New Corrosion Inhibitor for Steam-Generating Boilers

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Hydrazine (N_2H_4) is an oxygen scavenger to control corrosion in steam-generating systems, despite being a genotoxic carcinogen. Hydrazine has severe restrictions and must be replaced by 2020. Corrosion tests in boiling water showed corrosion rates dropped from 5.3 to 1.93 mpy for 50 ppm and 1.32 mpy for 100 ppm volatile corrosion inhibitor (VCI) addition. Corrosion tests in the steam closed loop system showed the corrosion rate of 8.2 to 8.9 mpy dropped to 0.72 to 0.74 mpy when washed with a 500 ppm VCI solution and inhibitor maintained at 100 ppm. Analysis showed that the new inhibitor stabilizes protective magnetite oxide (Fe_3O_4) on the pipe internals.

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 from the condensate where inleakage can occur.

Hydrazine (N_2H_4) 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.

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,[1-2] 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. 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.

Alternative oxygen scavengers include amine compounds, such as diethylhydroxylamine,[3-7] Helamine amine-based compounds, surface-active fatty alkyl polyamines, blends of amines of different volatilities (e.g., cyclohexylamine + aminoethanol + (Z)-N-9-octadecenylpropane-1,3-diamine), and cyclohexylamine-based corrosion inhibitors.[7-14] Amine-based water treatment has numerous beneficial properties when used as an oxygen scavenger in boiler feedwater systems: protects by forming a thin magnetite (Fe_3O_4) layer; prevents lime scale or mineral deposition on surfaces; 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 are very important in determining how much inhibitor is required to maintain an acceptable corrosion rate level (<1.0 mpy). An advantage of the amine-based compounds being volatile is that they are transported into the steam system and passivate surfaces, 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 underdeposit corrosion; and minimize general corrosion, thereby reducing the related maintenance costs. The other advantage of the new corrosion inhibitor is its very low toxicity, making it safe and easy to handle in typical application systems. For the oral toxicity test measure, lethal dose (LD_{50}) of the new corrosion inhibitor is 2,190 ppm for rats, whereas hydrazine's LD_{50} is only 15 to 22 ppm, indicating a very high toxicity.

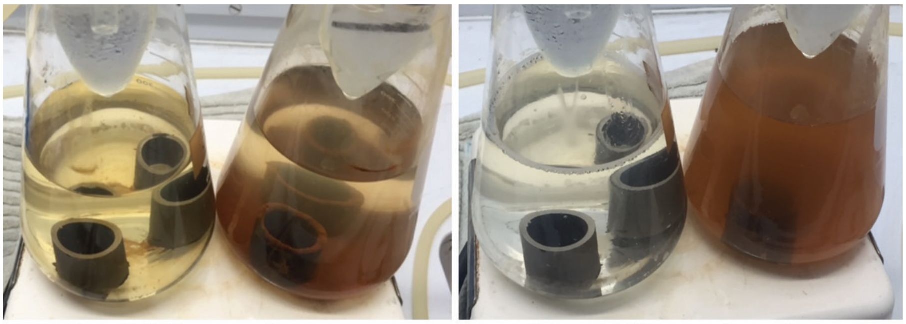

FIGURE 1 Corrosion behavior of the steel pipe samples in boiling water. Corrosion rate decreased to 1.36 mpy with 100 and 500 mg/L VCI addition (700 h).

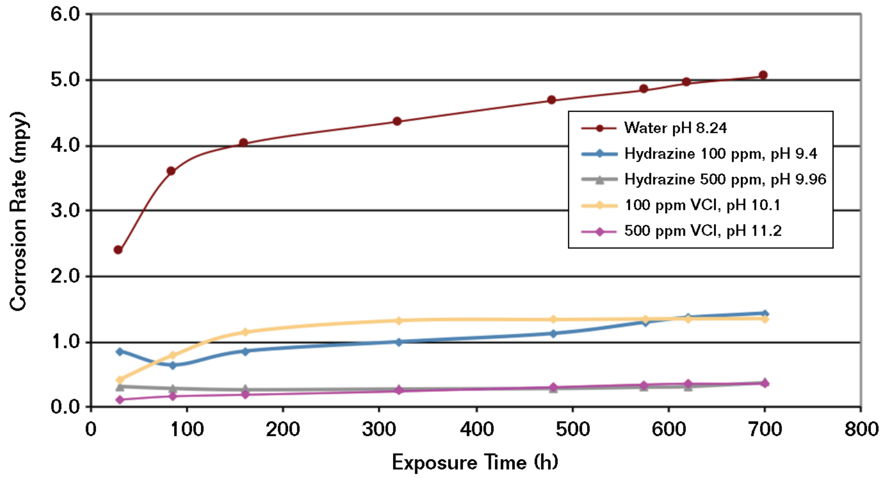

FIGURE 2 Corrosion behavior of steel pipes in hot water solution in 100 °C when exposed to control solution, 100 and 500 mg/kg VCI, and hydrazine.

Experimental Procedure

Corrosion behavior of low carbon steel (CS) pipe samples in the new amine-based volatile corrosion inhibitor (VCI) in steam/water loops at elevated temperature was investigated to explore its inhibiting effectiveness as an alternative to hydrazine. Corrosion behavior was assessed in boiling water while exposed to the new inhibitor. These tests were conducted in control solutions of 0.00, 50, 100, 200, and 500 mg/L VCI addition. The test duration was ~700 h.

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 °C and 90 psi. Tests were conducted on the control for a duration of 1,100 and 2,200 h for the 100 mg/L corrosion inhibitor. During these tests, corrosion rates were monitored using electrical resistance (ER) techniques.

Light microscopy, scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS) analysis, and x-ray photoelectron spectroscopy (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

Corrosion behaviors of the steel pipe samples in boiling water are shown in Figures 1 and 2 and were monitored for 700 h. The corrosion rate without an inhibitor was 5.3 mpy. When the 50 mg/L inhibitor was added, the corrosion rate decreased to 1.94 mpy, and for the 100 mg/L VCI addition, the corrosion rate dropped to 1.36 mpy. The addition of 200 mg/L VCI decreased the corrosion rate to 0.97 mpy, while the addition of 500 mg/L resulted in a very low corrosion rate of 0.37 mpy. The

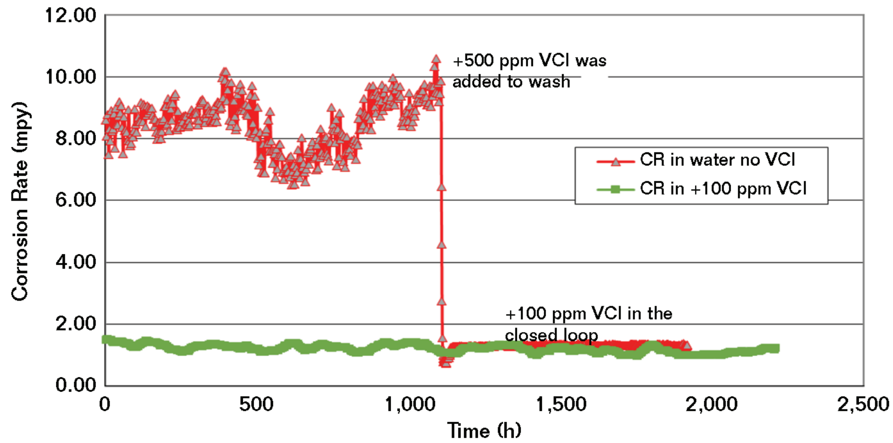

FIGURE 3 Comparison of corrosion rate measurements of the inhibitor-treated loop and control test after 2,200 h in hot steam/water closed loop.

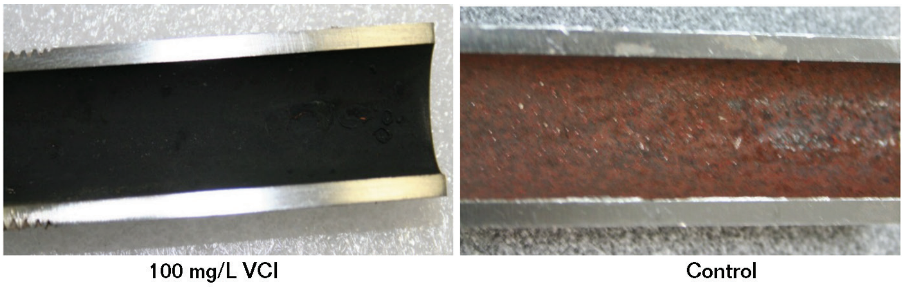

FIGURE 4 Comparison of steel pipe inner surface conditions of the inhibitor-treated loop and control test after 2,200 h in hot steam/water closed loop.

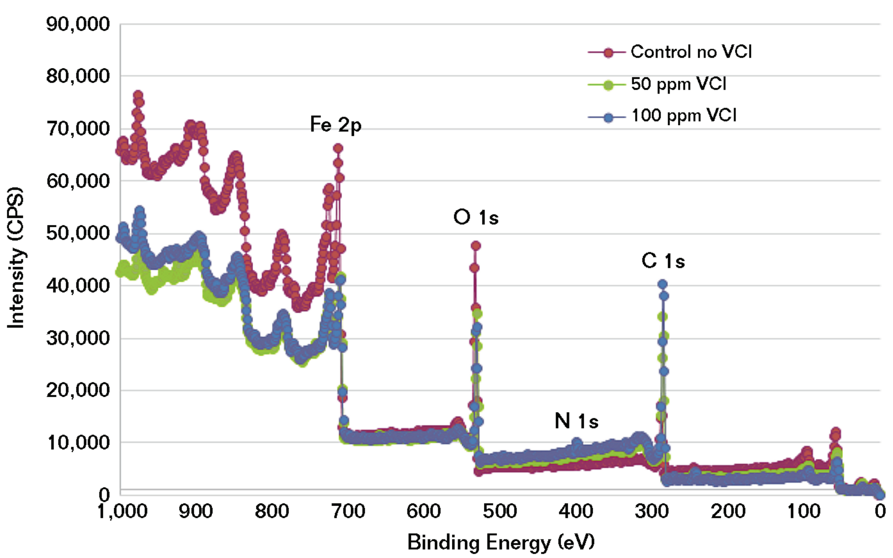

FIGURE 5 XPS analysis on the inner pipe surfaces after corrosion test in the hot steam loop shows more corrosion product on the control test.

corrosion rates for the solutions with different amounts of inhibitor had become steady at roughly 120 h (corrosion rates showed a logarithmic kinetic rate) while the nonprotected steel samples showed an increasing trend for the corrosion rate. From observation, the nonprotected steel samples showed heavy corrosion attack covered with hematite (Fe_2O_3) formation. To the contrary, the presence of inhibitor in low dosages (50 to 100 mg/L addition) resulted in an oxide formation of magnetite and no solution discoloration.

Elevated temperature corrosion tests on CS pipe samples in a steam/water loop were conducted using the electric boiler steam/water in a closed loop system that circulated and maintained hot steam at 90 psi and 118 °C (245 °F). The control test (without inhibitor) was conducted for 1,100 h and corrosion rates were monitored using electrical resistance techniques. Figure 3 shows the corrosion rate over time for the reference sample. The average corrosion rate was measured to be 8.2 to 8.9 mpy. After 1,100 h, the 500 mg/L VCI was injected into the closed loop system. This addition resulted in a significant drop in the corrosion rate to 0.72 mpy, indicating that the VCI inhibitor had successfully reduced the corrosion reaction and managed to stabilize formation of a protective magnetite on the internal surfaces.

The corrosion test in the steam/water closed loop was continued for 1,900 h in total 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 4 shows a comparison of steel pipe inner surface conditions of the inhibitor-treated loop and control test after 2,200 h in a hot steam/water closed loop. The average corrosion rate was measured at 1.09 to 1.24 mpy. During the boiler drainage, no sign of any rust formation in the discharged water was observed. The control ER 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. Comparison of these internal surfaces show that the control pipes internal surfaces are covered by thick hematite formation due to their high corrosion rate, while the test conducted with corrosion inhibitor VCI is mainly covered by a thin magnetite oxide.

XPS analyses were conducted on the internal surfaces of both the control sample and the inhibitor-treated steel pipe (Figure 5). High-resolution XPS analysis was also conducted on both control and inhibitor-treated steel pipes (Figure 6). 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 the internal surface of the control sample is hematite, Fe 2p, with binding energy 710.4 eV, whereas the oxide on the inhibitor-treated pipes is magnetite (Fe 2p) with a binding energy of 708.2 eV (Figure 6). 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 control performance.

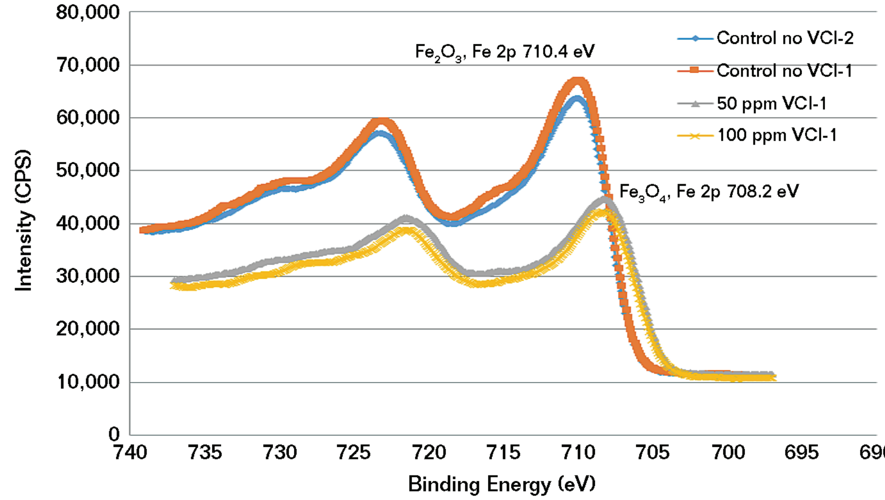

FIGURE 6 **High resolution XPS analysis on the inner pipe surface after corrosion test in the hot steam loop. Primary oxide seen on the inner diameter surface of nontreated pipes (control) is Fe_2O_3, while Fe_3O_4 is predominant oxide.**

Conclusions

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. The addition of 200 mg/L reduced the corrosion rate to 0.97 mpy, and the 500 mg/L resulted in a very low corrosion rate of 0.37 mpy.

The corrosion rates of pipe samples in a steam/water loop with and without inhibitor in a closed loop system showed a corrosion rate of 8.2 to 8.9 mpy. The corrosion rate in steam/water closed loop with 100 mg/L VCI addition decreased to 1.09 to 1.24 mpy. In a corroding system (control sample condition) when 500 mg/L VCI was injected into a closed loop system after 1,100 h, the corrosion rate dropped to 0.72 mpy. This indicates that the inhibitor successfully retarded corrosion reactions and managed to form a stable, protective magnetite layer on the pipe interior surfaces. This is a very impressive result, indicating 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 Fe_2O_3, while the oxide on the inhibitor-treated pipes was Fe_3O_4. These 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 excellent corrosion control performance.

The other advantage of the new VCI is its low toxicity, making it safe and easy to handle. The oral toxicity test measure, LD_{50} of the new VCI is 2,190 ppm for rats, whereas hydrazine's LD_{50} is 15 to 22 ppm.

This new amine-based 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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