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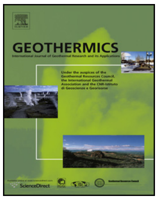

Galvanic corrosion study of carbon steel to arsenic and antimony couples

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ABSTRACT

Carbon steel has been observed to experience accelerated corrosion in pH adjusted geothermal brines. The damage mechanisms observed in service have included: heavy metal deposition, localised underfilm corrosion, galvanic corrosion and erosion corrosion. This paper describes progress in the study of the corrosion properties of galvanic couples of carbon steel to antimony and to arsenic using electrochemical techniques in simulated brine at temperatures up to 80 °C. The results show galvanic corrosion rates of carbon steel increased as temperature was increased. Aeration gave enhanced galvanic corrosion of carbon steel coupled to antimony, a reverse effect was observed with arsenic. The differing performance of arsenic was attributed to one of arsine production under cathodic polarisation and/or rapid oxidation of the arsenic electrodes used in this work.

1. Introduction

Geothermal energy is an economically reliable, safe and environmentally friendly alternative energy source which accounts for about 13% of New Zealand's national energy production. A limited number of service conditions have been observed to cause undesirable corrosion degradation of carbon steel facilities. This is predominantly due to chemical constituents in the geothermal fluids, specifically chlorides, hydrogen sulphide and carbon dioxide (Shannon, 1977; Lichti, 2007). Nevertheless, for most of the common engineering alloys in air-free geothermal fluids, the corrosion rates are sufficiently low to ensure adequate service life.

Of recent interest are the effects of heavy metal deposition on the performance of carbon steels in geothermal brines. Geothermal fluids in many cases may contain traces of heavy metals, such as gold, silver, thallium, arsenic, antimony and copper to mention a few (Brown and Simmons, 2003; Zhang et al., 2008). Under certain conditions, electrochemical reduction of these heavy metals, particularly of antimony, silver, arsenic or their combinations can results in deposited metallic scales forming on freely corroding carbon steel (Golubev et al., 1988; Gallup et al., 1995; Brown and Rock, 2010). Precipitation of unwanted scales and corrosion in processing facilities and pipelines causes major engineering challenges, leading to reduced availability, plant shutdowns, costly scale removal and limits on downstream use of fluids. Apart from that, these scales, formed in conjunction with oxidation of iron have subsequently been associated with localised galvanic corrosion, under scale pitting and erosion corrosion of the underlying carbon steel (Lichti and Brown, 2013; Amends and Yee, 2013). The chemical factors controlling the rate of damage accumulation have been difficult to deduce from the in-service history of corrosion.

The fluids of primary interest are mildly acidic brines which appear to be the main drivers for the electrochemical reduction and the subsequent galvanic corrosion. Under low pH conditions, both in two-phase fluids and brines, arsenic and antimony have been observed to precipitate in a metallic form (Brown, 2011). Acid well fluids are not encountered in New Zealand geothermal production; however, acid process conditions can be encountered either through deliberate modification of the environment (e.g. for silica scale control) or in power station circuits where the acidic geothermal gases (CO_2 and H_2S) are concentrated. In the case of arsenic and antimony, the deposition has been proposed to occur through the following oxidation and reduction reactions (Gallup et al., 1995):

$$\text{Oxidationofiron}: \quad Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$\text{Reductionofarsenic}: \quad AsO^+ + 2H^+ + 3e^- \rightarrow As + H_2O \tag{2}$$

$$\text{Reductionofantimony}: \quad SbO^+ + 2H^+ + 3e^- \rightarrow Sb + H_2O \tag{3}$$

Silver has also been observed in heavy metal scale deposits notably as silver–antimony alloy (Gallup et al., 1995). The process

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of oxidation/reduction has been observed to show pH dependence as it appears that iron ions must be rapidly taken into solution and not be precipitated as a protective corrosion product film for the elemental scales to form. An environment of relatively low pH is required for the reduction processes, as can be seen in Eqs. (2) and (3). Under alkali and near neutral to slightly acid brine solutions, where iron oxide and iron sulphide scales are stable and where silica rich scale form, heavy metal precipitation is not observed (Lichti and Brown, 2013). This observation may be a result of iron and silicon precipitation reactions that slow the oxidation reactions required for heavy metal reduction. Considering that both arsenic and antimony are less electronegative than carbon steels, it may be argued that processes resulting in deposition of non-continuous scales of antimony (Golubev et al., 1988), arsenic or a mix of the two could lead to localised corrosion. However, there has been no distinctive identification of factors which control the onset and/or propagation stage of such localised corrosion, e.g. pH, chloride content, heavy metal concentration, silica saturation index etc.

A corrosion study of heavy metal scales coupled to carbon steel was initiated in our laboratory with pure antimony and carbon steel, as antimony was readily available to manufacture a suitable and solid test electrode (Soltis and Lichti, 2013). Arsenic was not readily available in a form suitable for preparation of solid electrodes, and thus a series of tests with vapour-deposited arsenic and antimony layers on carbon steel were conducted to show that localised corrosion of carbon steel was most severe under antimony layers with pH 3 and pH 5.4 in aerated environments at 20 °C (Lichti et al., 2015). Our latest work also included attempts to manufacture solid arsenic electrodes, using the concept of powder metallurgy, but proved to be rather challenging when aiming to achieve a low degree of porosity in produced electrodes (Lichti et al., 2015).

The work presented here builds on the latest study (Lichti et al., 2015) and includes arsenic-coupled-to-carbon–steel electrochemical tests. The objective was to improve our understanding of effects which various environmental factors and geothermal power station production conditions can have on controlling localised corrosion of carbon steel in the presence of heavy metal scales so that operating conditions may be critically controlled and the risk of localised corrosion minimised. Although not discussed in the current work, as a part of this research programme, we also intend to review thermodynamic properties of arsenic and antimony and model stability of corrosion products which these metals could form at high temperatures, e.g. 90 °C and above in geothermal brines.

2. Experimental

2.1. Electrode preparation

High purity (99.999%) antimony (Goodfellow Materials, England) and carbon steel (AISI 1018) electrodes were prepared from, as received, 6 mm diameter rods.

High purity (99.999%) powdered arsenic (Goodfellow Materials, England) was used to prepare the arsenic electrodes. The sourced arsenic powder, average grain size estimated <100 μm, was compressed at ambient temperature and a pressure of 9 MPa to a 10 mm diameter disc; note that increasing temperature to 150 °C during the compression phase had no apparent influence of the final degree of porosity. Such prepared arsenic discs were then attached to a metal holder by a conductive (silver loaded) epoxy resin (RS silver loaded epoxy adhesive, RS 186-3616).

In order to provide electrical connection, a copper wire was soldered to one end of the carbon steel and antimony electrodes, and to the metal holder on the arsenic electrode. Each electrode was then mounted in K36 coating and laminating epoxy resin (Nuplex Industries Ltd., New Zealand) and stored in a desiccator at ambient temperature. Prior to each experiment, carbon steel and antimony electrode surfaces were ground using 1200 grit emery paper, rinsed with distilled water and cleaned with ethanol. In the case of the arsenic electrode, in order to minimise the effect of porosity on electrochemical measurements, the experimental surface was backfilled with the K36 resin and then re-polished. The test area of the exposed compressed arsenic powder electrode was estimated from scale photographs of the exposed metal surfaces.

2.2. Electrochemical measurements

All electrochemical measurements were obtained by using a PGZ 100 potentiostat (Radiometer Analytical) and EG&G Model 273A potentiostat (Princeton Applied Research). Measurements were conducted using a typical three-electrode electrochemical cell with a double-wall arrangement. Such a custom-made design allowed for hydronic heating of the experimental electrolyte, with both the heating mantle (Electrothermal, UK) and the peristaltic pump (Watson-Marlow 505S, UK) located outside a Faraday cage to minimise electromagnetic interference. A calomel electrode with saturated KCl (SCE) was used as the reference (all potentials reported were referred to SCE) and a platinum electrode as the auxiliary.

Experimental electrolytes were prepared using ultra-pure water and analytical grades of sodium and potassium chlorides (Scharlau Chemie S.A., Spain) at a ratio of 3.7:1 and a total concentration of chloride ions 1000 mg/dm^3. The chloride concentration of 1000 mg/dm^3 was chosen as a mid-level concentration, representative of New Zealand low chloride geothermal brines. The sodium to potassium ratios range from 3.7 to 7 in the New Zealand geothermal brines but ionic balance is seldom observed as the concentrations of $Cl > Na + K$ is common (Glover and Mroczek, 1995; Lichti et al., 1997, 2000; Mountain et al., 2013) The lower ratio was chosen to give less bias to the sodium salt. The desired pH of the electrolytes, i.e. 3–5.4, was obtained by the addition of small amounts of 0.05 mol/dm^3 solution of sulfuric acid. Oxygen-free environment was achieved by bubbling high purity nitrogen gas for 1 h prior to testing and was also used to shield the experimental atmosphere during measurements.

Potentiodynamic scans for each experimental material were conducted after a 360 s hold at the free corrosion potential, E_{corr}, and from the adopted E_{corr} in either anodic or cathodic direction at a scan rate of 0.1–0.2 mV/s. An alternative full scan (cathodic and anodic sweep) from approximately 700 mV below E_{corr} in the positive direction, passing through E_{corr} to approximately 400 mV above E_{corr} was also trialled.

A super-imposed method for estimating galvanic corrosion currents for the considered materials was used as discussed previously (Soltis and Lichti, 2013): solid antimony–carbon steel coupling and powdered arsenic–carbon steel coupling. This method super-imposes the anodic curve for carbon steel with the cathodic curves for solid antimony and powdered arsenic.

The Evans' experiment was used to give direct measure of the corrosion current at the mixed potential of heavy metal–carbon steel couples, where the more electronegative material (carbon steel) was used as the working electrode and the less electronegative materials (antimony and arsenic) were the auxiliary electrodes. Galvanostatic steps of 0.1–0.2 μA were applied with a drift threshold of 3 mV/min and maximum step duration of 30 s. The intersection of potential *vs.* current curves was used to establish the corrosion current, I_{corr}. Adjustment was made to account for the differences of the exposed surface areas (surface area ratio of 1:1 for working and auxiliary electrodes).