

CORROSION RATE ASSESMENT IN A GEOTHERMAL WATER CONVEYING SYSTEM

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Abstract:

The paper summarizes the results of analysis and field measurements performed for assessing the water corrosivity in a geothermal plant. Corrosion rates were measured on carbon steel, in an aqueduct used for conveying CO₂ containing water with moderate salinity, from production wells to reinjection wells in order to sustain vapor production of the geothermal field. The results were collected under different operating conditions. The corrosion rate was evaluated by means of linear polarization tests and weight loss tests as a function of flow rate, pressure, temperature, pH, oxygen and carbon dioxide content. The experimental results were discussed by considering models available in literature for predicting CO₂ corrosion.

Keywords:

Generalized corrosion, steel, CO₂ corrosion, geothermal plant, corrosion rate assessment.

1. Introduction

Geothermal energy production began in Italy about a century ago, in 1904 near Larderello (Tuscany). From 20's its worldwide diffusion grew, and today the annual production is 50 TWh/y, 0.3% of total electrical energy production. In Italy, the annual production of five plants is about 5 TWh/y.

Steam is obtained from geothermal reservoirs through drilling of wells [1]. Insulated carbon steel pipelines provide transportation to power plant. Steam mechanical energy is converted into electrical energy by means of turbines and generators, with a consumption of about 8000 kg of steam to produce 1 kWh of energy. After condensation, hot water passes through cooling towers and is transported by aqueducts to injection wells. Injection in the same geothermal reservoir is adopted in order to reduce environmental pollution and prevent soil subsidence, due to excessive suction of water.

In order to stimulate steam generation and to sustain vapour pressure of Larderello reservoir, the condensed steam injection is integrated by geothermal water drawn from three shallow wells. This water is directly transported to injection wells by a 20" pipeline conveying system, of about 4 km length, overcoming an elevation of 284 m. A pumping station increases pressure from 4 to 32 bars and provides 250 m³/h volumetric flow rate.

Aim of this work is the evaluation of corrosion rate of the carbon steel used for the conveying system. In situ linear polarization resistance measurements and weight loss tests were performed in order to obtain sound data for evaluating different approaches proposed for corrosion control.

2. Experimental

The average composition of water is shown in Table 1. The water has high sulphate content and hardness (203°F), with 2700 mg/L salinity and low chloride content. Gas evolution, principally nitrogen and carbon dioxide, can be noticed below 2 bar pressure. It is 1-8% volume at atmospheric pressure. CO₂ partial pressure was estimated about 0.34 bar. Temperature is in the range 40-50°C, typically 46°C. Flow rates range between 0.6 and 2.4 m/s, with two main operating conditions such as 1.7 m/s and 1 m/s.

Table 1 average water composition (mg/L).

pH	Cond. ^o μS/cm	Alk. meq/L	Ca ⁺⁺	Fe ⁺⁺	Mg ⁺⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ⁻⁻	B	Na ⁺	K ⁺	F ⁻	SiO ₂	susp. solids
6.62	2589	5.08	626	3.10	113	19.1	18.3	1580	4.40	16.4	5.5	2.8	38.7	11.8

^o value at 25°C

cell	φ _i (mm)	s (mm)
t1	49	16
t2	43	16
t3	22	12

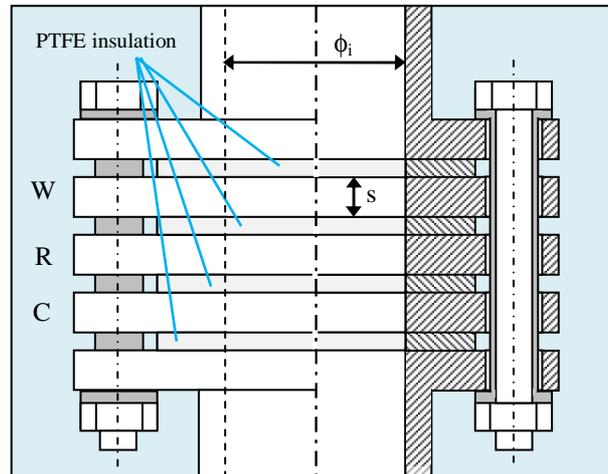


Fig. 1: electrochemical tubular cells assembled in the testing line parallel to the aqueduct.

The corrosion rate of steel was monitored by means of weight loss tests on cylindrical specimens, mounted through suitable equipments without stopping the plant. Specimens were exposed in critical areas of high turbulence immediately downstream of the pumps, curves and confluences of lines coming from different wells. The water flow directly impinges on lateral surface of the specimen.

Before weighing, the specimens were polished by means of emery paper and degreased. They were washed and cleaned with acetone in ultrasonic bath after exposure.

Polarization resistance (R_p) tests were performed both by potentiostatic and galvanostatic methods, with ± 10 mV polarization, on tubular steel cells (three electrodes) named t1, t2 and t3. The cell inner diameters, were 49, 43 and 22 mm respectively. The central electrode was used as reference electrode. The surfaces were polished by 400 grit emery paper. The cells were mounted into a testing line, derived by main line, equipped with manometer, valves for independent regulation of pressure and water flow. Temperature and oxygen content were evaluated through a membrane electrode.

Owing to the very high corrosion rates observed in the pipeline produce very low values of linear polarization resistance, R_p were corrected by considering ohmic drop contribution between reference (R) and working (W) electrodes, due to current circulation, through the following relationship

$$R_p = \frac{\Delta E_{WR}}{i} - R_{\Omega} \cdot S \quad (\text{eq.1})$$

where i is the current density on working electrode, ΔE_{WR} is potential between working electrode and central reference electrode of the cell, R_{Ω} is the ohmic drop resistance and S is the area of working electrode.

For similitude, R_{Ω} was assumed equal to half of ohmic drop resistance between working and counter electrode, measured by means of a conductimeter at 1000 Hz AC.

Corrosion current density (i_{cor}) was calculated by Stern and Geary equation.

The Stern and Geary constant can be estimated between 17 and 34 mV at room temperature from literature data. Values of 60-80 mV/decade are reported for Tafel slope of iron anodic process in neutral solutions [2]. For cathodic processes, limiting current conditions were assumed for oxygen reduction and 120 mV/decade slope for hydrogen evolution from carbonic acid reduction [3]. Afterwards, a value of 26 mV has been adopted for all environmental conditions.

4. Results and discussion

The specimens were covered by non-adherent black corrosion products after exposure and showed a pronounced non-uniform generalized attack, with average corrosion rates exceeding 2 mm/y, for brief exposure. A decreasing tendency was observed for longer exposure. The pipeline wall thickness was measured by means of ultrasonic probe confirming about 1-2 mm thinning after 13 months.

In situ R_p testing was carried out during three inspections after different periods of cell exposure: during first day, after 9 days and about 7 months.

After brief exposure, the tubular electrodes of cells for R_p measurements were covered by a thin and adherent layer of black corrosion products. The deposit was adherent, differently from specimens for weight loss test, which were exposed to high turbulent flow.

Thus for short exposures, the scale appears to act as a barrier that can reduce the rate of corrosion over the first few days of exposure, if flow conditions cannot promote insufficient erosive action on metal surface (Fig. 2).

However a complex behaviour can be noted. Corrosion rate decreases over first period due to formation of the thin scale, but it becomes higher as the scale grows over the time.

As the scale thickness increases, its adhesion to metallic substrate becomes lower. The scale reaches very high thickness, exceeding 1 mm (Fig 3, left). Sulphide traces were detected in the corrosion products, even if chemical analysis shows nil or very low values of H_2S content in the water.

After 7 months, corrosion rate increases again to 0.45-1.1 mm/y, in spite of the activation of a temporary degassing equipment to reduce carbon dioxide to 0.18 bar partial pressure. All three cells showed localized attack (Fig. 3, right), pointing out the non-protective nature of the scale after long term exposure, despite of its high thickness. As far as the effect of water flow rate is concerned, the scale showed lowest thickness in the cell with lowest inner diameter (t3), where high shear stress are induced on the wall by water flow. The results of R_p tests show detectable effect of oxygen content and flow rate, whereas the change of total pressure between 2 and 10 bar did not produce significant variations.

Oxygen content in the water is variable. Seasonal change is due to the geological characteristics of the aquifer. Furthermore, air slightly penetrates in the plant under some operating conditions. During testing, values ranged from very low concentration, below 0.1 ppm, up to 1.0 ppm. Linear polarization data show that corrosion rate significantly increases as the oxygen concentration and flow increase. 2-3 mm/y corrosion rate was found for 1 ppm oxygen concentration at 1 m/s flow rate during first periods of exposure. Water composition and pH are not favourable to calcareous scaling.

By comparing the results obtained for low oxygen concentration, in the range 0.03-0.07 ppm, as a function of flow rate, a different behaviour can be noted depending on exposure (Fig. 4). After brief time, the corrosion rate increases as the water flow rate increases. On the contrary, after 7 months, results show an opposite behaviour.

In the conditions of the plant, corrosion process is determined both by cathodic process of reduction of dissolved oxygen and by hydrogen evolution due to carbonic acid reduction. The rate of the first process is defined by the oxygen limiting current density, thus is

related with mass transport towards metallic surface. In absence of scale, the rate is determined by hydrodynamic conditions, mainly water flow rate, and oxygen content into water, considering the temperature in the conveying system is about constant. The corrosion by oxygen reduction is the main phenomenon for high flow rates and oxygen concentrations of about 1 ppm.

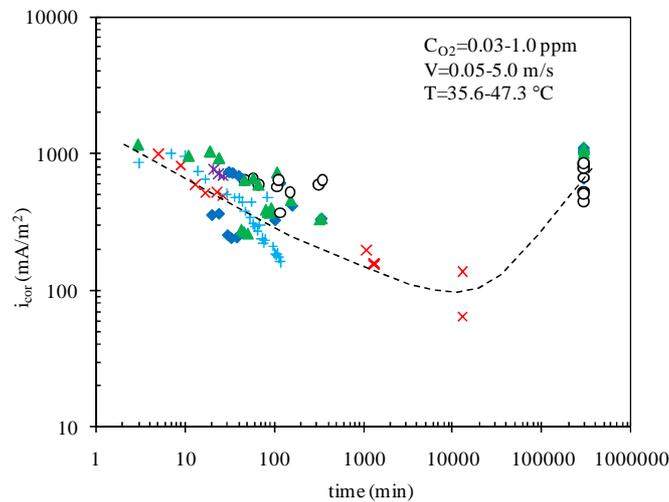


Fig. 2: corrosion rate from R_p tests as a function of exposure time.



Fig. 3: corrosion morphology after 7 months exposure (left: corrosion product scale on inner surface of the electrode; right: surface after sandblasting).

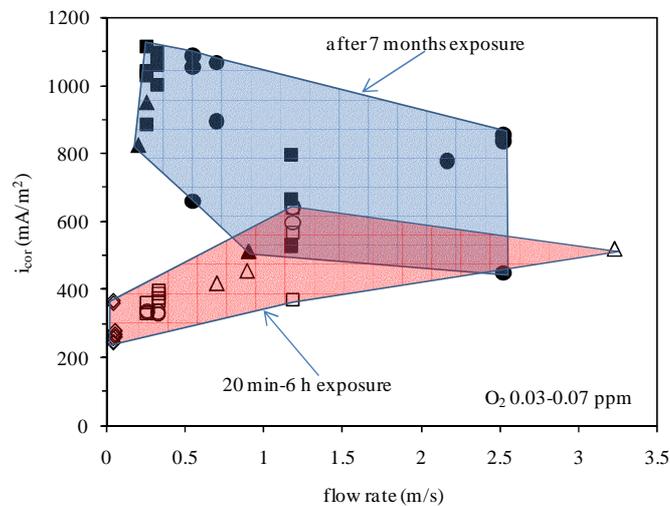


Fig. 4: effect of flow rate on corrosion rate from R_p tests.

The growth of a superficial scale opposes this process by creating a diffusion barrier. However, the experimental results do not permit an evaluation of the effect of oxygen in presence of the high thickness scale after 7 months exposure, because the measurements were performed under practical absence of oxygen.

At very low oxygen content or low flow rate, CO₂ corrosion (sweet corrosion) becomes the dominating attack in the conveying system, enhanced by operating temperatures. The cathodic process can occur either with activation (charge transfer) overpotential or limiting current. Water flow does not affect carbonic acid limiting current as oxygen limiting current, being CO₂ corrosion limited by slow chemical step of carbon dioxide hydration to carbonic acid. Kinetics are regulated by the dimensions of the reaction layer and its relation with diffusion layer, as a function of water flow [4]. Only at very high flow rate the diffusion layer is expected to become lower than reaction layer, producing higher limiting current and direct effect of flow rate on corrosion rate. At low flow rates, in the range of operating condition of the plant, the reaction layer is the determining step of maximum rate of carbonic acid reduction and the effect of flow rate should be negligible. However such limiting conditions are achieved only at low potentials.

Under limiting current conditions, corrosion rate is mainly determined by cathodic process and does not depend by the anodic process. However experimental data show that during brief exposure, the formation of a thin corrosion product scale significantly reduces corrosion rate. Such film, initially adherent, may reduce the anodic process and increase the anodic overpotential, without determining a real passivity condition. Furthermore it may increase the overpotential of carbonic acid cathodic process at noble potentials, where activation (charge transfer) overpotential is dominant. Both effects may explain the observed reduction of corrosion rate.

After some months, an opposite tendency was noticed. Corrosion rate increases again.

High corrosion rates could be favoured by environmental stagnant conditions in the thick scale, more aggressive than water far from surface. In this condition, carbonic acid reaction layer is thinner than scale thickness. Sulphides cumulating in the scale may contribute to aggressiveness, as they can act as a good cathode for hydrogen reduction. As the flow rate increases, a major replacement of the solution in the scale could reduce aggressiveness, reducing corrosion rate as a consequence.

Several models for CO₂ corrosion assessment have been developed for oil and gas industry, but they may be extended to mining and geothermal environments. An evaluation of corrosion rate has been carried out by using main literature models. DeWaard and Milliams model [5], Norsok standard [6] and mechanistic model by Netic et al. [7] were considered. The model proposed by Netic was modified by using different values of physical parameters. Furthermore, for anodic iron process, 80 mV/decade was assumed for Tafel slope from literature data concerning solution with pH similar to the examined water and exchange current density was assumed equal to 0.01 A/m², according to Song et al. [8]. The results of models have been compared with the experimental data by considering four different conditions shown in Table 2.

All models are in agreement with experimental values obtained through the R_p tests (Fig. 5) but some systematic differences can be noted with regard to the oxygen content and formation of corrosion scale.

Table 2 Environmental conditions for model comparison.

Conditions	Exposure	O ₂ ppm	CO ₂ bar
1	20 min-28 h	0.2-1	0.34
2	20 min-28 h	0.06	0.34
3	20 min-28 h	0.04-0.06	0.18
4	7 months	0.03-0.04	0.18

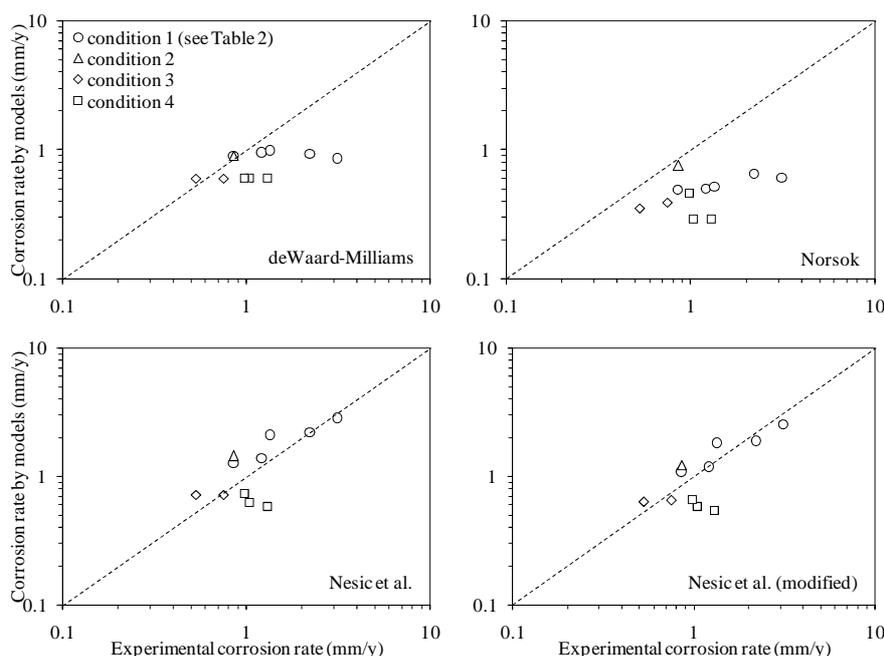


Fig. 5: comparison between experimental data and CO₂ corrosion model prediction (see Table 2).

Owing to the effect of oxygen is not taken into account, deWaard-Milliams and Norsok models lead to underestimation of corrosion rates at high oxygen concentration, i.e. conditions controlled by oxygen limiting current. On the contrary, the mechanistic models confirm their ability in extrapolation to environmental conditions wider then that found in oil and gas. However, at very low oxygen content, all models underestimate corrosion rates in presence of thick scale of corrosion products.

Conclusions

Corrosion rates were assessed, for different content of oxygen, carbon dioxide, and water flow, after brief and 7 months exposure. Time variations of corrosion rate were observed as corrosion product scale grows from thin and adherent film to thick porous scale. Model for predicting CO₂ corrosion in oil and gas industry were able to estimate magnitude of corrosion rates during first hours of exposure. Mechanistic models show their good ability to extrapolation at aerated waters with predominant oxygen attack. All models underestimated CO₂ corrosion under thick corrosion scale conditions, after 7 months of exposure.

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