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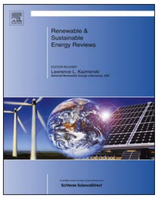

Corrosion in geothermal environment: Part 1: Fluids and their impact

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ABSTRACT

Energy production from geothermal resources can be challenging if geothermal fluid chemistry promotes metal corrosion of the production equipment's construction material. This fluid chemistry is normally unknown until deep production wells are drilled and tested. This paper reviews available literature on corrosion in geothermal environment due to different geothermal fluid chemistries. The existing geothermal fluid corrosiveness classification systems are also reviewed, compared and harmonized into a single classification system. In the harmonized system, the types of geothermal fluids identified from two existing classification systems were merged into one. New geothermal fluid chemistry types that were not considered in the two existing indices were also created. This new fluid types includes the very low pH and high salinity brines encountered in deep volcanic and sedimentary systems, A sub-class was similarly created for steam-dominated geothermal reservoirs, producing steam with HCl gas.

The geothermal power industry has reported a wide variety of corrosion problems. At least nine modes of corrosion were reported in this review from uniform corrosion to microbiologically induced corrosion (MIC). Varying degrees of uniform corrosion is most prevalent phenomena under any geothermal fluid condition and is mostly observed in carbon steel pipelines and equipment. Medium and high-strength carbon and alloy steels are susceptible to sulphide stress cracking under various conditions in geothermal fluid Erosion-corrosion occurs in the pipes for two phase flow transport which runs at high velocity. Designers of geothermal facilities and equipment need to properly match materials for any given type of geothermal resource fluid and process condition. Improper use of materials can lead to excessive corrosion damage that can result to catastrophic accidents and losses.

1. Introduction

Fluids produced by natural (conventional) geothermal resources bring to the surface many chemical impurities that can be corrosive to common construction materials such as metals and cement [3]. Corrosive chemical species normally found in geothermal fluids are: oxygen (very minimal due to reducing environment), hydrogen ion (pH), carbon dioxide, hydrogen sulphide species, ammonia, chloride ion, and sulfate ion [4]. Downstream processing of these fluids for power generation either removes or introduces other contaminants to these impurities [3]. In liquid dominated geothermal reservoirs, high temperature fluids from geothermal wells undergo processing in separators to isolate the brine and steam components. In a simple single-flash system, steam is transported to the power plant to run the turbine-generators while the brine is normally injected back into the geothermal reservoir [5]. Most of the liquid soluble chemical species are preferentially retained in the brine while the dissolved gas is concentrated in the separated steam [3]. Steam from vapor-dominated fields (those that yield dry or superheated steam at the wellhead, at pressures above atmospheric) such as Larderello and Monte Amiata (Italy), The Geysers (California) and Kamojang (Indonesia) are used directly for power generation [6]. Although steam in this case may have to go through a demister [7] or a steam scrubber [8] before entering the turbine. In both cases steam contains the gases CO_2, H_2S, and NH_3 (and others of lesser consequence). These may appear in different proportions and to a total of between 0.4% and 10% by weight [9] but may reach unusual levels of up to 80% [10,11]. In binary power plants the geothermal fluid's chemical concentrations are largely unchanged throughout the process flow; however, changes occur on physical properties of the fluid mainly due to temperature and pressure drop [12]. Temperature and pressure also affects the pH of geothermal fluids [13,14] and consequently the corrosiveness of the fluid [15].

The non-gaseous impurities are significant in water-phase corrosion in geothermal systems, while the gaseous impurities are important

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in steam-phase, condensate and atmospheric corrosion [4]. Wood [9] considers the following geothermal process environments for corrosion:

(a) At the two-phase pipeline before separation where water, steam and possibly some solid/rock particles are present.
(b) In steam pipes where initial contamination with 'carry-over' brine from the separation process is gradually diluted by condensed steam.
(c) At the entry to the turbine where the steam is almost dry or with slight super-heat.
(d) At exhaust from the turbine where the steam it is very wet.
(e) In the condenser where circulating water and air are both present,
(f) In the gas extraction circuit where air, gas, water and vapor are present.
(g) In the circulating water circuit where gases may be released and flashing water and gases are discharged from drains.
(h) In some systems, the brine undergoes downstream processing either through multiple stage separation or passed through heat exchangers. Acids are often added to minimize silica scaling [16,17].
(i) Cooling the brine in thermal ponds or sumps before re-injection where the resulting fluid is highly oxygenated and saline.

These corrosion environments are mainly on the surface where a variety of corrosion engineering solutions are available. In contrast, solutions to corrosion problems inside the wellbore are very limited. Down-hole conditions in geothermal wells are more extreme in terms of temperature and pressure and the selection of appropriate materials for equipment used over the entire lifetime of a well is technologically and economically complex [12,19]. Long term equipment includes casing, cement, and down-hole pumps or heat exchangers. Short-term equipment includes equipment used during actual drilling and completion operations as well as during logging and evaluation of the resource [20]. Equipment which contacts the fluid of the geothermal well is vulnerable to corrosion. The problem of reliability of materials used down-hole is a result of operations dictated by the physical nature of the formation being drilled but also due to the chemical composition of the resource fluids and gases encountered [21]. Geothermal systems commonly contain dissolved or free carbon dioxide (CO_2) and hydrogen sulphide (H_2S) gases that contribute to the corrosion problem. Hydrogen sulphide limits the materials that can be used for drilling equipment and also for casing to the lower strength steels [22], because higher strength steels will fail by sulphide stress cracking [23]. Other problems relating to well casing have occurred in large-scale geothermal-electric exploitation. These problems have resulted from thermal stress, sulphide stress cracking (SSC), cementing inadequacies, and internal or external corrosion of the casing [12,19,24]. Subsequent sections lay out the properties of geothermal fluids with particular emphasis on its classification with respect to its corrosive elements. Examples of corrosion damage to geothermal facilities and components are shown according to the forms of corrosion discussed. The goal is to establish the cause and effect of geothermal corrosion throughout the flow process from extraction, utilization and re-injection. Although different types of materials are used in different geothermal energy systems, the focus of this work is on geothermal fluids and their impact. This is to capture the recent experience and help in refining and focusing material selection in similar and new fluid environment.

2. Corrosive geothermal fluids classifications

Two major bodies of work have proposed corrosion classification systems for geothermal fluids. The first was the product of a research conducted by Radian Corporation and sponsored by the US Department of Energy [12]. Due to the importance of material selection on the economic viability of power generation, material studies were a major research area during the early years of US Federal government involvement in developing geothermal energy (US DOE GTP 2006). The first objective of the project was to "synthesize the corrosion experience from numerous worldwide geothermal operations into a rational, organized body of corrosion experience" [4].

The second was a collaborative work between Tohoku National Industrial Research Institute, AIST, MITI, Japan and Materials Performance Technologies, Industrial Research Limited, New Zealand and sponsored by International Energy Agency (IEA) Research Collaboration Program which started in 1997. The purpose of the research was to "collect and evaluate material results and experience relevant to the selection of materials for deep-seated geothermal developments" [25].

2.1. Geothermal fluids corrosivity index

This classification system is incorporated in a manual titled "Material Selection Guidelines for Geothermal Energy Utilization Systems" [1]. The data used for the classification comes from fields in: El Salvador, Iceland, Italy, Japan, Mexico, New Zealand and the United States. There were a total of 45 geothermal sites from the seven listed countries were reviewed for the project.

The study concluded that the produced geothermal fluids contain key chemical species that produce a significant corrosive effect on construction materials. These key species were identified from an extensive corrosion analysis and an examination of chemical composition data on fluids from both liquid-dominated and steam-dominated geothermal resources. These key species are: oxygen (usually from atmospheric contamination), hydrogen ion concentration (or pH), chloride ion, hydrogen sulphide (H_2S), carbon dioxide (CO_2), carbonate ($CO_3^{=}$), and bicarbonate (HCO_3^{-}) ions, ammonia (NH_3), ammonium ion (NH_4^{+}) and sulfate ($SO_4^{=}$) ion.

In the development of the classification system the term total key species (TKS) was proposed. Analogous to total dissolved solids (TDS), the TKS is the sum, in parts per million (mg/kg), of chloride, sulfate, carbon dioxide, bicarbonate, carbonate, total sulphide species and total ammonia species [4]. For most liquid dominated resources the bulk of the TKS is chloride, sulfate, and bicarbonate, with only minor weight contributions from ammonia and sulphides. Separated fluid chemistry was used as the basis for classifying liquid-dominated resources, since there is no available analytical data from un-flashed fluids. In the case of steam-dominated resources, the term TKS, as defined above has little significance and is replaced by the volume percent of non-condensable gases in the steam. Each class in the system is reviewed below [1].

2.1.1. Class I corrosivity

This class represents the hyper-saline type geothermal fluid encountered in the Salton Sea geothermal system (SSGS) and Imperial Valley geothermal system in the US. The total key species (TKS) in this fluid is greater than 100,000 ppm of which 99% is chloride (Cl^-). The geothermal fluid pH is < 5 in un-flashed condition and the fluid temperature in the reservoir is about 365 °C (690°F) [12]. Although the fluids from the geothermal field in Soultz-sous-Forêts, France [26] have very high TKS concentration ($Cl^- = 59{,}000$ ppm), the fluid from this resource does not qualify in this class based on the TKS defining parameters.

2.1.2. Class II corrosivity

This class represents the fluids from acidic liquid-dominated geothermal reservoir. The data source for this class is from Matsukawa geothermal field in Japan [27]. The concentration of total key species is from 1000 to 10,000 ppm. The un-flashed pH of the fluid in this class is < 4.5. The lower limit for the pH range was not defined.