Scaling and corrosion formation mechanism in geothermal piping system based on Pourbaix-Lindal diagram-Ryznar index and fluid velocity profile

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ABSTRACT. Geothermal fluid flow contains scale and corrosion species whose levels differ from each location of geothermal sources. The velocity of scale formation and corrosion mechanism due to specific parameters in case of total key species, flow rate, pressure and temperature of the geothermal fluid based on the Pourbaix-Lindal diagram -Ryznar index. The reduction in pipe diameter due to the scaling formation on the internal surface of the pipe correlates with the flow rate of geothermal fluid into the turbine, which drives the generator to produce electrical energy. This paper describes the mechanism of scale formation and the potential for corrosion on the internal surface of the piping through the momentum transfer approach of geothermal fluids to the turbine. Through this mechanism, curative and preventive measures can be taken to prevent premature degradation of the function and economic life of the geothermal piping system. The mathematical simulation results of fluid displacement momentum, the velocity of geothermal fluid flow, show that the velocity profile at the fluid-internal surface contact of the pipe is zero, which means that the species is at rest on the internal surface of the pipe. Thus, for scale species it will form a scale, while for corrosive species there will be a corrosion process on the internal surface of the pipe.

Keywords: Geothermal fluid, Total key species, Pourbaix diagram, Lindal diagram, Ryznar Index, Fluid velocity profile.

1. Introduction
Geothermal, wind, solar, and biomass are a group of new and renewable energy, environmentally friendly, but their contribution only reaches 12.36% of the total electricity demand [1]. In contrast to wind, solar and biomass energy which requires energy storage in the form of batteries, geothermal energy is abundant and a source of future energy, which can be directly utilized, such as hydropower, steam, coal and petroleum [2].

The geothermal piping system is an integral part of the power generation system which consists of a production well reservoir, a piping system, a pipeline, a turbine and a generator. The function of this piping system is to flow geothermal fluid from the reservoir to the turbine to drive a generator that will produce electrical energy. Geothermal fluid consists of steam containing non-volatile anions such as Cl⁻, SO₄²⁻, NH₄⁺, F⁻, I⁻, Br⁻ and cations such as Na⁺, K⁺, Mg²⁺, Mn²⁺, Fe²⁺, Al³⁺, and non-condensable...
gas (NCG), CO₂, H₂S, H₂ and the inert gas He and Ar and brine [3,4,5,6]. Some of these anion and cation species are also influenced by the character of production wells which have a composition of wet vapor, impurity gases, non-condensed gases, and a scale that has the possibility of solid particles.

Scale and corrosion due to contact on the internal surface of the piping system, which is a critical and complex problem in geothermal energy which is well known and disclosed by many researchers and practitioners [7-8]. The main problem that needs to be addressed is why does corrosion and scale occur in flowing geothermal fluids and how is the mechanism of scale formation and corrosion occurring in flowing geothermal fluid. This paper examines the mechanism of scale formation and corrosion based on the pH of geothermal fluids using the Pourbaix-Lindal diagram and Ryznar index approach which is correlated with the velocity profile of geothermal fluid flow. In answering the 2 (two) questions above, there are 2 hypotheses used, namely (1) both the formation of scaling and the corrosion reaction would occur at rest, (2) the Fe on the surface of the internal piping system was oxidized to form Fe²⁺ and Fe³⁺.

2. Geothermal fluids

2.1. Characteristics parameter

Characteristics of geothermal fluid parameters include key species, pH, TDS, Ω, T, P. During the flow of geothermal fluid in the piping system, there is a decrease in fluid temperature and at the same time there is a total key species interaction with the internal surface of the pipe. The temperature drop occurs due to heat transfer both by convection and conduction through pipe walls and insulators. Lindal diagram maps [9] temperature with fluid phase and its application. For electrical energy, the temperature of the geothermal fluid ≥ 120 °C where the temperature in the range 120-180 °C is known as binary steam, while 180-220 °C is known as superheated steam. A decrease in temperature will result in a decrease in the level of steam dryness, a change in pH value, a decrease in the solubility of key species, and a pressure. The correlation of the temperature decrease with the degree of steam dryness is stated

\[ X_w + X_s = 1 \]  

(1)

Where Xw is the weight fraction of water and Xs is the weight fraction of steam. A decrease in temperature can cause an increase in Xw and a decrease in Xs.

Changes in pH values and decreasing solubility of species as a result of decreasing geothermal fluid temperature have an impact on the tendency of scale formation and corrosion on the internal surface of the piping system. Decomposition of H₂S and formation of metal sulfides (MeS) as scales.

\[ H_2S \rightarrow S^2+ + 2H^+ \]  

(2)

\[ Me^{2+} + S^2+ \rightarrow MeS \text{ (where Me: Fe, Mn, Cu, Pb, etc)} \]  

(3)

H₂CO₃ decomposition and CaCO₃ precipitation (as scale) take place according to the reaction

\[ H_2CO_3 \rightarrow 2H^+ + \text{CO}_3^{2-} \]  

(4)

\[ Ca^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \text{ (as scale)} \]  

(5)

The solubility product, Ksp, is represented by CaCO₃ in the form of an equation

\[ Ksp = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \]  

(6)

Where the value of Ksp <1 means unsaturated; Ksp = 1 means saturated; Ksp> 1 means precipitated. Based on the water hardness classification (as ppm CaCO₃), CaCO₃ in 15-50 ppm is soft; CaCO₃ 50-100 ppm medium soft; 100-200 is hard, and CaCO₃ > 200 ppm is very hard.

The correlation of the descaling and corrosion trends was modeled by Ryznar [10], which was based on the saturation concept of calcium carbonate or calcite. RSI (Reyznar Saturation index) is calculated based on the pH of geothermal fluid and the calculation of pH saturation 2 (pHs) with the equation

\[ RSI = 2 \text{ (pHs) - pH} \]  

(7)

Calculation of pHs using equations

\[ \text{pHs} = (9.3 + A + B) - (C+D) \]  

(8)

where \[ A = \frac{\log_{10}[TDS] - 1}{10} \]; \[ B = -13.12 \times \text{log}_{10} (\text{°C} + 273.15) + 34.55 \];

and \[ C = \log_{10}[\text{Ca}^{2+} \text{ as CaCO}_3] - 0.4 \]; \[ D = \log_{10}[\text{alkalinity as CaCO}_3] \]
2.2. Pourbaix Diagram

Pourbaix Diagram is a diagram that correlated pH with chemical potential [11]. As is known, geothermal pipes are generally made of carbon steel and stainless steel with reference to practical recommendations such as API 5L Gr.B, ASTM A53 [12]. In geothermal fluids, corrosion is the reaction between the internal of a pipe surface and a type of corrosive key species in steam. Under acidic, neutral and alkaline conditions the Fe on the internal pipe surface is oxidized or polarized to Fe$^{2+}$ or Fe$^{3+}$ shown in Table 1

| No. | On the | Acid corrosion | Oxygen corrosion |
|-----|--------|----------------|-----------------|
| 1   | Anodic | Fe $\rightarrow$ Fe$^{2+}$ + 2e$^-$ | Fe $\rightarrow$ Fe$^{2+}$ + 2e$^-$ $\rightarrow$ Fe$^{3+}$ + e$^-$ |
| 2   | Cathodic | 2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$ | O$_2$ + 2H$_2$O + 4e$^-$ $\rightarrow$ 4OH$^-$ |
| 3   | Overall | Fe + H$^+$(aq)$\rightarrow$Fe$^{2+}$(aq) + H$_2$(g) | 4Fe + 3O$_2$ + 2H$_2$O $\rightarrow$ 4FeOOH |

2.3. Fluid flow velocity profile

Geothermal fluid flow in the pipe is divided into convective momentum transfer in the direction of the geothermal fluid flow and viscosity momentum transfer in the radial direction shown in Figure 1 [13,14,15].

As it is known that the momentum flux is the shear force expressed, $\tau = \eta (d v/d r)$ so that it is obtained

$$\tau_{rz} = \left( \frac{\Delta P}{L} + \rho g \right) \frac{r}{2}$$ (9)

In fully developed conditions, the fluid flow velocity profile forms a boundary layer as shown in equation (10) and Figure 1.

$$v_z = \left( \frac{\Delta P}{L} + \rho g \right) \frac{R^2 - r^2}{4\eta}$$ (10)

The flow velocity at the part in contact with the pipe surface is 0 (at $r = R$, $v = 0$, the fluid is in idle or static condition).
3. Corrosion Mechanism and Scale Formation

Geothermal fluid has characteristic parameters for total key species, pH, TDS, resistivity, and chemical composition. Meanwhile, the geothermal fluid properties include density ($\rho$), viscosity ($\eta$), and flow velocity ($v$), and pipe diameter ($D = 2R$). The combination of the interaction of the geothermal-piping system fluid contact interface and the viscous momentum of the radial direction has an important role in the formation of scale and corrosion on the internal surface of the pipe. In simple terms, the approximate parameters and characteristics of geothermal fluid flow are shown in Figure 2.

![Figure 2. Causal-effect diagram of scale formation and corrosion mechanism](image)

4. Discussion

4.1. Change in pH and RSI value

At RSI $\leq 6$ there tends to be scale formation, while RSI $\geq 6$ tends to corrode, as shown in Figure 3. The range of RSI and the tendency for scale formation and corrosion is shown in Table 2 [10].

| Ion S$^2$, CO$_3^2$, O$_2$, OH$^-$ and TSD, CaCO$_3$, MgCO$_3$, MeS | Ksp $>1$ Precipitation (TDS) |
|---|---|
| Corrosion: FeCO$_3$, FeS, Fe(OH)$_2$, FeOOH, | |
| Scaling formation: FeCO$_3$, FeS, CaCO$_3$, CaSiO$_3$ | |

| Fluids characteristics parameters |
| Key species, pH, TDS, $\Omega$, T, P |

| Fluids flow Properties |
| $\rho$, $\eta$, $R$, $v$ |

| Governing equation |
| $-\frac{d(r\tau_{rz})}{dr} - \frac{dP}{dL} + \rho g r = 0$ |

| Fluids flow Properties |
| $\tau_{rz} = \frac{(\Delta P + \rho g)}{R^2 - r^2}$ |

| Profile of velocity |
| $v_x = \frac{(\Delta P + \rho g)}{4\eta} \frac{R^2 - r^2}{L^2}$ |

| $r = R$ |
| $v_x = 0$, $\tau_x = \text{max}$ |

| $r = 0$ |
| $v_x = \text{max}$, $\tau_x = 0$ |

Fe$^{3+}$ on surface internal piping system and viscous momentum
4.2. Corrosion mechanisms and scale formation

During geothermal fluid flows, the internal pipe surface, Fe oxidized to Fe2+, is on the entire internal surface of the piping system. When it meets CO\textsubscript{3}\textsuperscript{2-} it will react to form FeCO\textsubscript{3} (siderite), \(\text{S}_2\) ions to form FeS (pyrite), steam FeOOH, Fe(OH)\textsubscript{2}, oxygen to form FeO, Fe\textsubscript{2}O\textsubscript{3}. As for Ca\textsuperscript{2+} with CO\textsubscript{3}\textsuperscript{2-}, SiO\textsubscript{2}, respectively form CaCO\textsubscript{3}, CaOSiO\textsubscript{2}.

The mechanism of corrosion and scale occurs in piping systems in geothermal fluid flow only and only occurs in fully developed flow conditions, at \(r = R\), where flow velocity, \(v = 0\). This has been proven in the research of [13], using Comsol software, [14] using Ansys software, [16] using the Ansys student version software as shown in Figure 5. Thus, the conditions for the formation of scale and corrosion or both are due to the oxidation of the steel pipe on the internal surface of the pipe, viscous momentum, Ksp > 1.

Table 2. Scale and corrosion tendency

| RSI value range | Interpretation tendency |
|-----------------|------------------------|
| RSI < 5.5       | High Scaling formation |
| 5.5 < RSI < 6.2 | Medium Scaling formation |
| 6.2 < RSI < 6.8 | No scale and corrosion |
| 6.8 < RSI < 8.5 | Medium corrosion       |
| RSI > 8.5       | High corrosion         |

Figure 3. Effect of pH on RSI

Figure 4. (a). Mechanism for scaling and corrosion in surface internal pipeline; (b). Scaling products

Figure 5. Fluid velocity profile in vertical flow (right) [13, 14]. (A) Simulation of flow patterns in pipes; (B) Flow patterns if there is a corrosion coupon or ER / LPR Probe horizontal flow (left) [16]

Corrosion and scale mechanisms occur in piping systems in geothermal fluid flow only and only occur in fully developed flow conditions, at \(r = R\), where flow velocity, \(v = 0\). The Metallurgical Engineering Chemical and Corrosion Laboratory, FTM, UNJANI has developed a closed flow loop simulator (CFLS).
to test the corrosivity of fluids in a particular pipe material. The line pipe specifications have been tested, i.e. API 5L X52, API 5L X65, API 5LC (X65 + Ni Base Alloy 825) etc. In the closed-loop simulator design we use computational fluid dynamic (CFD) for velocity profile mapping to describe the visual conditions on the pipe surface and if inside the pipe fitted with corrosion coupons, ER / LPR Probes (Figures A above and below, A and B). [16]

5. Conclusion
Prediction of the tendency of scale formation and corrosion based on pH, temperature, and content of key species using Lindal diagrams, Pourbaix diagrams, and RSI. The mechanism for the formation of corrosion and scale on the inner surface of pipes that flow geothermal fluids tends to occur in fully developed flow conditions where on the internal pipe surface there is oxidation or polarization of Fe to Fe$^{2+}$ and Fe$^{3+}$ and flow velocity, $v = 0$ and this means key species are in contact and at rest on the inner surface of the pipe. The geothermal fluid flow velocity = 0, in the form of a boundary layer at $r = R$, is proven using equation (9) and equation (10) and the simulation shown in Figure 4.

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