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Development of a New Vapor Phase Corrosion Inhibitor for Steam Generating Systems and Boilers

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ABSTRACT

Hydrazine is used as an oxygen scavenger to control corrosion in steam generating systems, despite being a genotoxic carcinogen. The International Conference on Chemicals Management in 2006 adopted the Strategic Approach to International Chemicals Management designed to implement the Johannesburg Plan. The European Union has also implemented the new Regulation on Registration, Evaluation, Authorization, and Restriction of Chemicals to achieve the World Summit on Sustainable Development goals by 2020. Hydrazine is one those chemical that severe restriction has been imposed on and must be replaced by 2020. Alternative chemicals, nontoxic corrosion inhibitors or new oxygen scavenger-free water treatment technologies are preferred. A newly developed amine-based vapor phase corrosion inhibitor was investigated. Electrochemical tests were conducted and showed a significantly lower corrosion rate in boiling water. Short term corrosion tests in boiling water showed a decreased corrosion rate from 5.3 mpy to 1.93 mpy for 50 ppm VCI and 1.32 mpy for 100 ppm VCI addition. Long term corrosion tests in the hot steam generating closed loop system showed a decreased corrosion rate from 8.2-8.9 mpy for the control sample to 0.72-0.74 mpy when washed with 500 ppm VCI solution and subsequently

maintained at 100 ppm inhibitor for the test remainder. ~~When~~ Inhibitor added at the beginning of testing resulted in a corrosion rate of 1.09-1.24 mpy (with 100 ppm VCI). XPS analysis showed that the amine-based inhibitor promoted and stabilized a protective (Fe_3O_4) magnetite oxide on the pipe internals.

Keywords: corrosion inhibitor, hydrazine, steam generating closed loop system, boilers

INTRODUCTION

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

Hydrazine has been used as an oxygen scavenger and corrosion inhibitor for corrosion control in steam generating systems. Although hydrazine is very effective, 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 drum boilers and heat recovery steam generator boilers.

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 the Earth Summit Agenda 21[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 compounds such as diethylhydroxylamine[10-14], Helamine amine-based compounds[21-24] surface-active fatty alkyl polyamines, and blends of amines of different volatilities, e.g., cyclohexylamine + aminoethanol + (Z)-N-9-octadecenylpropane-1,3-diamine, and cyclohexylamine-based corrosion inhibitors.[8, 9, 15-20] These amine-based compounds were introduced as an alternative to oxygen scavenging-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 when used as an oxygen scavenger in boiler feed water systems: protects by forming a thin magnetite (Fe_3O_4) layer; prevents lime scale or mineral deposition on surfaces ~~installations~~; removes old deposits without causing damage; disperses impurities, inorganic salts and oxides of iron; alkalinizes vapor networks, including condensate return, 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 (< 1.0 mpy). In low to moderate pressure industrial boiler systems, an initial feed water inhibitor dosage of 100-500 mg/L is recommended.[23] However, during operation, an adjusted product feed rate is recommended until a consistent inhibitor residual of 80-120 mg/L is established in the condensate.

Volatile Corrosion Inhibitors (VCI)

Volatile Corrosion Inhibitors 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.[16-25] In closed vapor spaces, such as shipping containers, larger nitrogen-containing molecules are used, such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine. When these inhibitors come in contact with a 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 being a result of high volatility, while enduring protection is a result of low volatility and complex compound formation.

In addition to oxygen scavenging and metal passivating capabilities, another key advantage of amine-based inhibitors is their volatility. Not only do they scavenge oxygen and passivate metal in the feed water and boiler portions of a steam boiler cycle, they also enter the vapor phase (volatilize) with the steam to provide complete system protection. 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 [consider this alternative: An enormous advantage of the amine-based compounds being volatile is that they are transported into the steam system and then the condensate portion of the system where they passivate condensate system metallurgy, thereby preventing corrosion; scavenge oxygen that enters the condensate system, preventing corrosion; reduce corrosion byproduct transport to the boiler, reducing the potential for boiler deposition and under deposit corrosion; improve equipment reliability and efficiency; and minimize overall condensate system corrosion, thereby reducing the related maintenance costs.

One the major advantage of the new corrosion inhibitor is its very low toxicity, making it safe and easy to handle in typical application systems. The oral toxicity test measure, LD_{50} "Lethal Dose" of the new corrosion inhibitor is 2190 mg/Kg (ppm) for rats, whereas hydrazine's LD_{50} is only 15-22 mg/Kg (ppm), indicating a very high toxicity.

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, which is limited per ~~the~~ European Union regulations. 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 the new amine-based VCI versus hydrazine in providing corrosion protection for the boiler steam/water system internal surfaces through the phases of the steam system (water, transition, steam). Prior to investigating this new VCI in a closed loop system, some preliminary testing was conducted at high temperatures (roughly 182^{o}C) to determine when it would start to ~~boil~~ vaporize; for comparison, hydrazine's boiling point is 114^{o}C. The assumption was that if hydrazine can survive the steam cycle, then this new VCI should provide effectiveness and good functionality in those conditions. The auto-ignition temperature for both hydrazine and new VCI is around 288-293^{o}C. 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 118^{o}C. The objectives were to investigate electrochemical behavior of carbon steel pipe samples (ASME B31.1 pipes)[26] under the following conditions: 1) exposed to the new VCI and a control solution; 2) total immersion in boiling water with new VCI and without inhibitor (control-reference); 3) in steam/water closed loop system with VCI and without inhibitor (control-reference). Post-test evaluation was conducted by SEM/EDS analysis and XPS (X-Ray Photoelectron Spectroscopy) analysis of surface conditions for samples with inhibitor.

EXPERIMENTAL PROCEDURE

Corrosion behavior of low carbon steel pipe samples in the new amine-based VCI in steam/water loops at elevated temperature was investigated to explore its inhibiting effectiveness as an alternative ~~for~~ to hydrazine. Electrochemical polarization behavior was conducted in 50 to 500 mg/L inhibitor solutions. Samples were polished (1.0 μm surface finish), placed in a flat cell and tested in deionized water solutions containing 50 to 500 mg/L VCI inhibitor at elevated temperatures. Corrosion behavior of carbon steel pipe samples was assessed during complete immersion in boiling water while exposed to the new VCI and without inhibitor. Apparatus for testing was similar to that recommended in ASTM G123[27] (Erlenmeyer flask and condenser, hot plate to maintain solution at its boiling point, Figure 2). These tests were conducted in control solution (filtered water, no inhibitor), 50, 100, 200 and 500 mg/L VCI addition. Test duration was about 700 hours.

The steam/water loop system included an electric boiler and steel pipe loop, to produce low or high pressure steam (~100 psi). A closed loop system was assembled to circulate and maintain steam at 118^{o}C (245^{o}F), 90 psi. Tests were conducted on the control (no inhibitor was used) for a duration of 1,100 hours. Test duration for the 100 mg/L corrosion inihibitor was 2,200 hours. During these tests, corrosion rate measurements were monitored using electrical resistance (ER) techniques.

Light microscopy, scanning electron microscopy (SEM/EDS analysis) and XPS analysis were performed after the corrosion tests to verify the extent of corrosion damage on the exposed surfaces after each test, using image analysis and SEM/EDS, followed by surface chemistry post-corrosion tests using high resolution XPS analysis.

RESULTS and DISCUSSIONS

Electrochemical polarization behaviors of the steel pipes in different concentrations of corrosion inhibitors at different temperature are shown in Figure 1. Results indicated that the new VCI is an anodic corrosion inhibitor capable of lowering corrosion rates and expanding the passivation range for steel pipe in working condition of hot steam/water system. Corrosion rates based on the cyclic polarization test results are as follows: for the control, 17.2 μA/cm^2 (7.91 mpy); in presence of 100 mg/L VCI, 4.73 μA/cm^2 (2.18 mpy); and when a 200 mg/L VCI was added to solution, the corrosion rate decreased to 2.86 μA/cm^2 (1.24 mpy). In general, the boiler industry assumes approximately 1.0 mpy corrosion rate to be an acceptable range for the open circulating system.

Corrosion behaviors of the steel pipe samples in boiling water are shown in Figures 2-3, and were monitored for 700 hours of continuous immersion at boiling temperature. The corrosion rate (determined from weight loss measurement) for the steam environment with no inhibitor was 5.3 mpy. When 50 mg/L inhibitor VCI was added, the corrosion rate decreased to 1.94 mpy, and for 100 mg/L VCI addition, the corrosion rate dropped to 1.36 mpy. Addition of 200 mg/L VCI decreased the corrosion rate to 0.97 mpy, while addition of 500 mg/L resulted in a very low corrosion rate of 0.37 mpy. The corrosion rates for the solutions with different amounts of inhibitor had become steady at roughly 120 hours (corrosion rate showed a logarithmic kinetic rate) while the non-protected steel samples showed an increasing trend for the corrosion rate. From observation, the non-protected 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 inhibitor in low dosages (50-100 mg/L 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 mg/L), no color change was observed on the steel samples or their solutions, which correlates with the measured, low corrosion rates.

Elevated temperature corrosion tests on carbon steel pipe samples in a steam/water loop with VCI and without inhibitor (control-reference) were conducted using the electric boiler steam/water in a closed loop system that circulated and maintained hot steam at 90 psi, 118ºC (245ºF). The control-reference test (without inhibitor addition) was conducted for 1,100 hours and corrosion rates were monitored using electrical resistance (ER) techniques. Figure 4 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 mg/L VCI inhibitor was injected into closed loop system. This addition resulted in a significant drop in the corrosion rate to 0.72 mpy. This indicates that VCI 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 mg/L. The 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 5 shows a comparison of steel pipe inner surface conditions of the inhibitor treated loop and control test after 2,200 hours corrosion test in a hot steam/water closed loop. The average corrosion rate was measured at 1.09-1.24 mpy. During the boiler drainage (blowdown), no sign of any rust formation in the discharged water was observed. The control probe showed heavy rust formation on its surface, while the 100 mg/L VCI ER probe showed a thin layer of black magnetite and relatively clean surfaces. Figure 5 shows 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 VCI is mainly covered by a thin Fe_3O_4, magnetite oxide.

XPS analyses were conducted on the internal surfaces of both control sample and inhibitor treated steel pipe. Results are shown in Figure 6. High Resolution XPS analysis was also conducted on both control and inhibitor treated steel pipes, Figure 9. The nature of surface oxide was compared after 2.0 nm of the top surface deposits were etched to remove ambient changes or accidental surface contamination. XPS data showed that the oxide on internal surface of the control sample (no inhibitor) is hematite (Fe_2O_3), Fe 2p, with binding energy 710.4 eV, whereas the oxide on the inhibitor treated pipes ~~were~~ is magnetite (Fe_3O_4), Fe 2p, with a binding energy of 708.2 eV (Figure 7). These observations reaffirmed that VCI presence in water promotes the formation of a protective thin layer of black magnetite, which adheres very well to steel pipe surfaces due to its magnetic properties, and provides excellent corrosion performance.

CONCLUSIONS

The corrosion behavior of low carbon steel pipe material samples in a steam/water loop, with and without VCI corrosion inhibitor, was investigated. Electrochemical polarization behavior showed the VCI ~~is~~ to be 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 control sample to be roughly 5.3 mpy; when 50 mg/L inhibitor VCI was added, it decreased to 1.94 mpy, and for 100 mg/L addition, it decreased to 1.36 mpy. Addition of 200 mg/L reduced the corrosion rate to 0.97 mpy, and 500 mg/L resulted in a very low corrosion rate of 0.37 mpy. In boiling water, the corrosion rate for the reference steel sample was about 5.3 mpy. For 100 mg/L Hydrazine addition, the corrosion rate was 1.46 mpy; and for 500 mg/L hydrazine addition, 0.38 mpy was achieved.

The corrosion behavior of the low carbon steel pipe material samples in a steam/water loop with and without inhibitor in a closed loop system of 90 psi at 118^{o}C showed a corrosion rate of 8.2-8.9 mpy. The corrosion rate in steam/water closed loop with 100 mg/L VCI inhibitor addition decreased to 1.09-1.24 mpy. In a corroding system (control sample condition) when 500 mg/L VCI inhibitor was injected into a closed loop system after 1,100 hours, the corrosion rate dropped to 0.72 mpy. This indicates that VCI inhibitor successfully retarded corrosion reactions and managed to form a stable, protective Fe_3O_4 (magnetite) layer on the pipe interior surfaces. This is a very impressive result; a corroding closed loop steam/water system can be recovered with the addition of 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, Fe_3O_4. These observations reaffirmed that the VCI presence in water promotes the 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 [consider: excellent] corrosion performance.

In summary, this investigation confirmed that for steel materials exposed to hot steam/hot environments, the new vapor phase corrosion inhibitor can be an effective replacement for toxic hydrazine. The major advantage of the new VCI is its very low toxicity, making it safe and easy to handle in typical application systems. The oral toxicity test measure, LD_{50} of the new VCI is 2190 mg/Kg for rats, whereas hydrazine's LD_{50} is 15-22 mg/Kg .

The new amine-base corrosion inhibitor displays excellent properties that 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.

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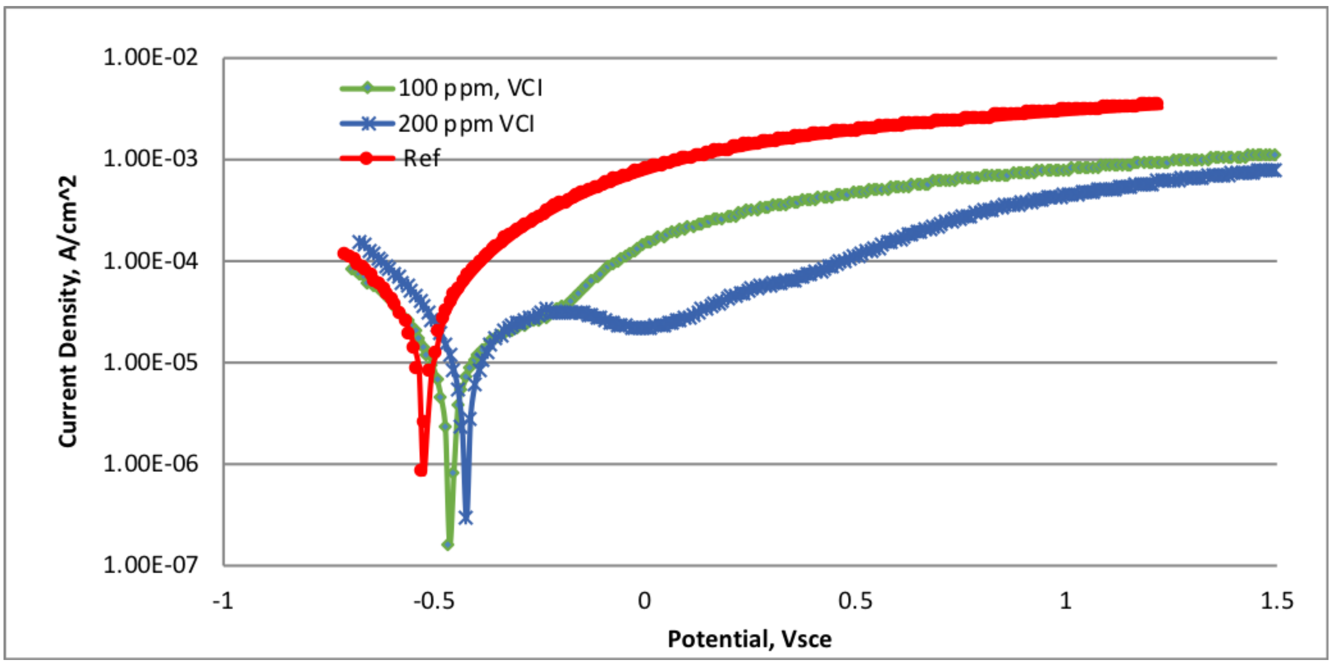
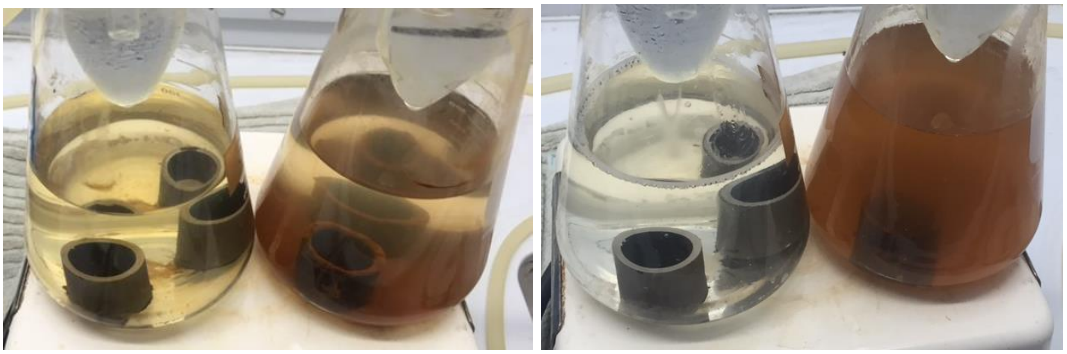


Figure 1: Comparison of cyclic polarization behavior of steel pipe in hot water solution in 100°C when exposed to control solution, 100 and 200 mg/L VCI.



100 mg/L VCI control water 500 mg/L VCI control water

Figure 2: Corrosion behavior of the steel pipe samples in boiling water. Corrosion rate decreased to 1.36 mpy with 100 and 500 mg/L VCI addition, (700 hours).

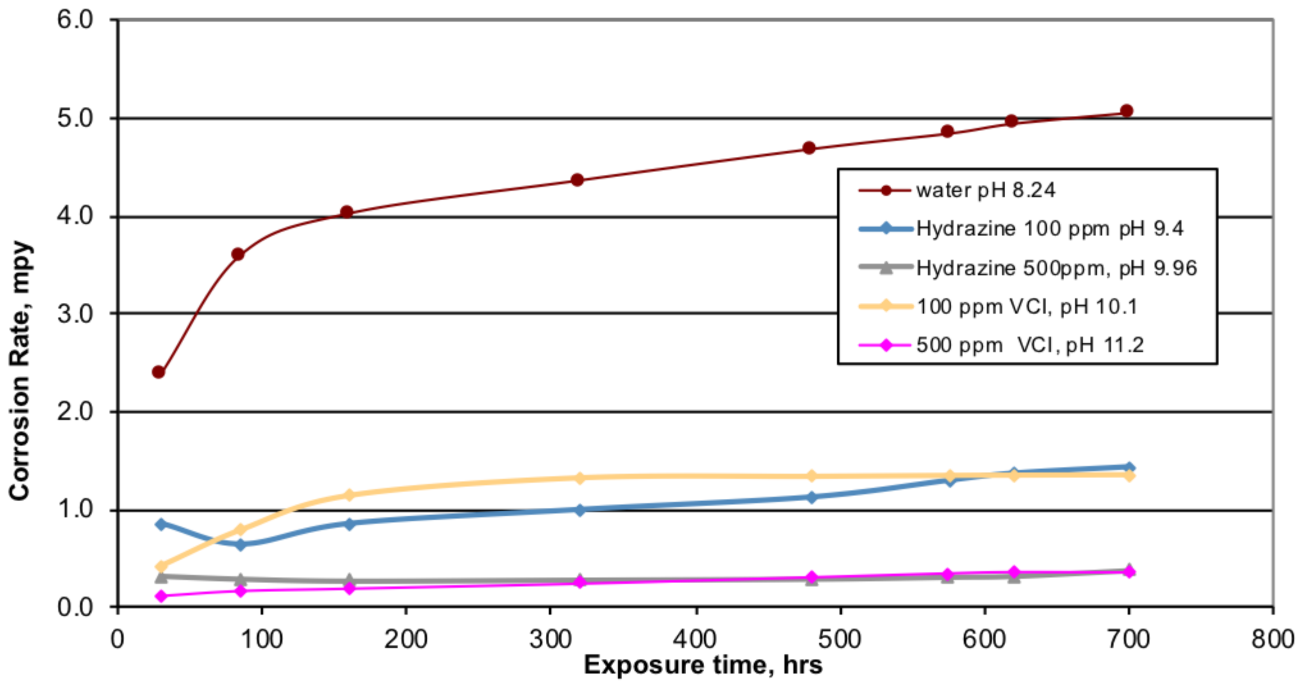


Figure 3: Corrosion behavior of steel pipes in hot water solution in 100°C when exposed to control solution, 100 and 500 mg/Kg VCI, and Hydrazine.

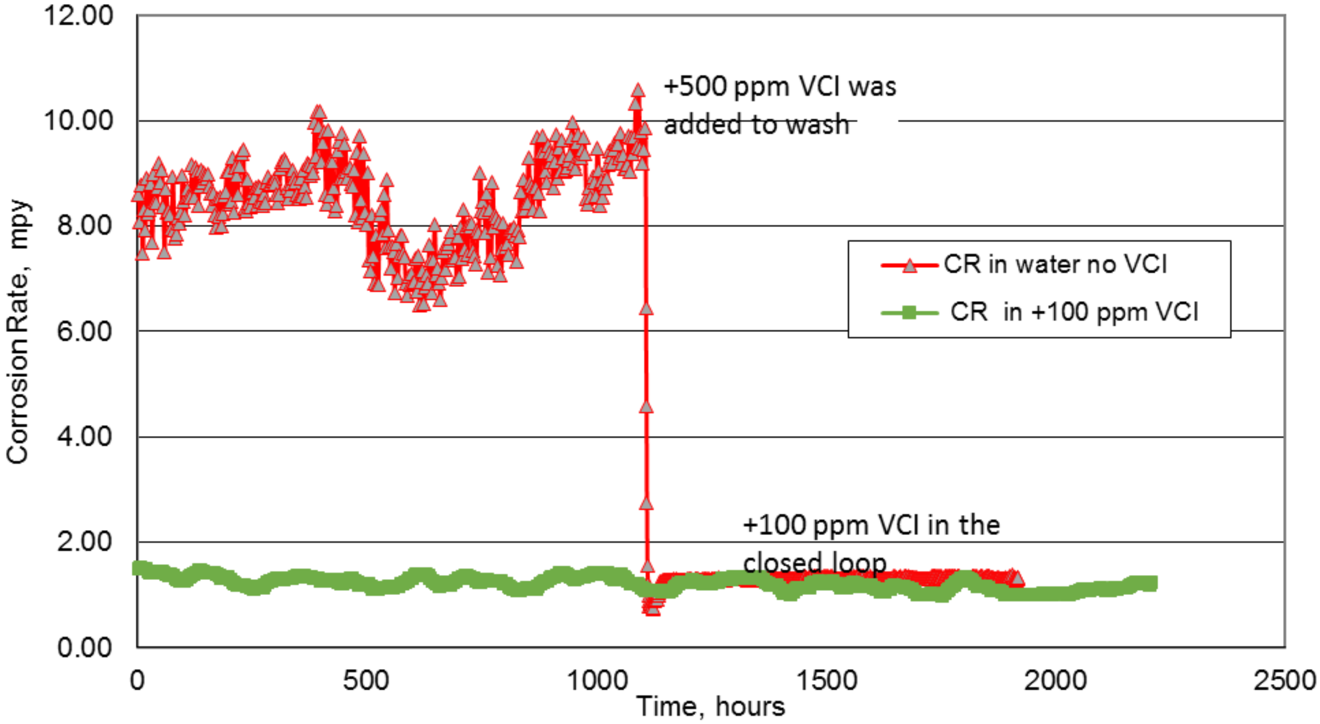
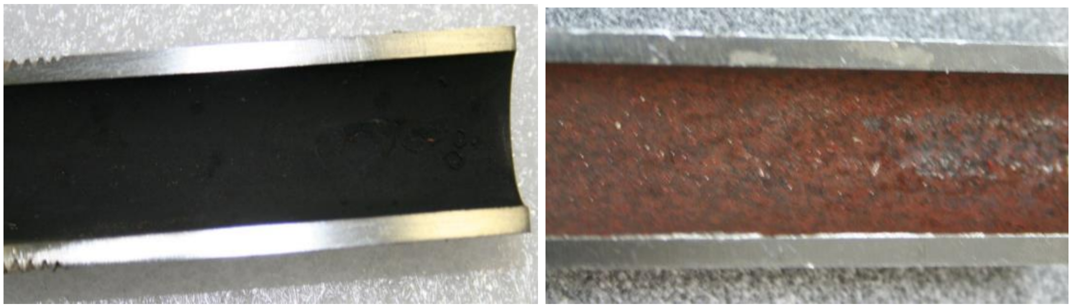


Figure 4: Comparison of corrosion rate measurements of the inhibitor treated loop and control test after 2,200 hours corrosion test in hot steam/water closed loop.



100 mg/L VCI Control

Figure 5: 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.

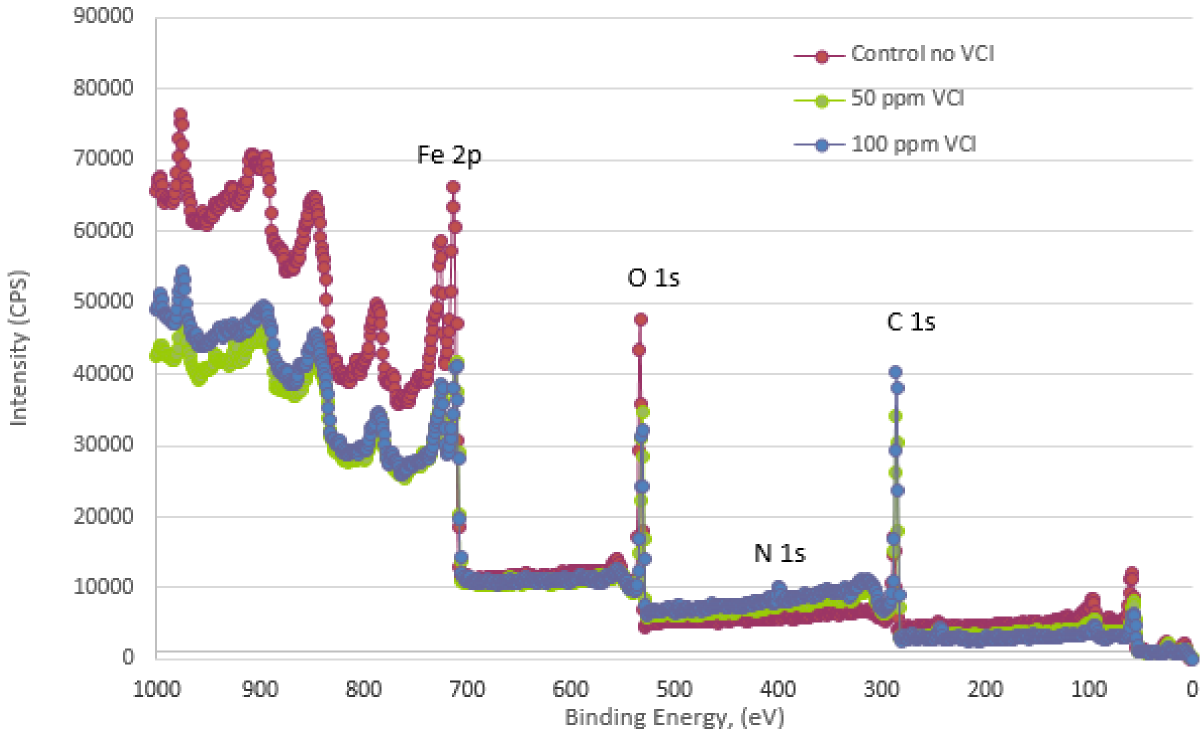


Figure 6: XPS analysis on the inner pipe surfaces after corrosion test in the hot steam loop shows more corrosion product on the control test.

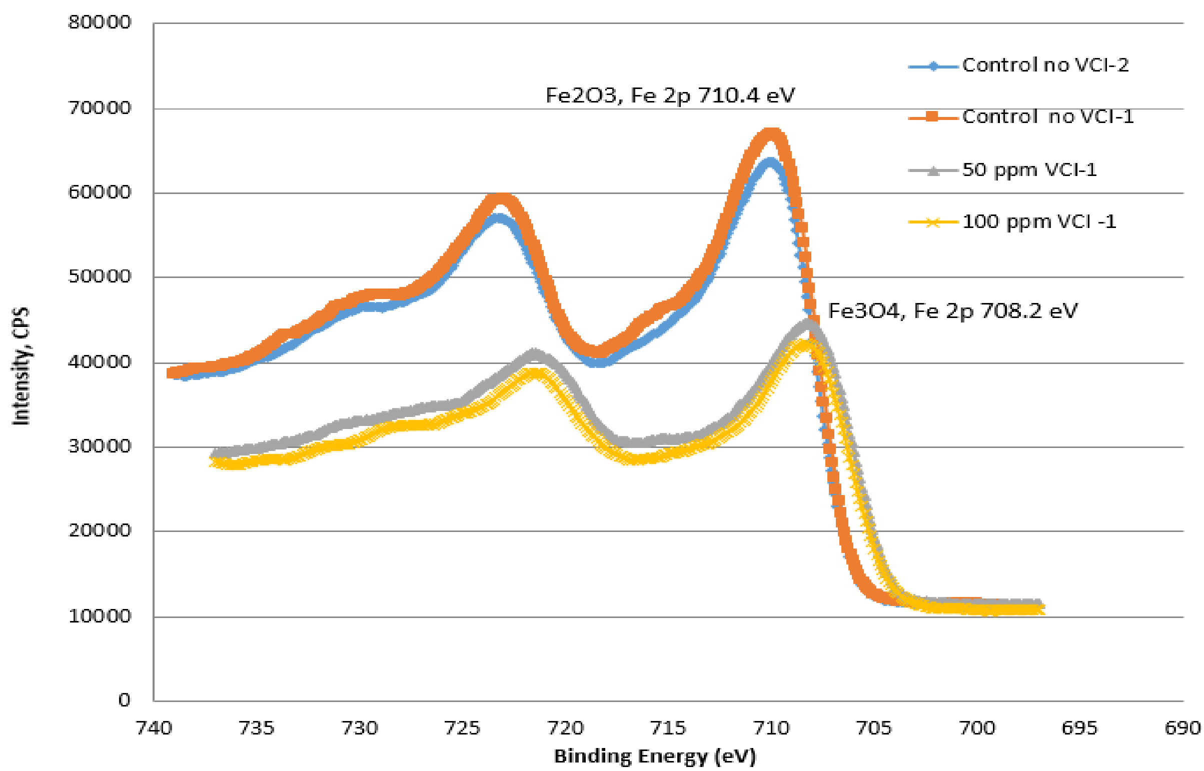


Figure 7: High Resolution XPS analysis on the inner pipe surface after corrosion test in the hot steam loop. Primary oxide seen on ID surface of non-treated pipes (control) is hematite, while magnetite is predominant oxide on ID surface of VCI treated pipes.