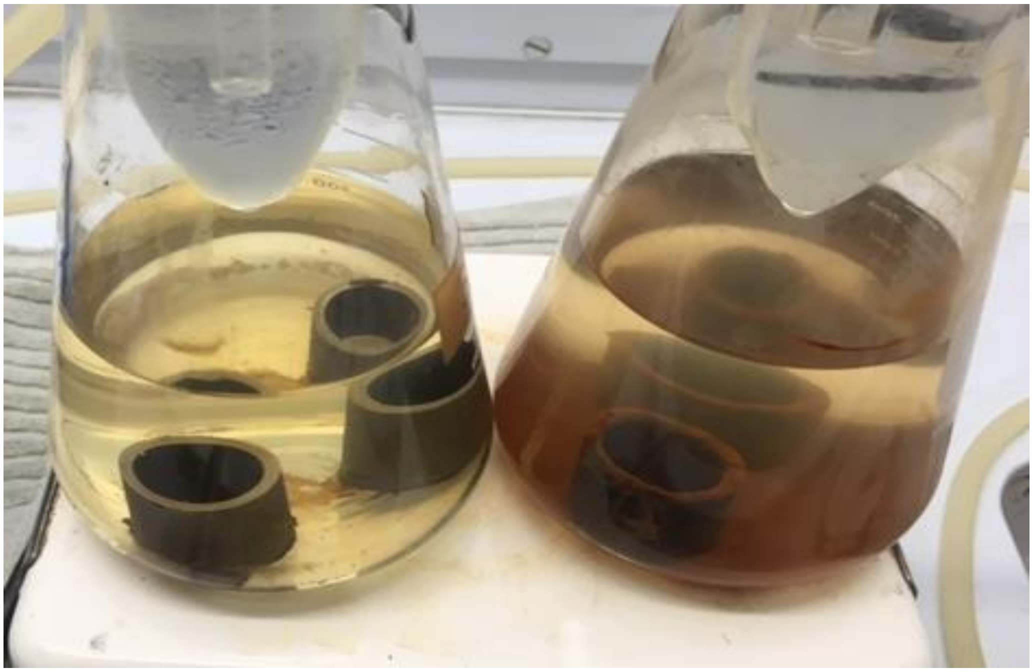


Figure 8: Corrosion behavior of steel pipe in hot water solution in 100 C when exposed to control solution, 50, 100, 200 and 500 ppm VCI S-15.



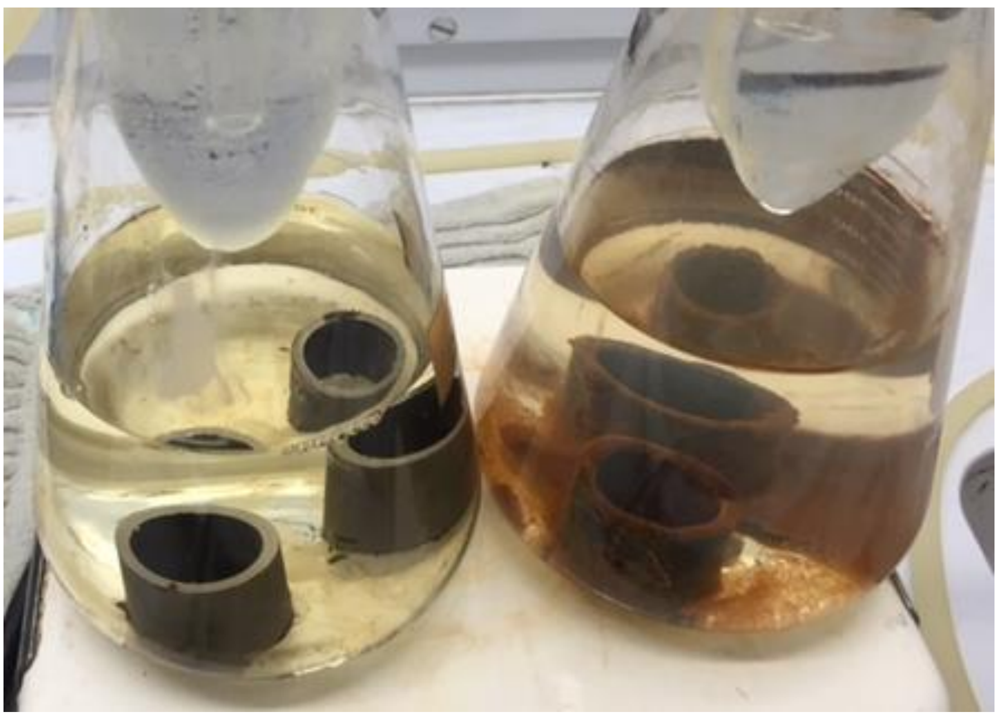
50 ppm S-15 VCI water

Figure 9: Corrosion behavior of the steel pipe samples in boiling water; rates were monitored for 700 hours of continuous immersion at boiling temperature. Corrosion rate was 5.3 mpy for the steam environment with no inhibitor. When 50 ppm inhibitor S-15 VpCI was added corrosion rate decreased to 1.94 mpy.



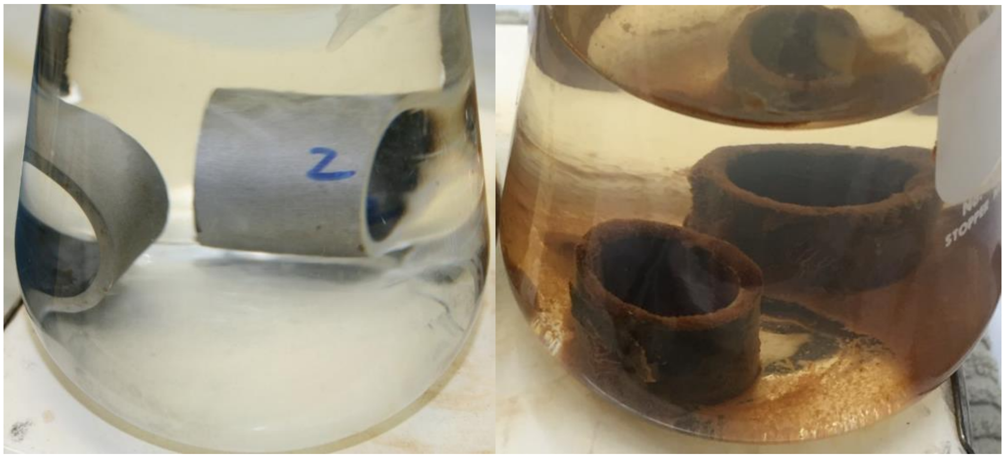
100 ppm S-15 VCI control water

Figure 10: Corrosion behavior of the steel pipe samples in boiling water. Corrosion rate decreased to 1.36 mpy with 100 ppm S-15 V_pCI addition.



200 ppm S-15 VpCI water

Figure 11: Corrosion behavior of the steel pipe samples in boiling water. Addition of 200 ppm S-15 VpCI decreased the corrosion rate to 0.97 mpy.



500 ppm S-15 VpCI water

Figure 12: Comparison of behavior of steel pipe in hot water solution with addition of 500 ppm resulted in a very low corrosion rate of 0.37 mpy.

500 ppm S-15 in water (215 F) water (215 F), 720 hrs.

Figure 13: Comparison of corrosion behavior of steel pipe in hot water solution: 500 ppm VCI S-15 and after 720 hours continuous immersion in control solution (no inhibitor).

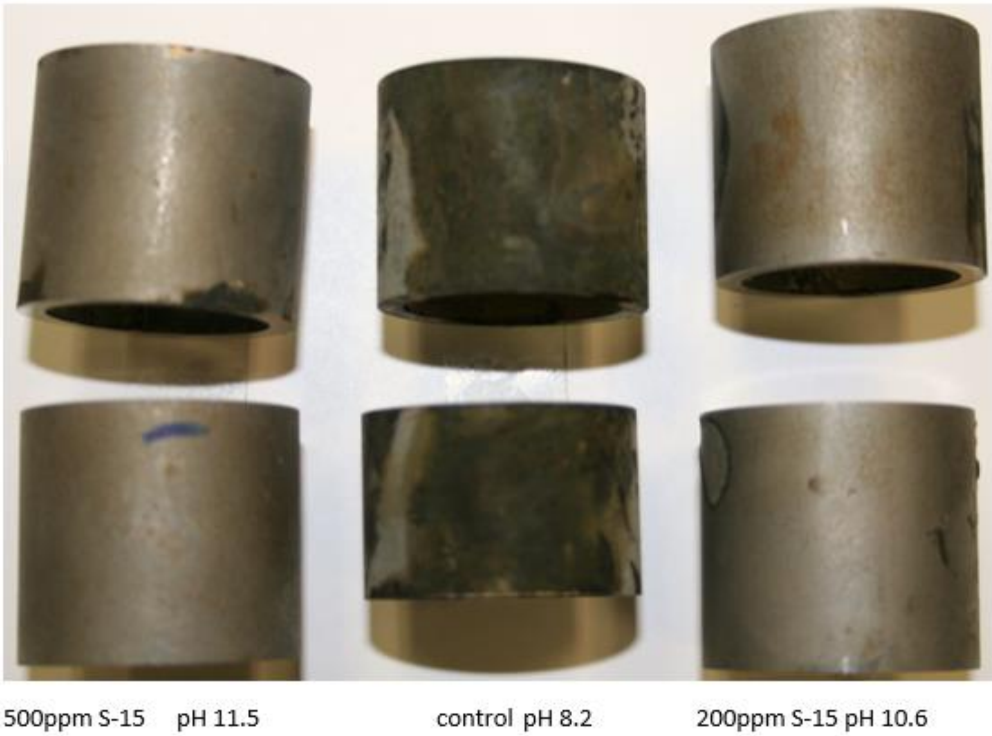


Figure 14: Comparison of behavior of steel pipe in hot water solution in 100 C when exposed to control solution, 200 and 500 ppm VCI S-15, after 720 hours continuous immersion in solution.

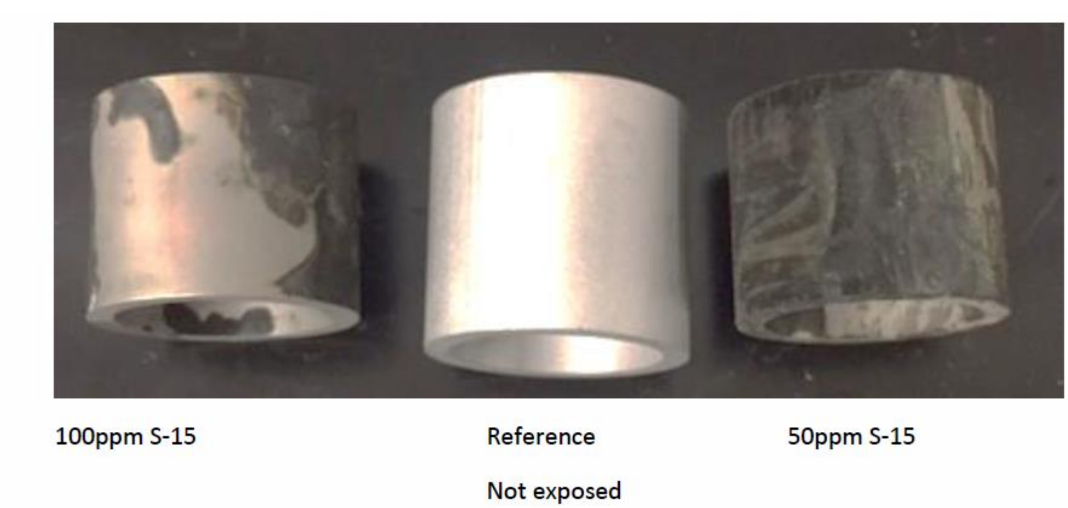
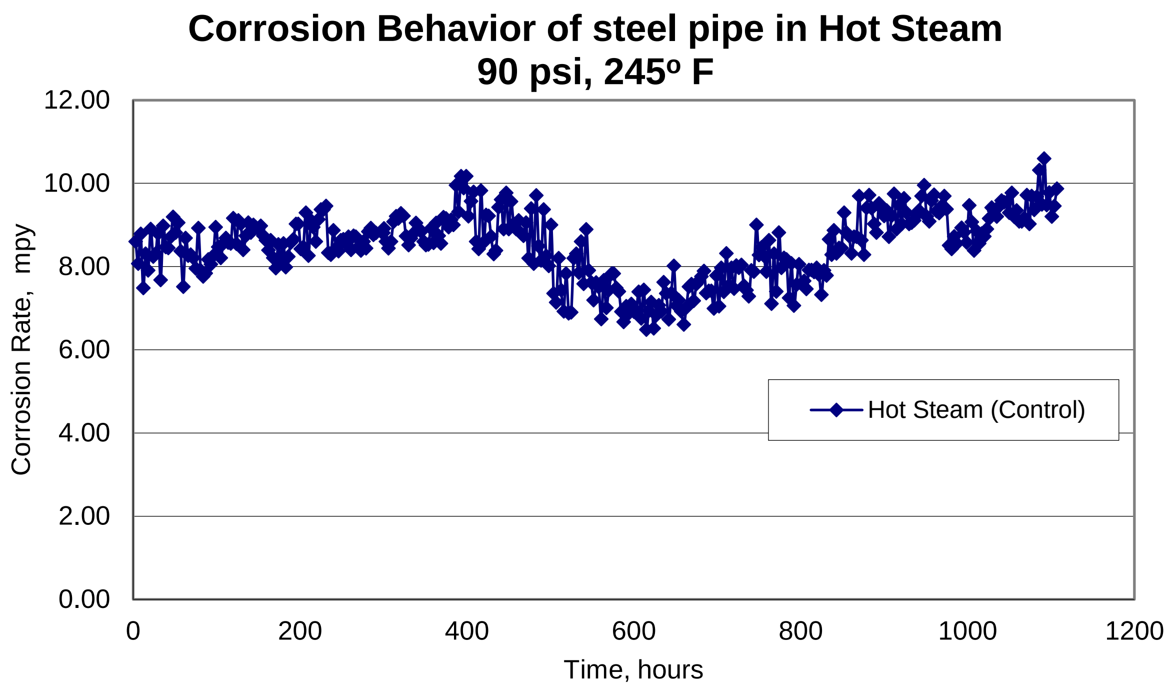


Figure 15: Comparison of behavior of steel pipe in hot water solution in 100 C when exposed to control solution, 50 and 100 ppm VCI S-15, after 720 hours continuous immersion in solution.

Figure 16: The Chromalox Packaged Electric Steam and hot water boiler with its closed loop piping system used for the corrosion tests in the high pressure/hot steam condition. Electrical resistance (ER) probes were used to monitor corrosion rate during testing.

Corrosion Behavior of steel pipe in Hot Steam 90 psi, 245° F

Figure 17: Electrical resistance (ER) probes of the control sample surface condition after 1,100 hours corrosion test in hot steam/water closed loop.



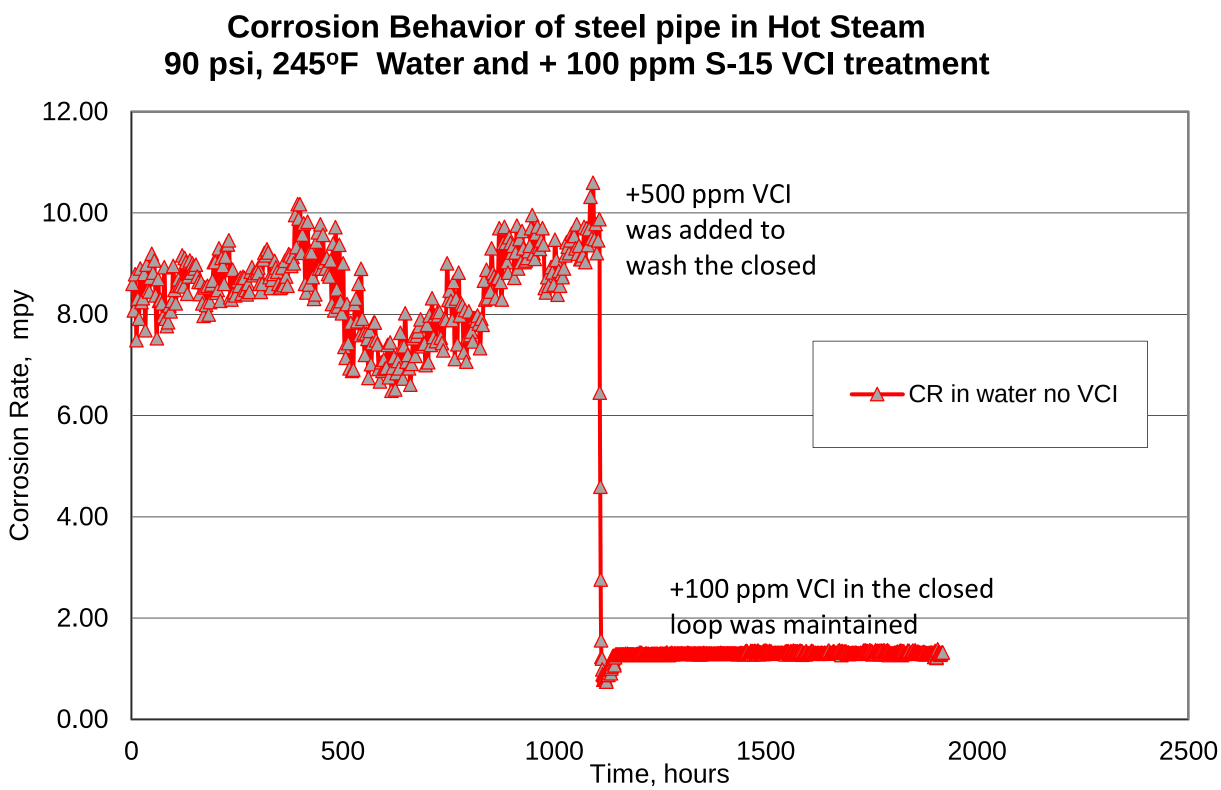


Figure 18: Corrosion rate measurement of the control sample surface condition after 1,100 hours corrosion test in hot steam/water closed loop, and changes that occurred after inhibitor was added to loop.

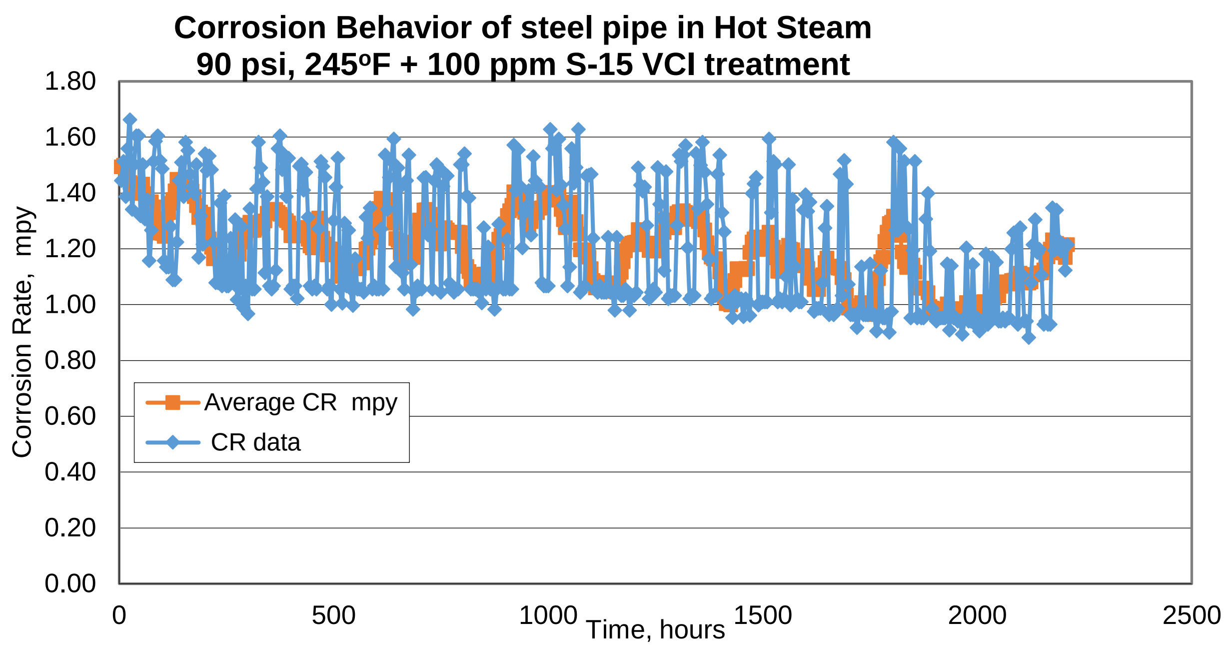


Figure 19: Corrosion rate measurement of the inhibitor treated loop after 2,200 hours corrosion test in hot steam/water closed loop.

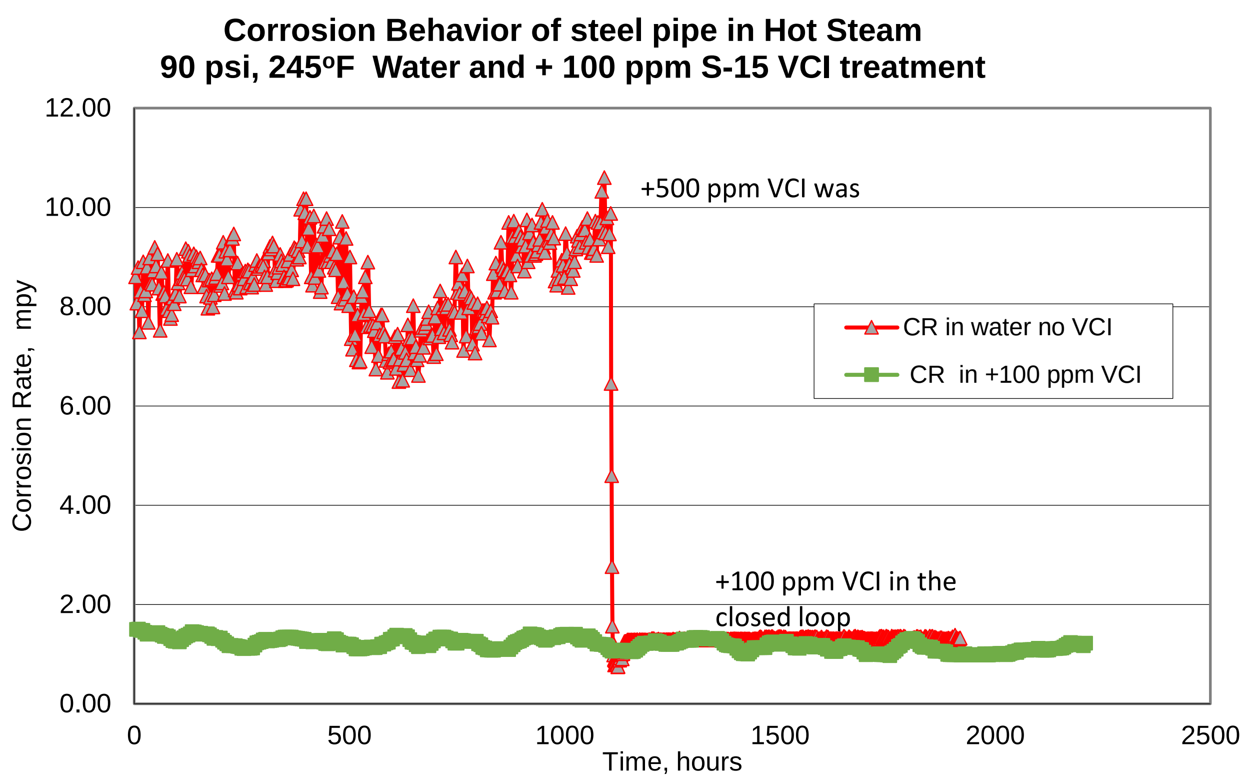
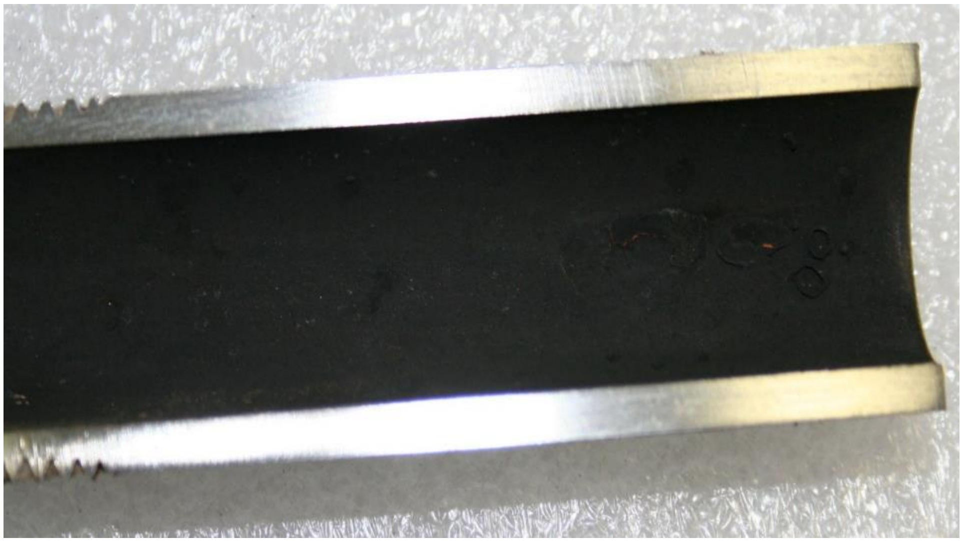


Figure 20: Comparison of corrosion rate measurements of the inhibitor treated loop and control test after 2,200 hours corrosion test in hot steam/water closed loop.

Figure 21: Comparison of corrosion ER probe surface condition of the inhibitor treated loop and control test after 2,200 hours corrosion test in hot steam/water closed loop.



100 ppm VCI

Control

Figure 22: Comparison of steel pipe inner surface conditions of the inhibitor treated loop and control test after 2,200 hours corrosion test in hot steam/water closed loop.

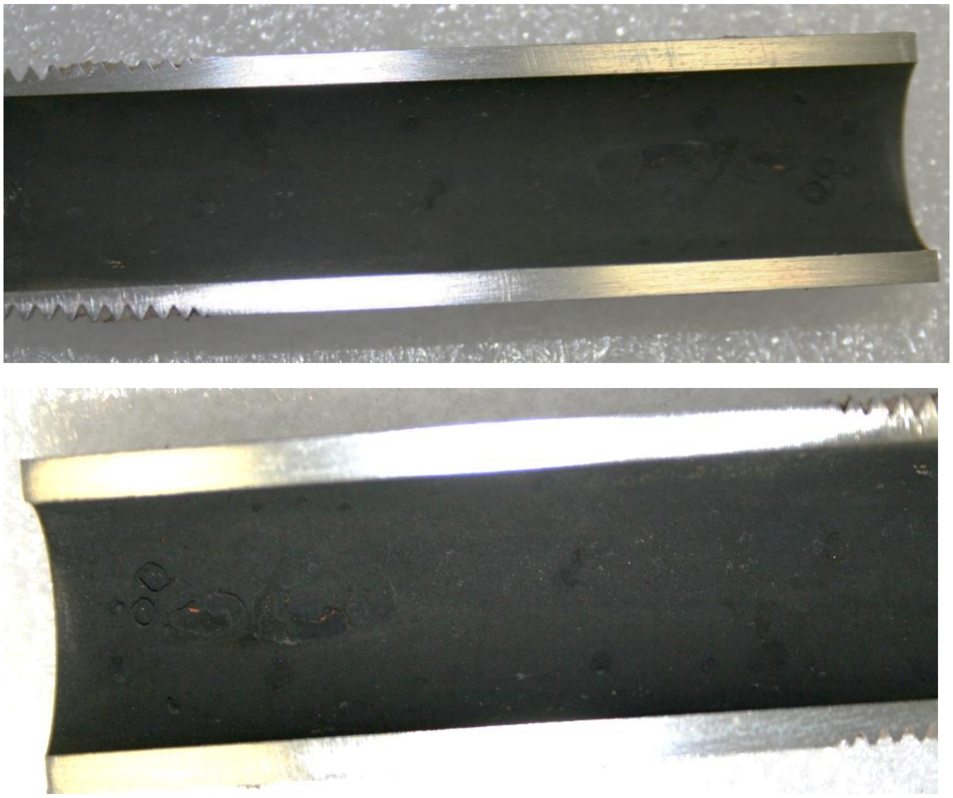


Figure 23: the steel pipe inner surface conditions of the inhibitor treated loop after 2,200 hours corrosion test in hot steam/water closed loop.

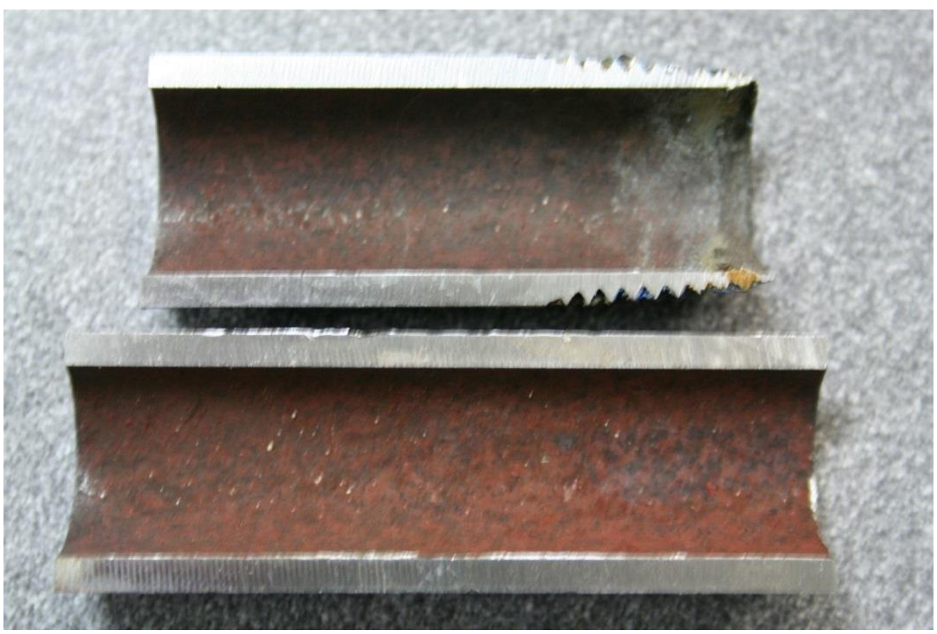


Figure 24: the steel pipe inner surface conditions of the control test after 2,100 hours corrosion test in hot steam/water closed loop.

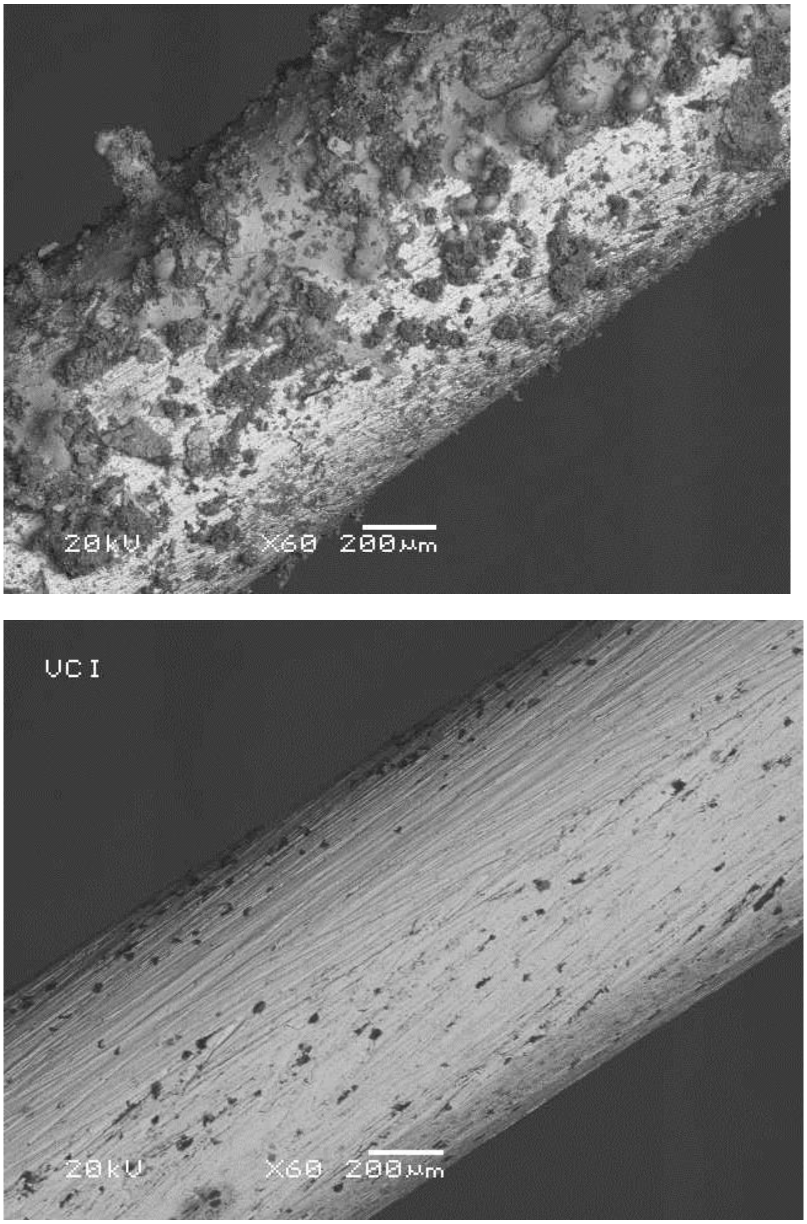


Figure 25: SEM micrographs on ER probe shows heavy corrosion on control (reference) compared with VCI treated.

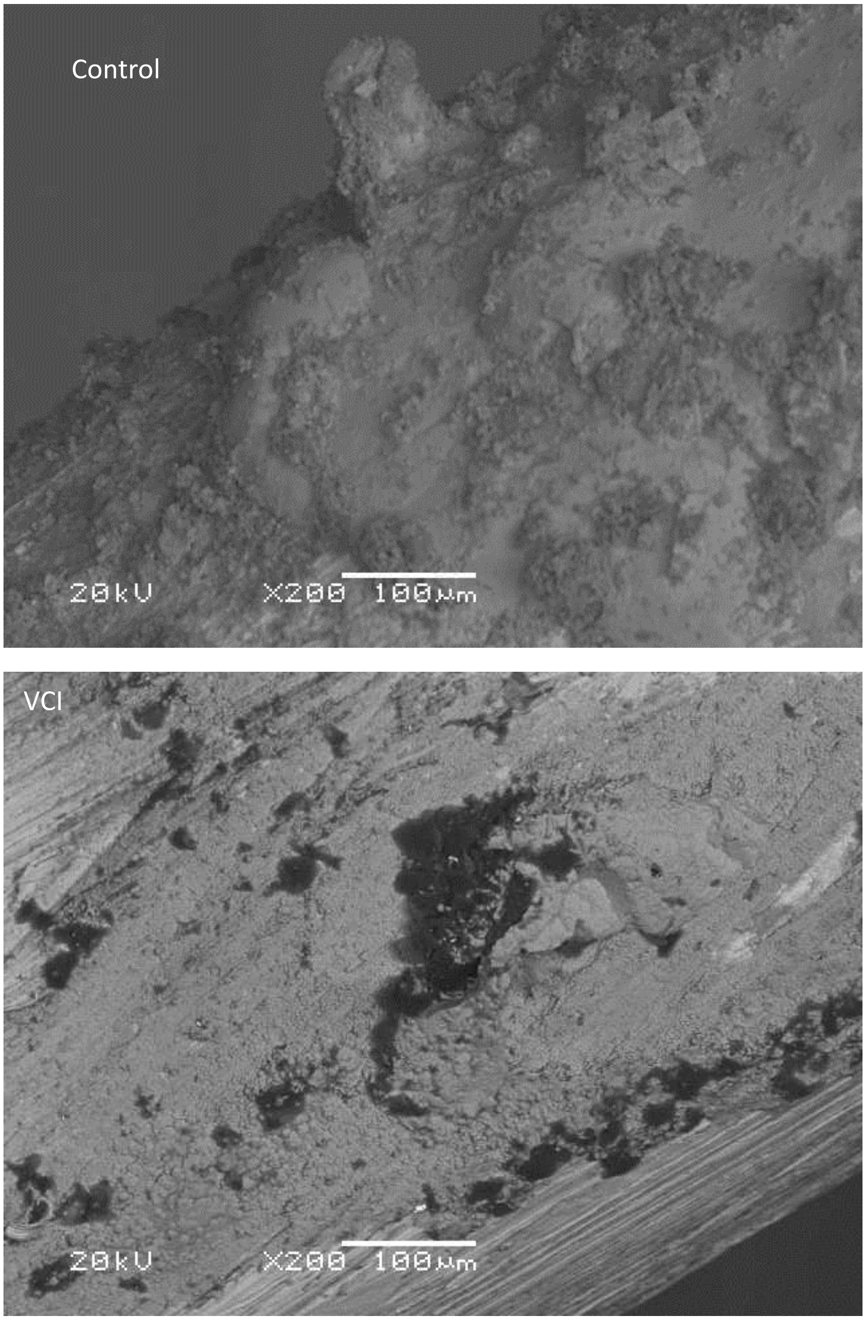


Figure 26: SEM micrographs on ER probe shows heavy corrosion on control (reference) compared with VCI treated.

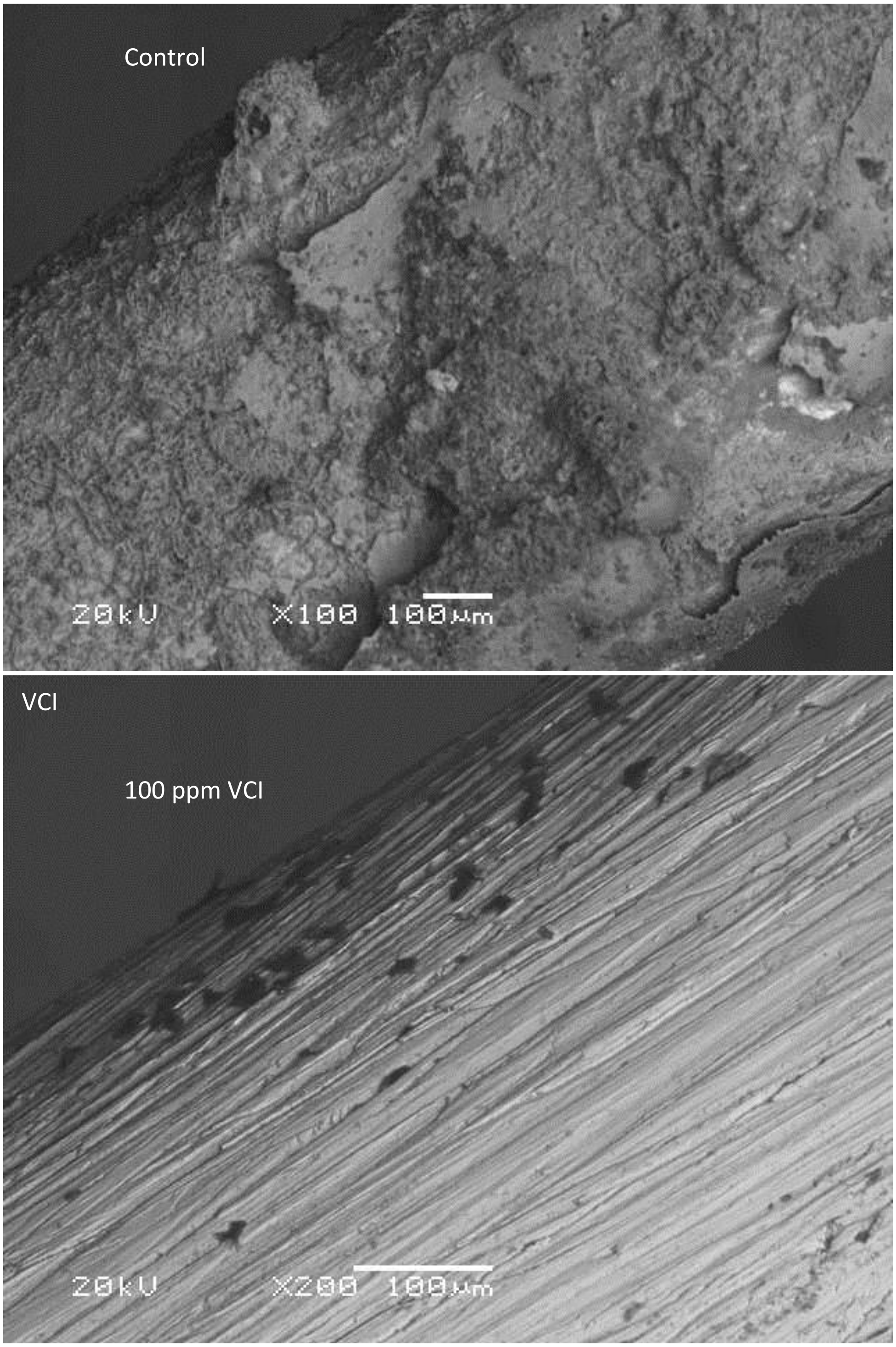


Figure 27: SEM micrographs on ER probe shows heavy corrosion on control (reference) compared with VCI treated.

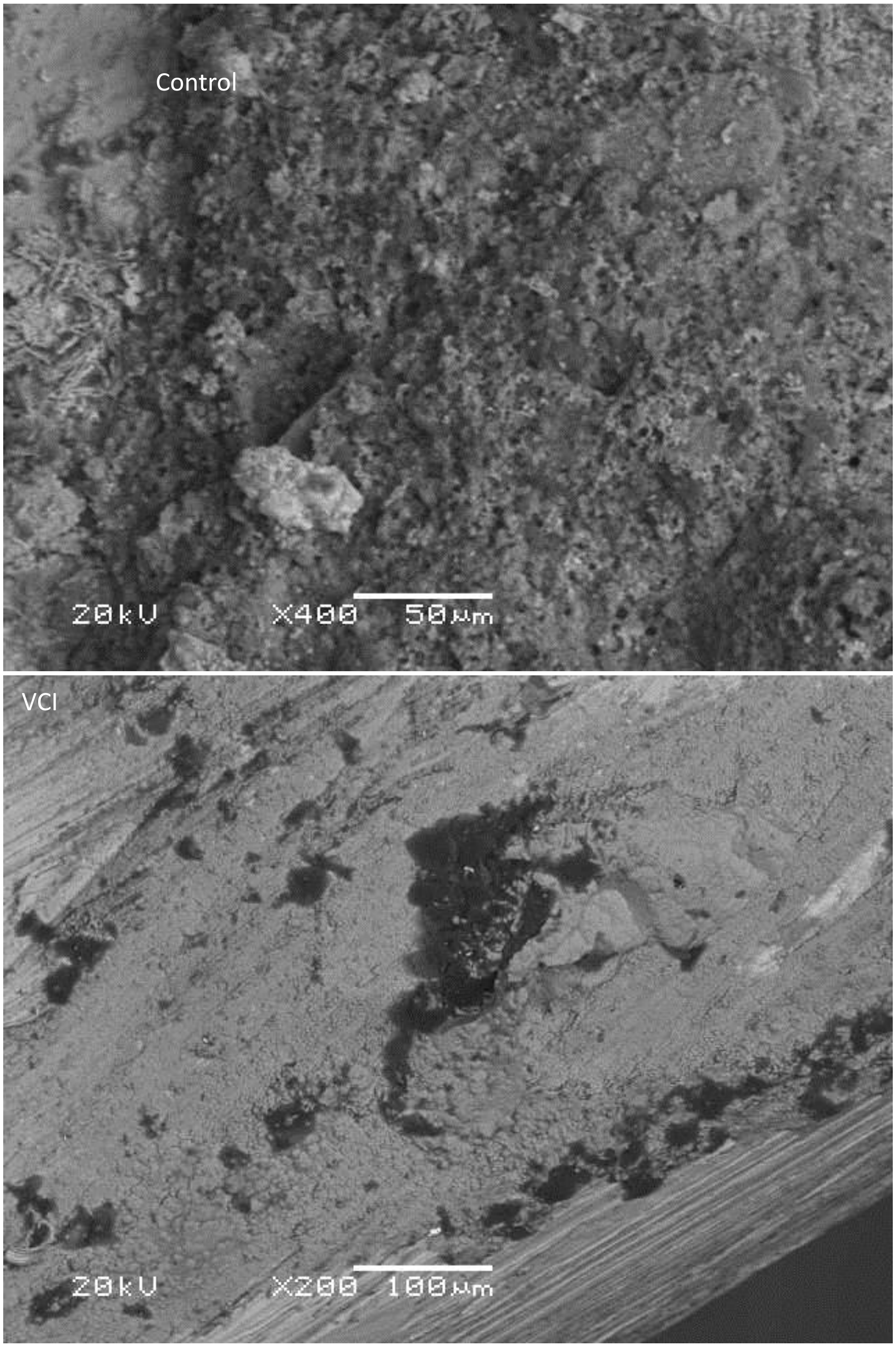
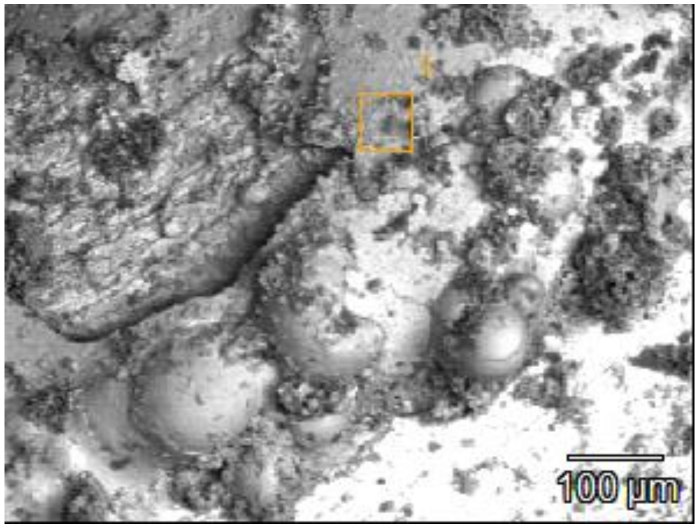
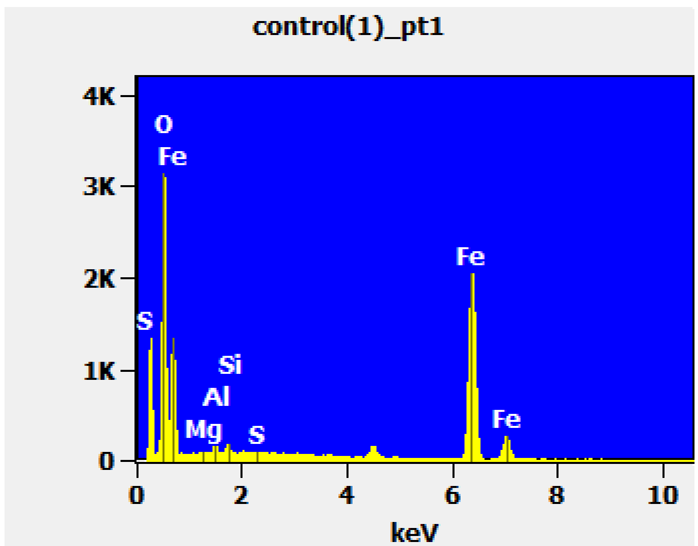


Figure 28: SEM micrographs on ER probe shows heavy corrosion on control (reference) compared with VCI treated.

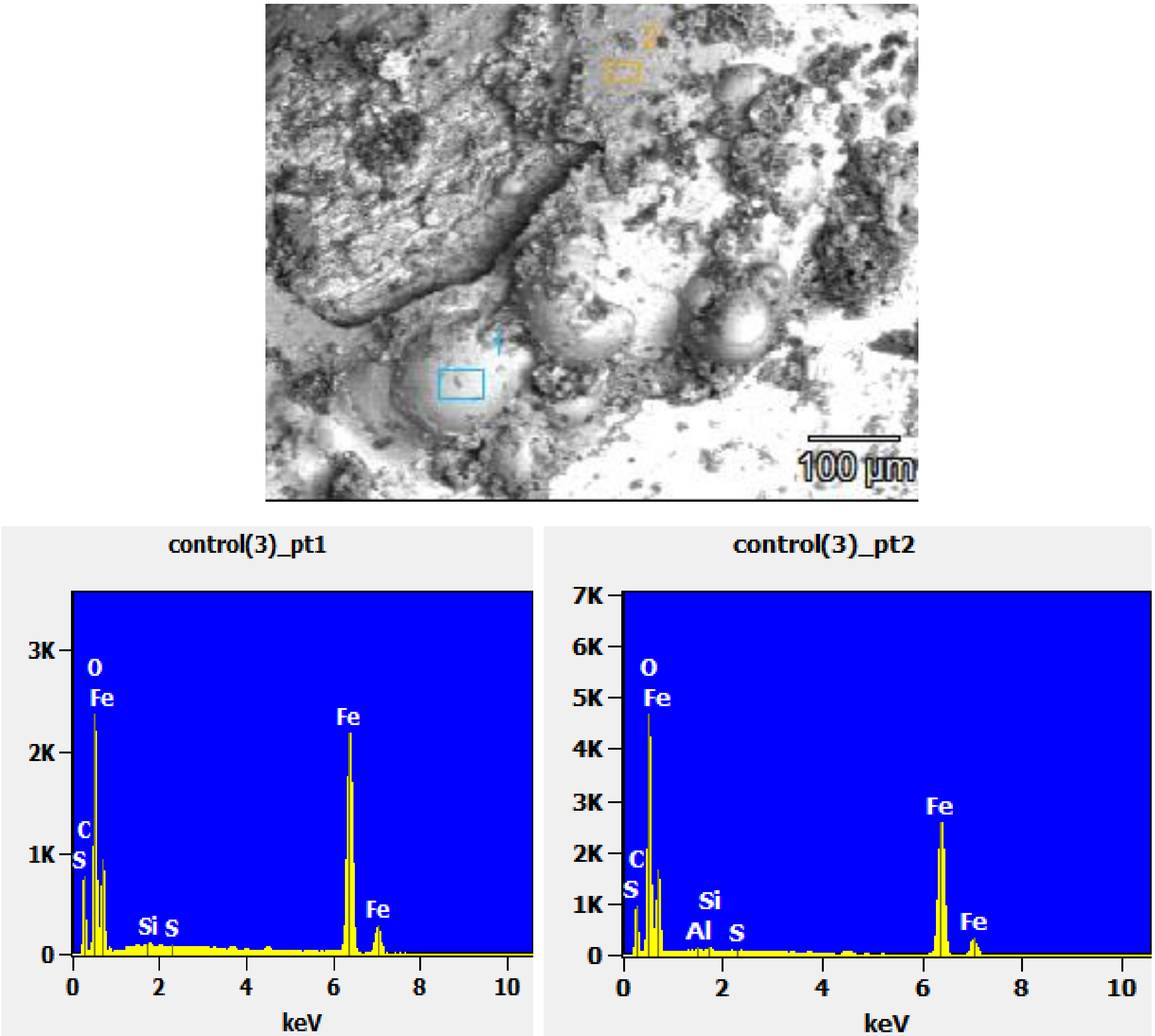




Weight %

	O	Mg	Al	Si	S	Fe
control(1)_pt1	38.22	0.18	0.81	0.88	0.13	59.77

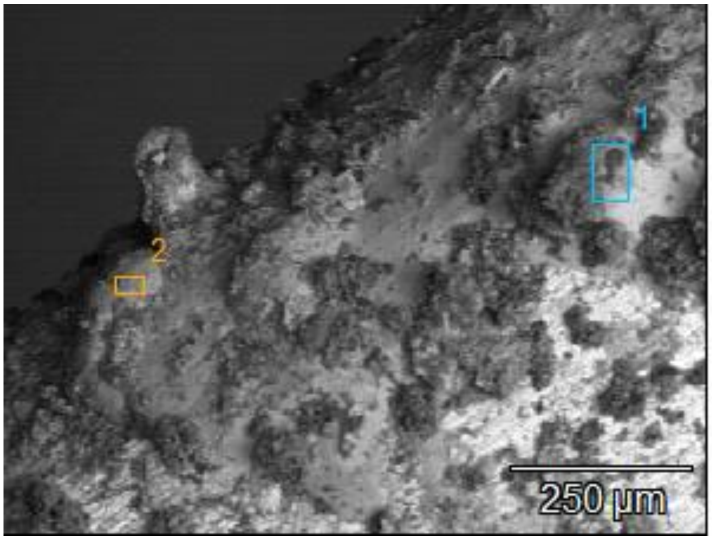
Figure 29: SEM/EDX analysis on the ER probe of control (reference) test shows heavily corroded (rich in oxygen oxide).

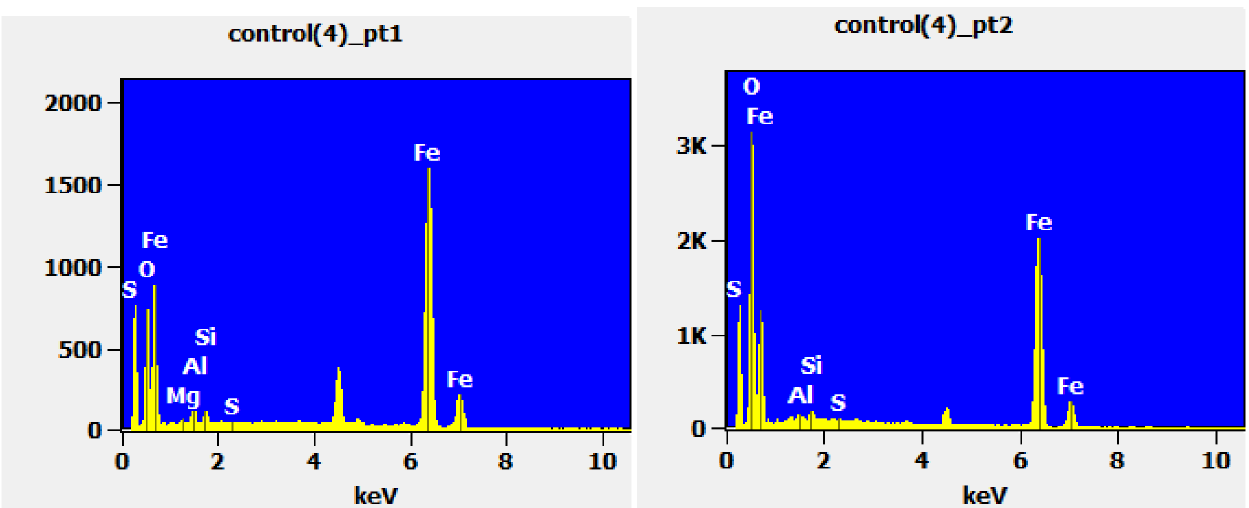


Weight %

	O	*Al*	*Si*	*S*	*Fe*
control(3)_pt1	29.29		0.37	0.02	70.32
control(3)_pt2	42.72	0.21	0.34	0.05	56.67

Figure 30: SEM/EDX analysis of the ER probe for control (reference) test shows heavily corroded (rich in oxygen oxide).

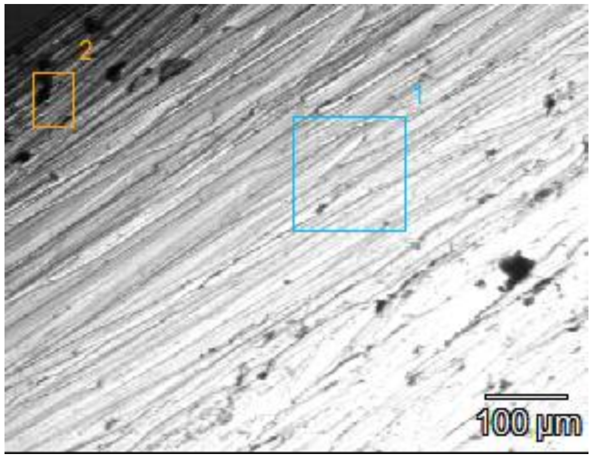


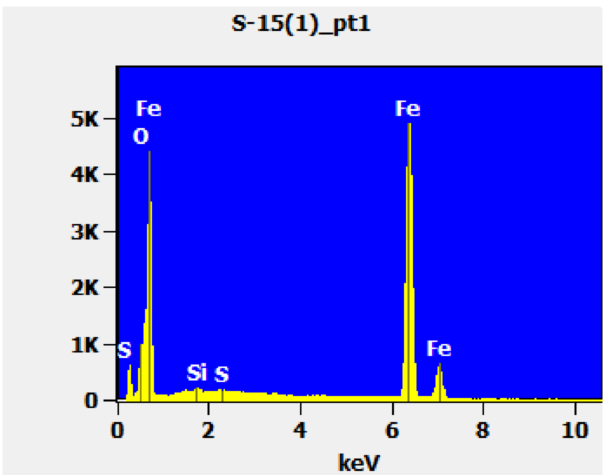


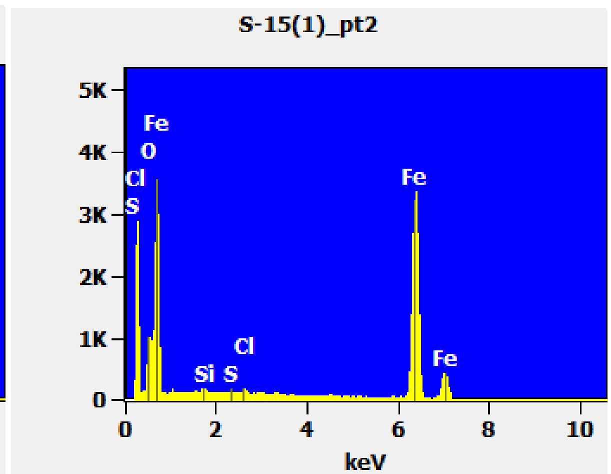
Weight %

	O	Mg	Al	Si	S	Fe
control(4)_pt1	20.19	0.71	1.80	1.35	0.14	75.80
control(4)_pt2	37.42		0.73	0.91	0.10	60.84

Figure 31: SEM/EDX analysis of the ER probe from control (reference) test shows significant corrosion product (rich in oxygen oxide).



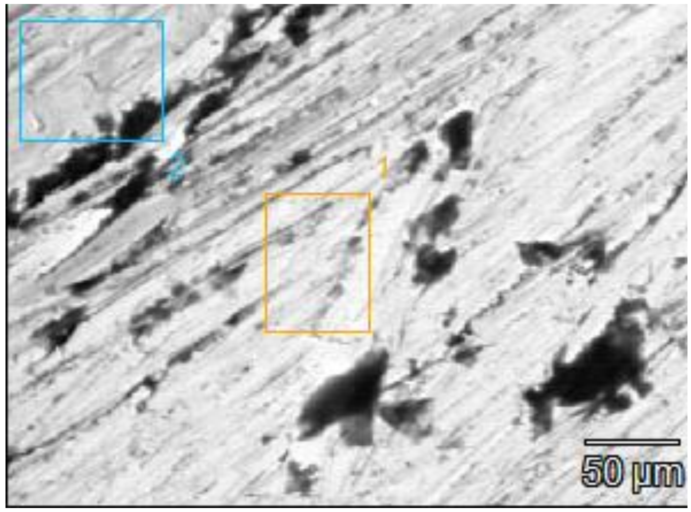


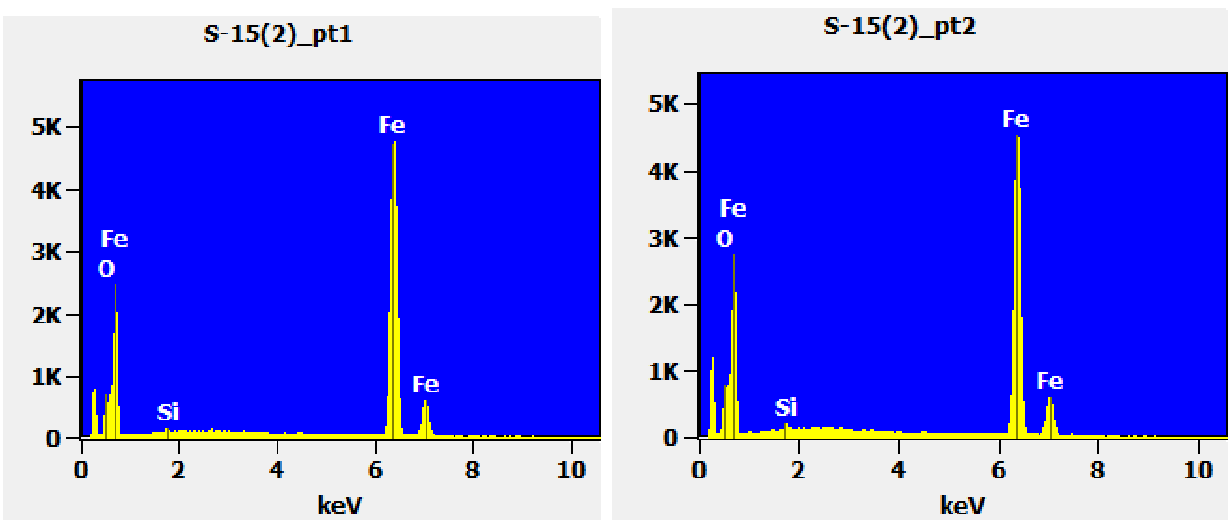


Weight %

	O	*Si*	*S*	*Cl*	*Fe*
S-15(1)_pt1	5.66	0.50	0.15	0.24	93.45
S-15(1)_pt2	11.99	0.57	0.22	0.55	86.66

Figure 32: SEM/EDX analysis of the ER probe for VCI treated test shows significantly less corrosion attack (rich in iron).

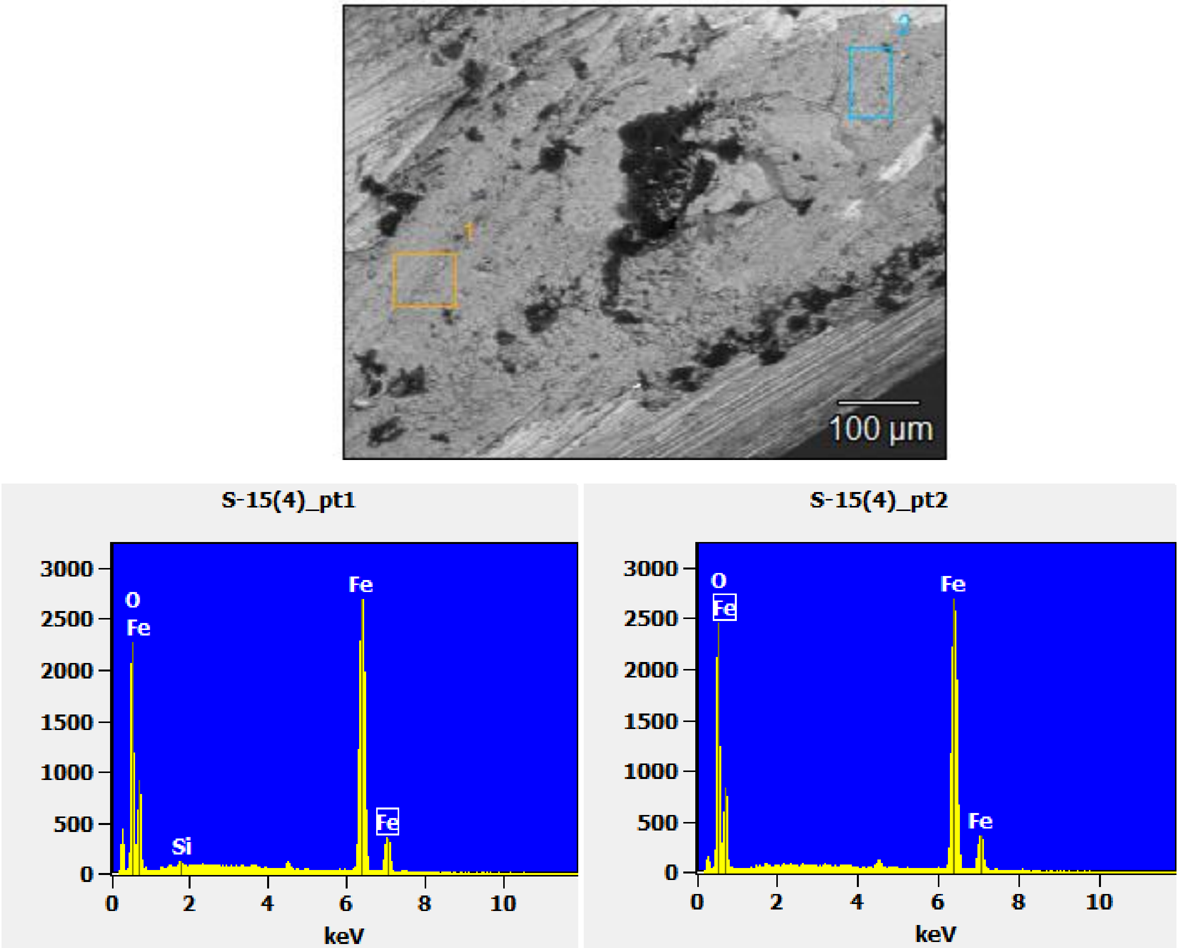




Weight %

	O	Si	Fe
S-15(2)_pt1	4.73	0.36	94.91
S-15(2)_pt2	6.45	0.60	92.95

Figure 33: SEM/EDX analysis on the VCI treated ER probe shows significantly less corrosion attacks (rich in iron).



Weight %

	O	*Si*	*Fe*
S-15(4)_pt1	24.94	0.39	74.67
S-15(4)_pt2	27.83	0.12	72.06

Figure 34: SEM/EDX analysis of the VCI treated ER probe shows significantly less corrosion attack (rich in iron).

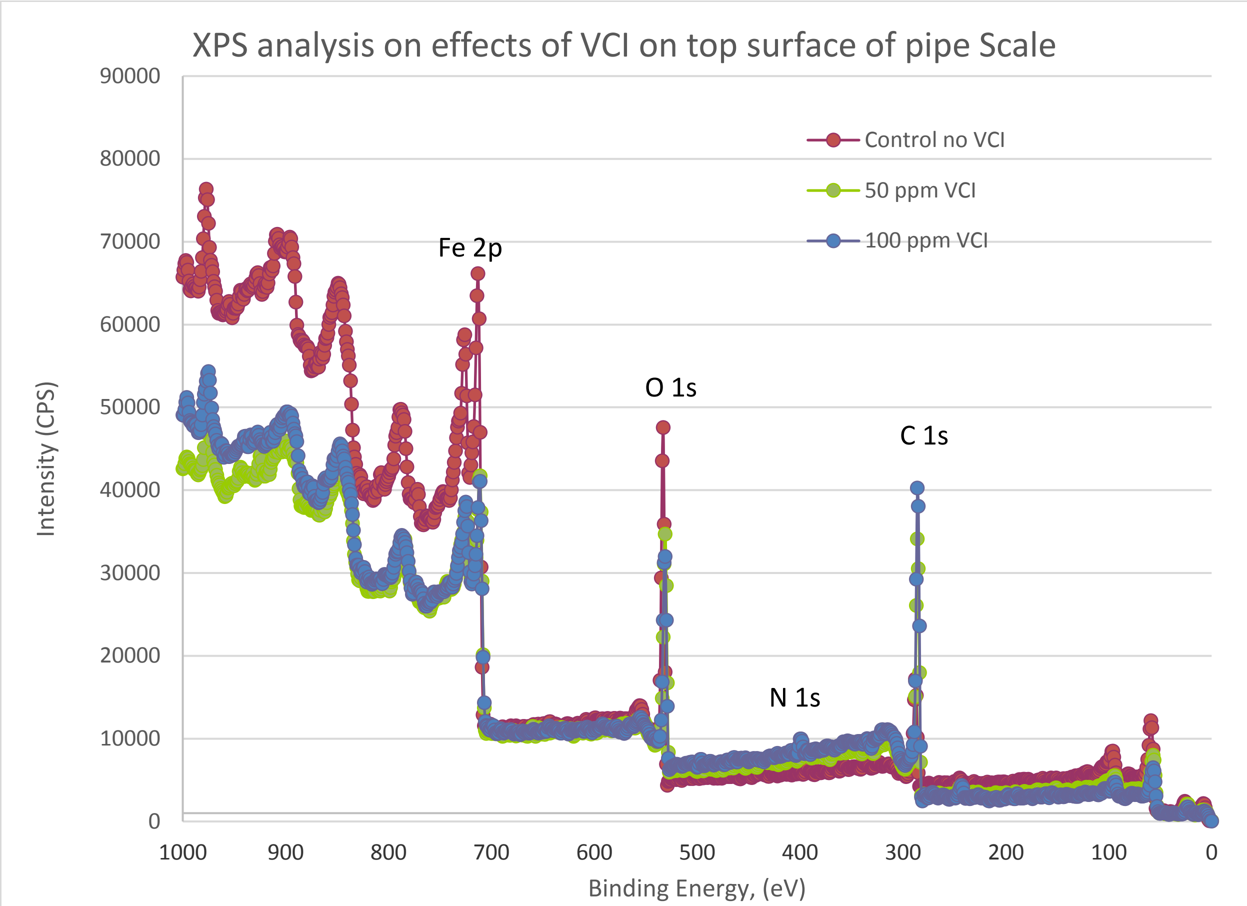


Figure 35: XPS analysis on the inner pipe surfaces after corrosion test in the hot steam loop shows more corrosion product on the control test.

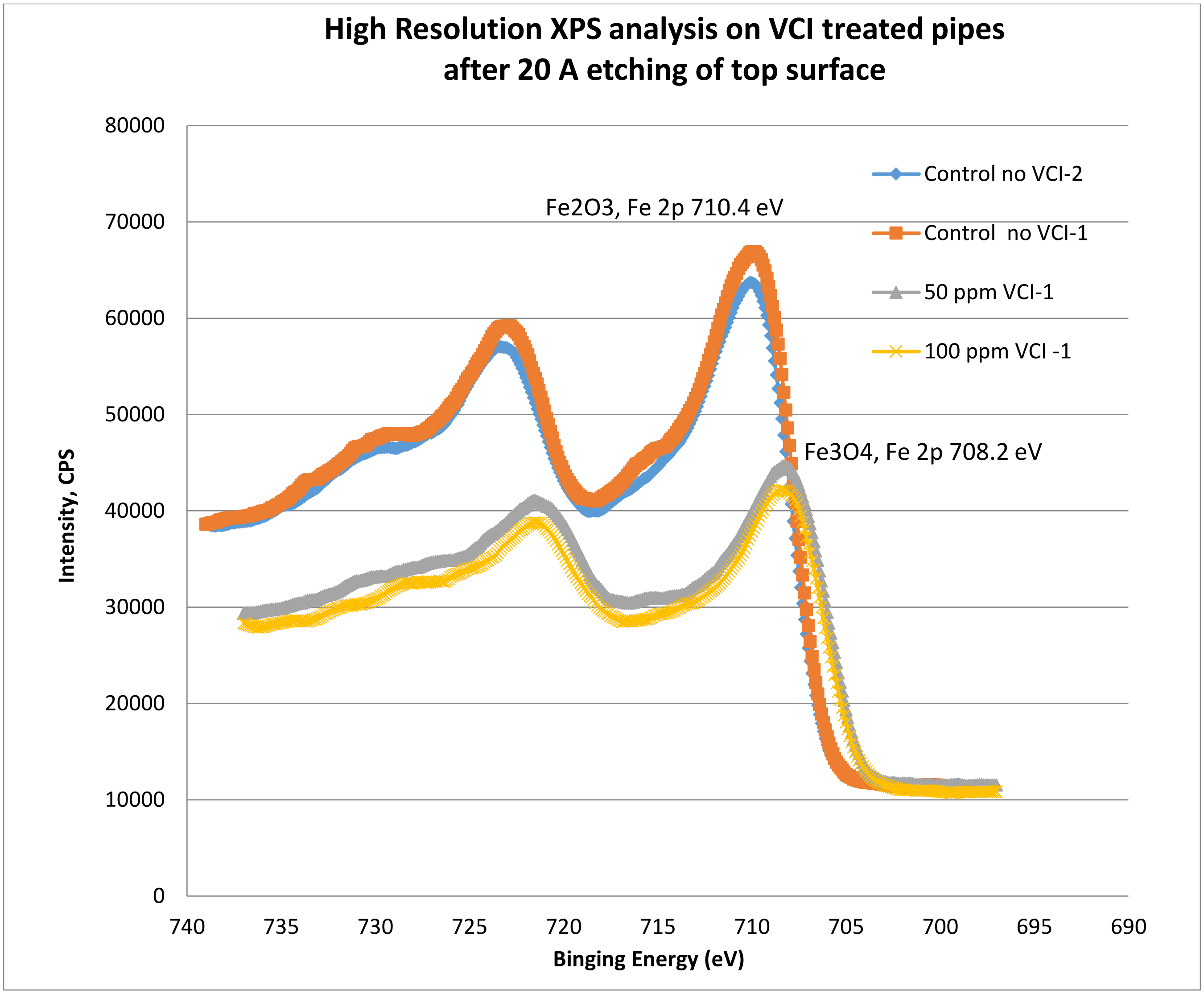


Figure 36: High Resolution XPS analysis on the inner pipe surfaces after corrosion test in the hot steam loop. Primary oxide seen on ID surface of non-treated pipe (control) is Fe_2O_3 (hematite), while Fe_3O_4 (magnetite) is predominant oxide on ID surface of VCI treated pipe.

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