VCI Technology in Chloride-Containing Electrolytes at Elevated Temperatures

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Industrial objects, facilities, and equipment are often damaged by harsh weather conditions. When a nuclear power plant experiences some damage and overheating, seawater may be used to cool the nuclear fuel. This article discusses the study of the effectiveness of vapor phase corrosion inhibition on carbon and stainless steel, brass, and aluminum under these conditions.

Vapor phase corrosion inhibitors (VCIs) may often be a complex mixture of volatile bases or their salts containing weak acids (e.g., carboxylic acids), which may have contact film-forming components. Such substances can be transported from their source, through the vapor phase and contact metal to form a protective adsorption layer. These substances also can be combined with other organic or nonorganic inhibitors to enhance corrosion protection in the liquid phase.

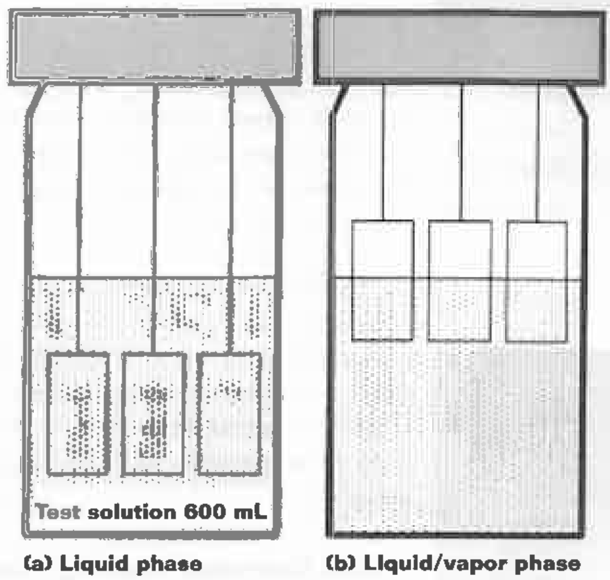
Surface-active inhibitor components will strongly adsorb at active sites having energy levels of the polar groups, thereby forming a tight, uniform protective layer over the metal surface.[1-2] Specific VCIs protect the majority of metals from corrosion including ferrous, yellow, and aluminum and will significantly delay the development of stress and crevice corrosion.[3] Although stainless steel (SS) is used for corrosion resistance, it can also suffer from pitting, stress corrosion, and cracking corrosion in electrolytes with high concentrations of chlorides, especially under elevated temperatures.[4]

TABLE 1

Components of artificial seawater

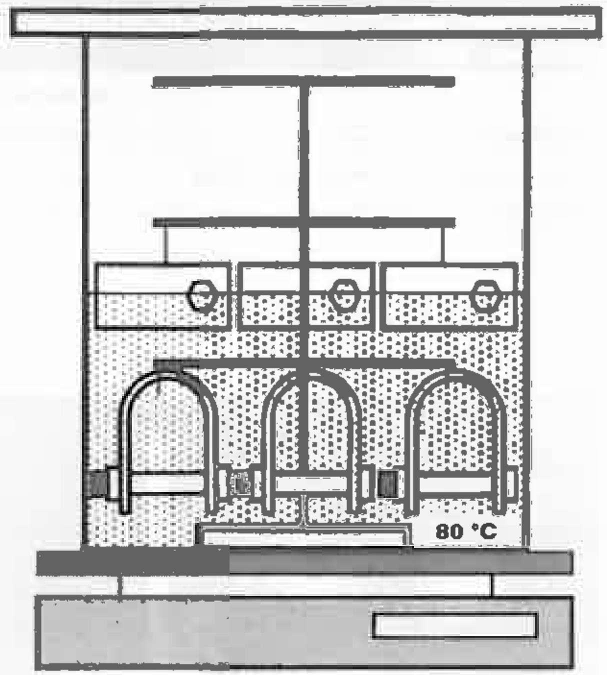
Magnesium chloride ($MgCl_2$) ($6H_2O$): 222.2 g
Calcium chloride ($CaCl_2$) ($2H_2O$): 30.7 g
Strontium chloride ($SrCl_2$): 0.85 g
Potassium chloride (KCl): 13.89 g
Sodium hydrogen carbonate ($NaHCO_3$): 4.02 g
Potassium bromide (KBr): 2.01 g
Boric acid (H_3BO_3): 0.54 g
Sodium fluoride (NaF): 0.06 g
Sodium chloride (NaCl): 490.68 g
Sodium sulfate (Na_2SO_4), anhydrite ($CaSO_4$): 81.88 g
Deionized (DI) water: 19 kg

FIGURE 1



Immersion and partial immersion corrosion test setup.

FIGURE 2



SCC test setup.

Materials

Specific VCI formulas contain film formers, amino-carboxylate-based VCIs, and a triazole-based component for yellow metal protection. Different concentrations were tested from 3.3 to 20 wt%. Metal panels made from SAE 1018 carbon steel (CS) (UNS G10180), Type 304 SS (UNS S30400) heat-treated at 620 °F (326 °C) for 24 h, Type 260 yellow brass (UNS C26000), and Type 1100 aluminum (UNS A91100) were used in corrosion immersion tests. U-bend specimens for stress corrosion cracking (SCC) tests were also Type 304 SS heat-treated at 620 °F for 24 h.[5]

Immersion corrosion and SCC tests were performed in artificial seawater prepared according to a standardized formula (Table 1).

Test Methods

Electrochemical polarization tests were performed in artificial seawater and solutions of NaCl in DI water with 6,000 and 2,000 ppm of chloride ion concentrations and fresh water.

Compatibility Tests

These tests were performed to confirm that the suggested inhibitors would not be affected by radiation and would not cause precipitation or cloudiness when added to artificial seawater. This was done using different concentrations of specific VCI formulations in artificial seawater with a pH of 9 and 11. The electrolytes were filtered through No. 4 filter paper and VCIs were added at a concentration of 15 wt%. Clarity of the solutions was visually inspected and photographed.

Immersion and Partial Immersion Corrosion Tests

Three test panels were immersed or partially immersed in various solutions (Figure 1). All samples were placed in the laboratory oven, set at 80 °C for 150 h. After the completion of the test, the panels were visually inspected and photographed.[6]

Electrochemical Tests

Using Potentiostat/Galvanostat/ZRA PCI 4/300[†] and DC 105 Corrosion Techniques[†] software, tests were performed per ASTM G5[7] in a glass polarization cell with a saturated calomel as a reference electrode and high-density graphite as a counter electrode. Cylindrically shaped working electrodes were made from SAE 1010 CS and heat-treated Type 304 SS. Before testing, they were polished with 600 grit sandpaper and washed with laboratory-grade methanol.

The testing cell containing the electrolyte was placed on the hot plate and heated to 80 °C. The working electrode was then immersed into the electrolyte and left there for 1 h for preconditioning. Polarization curves were obtained in potentiodynamic and cyclic polarization modes with a scan rate of 0.2 or 0.5 mV/s.[8-9]

Pitting was electrochemically developed on the electrodes made from sensitized SS. For this purpose, electrodes were subjected to 200 mV vs. E_{corr} anodic polarization for 2 min in artificial seawater with pH 8.2. The difference between E_{corr} and E_{pit}, where E_{corr} is the

[†]Trade name.

TABLE 2

Corrosion test results on CS in artificial seawater with and without VCI

	Appearance		
Electrolyte	CS	Aluminum	Brass
Artificial seawater	Heavy, deep pitting	Heavy corrosion	Corrosion
15% VCI	Few spots on the surface	Light corrosion	No corrosion
20% VCI	One to two-surface spots	Very light corrosion	No corrosion

FIGURE 3

(a) (b)

Appearance of the CS panels after immersion in (a) artificial seawater and (b) artificial seawater with 15% VCI.

FIGURE 4

Control 15% 20%

Appearance of the aluminum panels after immersion in artificial seawater with and without VCI.

corrosion potential and E_{pit} is the potential of the pitting corrosion, was determined on polarization curves and used as the criteria of the relative resistance to pitting corrosion.[10-12]

Cyclic Polarization Curves

This test evaluated the probability of pitting propagation by analyzing the shape of the hysteresis loop. Zero or negative hysteresis means that development or propagation of pitting is unlikely.[13-14]

Stress Corrosion Cracking Test

The effect of the inhibitor on SCC was evaluated according to ASTM G30.[5] Specimens were made from Type 304 SS sensitized at 620 °C for 24 h. Steel was polished with 240 grit and bent with accessories. Specimens were immersed or half immersed in artificial seawater with added VCI (Figure 2). The solution of artificial seawater was used as a control.

Results

Compatibility Test

The requirement of the VCI was to prevent any hydrolysis or change in electrolyte at high temperatures and radiation. Testing shows that the addition of 20% VCI to artificial seawater with pH 9 or 11 did not cause changes in the appearance of the solution. It was additionally shown that the VCI solution did not change in physical or chemical properties after treatment with gamma radiation. These results were reported by the laboratory of Toshiba, Japan.

Corrosion Tests Results

Table 2 and Figures 3 through 5 show the result of the half immersion corrosion tests. Figure 3 shows that the addition of VCI decreases the pitting corrosion on CS. In Figures 4 and 5, aluminum and brass panels have no or minor changes in appearance after exposure to seawater with VCI; after testing for the same amount of time in the electrolyte without VCI, the surface is significantly corroded.

The results of the immersion and half immersion tests on Type 304 SS were not conclusive.

Electrochemical Tests Results

Corrosion Protection of Carbon Steel

Figure 6 and Table 3 show polarization curves and corrosion rate data of SAE 1018 CS in artificial seawater and seawater with VCI. Data showed that the addition of VCI lowered the rate of both cathodic and anodic electrochemical reactions on CS. At the same time, the shift of the E_{corr} in the anodic direction after addition of the VCI shows that the affect on the anodic reaction is stronger than the cathodic.[13] Table 3 shows that the corrosion rate of CS is significantly lower in seawater with VCI than in seawater without VCI.

Corrosion Protection of Stainless Steel

The means of corrosion potential (E_{corr}) and differences between corrosion potential and pitting potential ($E_{corr} - E_{pit}$) were obtained from potentiodynamic polarization curves. Figure 7 shows that by increasing the VCI concentration up to 20%, the pitting potential became more anodic, and there are similar changes in ($E_{corr} - E_{pit}$). According to the literature,[10-12] these results show that increasing the concentration of the VCI reduces the pitting on sensitized Type 304 SS with preexisting pitting.

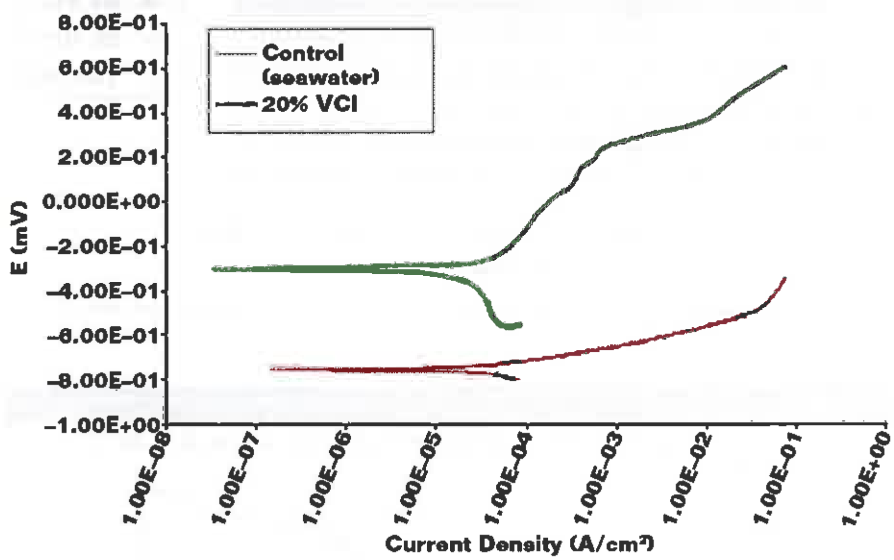
Figure 8 also shows that pitting corrosion will likely develop on sensitized Type 304 SS in water with the presence of chloride ions at concentrations ranging from 2,000 to 6,000 ppm. The addition

FIGURE 5

Control 15% 20%

Appearance of the brass after immersion in artificial seawater and artificial seawater with VCI.

FIGURE 6



Tafel polarization curves on SAE 1018 CS in seawater and seawater with VCI.

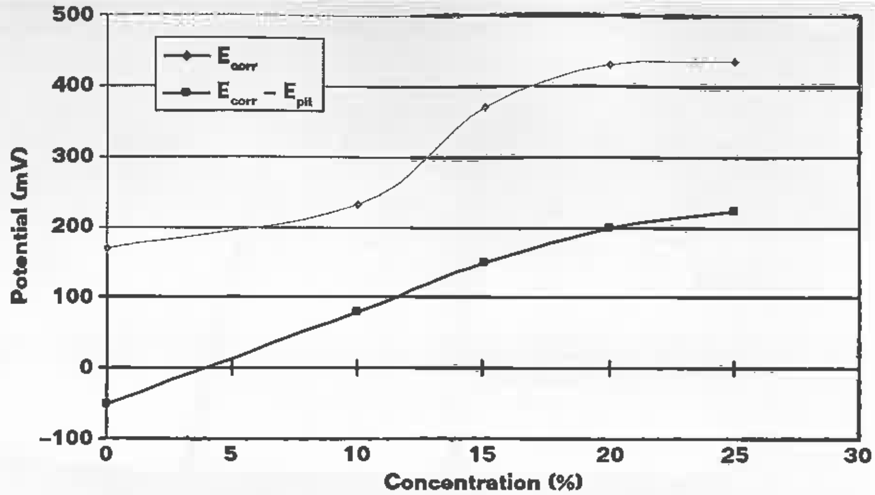
TABLE 3

Corrosion rate of CS SAE 1018 in seawater and seawater with VCI

Material	E_{corr} (mV)	Corrosion Rate (mpy)	Percent of Corrosion Protection (Z%)[A]
Control (seawater)	-751.5	118.8	—
20% VCI	-532.6	6.9 × E-3	~100

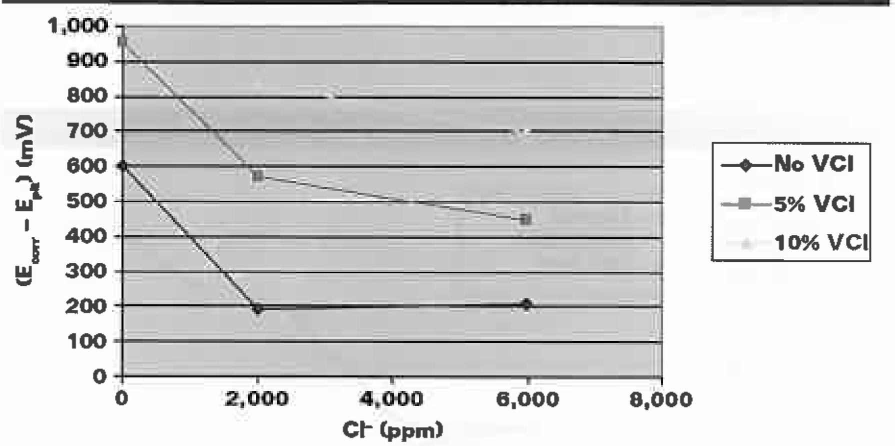
[A]Z = 100% (corrosion rate control – corrosion rate inhibitor): corrosion rate control.

FIGURE 7



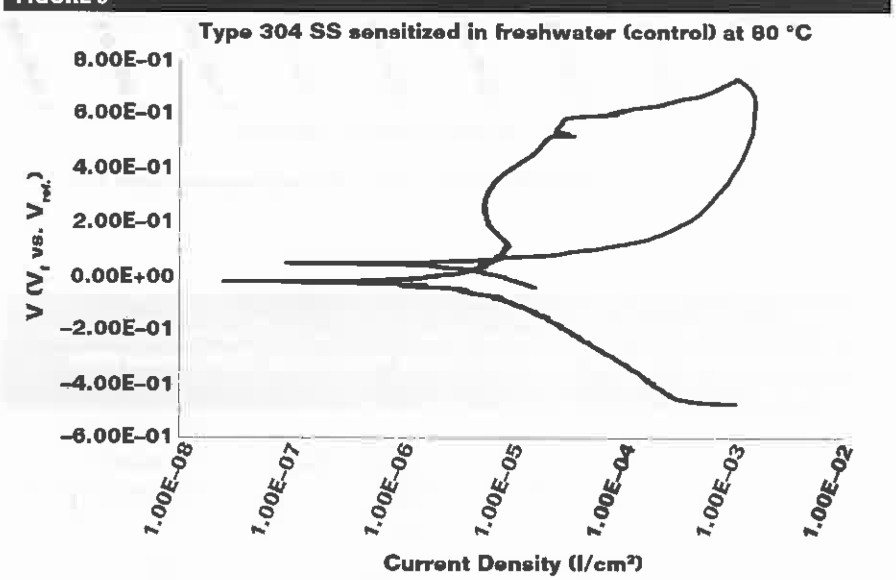
Effect of VCI concentration on pitting corrosion of sensitized Type 304 SS in seawater.

FIGURE 8



Affect of the chloride concentration on pitting corrosion of sensitized Type 304 SS in seawater.

FIGURE 9



Cyclic polarization curve of Type 304 SS sensitized with pre-existing pitting, in freshwater.

of VCI increases the difference in $E_{corr} - E_{pit}$, which leads to a reduced probability of pitting development.

Cyclic polarization curves were obtained in fresh water on Type 304 SS sensitized with pre-existing pitting (Figures 9 and 10). Analyses of the hysteresis of these curves shows that the use of the inhibitor stops pitting from further development. Without the inhibitor, the cyclic polarization curve has a positive hysteresis, which shows that the probability of the pitting propagation still exits. Another curve exhibited a negative hysteresis (the back scan shows more noble E_{corr} and lower current levels than on the direct curve).

Stress Corrosion Cracking Test Results

In the SCC test, corrosion started to develop on partially immersed U-bend samples in seawater without inhibitor at the end of the second week. After 20 days of testing, this sample showed signs of stress fracturing from corrosion above the liquid in the vapor phase (Figure 11).

All other samples that were immersed or partially immersed in the solution of seawater containing VCI showed no signs of corrosion or cracking. This test shows that the combination of the corrosive environment and mechanical tensile stress increases the corrosion rate and, in this particular case, causes SCC. Adding VCI prevents corrosion and cracking of the partially immersed U-bend sample.

Conclusions

1) Based on the test results, VCI inhibitors provide corrosion protection for CS, SS, aluminum, and brass in seawater at elevated temperatures up to 80 °C.
2) The addition of VCI to seawater protects CS and sensitized SS against pitting in the presence of chlorides.

3) VCI, when added to seawater, prevents SCC of sensitized SS.
4) VCI is not affected by gamma radiation.

Acknowledgment

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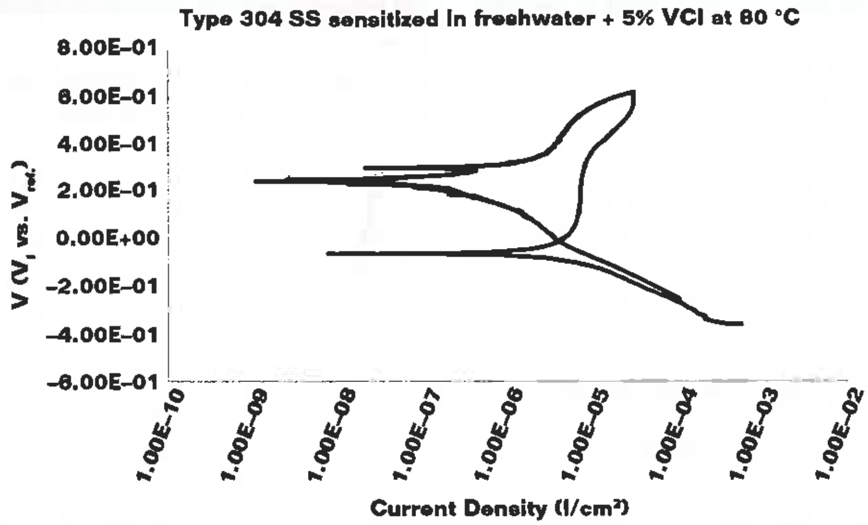
FIGURE 10



Cyclic polarization curve of Type 304 SS sensitized with pre-existing pitting, in freshwater with 5% of VCI.

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FIGURE 11

U-bend sample made from sensitized Type 304 SS after partial immersion in seawater for 20 days. The corrosion is seen on the surface with a line running across the panel where the stress crack is formed.