

Volatile Corrosion Inhibition of Stress Corrosion Cracking in a Steam Turbine

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The accumulation of damage caused by localized corrosion, pitting, stress corrosion cracking, and corrosion fatigue in low-pressure steam turbine components such as blades, discs, and rotors has been consistently identified as the main cause of turbine failure. The development of effective localized corrosion inhibitors is essential for the successful avoidance of unscheduled downtime in steam turbines or other complex industrial and infrastructure systems. Commercially available inhibitors were investigated for their effectiveness in reducing and controlling the steel equipment's susceptibility to corrosion.

Steam turbines and other complex industrial systems are susceptible to stress corrosion cracking (SCC) and other forms of corrosion because of the hostile environments in which they operate. The majority of damage occurs during shutdown periods because of chemistry changes and stagnant conditions in localized areas. The environmental changes during the shutdown period are the primary contributing factors that determine the probability of blade and disc failures in low-pressure steam turbines. Oxygen, chlorides, temperature, pH, and time spent under aerated conditions during the shutdown period increase the likelihood of localized corrosion attack. Increases in Cl^- concentration and pH changes affect the stability of protective oxides, and eventually pitting, SCC, and corrosion fatigue (CF) can occur.

In general, it is believed that by lowering Cl^- below 35 ppm, the susceptibility to localized corrosion decreases significantly. If chloride concentration on the surfaces is reduced immediately upon shutdown, this will provide a corrective strategy for minimizing or even eliminating the failure of discs and blades. This is most easily accomplished by washing the blade and disc surfaces with chloride-free water immediately upon shutdown of the turbine. In fact, an even more effective strategy would be to combine turbine surface washing with dehumidification or nitrogen blanketing.

For the accessible surfaces, this strategy can work, but for the restricted geometries such as crevices, notches, and cavities, reaching these surfaces is very difficult and it is dangerous to assume that those areas have been washed effectively. Accumulation of corrosive species and pH changes inside these restricted geometries can alter the electrochemical reactions to initiate pitting or crevice corrosion that eventually leads to SCC and CF.

Low-pressure rotors are typically constructed of forgings conforming to ASTM A470,¹ 3.5NiCrMoV (Class 2 to 7). Shrink-on discs are made of ASTM A471² (Class 1 to 3). The strength and hardness of turbine components must be

limited because the stronger and harder materials become very susceptible to SCC and CF, particularly turbine rotors, discs, and blades. The crack propagation rate increases with yield strength and hydrogen embrittlement (HE) can occur. This susceptibility limits the use of high-strength materials for turbine discs in power plants (a yield strength <140 ksi [965 MPa] is recommended). However, in turbo machinery, the common impeller and turbine are 7xxx series high-strength aluminum alloys, mainly 7050 (UNS A97050) forged aluminum alloy. Some of the main reasons for selecting this alloy for turbine applications are light weight, toughness, and corrosion resistance. However, residual stresses induced by the heat treatment in conjunction with those from the machining process make these materials sensitive to SCC. To improve SCC and CF resistance, this alloy is used in T74 tempered condition. Corrosion protection is critical to maintain the functionality of these systems.

Vapor Phase Corrosion Inhibitors

Several groups of organic compounds have corrosion inhibiting effects for different alloys. The extent of adsorption of an inhibitor depends on many factors: the nature and surface charge of the metal, the inhibitor adsorption mode, and the inhibitor's chemical structure. The presence of heteroatoms (oxygen, nitrogen, sulfur, phosphorus), triple bonds, and aromatic rings in the inhibitor's chemical structure enhance the adsorption process. Coating-to-substrate adhesion and the diffusion of water and other species from an external environment to the coating/substrate interface are critical factors for the corrosion inhibition of organic protective coatings.

One possibility for turbine materials protection is a volatile corrosion inhibitor (VCI), where protective vapors deposit on the exposed surfaces, including cracks and crevices, and condense to form a thin barrier of tiny crystals. The crystals dissolve when in contact with water, causing the adsorption of a monomolecular coat-



Turbine machinery blades.

ing to the metal surface that helps repel water. A VCI can also neutralize the pH and other corrosive species, which is an effective way to adjust the localized chemistry inside a crevice, pit, or crack.

VCIs are often a complex mixture of amine salts and aromatic sulfonic acids that provide direct contact inhibition and incorporate volatile carboxylic acid salts as a vapor phase inhibitor for metal surfaces not sufficiently coated. The thin polar layer of surfactants is tightly bound to the metal surface through chemisorption. Between this thin polar layer and the corrosive environment is the thicker barrier layer of hydrocarbons. The sul-

fonate part of the inhibitor displaces water from the metal surface and promotes chemisorbed inhibitor to the surface. A surface-active inhibitor component will be strongly chemisorbed or adsorbed to the surface.³ Active sites having energy levels complementary to the energy levels of the polar group form a tighter, more uniform layer over the metal surface.

The barrier layer has three important characteristics: 1) low permeability by moisture and other corrosives, 2) compatibility with the oleophilic ends of the polar layer molecules so that the barrier is held firmly in place, and 3) good solubility in

FIGURE 2



Steam turbine system.

the carrier to attach the polar and barrier layers to the metal surface.⁴The VCI film barrier replenishes through further evaporation and condensation of the inhibitor on the metal surface.

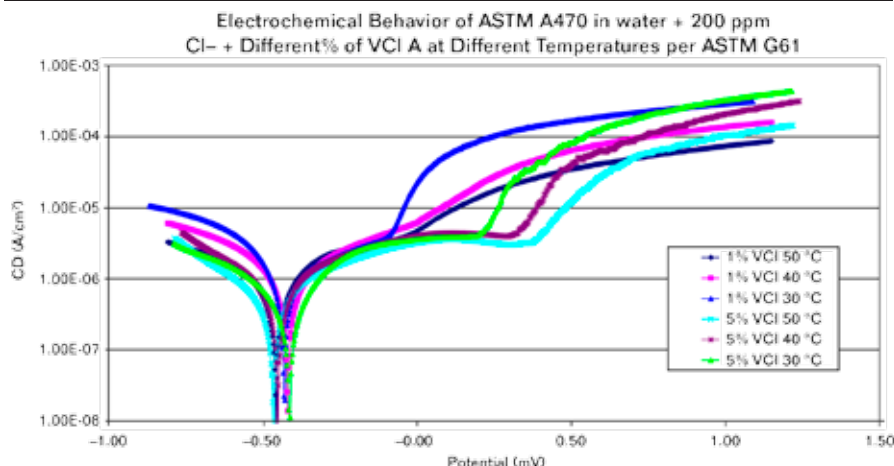
Turbo Machinery Maintenance

Turbo machinery systems (Figures 1 and 2) have regular service maintenance and unexpected shutdowns. During scheduled maintenance, components are frequently washed to dilute or remove any surface contaminants, such as salt, dirt, grease, and oil. There are three main types of cleaning: aqueous, organic solvent, and abrasive. Aqueous cleaning covers a wide variety of methods, including the use of detergents, acids, and alkaline compounds. The proposed inhibitors investigated in this program are heavy-duty, biodegradable, water-based alkaline cleansers and degreasers. The compounds function by altering hydrocarbons (grease) so that the deposits can be removed with water. Any conventional equipment (power washers, steam cleaners, dip tanks) can be used for multi-metal corrosion protection. Ethoxylated alcohols, the active ingredient in the inhibitors, are based on short-chain alcohols giving fast penetration of soil and improved performance on hard surfaces.

Adsorption Isotherm Models

An adsorption isotherm is a mathematical function that relates to the coverage of a chemical on a surface (usually a metal) to the concentration of the chemical. Identification of the surface adsorption isotherm is important in that it and classical thermodynamics can lead to the determination of a mechanism. It is assumed that the corrosion current density (CD), which is directly related to the corrosion rate, is representative of the number of corrosion sites. Therefore, adding inhibitor to the environment should diminish the number of corrosion initiation sites by displacing water molecules on the

FIGURE 3



Electrochemical polarization behavior of A470 steel in different percentages of VCI A solutions.

surface with inhibitor molecules, thereby decreasing the corrosion rate. By measuring the CD of a solution with no inhibitor (blank) and an inhibited solution (or by measuring the polarization resistance), the surface coverage, θ , can be defined by the following formula:

$$\theta = \frac{I_{\text{corr}}(\text{B}) - I_{\text{corr}}(\text{I})}{I_{\text{corr}}(\text{B})} \quad \text{or} \quad \theta = \frac{\frac{1}{R_p(\text{B})} - \frac{1}{R_p(\text{I})}}{\frac{1}{R_p(\text{B})}} \Rightarrow$$

$$\theta = \frac{R_p(\text{I}) - R_p(\text{B})}{R_p(\text{I})} \quad (1)$$

where $I_{\text{corr}}(\text{B})$ and $R_p(\text{B})$ are the corrosion current and polarization resistance of the blank solution, respectively. $I_{\text{corr}}(\text{I})$ and $R_p(\text{I})$ are the corrosion current and polarization resistance for the inhibited solution, respectively.

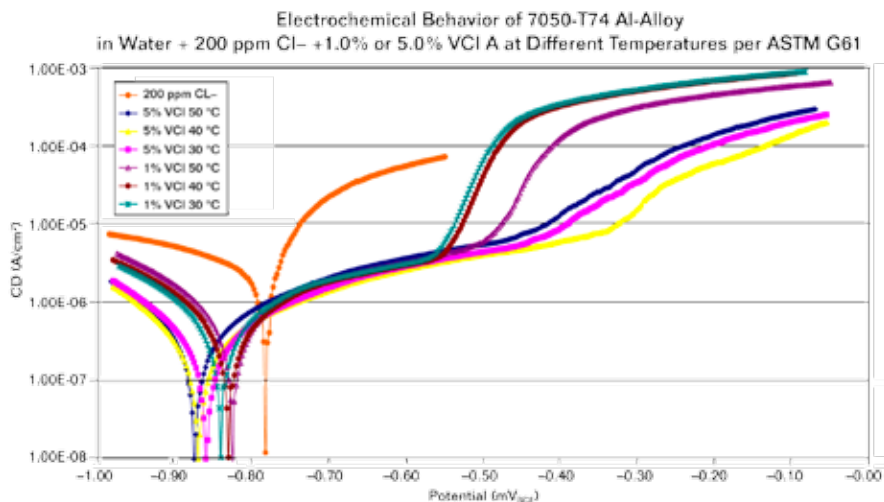
Experimental Procedures

Corrosion inhibition of VCI 337[†] (VCI A) and Ecoline 3690[†] (VCI B) were investigated for 7050 aluminum alloy and ASTM A470 steel in the turbo expander and steam/gas turbines industry. The A470 steel is common for constructing low-pressure steam turbine discs and rotors. Its chemical composition contains 3.5% Ni, 1.5% Cr, 0.8% Mo, and 0.25% V. The samples for investigation were annealed for 24 h and air-cooled. A Rockwell C hardness of 32 was achieved after heat treatment. The 7050 alloy contains 6.5% Zn, 2% Mg, and 2% Cu that was used in T74 tempered condition. Rockwell B hardness was 82 to 84, while electrical conductivity was 38% IACS (International Annealed Copper Standard).

Electrochemical polarization per ASTM G61⁵ was used to evaluate the electrochemical behavior of these inhibitors on the A470 steel and 7050 alloy. These techniques can provide useful information regarding the corrosion mechanisms, corrosion rate, and localized corrosion susceptibility of the material for a given environment. The studies were conducted using a Gamry PC4/750[†] potentiostat/galvanostat/zero resistance

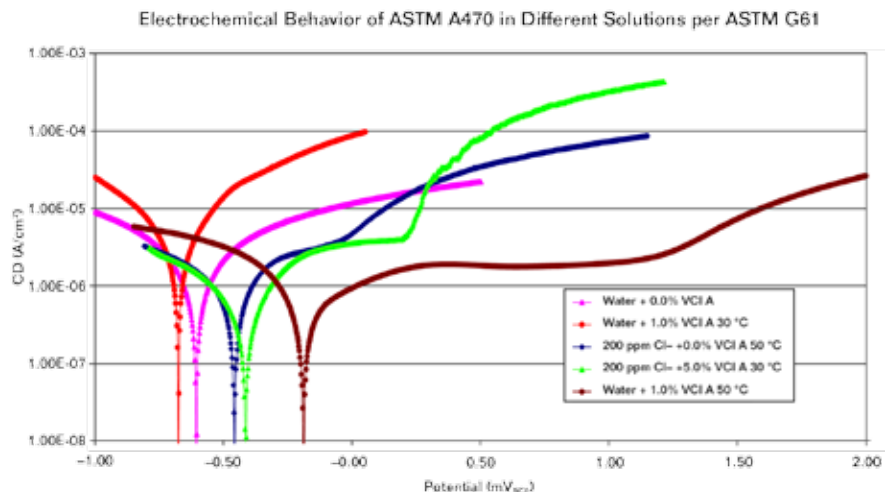
[†]Trade name.

FIGURE 4



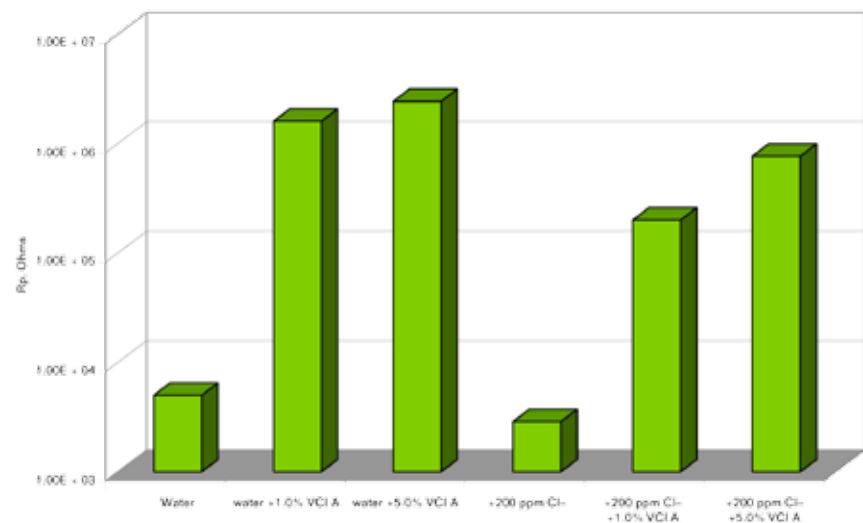
Effects of temperature on the electrochemical polarization behavior of 7050-T74 alloy in different percentages of VCI A solutions.

FIGURE 5



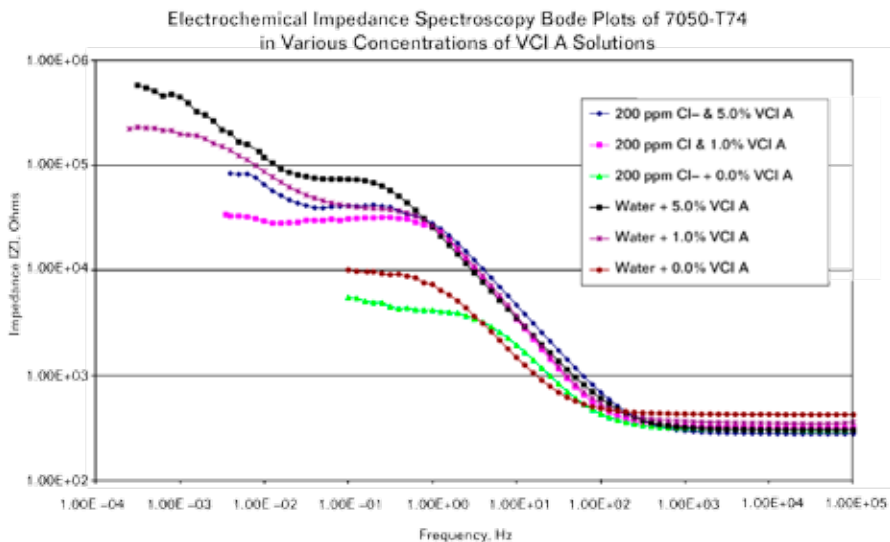
Electrochemical polarization behavior of A470 steel in different percentages of VCI A solutions.

FIGURE 6



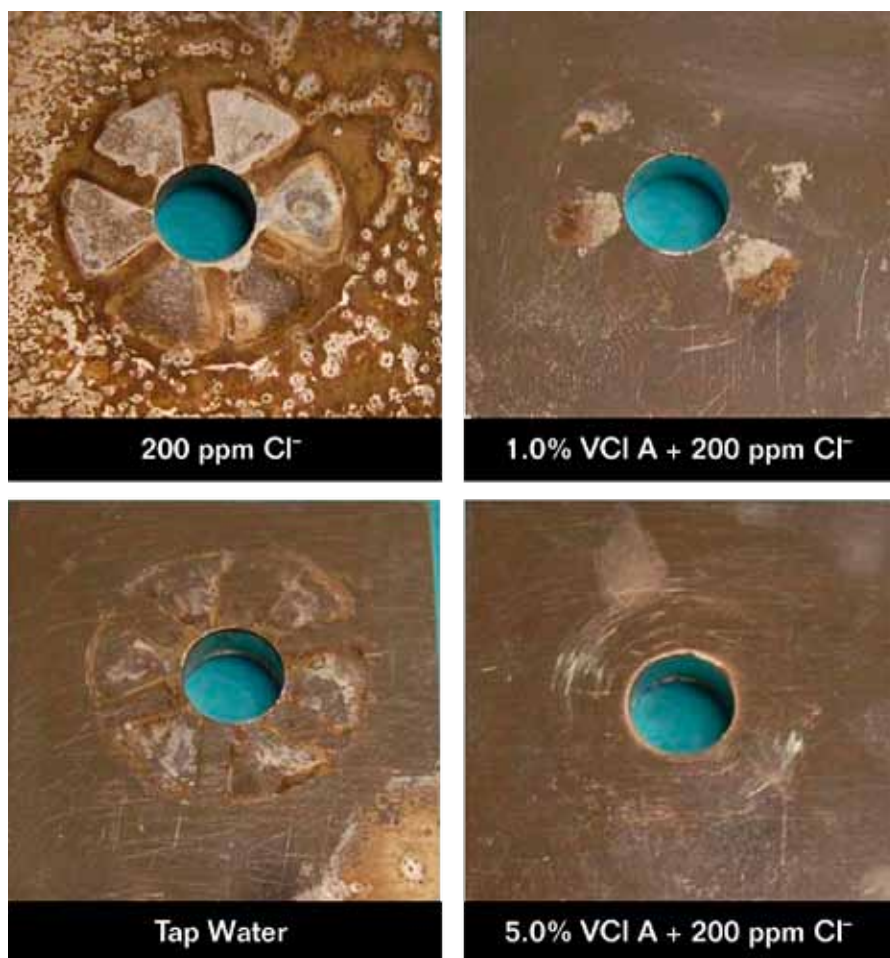
Effects of VCI A on the resistance polarization of ASTM A470 in different solutions.

FIGURE 7



EIS Bode plots of 7050-T74 alloy in various concentrations of inhibitor VCI A.

FIGURE 8



Crevice corrosion tests on 7050-T74 alloy in alternate immersion for 200 h.

ammeter and DC105[†] corrosion test software. These alloys were tested in a solution of 1.0% and 5.0% inhibitor with 200 ppm Cl⁻. A series of cyclic polarization tests was performed to investigate the effect of temperature on the VCI/metal behavior. For the cyclic polarization tests, samples were polished with 600 grit sandpaper, placed in a flat cell, and tested in different inhibitor concentrations of deionized water and 200 ppm Cl⁻ solutions.

The potentiostat with electrochemical impedance spectroscopy (EIS) software (EIS300[†]) was used to further investigate the inhibitor effectiveness on these alloys and gather data for adsorption isotherms in different inhibitor concentrations of deionized water plus 200 ppm Cl⁻. Electrochemical impedance was measured by applying a sinusoidal signal to an electrochemical cell and measuring the current. The Rp value (determined from the Bode plot) was used to fit the data into adsorption isotherm models.

Crevice Corrosion Investigation

Both the A470 and 7050 alloys were tested in an eight-station alternate immersion system. The samples were immersed in various concentrations of corrosion inhibitor, sodium chloride (NaCl), and tap water. Alternate immersion, an aggressive procedure, was performed to evaluate the inhibitors' ability to resist crevice corrosion. The testing cycle immersed the samples for 10 min, then exposed them to air for 50 min per ASTM G44⁶ and G47.⁷ After 200 cycles of testing, the samples were disassembled, examined, and photographed to document crevice corrosion resistance.

SCC Investigation

The slow strain rate tests were conducted on cylindrical samples under controlled electrochemical conditions using a strain rate of $5 \times 10^{-7} \text{ sec}^{-1}$. To evaluate an inhibitor's effectiveness, these alloys were tested in a 1.0 and 5.0% VCI solution (a typical concentration

[†]Trade name.

recommended to retard corrosion attack) and the reference samples were tested in tap water and +200 ppm Cl⁻ solutions without inhibitor. To determine the degree of inhibitor effectiveness, anodic potentials of -400 mV vs. saturated calomel electrode (SCE) (for the 7050 alloy) and -200 mV vs. SCE were applied to the samples during the test. These potentials are close to the passive film breakdown potentials for these alloys, and are the most critical range of potential to initiate localized corrosion. Twenty-four tests per alloy were completed to assess the degree of SCC susceptibility of each alloy in different solutions.

Results

Cyclic Polarization Behavior

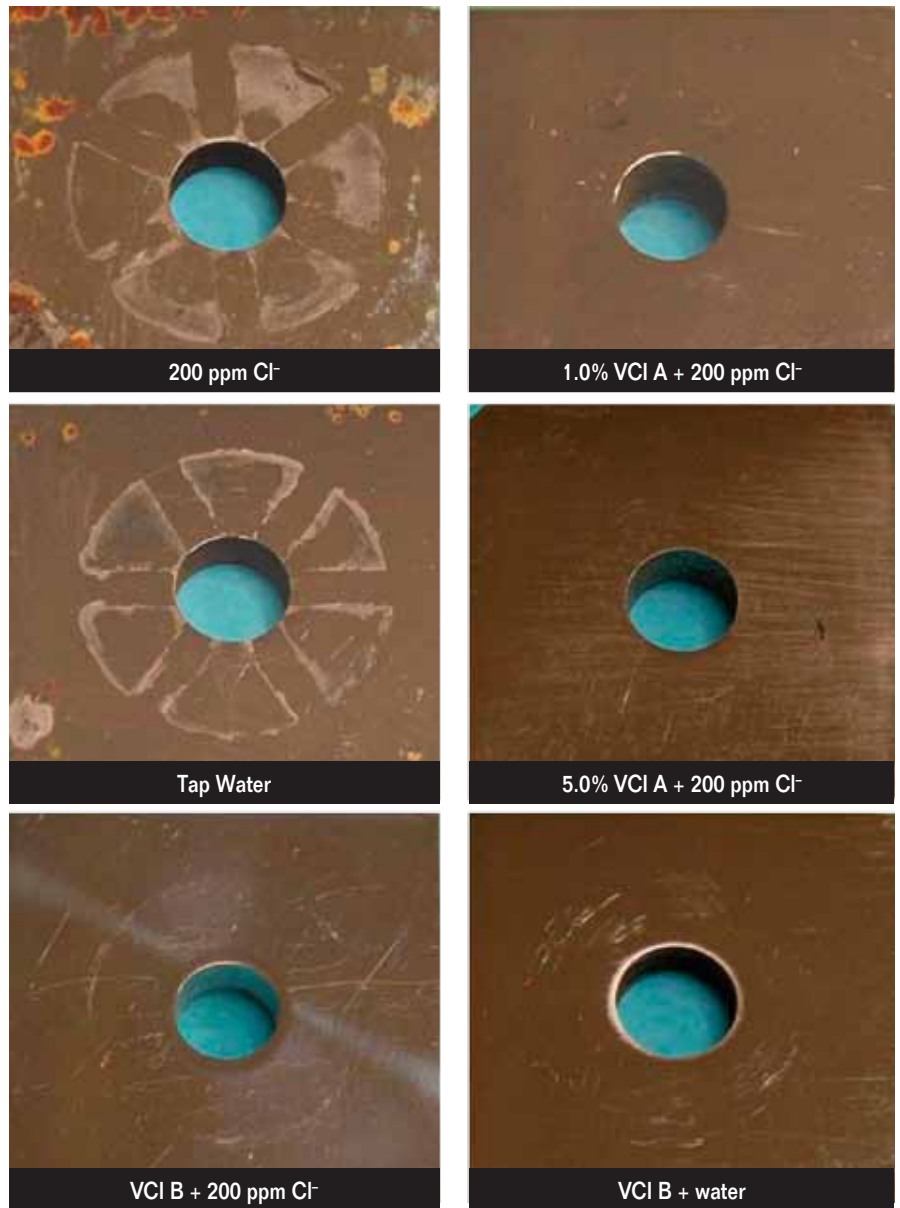
Figures 3 to 6 and Tables 1 to 3 show the polarization behavior of both alloys in different solutions. Most noticeable changes are the positive shift in the breakdown potentials by more than +500 mV for alloys in the VCI A inhibitor solutions. The inhibitor altered the electrochemistry, increased the passivation rate significantly, and had beneficial consequences for reducing localized corrosion. As demonstrated in the polarization curves, extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range, resulting in a more stable passive film.

Figure 7 shows EIS test results of the 7050 alloy in different solutions and inhibitor concentrations. VCI B increased the resistance polarization. The increased polarization resistance can be attributed to the film formation on the metal surfaces and neutralizing of corrosive species. However, it appears that VCI A is more protective on A470 steel. Similar inhibition effectiveness was observed for VCI B.

Crevice Corrosion

Figures 8 and 9 show photos of 7050-T74 aluminum alloy and A470 samples, respectively, after 200 h of alternate immersion in various solutions. The samples immersed in tap water and +200 ppm Cl⁻ show severe corrosion damage. The corrosion damage was reduced with the addition of inhibitor to the environments

FIGURE 9



Crevice corrosion tests on A470 in alternate immersion for 200 h.

TABLE 1

CYCLIC POLARIZATION (ASTM G61) AND EIS (ASTM G106⁸) CORROSION TESTS ON ASTM A470 (3.5 NI-1CR-1MO-0.25V) AND 7050 AL-ALLOYS IN DIFFERENT SOLUTIONS OF VCI A AND VCI B.

Environment	Inhibitor Concentration, %	# of Tests Each Alloy
Water	0.0	4
Water + ppm Cl ⁻	0.0	4
Water	1.0	4
Water + 200 ppm Cl ⁻	1.0	4
Water	5.0	4
Water + 200 ppm Cl ⁻	5.0	4

TABLE 2

CREVICE CORROSION TESTS ON ASTM A470 (3.5Ni-1Cr-1Mo-0.25V) AND 7050 Al-ALLOYS USING ARTIFICIAL CREVICE SAMPLES IN DIFFERENT SOLUTIONS, ALTERNATE IMMERSION TEST ASTM G48⁹ AND ASTM G44

Environment	VCI A Concentration, %	# of Tests Each Alloy
Water	0.0	2
Water + ppm Cl ⁻	0.0	2
Water	1.0	2
Water + 200 ppm Cl ⁻	1.0	2
Water	5.0	2
Water + 200 ppm Cl ⁻	5.0	2

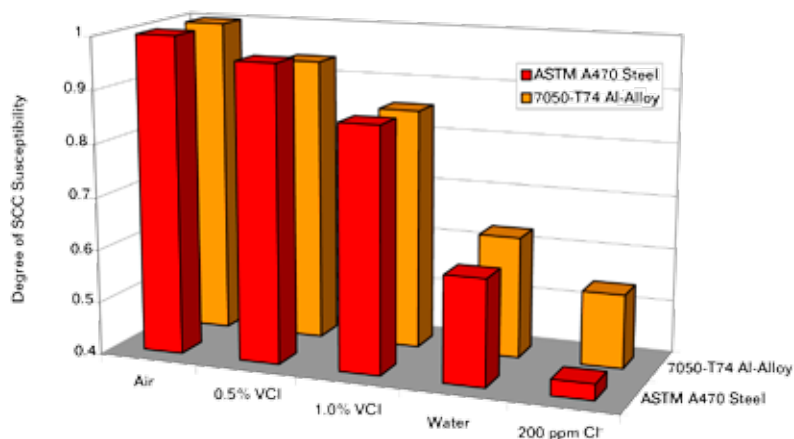
TABLE 3

CREVICE CORROSION TESTS ON ASTM A470 (3.5Ni-1Cr-1Mo-0.25V) AND 7050 Al-ALLOYS USING ARTIFICIAL CREVICE SAMPLES IN DIFFERENT SOLUTIONS, ALTERNATE IMMERSION TEST ASTM G48 AND ASTM G44

Environment	VCI A Concentration, %	# of Tests Each Alloy
Water	0.0	2
Water + ppm Cl ⁻	0.0	2
Water	coated	2
Water + 200 ppm Cl ⁻	coated	2

FIGURE 10

Slow Strain Rate Tests on 7050-T74 Al-Alloy ($-400\text{ mV}_{\text{SCE}}$) and ASTM A470 ($-200\text{ mV}_{\text{SCE}}$), ASTM G128, in Different Solutions at 5×10^{-7}



Comparison of SCC susceptibility of ASTM A470 and 7050 in different solutions.

(solutions). The passive film stability improved the corrosion resistance for the inhibitor-treated samples. Coated samples with VCI B did not show any corrosion attacks. Due to the hydrophobic nature of this inhibitor, aggressive species could wet the surface and still have corrosion protection.

Stress Corrosion Cracking

Susceptibility to SCC was determined for these two alloys using the slow strain rate test per ASTM G128.¹⁰ At applied potentials close to the passive film breakdown potential, a noticeable increase in susceptibility was seen for the samples tested without inhibitor. The greatest reduction in the degree of susceptibility is seen around -200 mV vs. SCE for the A470 steel and around -400 mV vs. SCE for the 7050-T74 alloy. Figure 10 shows a comparison of the SCC susceptibility of the A470 steel and 7050 alloy in different solutions.

Verification of the Inhibition Mechanism

The corrosion inhibition mechanism of VCI A was investigated using the data acquired from the EIS tests. EIS, when modeled correctly, is a powerful tool for the analysis of complex electrochemical systems. A modified Randles model was used to obtain the polarization resistance (R_p) values. The Bode plots showed that VCI increases the polarization resistance of both alloys, with higher concentrations resulting in higher R_p values. The increased polarization resistance can be attributed to the adsorption of inhibitor molecules on the metal surfaces. The addition of inhibitor increased the R_p value from $2.8\text{ k}\Omega$ for A470 in the blank solution (0 ppm concentration) to $220\text{ k}\Omega$ for 1.0% VCI, and $766\text{ k}\Omega$ for 5.0% VCI in solution. The high R_p value is due to the progressive adsorption of inhibitor molecules and film formation on the metal surface. The data obtained from the EIS experiment best fit the Lang-

muir adsorption isotherm, where $\ln(\theta)$ (concentration) vs. $[\ln \theta - \ln(1 - \theta)]$ resulted in good linearity.

The analysis on VCI A showed the enthalpy of adsorption to be about -14 to -18 kJ/mol; this suggests that this product is borderline between a strong physisorption and a weak chemical adsorption to the metal surface. Generally, chemisorption makes strong bonding between the inhibitor and the surface of the substrate, resulting in a more stable protective film. But, the majority of corrosion damage to turbo-machinery systems occurs during shutdown periods due to chemistry changes and stagnant conditions in localized areas; therefore, a strong physisorption corrosion inhibitor will provide satisfactory protection.

Conclusions

A comprehensive investigation was undertaken to characterize the corrosion behavior of turbo-machinery systems in VCIs. Effectiveness of the inhibitor was confirmed with electrochemical impedance spectroscopy and cyclic polarization in room temperature and elevated temperature studies. As well, identification of the adsorption mechanism and corrosion activation energy was explored. The data acquired from EIS tests showed that inhibitor adsorption to these alloy surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption is about -14 to -18 kJ/mol, suggesting that this product is a strong physisorption or at least a relatively weak chemisorption compound.

Cyclic polarization behavior for samples in the VCI showed a shift in the passive film breakdown potential by roughly $+500$ mV. This increase in the passive film range will improve localized corrosion resistance. Crevice corrosion test results showed improved corrosion inhibition behavior compared to unprotected samples. The SCC studies revealed significant reduction in SCC susceptibility in environments with added VCI. Furthermore, ductile overload

failure mode was observed for the alloys tested in 5% VCI A and VCI B inhibitor solution. In summary, both VCI A and VCI B provide effective corrosion protection for both A470 and 7050 alloys during the shutdown period for blades and discs in low-pressure steam turbines.

Acknowledgements

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