The Influence of Minerals on Equipment Corrosion in Geothermal Brines

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Industrial minerals, extracted from geothermal brines, play an important role in the economy of many countries, which own and operate geothermal fields and geothermoelectric plants. These minerals are the raw materials for the chemical, fertilizer, metal, ceramic and building industries.
Corrosion affects the different types of equipment, machinery and structures, made from two basic engineering materials: steel and concrete, used in geothermal plants and installations. Minerals undergo ionic dissociation in the brines, contribute to their salinity, chlorinity, and electrical conductivity; alter their pH and increase their corrosivity. Other corrosive substances are present in the brines such as dissolved gases: Oxygen (O_2) carbon dioxide (CO_2), ammonia (NH_3) and hydrogen sulfide (H_2S). Some minerals, depending on their chemical nature and solubility, deposit on metallic surfaces as a hard scale and corrosion appears underneath.
Corrosion control engineering applies methods and techniques of prevention and protection, to avoid the interaction of the equipment and structures with the corrosive constituents of the geothermal brines. Typical cases of corrosion in geothermal brines in USA, Mexico and Israel will be presented, illustrated and discussed.

Introduction

Industrial minerals, extracted from geothermal brines, play an important role in the economy of many countries, which own and operate geothermal fields and geothermoelectric plants. These minerals are the raw materials for the chemical, fertilizer, metal, ceramic and building industries. On the other hand, minerals undergo ionic dissociation in the brines, increase their salinity, chlorinity, and electrical conductivity; alter their pH and increase their corrosivity.
Corrosion control in natural and industrial environments, such as geothermal wells and brines, contributes to the preservation and protection of the environment quality around the geothermal field. Corrosion causes severe damage due to the deterioration of materials and structures, loss of production, and safety hazards to personnel, etc.

Geothermal Brines

Geothermal brines contain a high concentration of dissolved; ionized mineral salts mainly chlorides and sulfates, which are aggressive ions in the context of corrosion. Their amount, relative to carbonates and bicarbonates, are of primary importance in any assessment of the corrosion characteristics of the brines. The chemical composition of a typical geothermal brine is presented in table 1.

Component	**Na**	**K**	**Mg**	**Ca**	**Cl**	**SO_4**	**SiO_2**	**HCO_3**
ppm	6429	1176	18.6	347	11735	15	1133	303

Table1. Chemical composition of a typical Cerro Prieto geothermal brine.

The corrosion dominant factors are salinity and the concentration of dissolved oxygen (DO). Salinity influences the brine electrical conductivity; the chloride (Cl^-) ion also affects the oxide layer, penetrating the passive film; it can initiate pitting and crevice corrosion at localized sites. Localized attack results from differences in aeration, concentration, temperature, velocity and pH. It occurs as pits, crevices, cracks, grooves and eroded parts.

Geothermal Plants Equipment

The industrial equipment, structures and installations of geothermal fields are built of two basic materials: Steel and reinforced concrete, the latter with a surface of low porosity to avoid the penetration of the brine dissolved minerals and future corrosion. Other plastic and modern composite materials, with high corrosion resistance are replacing metallic materials. An abridged list of equipment for geothermal wells and brines is given in table 2.

Equipment	Materials of Construction
Pipes, tubes and ducts	Steel, reinforced concrete
Pumps, vertical and centrifugal	Steel, brass, bronze
Valves, diverse types	Steel
Fittings and flanges	Steel
Silencers	Reinforced concrete
Brine canals	Reinforced concrete
Geotextiles, sedimentations ponds	Plastic, rubber
Monitoring and safety instrumentation	Metallic, plastic

Table 2. Equipment for geothermal wells and brines.

This equipment suffers from different forms of wear: erosion, abrasion, fatigue, disintegration, stress, aging, and particular wet corrosion. Several geothermal power plants in the Imperial Valley, CA use stainless steel, titanium alloy and cement-lined carbon steel tubes to prevent and / or minimize corrosion by acidic components and scaling by silica (SiO_2) in the casings of their geothermal wells. Silica is utilized as an additive for road pavimentation and roofing tiles materials. Calcite and aragonite scaling are frequently encountered in other countries geothermal well fluids.

It is worthwhile to mention in the context of this work, the peculiar corrosion behavior of two salty water bodies: the Salton Sea, CA, and the Dead Sea(called the Salt Sea in the Bible) Israel and Jordan. They contain an high concentration of mineral salts: 45g/l and 280 g/l respectively. These massive desert seas, without a natural outlet, located at 60m and 400m below sea level, continually evaporate rising their salinity. As a result of this salt content, DO reach condition of hypoxia: 2 to 4 mg/l in the Salton Sea or anoxia: 0.1 mg/l in the Dead Sea. Therefore, the harvest of the solid Na, K and Mg salts in the evaporation ponds for the production of chemicals, fertilizers and Mg metal in Dead Sea Works plants is carried out by unprotected steel-made barges, pumps and pipelines without any practical corrosion.

Corrosion, Scaling, and Fouling

Corrosion, scaling and fouling phenomena often appear simultaneously in equipment and installations handling geothermal wells and brines. Minerals scales and deposits, associated with brines composition and circulation, have a marked effect on corrosion. They occur in the brines depending on their physicochemical interaction with the equipment surface, the operational conditions such as pH (4 to 8), DO content (4 to 6 mg/l) flow–regime and temperature (30 to 250 C).

The mineral salt concentration affects the corrosion rate of carbon steel (Figure 1). The rate increases to a maximum at the concentration of seawater (3.5%) and then decreases nearing cero at the saturation concentration (25%) because DO content reaches a minimum value near zero.

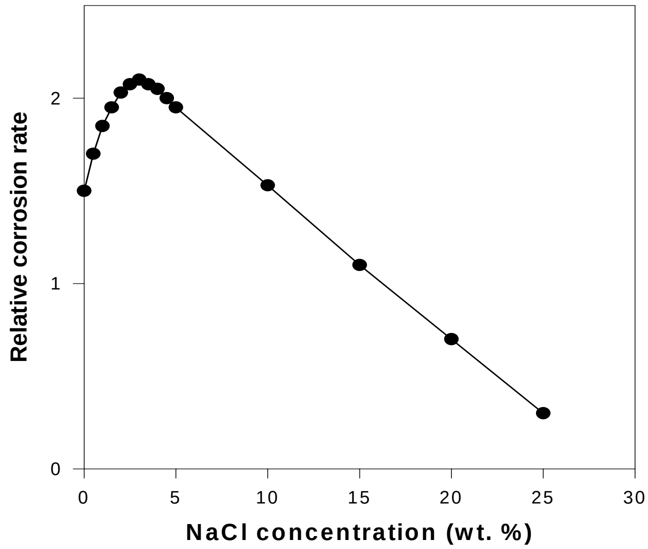

Figure 1. Effect of salt concentration on corrosion of steel in saline water.

The acidic salts $MgCl_2$ and $MgSO_4$ damage concrete surfaces during hydrolysis, corroding the internal reinforcing steel bars, too.

Various corrosive agents and processes occur in geothermal brines:

- **Hydrogen sulfide (H_2S),** a reductant, toxic and corrosive acid, which originates from the well hydrothermal pyrites by natural acidification, corrodes steel and ductile iron:

$$Fe + H_2S \longrightarrow FeS + H_2 \qquad (1)$$

forming a suspension and/or deposit of black iron sulfide, typical of sulfide attack. The H_2S content of well water in several geothermal fields in Mexico varies from 0.6 to 7.7 ppm.

- **Oxygen O_2/ Carbon dioxide CO_2.** The corrosion of active metals e.g iron and steel depends on the concentration of DO, producing rusted surfaces:

$$2Fe + 3H_2O + 1.5\ O_2 \longrightarrow Fe_2O_3.3H_2O \qquad (2)$$

CO_2 is generated by thermal and/or acidic decomposition of the brine carbonates and bicarbonates, reducing its pH value. A decrease in pH increases corrosion.

- **Ammonia.** NH_3 gas is generated by the chemical decomposition of compounds containing nitrogen such as kerogen. Ammonia and its ammonium salts corrode copper alloys: Brass and bronze moving parts of pumps wells.

Corrosion Control

The cost of the aging infrastructure maintenance and repair are considerable and increasing. A recent NACE report estimated that 20 to 30% of this cost could be saved by application of corrosion control technologies.
The principal means of corrosion control in the geothermal industry are correct selection of materials of constructions for equipment and structures, use of special paints, coatings and linings resistant to concentrated brines and cathodic protection by impressed current and/or sacrificial magnesium or aluminum anodes.
Today, the main and fastest source of information on corrosion control of industrial equipment, plants and facilities is the internet. Data bases and computer – based expert systems, dealing with selection of materials, their properties and corrosion control for many environments and industries are listed in Roberge´s Handbook.

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