A green MnMgZn phosphate coating for steel pipelines transporting CO_2 rich fluids

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ABSTRACT

The transport of CO_2 rich fluids via steel pipelines in the CO_2 capture and storage (CCS) process requires a strategy for internal corrosion protection in cases where the stream is acidic and hence corrosive due to the formation of carbonic acid. Such protection strategies have been scarcely studied and will need significant research. In this study, one possibility to protect the steel pipelines from internal corrosion during CO_2 transport is presented based on treatment of the internal surface with a vanadate-based MnMgZn phosphate coating. The addition of sodium orthovanadate (Na_3VO_4) in a MnMgZn phosphate bath leads to a significant change in the microstructure of the phosphate coating, which will alter corrosion behaviour significantly. Herein, the effect of vanadate concentration (0.0625, 0.125, 0.25 mM) in the phosphate bath is studied with respect to the resultant microstructure and corrosion behaviour of the phosphate coatings. Electrochemical studies such as polarization curves and electrochemical impedance spectroscopy (EIS) were performed in diluted HCl solution at pHs 2–4 to investigate the corrosion behaviour and distinguish the dielectric and electric properties of the phosphate coating.

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1. Introduction

In CO_2 capture and storage (CCS) carbon dioxide (CO_2) corrosion is the primary factor affecting the life of steel pipelines. If the water content of a CO_2 stream is above the solubility limit then a separate aqueous phase will exist. This aqueous phase may not only permit, but also induce corrosion depending on its form and chemical composition [1]. The pH value varies depending on the water mole fraction and other additives (H_2S, SO_2, NO_3^-) in CO_2 transport. As the water contaminant mole fraction increases, the aqueous phase immersed in CO_2 stream will absorb CO_2 (at pressure 8 MPa) to form carbonic acid and drops the pH value to ~3.3 [2]. In the presence of other contaminants (H_2S, SO_2, NO_3^-) the pH value drops to <3 with a recent review indicating that high corrosion levels occur [3]. Appropriate gas cleaning prior to transport may be able to limit the level of additional contaminants, however as indicated above if an aqueous phase exists, then that aqueous phase will have a pH between 3 and 4. Thus for both CCS and for transport of oil or gas a coating that can protect pipelines at pH values below 4 is required. Wet chemistry processes could play important role in the internal protection strategy of pipelines.

Corrosion control by developing an optimum approach that includes both inspection and corrosion prevention strategies is critical to the future safety and the cost-effective operation of transmission pipelines. In pipeline manufacturing there has been considerable effort applied to protect the external surface of on-shore and off-shore pipelines from

corrosion [4–9]; however, the internal surface remains vulnerable and requires corrosion protection. Currently, different organic corrosion inhibitors (amine-based organic inhibitors) are applied to minimize the internal corrosion of carbon steel pipelines during oil and gas transport [10–15]. There is a strong need to design protection systems for reducing the inhibitor cost as well as the replacement and maintenance cost of failure in the transmission pipeline system by minimizing the internal localized CO_2 corrosion in steel pipelines.

At present there is no standard coating system for the interior surface of the pipelines, except for the use of inhibitors. The different contaminants that may be piped along with captured CO_2 may vary from source to source and drop the pH value on the surface. Four regimes with different risks of corrosion were outlined for supercritical CO_2 transport by Cole et al. [3].

A) Very low contaminant levels and extremely low water content.
B) Low contaminant levels and water content below the solubility content.
C) Low contaminant levels and water content above the solubility content.
D) Moderate contaminant levels and water content above the solubility limit.

Each contaminant level needs a specific coating system suitable for the change in pH. Choi et al. [1] found that the aqueous phase pH was between 3.1 and 3.2 for pressures from 5 to 15 MPa (50 to 150 bar) and temperatures from 32 to 42 °C. Ayello et al. [16] modelled the aqueous chemistry when additional contaminants were added to a CO_2–H_2O

mixture. In general they found that the aqueous phase in CO_2 would have a pH of 3.1 but the addition of 1 g HCl per kg CO_2 would drop the pH to -4.1 while 1 g of HNO_3 would drop the pH to -3.1.

Zinc phosphate conversion coatings are an economical and environmentally friendly technology commonly used to protect steel, Al and Mg alloy surfaces against corrosion in many industries such as automotive, steel forming and as a primer for steel and aluminium paint. Phosphate coatings enhance the adhesion of the paint to the substrates [17–20]. The structure of zinc phosphates enables them to carry and store organic and inorganic inhibitors due to their porous structure. The zinc phosphate coating has a porous structure and works with high efficiency when it is sealed with oil. This makes zinc phosphate a suitable coating for the internal surface of steel pipelines in gas and oil transport. In a previous work [21] the MnMgZn phosphate plus vanadate was considered as a possible candidate for internal protection of steel pipelines under the condition of corrosion caused only by acidification with carbonic acid (regime A). Vanadium compounds were reported as effective corrosion inhibitors in a number of anti-corrosion applications of aluminium [22–24]. Vanadium compound inhibition is due to the formation of an insoluble oxide thin film (500 nm) over a wide range of pH and environmental conditions [25–27].

The present study will report MnMgZn phosphate solution with vanadate for protecting the interior surface of pipelines with solid phosphate inhibitor. The presence of vanadate in the phosphate bath extensively affects the morphology and size of the phosphate crystals, which has an impact on increasing the performance of the phosphate coating protection by reducing the crystal size as well as acts as potential inhibitor. Electrochemical tests (polarization and EIS) were performed to investigate the coating performance with the addition of vanadate at different pH and concentration.

2. Experimental

2.1. Zinc phosphate treatment

The investigated MnMgZn phosphate bath was prepared by dissolving approximately 3.0 g zinc oxide, 0.01 g $MnCO_3$ and 0.05 g $MgCO_3$ in 2.7–3.00 ml nitric acid (C: 61%) and 3 ml phosphoric acid (C: 85%) in 100 ml de-ionized water. The phosphate bath was diluted to 1 l with de-ionized water. The bath acidity was adjusted at pH 2.5 using sodium hydroxide. Upon immersion in the phosphate bath, steel panels chemically react with primary zinc phosphate ($Zn(H_2PO_4)_2$) solution and insoluble zinc phosphate crystals (hopeite-$Zn_3(PO_4)_2 \cdot 4H_2O$) of grey colour are grown and adhere to the surface according to the following reactions:

$$\underset{\text{Primary phosphate}}{Zn\,(H_2PO_4)_2} \rightarrow \underset{\text{secondary phosphate}}{ZnHPO_4} + \underset{\text{free acid}}{H_3PO_4} \tag{1}$$

$$3ZnHPO_4 \rightarrow Zn_3(PO_4)_2(\text{Hopeite}) + H_3PO_4. \tag{2}$$

In phosphate solution, a classic acid (phosphoric) and metal (steel) reaction takes place which locally depletes the hydroxonium (H_3O^+) ions, raising the pH, and causing the dissolved primary phosphate salt to fall out of solution and be precipitated on the surface as tri-zinc phosphate (insoluble).

Sodium orthovanadate (Na_3VO_4) solution of 0.1 M was prepared as stock solution. Three phosphate solutions with different vanadate concentrations (0.0625 mM, 0.125 mM, 0.25 mM) were prepared by adding the required volume of stock vanadate solution to the phosphate bath.

Prior to the phosphate treatment, the steel specimens of dimension $50 \times 50 \times 2$ mm^3 have been abraded (emery grade: 180 and 400), degreased with ethanol and rinsed with water before immersion in diluted zinc phosphate bath at 60 °C. The immersion time is 5 min

followed by rinsing with de-ionized water and drying with compressed air.

The surface morphology of zinc phosphate crystals was observed using a Philips XL30 FE-SEM with a LinkISIS X-ray analysis system (Oxford Instruments).

A JEOL JDX-3530M X-ray diffractometer system was employed to analyse the phase structure of the zinc phosphate coatings.

2.2. Electrochemical testing

A Solartron potentiostat/galvanostat – model 1280B with an attached frequency analyser unit-model 1260A – was employed in the polarization and electrochemical impedance measurements (EIS). A three-electrode cell has been used in electrochemical tests with mild steel (coated or uncoated zinc phosphate) as the working electrode, titanium mesh as counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The surface area of the working electrode exposed to the electrolyte is approximately 3.14 cm^2. For electrochemical polarization investigations, both the MnMgZn phosphate coated steels and mild steel strips of the same composition were cleaned by ethanol and de-ionized water and fixed in a perspex electrochemical cell. All polarization and EIS measurements were carried out at room temperature. The specimens were immersed in the electrolyte for a period of 30 min to allow them to reach the equilibrium state prior to running the polarization measurements. The polarization measurements were carried out at pH 3 by adjusting the pH of de-ionized water (>10 MΩ) using 1 M hydrochloric acid solution. All the measurements were made in a 200 ml working solution. The EIS device is attached to computer with Z-plot and Z-view software installed to record the impedance (real, imaginary) and phase angle at applied AC potential in the frequency range from 0 Hz to 65 MHz. EIS measurements were carried out at an open circle potential with 10 mV AC potential. The working electrolyte for EIS tests was diluted hydrochloric acid (Conc. 32%) in de-ionized water maintained at different pH values of 2–4.

2.3. ICP-AES analysis

An Agilent 730 simultaneous axial atomic emission spectrophotometric ICP-AES system was applied to detect and evaluate the elemental metal ion concentration (Fe, V, Zn) in the solutions after dissolving the zinc phosphate layer in 50 ml HCl acid solution at pH 2 for 20 min. The solutions were diluted to 1:50 by de-ionized water.

3. Results and discussion

3.1. Coating microstructure and phase analysis

Fig. 1 shows the scanning electron microscope (SEM) images showing the different crystals of MnMgZn phosphate coatings at different concentrations of sodium orthovanadate (0, 0.0625, 0.125 and 0.25 mM). The images reveal significant changes in the microstructure and the crystal size of the phosphate coatings by increasing the vanadate (VO_4^{3-}) content in the phosphate bath. The grain size decreased as the vanadate concentration increased from 0 to 0.25 mM. The images show that vanadate-free and 0.0625 mM vanadates MnMgZn phosphate coatings have fingered-shape crystals with a grain size range of 3–12 μm. However, phosphate coatings with 0.125 and 0.25 mM vanadate consist of fine rod-shaped grains with a uniform size of 0.5–2 μm. The grain size of MnMgZn phosphate coatings was reduced to approximately 50% as the amount of vanadate was doubled from 0.125 to 0.25 mM in the phosphate bath. The grains are uniformly distributed on the steel surface. The difference among the coatings is primarily in the morphology, distribution and size of the crystals formed during the phosphating process. As the grain size decreases, the coating becomes dense with low porosity compared to coating with coarse crystal. Grain-size reduction has a benefit of reducing the porosity and improving the phosphate coverage on