

ZnCr and ZnNb Cold Spray Coatings

Lucas Teeter

U.S. Department of Energy, National Energy
Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321
USA

Joseph Tylczak

U.S. Department of Energy, National Energy
Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321
USA

Margaret Ziomek-Moroz

U.S. Department of Energy, National Energy
Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321
USA

Grant Crawford

South Dakota School of Mines and Technology
501 E. Saint Joseph St.
Rapid City, SD 57701
USA

ABSTRACT

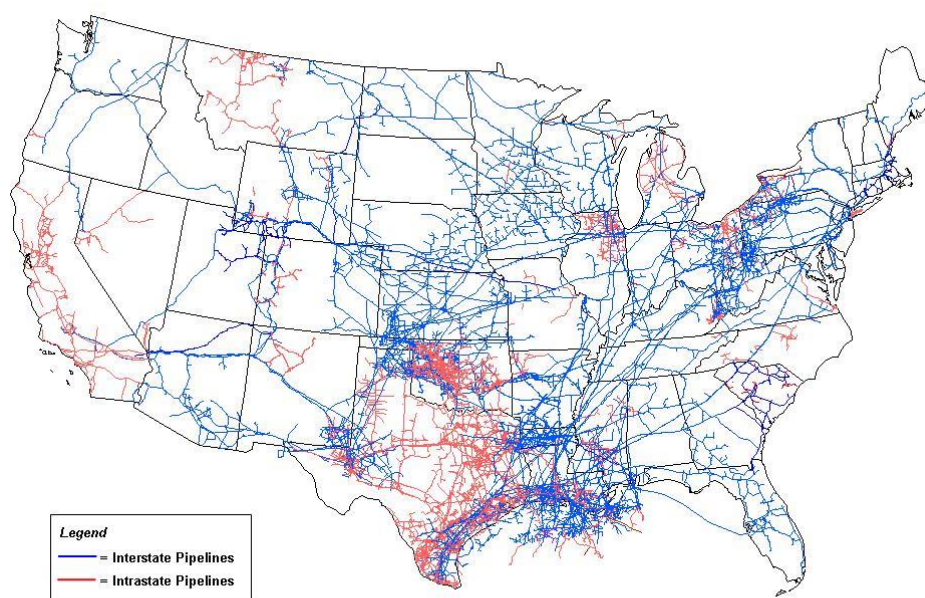
Novel cold spray zinc-based alloy coatings have been investigated for corrosion protection of API 5L low carbon steel pipelines used in transporting natural gas. These different zinc alloy coatings are designed for use to help prevent internal corrosion and improve the lifespan of steel pipelines via sacrificial anodic protection. The corrosion behavior of these cold deposited zinc alloy coatings was investigated in CO₂ saturated 3.5 wt.% NaCl solutions under simulated natural gas pipeline conditions.

Electrochemical tests were conducted at 25 and 40 °C to determine the polarization resistance and galvanic current between each coating and the steel substrate in the galvanic couple. Tests were conducted at atmospheric, 1 bar, pressure. The results indicate that use of these coatings has the potential to increase the lifespan of steel pipelines above what a zinc coating alone could provide.

Key words: Corrosion control, Zn-based alloy coatings, cathodic protection, galvanic corrosion

INTRODUCTION

In the US, natural gas accounts for one third of the energy consumed [1]. The gas pipeline network consists of more than 210 individual pipeline systems and nearly 300,000 miles, Figure 1, which makes it the most the most extensive pipeline delivery system in the world [2] [3]. The majority of the line pipe in current service was installed in the 1950's and 1960's. These pipelines are made of high grade carbon steel regulated by the American Petroleum Institute (API) [3] [4]. Failure of this pipeline can cause disruption in service and gas release into the environment. Corrosion is a primary failure concern, as carbon steel does not resist corrosion particularly well. Developing inexpensive, practical methods to increase the life of new and existing pipelines is of significant importance.



Source: Energy Information Administration, Office of Oil & Gas, Natural Gas Division, Gas Transportation Information System

Figure 1: US Natural Gas Pipeline Network, 2009 [3]

Natural gas pipelines are usually buried underground, which puts them in contact with potentially corrosive soils. Currently coatings and impressed current systems are used to protect the external pipe from corroding [5]. The impressed current method works by supplying a remote external anode with a direct current, with the soil acting as the electrolyte. However, this only protects the external surface of the pipeline. Natural gas consists primarily of methane (CH_4); some hydrocarbons, water; and gases, such as carbon dioxide (CO_2); and dissolved ions, such as Cl^- [3] [6]. While designed to be dry, usually less than 7 lbs. of water per MMCF of gas, it is not unusual to find liquid water. It has been shown when CO_2 dissolves in water it forms a corrosive solution that can cause severe internal corrosion [7]. When transporting natural gas that contains corrosive species, the internal pipe has neither an anode nor an abundant electrolyte on which an impressed current can be utilized, but rather pockets of localized areas of attack.

Developed and potential methods for mitigating internal pipeline corrosion include regular maintenance, such as mechanical(pigging)/chemical cleaning; changing the fluid composition, by eliminating contaminants or introducing corrosion inhibitors; or adding internal liners or coatings. Of these methods, liners and coatings allow for the current natural gas industry practices to continue without significant alterations to current practices.

Liners and organic coatings can be very good at providing barrier protection; however, these barriers tend to become damaged during shipment or in use and would then themselves be subject to regular maintenance. Metallic coatings also provide barrier protection and can be subdivided into two classes: noble coatings and sacrificial coatings [8]. Noble coatings only provide a barrier coating. Sacrificial coatings provide both a barrier coating and cathodic protection. In salt water, sacrificial metals, such as zinc, have been shown to cathodically protect exposed steel several feet removed from the coating [8].

Sacrificial coatings that are of interest for protecting carbon steel include magnesium, zinc, and aluminum. The National Energy Technology Laboratory (NETL) is investigating corrosion protection capability for X-65 carbon steel using cold spray Zn-based alloy coatings containing Cr or Nb. Cold spray is a process wherein powder particles (in this case the Zn-alloy coatings) are accelerated at very high velocities and temperatures below melting into a surface [9]. Cold spray, as opposed to thermal spray, has multiple benefits. First, cold spraying metals does not need the additional protective atmosphere or vacuum that thermal spray requires. Second, when the particles impact the surface, rapid plastic deformation occurs which breaks up surface oxides on both the particles and the surface, increasing bond strength and deposition efficiency and lowering oxygen content [9]. Third, cold spray does not have residual stresses introduced through solidification, allowing for thicker and less porous coatings to be achieved [9].

Cold spray technique could be a practical manner in implementing corrosion protection for natural gas pipelines. This work focuses on the behavior of two different Zn-alloys, one with Cr and the other with Nb. These Zn-alloys are compared to pure Zn and X65 in order to determine the potential for use in these systems.

EXPERIMENTAL PROCEDURE

The materials and testing conditions are listed in Table 1. The materials included in this study are API 5L (X65), the pipe base material; ZnCr and ZnNb alloy coatings cold sprayed onto X-65, and Zn for comparison. The materials were tested in 3.5 wt.% NaCl with bubbling CO₂ at 25 and 40 °C to simulate conditions of the corrosive species. Additionally, one experiment was conducted on ZnCr with bubbling air in order to indicated use outside of the natural gas pipeline environment.

Table 1: Materials and testing conditions

Alloy	Alloy Description	Density (ρ) g/cm ³	Equivalent Weight (EW)	Electrolyte	Gas Bubbled	Temperature and Pressure
X65	Carbon Steel API 5L	7.74	27.45	3.5 wt.% NaCl	Saturated with CO ₂ *	25 or 40 °C 1 bar
ZnCr	Zinc coating with chromium	7.14	29.36			
ZnNb	Zinc coating with niobium	7.18	32.64			
Zn	Zinc with minor impurities	7.14	32.69			

*ZnCr experiments also include a set with air bubbled instead of CO₂ for comparisons

Samples were cut to an appropriate size for use in the 1 cm² flat cell testing area. The exposure surface of the samples was polished to 600 grit, rinsed with deionized water, with a final cleaning in an isopropanol ultrasonic bath.

Materials were tested using Potentiodynamic Polarization (PDP), Linear Polarization Resistance (LPR), and Electrochemical Impedance Spectroscopy (EIS) methods at 25 and 40 °C at 1 bar in a flat cell.

Galvanic tests were also performed in a flat cell at 25 and 40 °C and 1 bar using Zero Resistance Ammetry (ZRA) method.

The setup for the 1 bar PDP, LPR, and EIS experiments is displayed in Figure 2 with a counter electrode made of Pt. The 3.5 wt.% NaCl electrolyte was saturated overnight with bubbling CO₂ (or air for the air exposure). For the 40 °C exposures, the electrolyte was also preheated to 40 °C overnight while bubbling gas. Samples were loaded into one side of the flat cell with a 1 cm² exposed surface area. The counter electrode was platinum and the reference electrode was a saturated Ag/AgCl electrode. During the exposure, gas bubbling was controlled to 20-40 mL/min. The 40 °C exposures also included a water bath controlling the flat cell temperature and a plastic liner separating the flat cell from the water bath. The flat cell for galvanic ZRA measurements is displayed in Figure 2 with a second working electrode. The testing material was inserted on Working Electrode #2 side of the flat cell and X65 inserted on the Working Electrode #1 side, which had the reference electrode Luggin capillary.

PDP tests were conducted from -0.25 to 1.6 V vs open circuit potential (OCP) at a scan-rate of 1 mV/s. LPR tests were conducted from -5 to 5 mV vs OCP at a scan-rate of 0.125 mV/s. EIS tests were conducted from 10⁵ to 10⁻² Hz at 10 points/decade with an amplitude of 10 mV rms. ZRA tests were run for two hours to achieve a steady state galvanic current density, I_{gal} , and galvanic potential, E_{gal} .

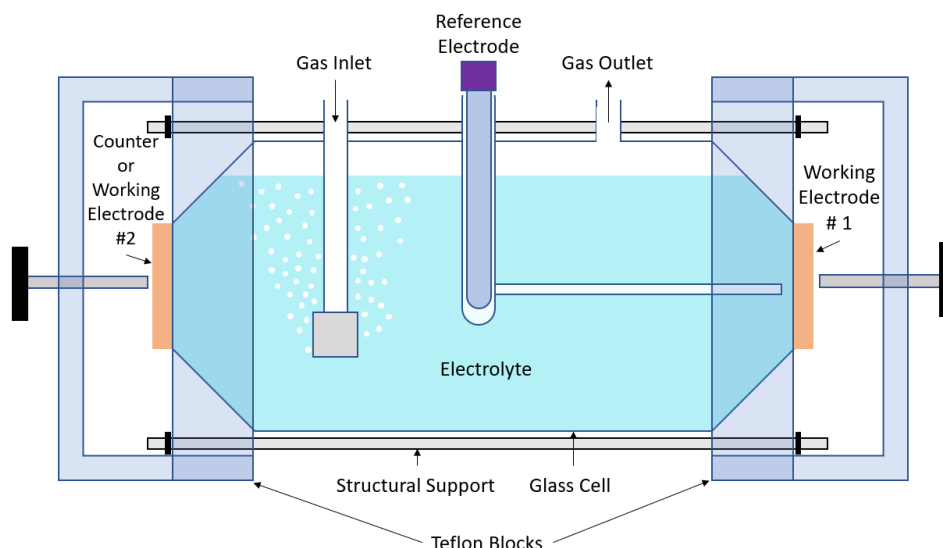


Figure 2: Flat cell setup with counter electrode for PDP, LPR, and EIS experiments or setup with working electrode #2 for galvanic ZRA experiments

The corrosion rates and polarization resistance for each condition and alloy were calculated from PDP, LPR, and EIS experiments. The corrosion rate was determined via Equation 1 [10], where K is a constant (3,272 mm²g/A), EW is the calculated dimensionless equivalent weight (Table 1), ρ is the density of the metal (Table 1), and A is the sample area (1 cm²). The corrosion current for polarization resistance was determined directly from experimentation.

The corrosion current for EIS and LPR was determined using the Stern-Geary Equation, Equation 2 [11], where β_a and β_c are the anodic and cathodic Tafel slopes measured during polarization resistance tests, and R_p is the polarization resistance. Using EIS the solution resistance was determined, and the effect was subtracted from the both the LPR and EIS measured R_p .

$$CR = I_{corr} \frac{K \cdot EW}{\rho \cdot A} \quad (1)$$

$$I_{corr} = \frac{\beta_a \cdot \beta_c}{2.3 \cdot R_p \cdot (\beta_a + \beta_c)} \quad (2)$$

RESULTS AND DISCUSSION

The results section is subdivided between temperature. Each temperature subsection contains results and interpretations for PDP and EIS, and galvanic ZRA measurements for the investigated materials.

25 °C at 1 bar

The PDP results for Zn, X-65, ZnCr coating, and ZnNb coating are displayed in Figure 3. X65 has a higher OCP than Zn and Zn-based coatings. This indicates that higher negative potential of the Zn/Zn-alloys should work to protect X65 from corrosion, recommended minimum of -0.3 V shift [10]. In this electrolyte, all the investigated materials show active dissolution. The Tafel slopes, β_a and β_c , determined from the PDP experiments, the corrosion rates, and the calculated polarization resistances are tabulated in Table 2.

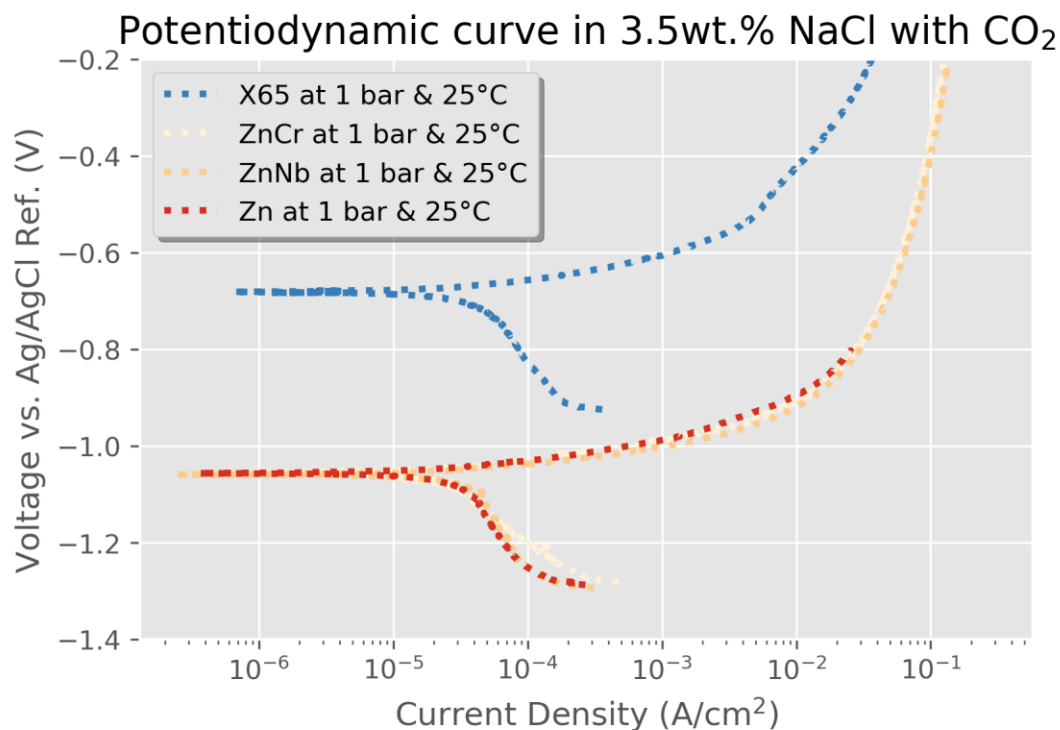


Figure 3: PDP curves for materials tested at 25 °C

The EIS Nyquist results for the material tested at 25 °C are displayed in Fig. Figure 4 and Figure 5. EIS measurements for X65, were modeled as a high frequency capacitive loop and low frequency inductance loop. The high frequency capacitive loop described charge transfer of the X65 metal corroding, and the secondary inductance loop can be attributed to surface adsorption [13]. EIS measurements for the Zn/Zn-alloys, were modeled as a double capacitance loop. As with X65, the high frequency capacitive loop described charge transfer for the Zn/Zn-alloys; however, the second capacitance loop is attributable to a diffusion process of a finite thickness [14]. This diffusion process would invalidate the Stern-Geary equation for use in corrosion rate measurements because it assumes no mass transfer, only charge transfer. The measured solution resistance (R_e) was subtracted from the measured polarization resistance to get the true polarization resistance (R_p). This EIS R_p as well as the LPR R_p are tabulated