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

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Hydrazine is used as an oxygen scavenger to control corrosion in steam-generating systems, despite being a genotoxic carcinogen. Alternative chemicals, nontoxic corrosion inhibitors, or new oxygen scavenger-free water treatment technologies are preferred. A newly developed amine-based vapor phase corrosion inhibitor (VCI) was investigated. Electrochemical tests were conducted and showed a significantly lower corrosion rate in steam-generating boilers and boiling water. Short-term (720-h) corrosion tests in boiling water showed a decreased corrosion rate from 5.3 mpy to 1.93 mpy for 50 mg/L VCI and 1.32 mpy (0.001 metal loss per year) for 100 mg/L VCI addition. Long-term (2,200-h) corrosion tests in the hot steam-generating closed loop system showed a decreased corrosion rate from 8.2 to 8.9 mpy for the control sample to 0.72 to 0.74 mpy when washed with 500 mg/L VCI solution. The closed loop system was subsequently maintained at 100 mg/L inhibitor for the test remainder. Inhibitor added at the beginning of the test resulted in a corrosion rate of 1.09 to 1.24 mpy (with 100 mg/L VCI). X-ray photoelectron spectroscopy analysis showed that the amine-based inhibitor promoted and stabilized a protective magnetite oxide (Fe₃O₄) on the pipe internals. This investigation confirmed the inhibitor can be an effective replacement for toxic hydrazine.

The presence of dissolved oxygen in metal 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 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.

 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, 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 Johan-
nesburg 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, diethylhydroxyl-
amine,10-14 helamine (amine-based comp-
ounds),15-18 surface-active fatty alkyl polyamines, and amines of different vola-
tility (cyclohexylamine + aminoethanol + (Z)-N-9-octadecenylpropane-1, 3-diamine),
and cyclohexylamine-based corrosion inhibitors.8,9,19-24 These amine-based com-
pounds were introduced as an alternative oxygen scavenger to hydrazine, offering the advantages of very low toxicity and the vola-
tility of a neutralizing amine. Like hydrazine, amine-based compounds also promote the formation of a passive magnetite film on low carbon steel (CS) surfaces, minimizing cor-
rosion in the system.11 Amine-based water treatment has numerous beneficial proper-
ties as an oxygen scavenger in boiler feed-
water systems: protects by forming a thin magnetite oxide (Fe₃O₄) layer; prevents lime scale or minerals on surface installations; removes old deposits without causing dam-
age; disperses impurities, inorganic salts, and oxides of iron; alkalinizes vapor net-
works, 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 (<1.0 mpy). In low to moderate pressure industrial boiler systems, an initial feedwater inhibitor dosage of 100-500 mg/L is recommended.17 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.

### Volatile Corrosion Inhibitors

Volatile corrosion inhibitors (VCIs) are compounds transported in a closed loop environment to the site of corrosion by vol-
utilization 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 (CO₂) or by shifting surface pH toward less acidic and corrosive values.15-18, 20-25 In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohex-
ylamine, cyclohexylamine, and hexamethy-
lene-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 quali-
ties depend on the volatility of these com-
pounds; fast action wanting high volatility while enduring protection requires low vol-
tility 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 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. 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, prevent-
ning corrosion; reduce corrosion byproduct transport to the boiler, minimizing the potential for boiler deposition and under-deposit corrosion; improve equipment reli-
ability and efficiency; and minimize overall condensate system corrosion, reducing the related maintenance costs.

### Research Objectives

Corrosion of the steam/watertside inte-
riors during the various stages of the steam cycle is a major problem for steam-generat-
ing and power plant operators. The industry standard for corrosion protection in operat-
ng systems is the use of hydrazine required to be limited per the European Union. 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 con-
densate system. The purpose of this investig-
agation was to compare the performance of the new amine-based VCI vs. the hydrazine capabilities to provide corrosion protection for the boiler steam/water system internal surfaces through the phases of the steam sys-
em (water, transition, steam). Prior to investi-
gating this new VCI in a closed loop system, some preliminary testing was conducted at high temperature (roughly 182 °C [357 °F]) to determine when it would start to boil; the hydrazine boiling point is 114 °C (238 °F). The assumption was that if hydrazine can survive the steam cycle, then this new VCI

#### 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).
VAPOR PHASE CORROSION INHIBITORS

should provide effectiveness and good functionality in those conditions. The auto-ignition temperature for both hydrazine and new VCI is around 288 to 293 °C (553 to 555 °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 118 °C (245 °F). The objectives were to investigate electrochemical behavior of CS 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); and 3) in steam/water closed loop system with VCI and without inhibitor (control-reference). Post-test evaluation was conducted by scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) analysis and x-ray photoelectron spectroscopy (XPS) analysis of surface conditions for samples with inhibitor.

Experimental Procedure
Corrosion behavior of 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 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 at elevated temperatures. Corrosion behavior of CS pipe samples was assessed during complete immersion in boiling water while exposed to the new VCI and without inhibitor (control sample). Apparatus for testing was similar to that recommended in ASTM G12327 (Erlenmeyer flask and condenser, hot plate to maintain solution at its boiling point, Figure 1). These tests were conducted in control solution (filtered water, no inhibitor), with 50, 100, 200, and 500 mg/L VCI addition. Test duration was ~700 h.

The steam/water loop system included a Chromalox electric boiler and steel pipe loop. The system is a safe and versatile heat source to produce low- or high-pressure steam (~100 psi). A closed loop system was assembled that can circulate and maintain steam at 118 °C and 90 psi. Tests were conducted on the control (no inhibitor was used) for a duration of 1,100 h. Test duration for the 100 mg/L VCI was 2,200 h. 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, SEM/EDS analysis, and XPS analysis were performed after 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 Discussion
Electrochemical polarization behavior of the steel pipes in different concentrations of corrosion inhibitors at different temperatures are shown in Figure 2. Results indicated that the new VCI is an anodic corrosion inhibitor capable of lowering corrosion rate and expanding the passivation range for steel pipe in the working condition of hot steam/water systems. The corrosion rate based on the cyclic polarization test results were as follows: for the control, 17.2 μA/cm² (7.91 mpy); in the presence of 100 mg/L VCI, 4.73 μA/cm² (2.18 mpy); and when a 200 mg/L VCI was added to solution, the corrosion rate decreased to 2.86 μA/cm² (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 behavior of the steel pipe sam-

°Trade name.
samples in boiling water are shown in Figures 1 and 3. Corrosion rates were monitored for 700 h of continuous immersion at boiling temperature. The corrosion rate was 5.3 mpy (determined from weight loss measurement) for the steam environment with no inhibitor. When 50 mg/L of VCI was added, the corrosion rate decreased to 1.94 mpy and for 100 mg/L VCI addition, 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 corrosion rates for the solutions with different amounts of VCI had become steady at roughly 120 h (corrosion rate showed a logarithmic rate) while the nonprotected steel samples showed an increasing trend for the corrosion rate. From observation, the nonprotected steel samples (control-reference) showed heavy corrosion attack with hematite (Fe₂O₃) (brown color solution, an indication of heavy rust formation). To the contrary, the presence of VCI in low dosages (50 to 100 mg/L addition) resulted in an oxide formation of magnetite (Fe₃O₄) and no significant change in solution color was observed. At higher dosages (200 to 500 mg/L), no color change was observed on the metal surfaces or their solutions, which correlates with the (measured) low corrosion rates.

Elevated temperature corrosion tests on CS pipe samples in the steam/water loop with VCI and without inhibitor (control reference) were conducted using the electric boiler steam/water in a closed loop system that could circulate and maintain hot steam at 90 psi and 118 °C. The control reference test (without inhibitor addition) was conducted for 1,100 h and the corrosion rate was monitored using 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 to 8.9 mpy.

After 1,100 h, 500 mg/L of VCI was injected into the closed loop system. This addition resulted in a significant drop in the corrosion rate to 0.72 mpy. This indicates that the VCI had successfully retarded the corrosion reaction and managed to stabilize formation of protective magnetite on the internal surfaces. The corrosion test in the steam/water closed loop was continued for 1,900 h in total (800 h beyond introduction of inhibitor to the 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 also shows the corrosion rate over time for the corrosion test in the steam/water closed loop with 100 mg/L VCI addition for 2,200 h. The average corrosion rate was measured at 1.09 to 1.24 mpy. During the boiler drainage (blowout), no sign of any rust formation in the discharged water was observed.

Figure 5 shows the comparison of the ER probes that were used to monitor corrosion rate during these investigations. Figure 6 shows the comparison of corrosion rate measurements for the inhibitor treated loop and control reference after 2,200 h corrosion test in hot steam/water closed loop. The nature of the surface oxide was compared after 2.0 mm of the top surface deposits were etched to reveal ambient changes or accidental surface contamination. XPS data showed that the oxide on the internal surface of the control sample (no inhibitor) is hematite, Fe₂O₃, with binding energy 710.4 eV, while the oxide on the
inhibitor-treated pipes is magnetite oxide, \( \text{Fe}_2\text{p} \) with a binding energy of 708.2 eV (Figure 8). These observations reaffirmed that VCI 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 CS pipe material samples in a steam/water loop with and without VCI was investigated. Electrochemical polarization behavior showed the VCI is an anodic corrosion inhibitor and when present in the environment, expands the region of stability of a magnetite \( \text{Fe}_3\text{O}_4 \) 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 VCI was added, it decreased to 1.94 mpy; and for 100 mg/L addition, the corrosion rate dropped to 1.36 mpy. The addition of 200 mg/L reduced 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. In boiling water, corrosion rates for the reference steel sample was ~5.3 mpy; for 100 mg/L hydrazine addition, the corrosion rate was 1.46 mpy; and for 500 mg/L hydrazine addition, a 0.38 mpy rate was achieved.

Corrosion behavior of CS pipe material samples in a steam/water loop with VCI and without inhibitor in a closed loop system of 90 psi at 118 °C showed a corrosion rate of 8.2 to 8.9 mpy; while the corrosion rate in the 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 the closed loop system after 1,100 h, the corrosion rate dropped to 0.72 mpy. This indicates that the VCI successfully retarded corrosion reactions and managed to form stable protective oxide of 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, while the oxide on the inhibitor-treated pipes was magnetite oxide. These observations reaffirmed that the VCI 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 control performance.

In summary, this investigation confirmed that the new VCI can be an effective replacement for the toxic hydrazine for steel materials exposed to hot steam/hot environments. 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 of the LD50 “Lethal Dose” of the new VCI is 2,190 mg/L for rats. Hydrazine has an LD50 of only ~15–22 mg/L, indicating a very high toxicity.

The new amine-based VCI corrosion inhibitor is very promising and can reduce environmental impact, improve the work environment, reduce deposition that minimizes the frequency of chemical cleaning for through-flow boilers, and reduce pipe wall thinning due to flow-accelerated corrosion.

References

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