EFFECT BY ELECTROLYSIS FOR DISSOLUTION AND PRECIPITATION OF CALCITE SCALE IN A COOLING WATER LINE OF A HEAT EXCHANGE SYSTEM

Norio YANAGISAWA[1], Takahiro MATSUMURA[2]

[1]Institute for Geo-Resources and Environment, AIST, Japan
[2]REIKEN Co. Ltd, Japan

Keywords: scale, calcite, electrolysis process, precipitation rate, dissolution rate, pH

SUMMARY - A high-frequency electrolysis method was used to reduce the calcium in a circulating cooling water line by precipitating calcite on the electrodes. Therefore, this electrolysis system was useful to remove calcite scales in the flow line. In super-saturation solution for $CaCO_3$, Ca and HCO_3 concentration 100 mg/l solution, calcite scale on the stainless plate in the flow line dissolved with pH decreasing using electrolysis power supply. In contrast, no power supply, calcite precipitated more on stainless plate with pH slightly increasing.

When power supply, average dissolution rate was about 0.1 $mg/m^2/s$ and changed with pH decreased.

1. INTRODUCTION

Calcite ($CaCO_3$) scale precipitates in pipelines in factories or geothermal plants using heating and cooling processes especially at the heat exchanger. Because the precipitation of scale in pipes decreases the heat-transfer performance and prevents water flow, much research has been carried out to prevent the precipitation of scale.

Usually, in geothermal fields, the scale inhibitor, Sodium polyacrylate, C_2H_3COONa, is commonly used to prevent calcite precipitation (Ramous-Cardelaria et al., 2000) and in a Hot Dry Rock test field (Yanagisawa et al.,2006a).

Recently, electrolysis methods have been developed to prevent the precipitation of scale for a factory cooling pipeline (Gabrielli et al., 1999; Morizot et al., 1999; Neville and Morizot, 2000; Rinat et al., 2005).

We developed a high-frequency electrolysis system (Yanagisawa et al., 2006b). Using this system, the concentration of Ca and HCO_3 ions are reduced by the forced precipitation of $CaCO_3$ on the electrodes, which prevents the precipitation of $CaCO_3$ in other sections of the pipeline. And more precipitated calcite in the pipeline is removed by using this system.

In this study, we have clarified the details of the mechanism of $CaCO_3$ precipitation from changes in the chemical properties of aqueous solutions using an electrolysis method. And we have clarified the details of the mechanism of removal and dissolution of $CaCO_3$ scales precipitated previously using an electrolysis method.

2. EXPERIMENTAL

High-frequency electrolysis experiments were carried out using a Dynakleen-D150T electrolysis system (Reiken Inc., Japan). The Dynakleen-D150T system consists of a control unit and an electrode unit with three electrodes as shown in Figure 1.

In this work, the Dynakleen-D150T system was placed in a 50-liter water tank and the measuring electrodes used to sense the pH, electrical conductivity (EC), water temperature, and oxidation–reduction potential (ORP) were also immersed in the water tank, as shown in Figure 1. The measuring electrodes were connected to a PC, and the pH, EC, and ORP data were continuously acquired

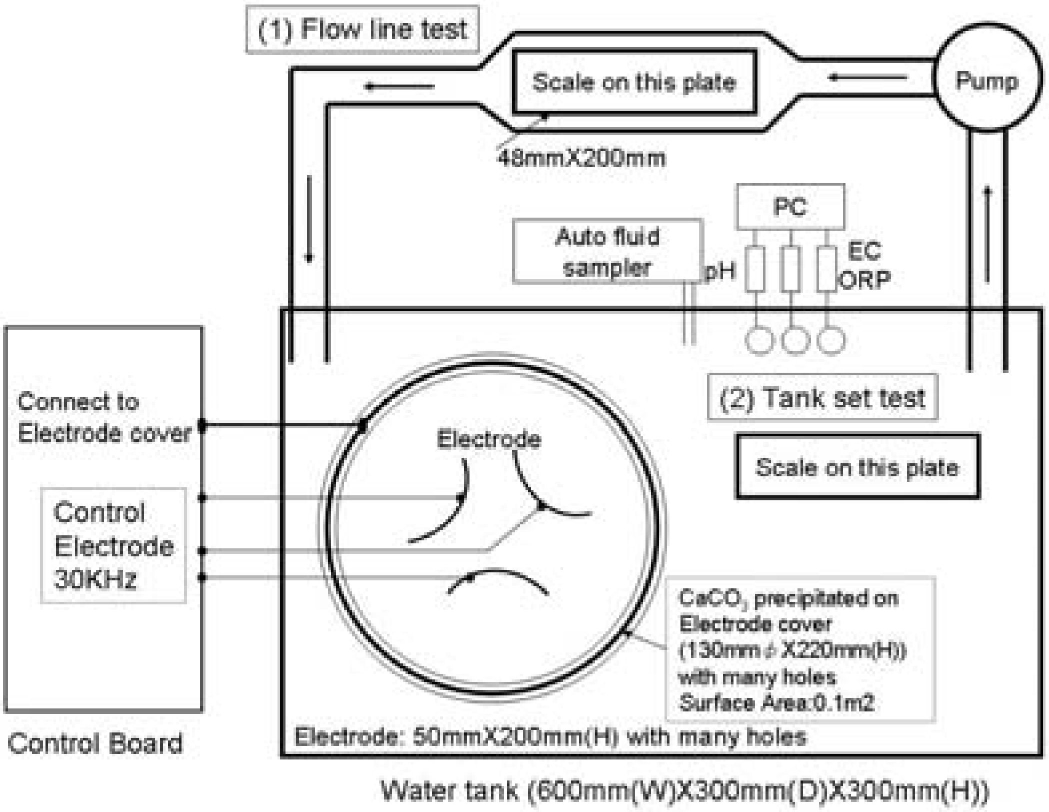

Figure 1: The Dynakleen-D150T experimental system with flow system

An experimental solution consisting of dissolved calcium lactate and sodium hydrogen carbonate in distilled water was used for the Ca and HCO_3 ions, respectively. The samples were periodically collected to measure the Ca and HCO_3 ion concentrations using an auto fluid sampler. The experiment was carried out with an initial Ca concentration at 50-200 mg/l and HCO_3 ion concentration at 100 mg/l.

The electric power supplied to the electrode had a mean voltage of 15 V and a current of 1.6 A. During the experiments, the water temperature was maintained at a constant temperature of 20 °C.

And we prepared the stainless plate with $CaCO_3$ adhesion on the surface. This stainless plate was 48 mm wide and 200 mm length and was set in the pipeline of polyvinyl as shown in Figure 1 (1). The solution in tank was pumped and it flowed along the plate in the pipeline. The flow rate was 15L/min. Fluid circulation was carried out during 118 h. in Ca super-saturation condition. To survey the detail of the dissolution rate, we set the stainless plate in a water tank as shown in Figure 1 (2) and carried out the dissolution test. We measured the weight change of the stainless plate several times during tank test. Stainless plate was taken out of the water tank and weighed after it was dried.

The HCO_3 ion concentration in the solutions was measured using the H_2SO_4 titration method, and the calcium ion concentration was determined using ion chromatography. We calculated the $CaCO_3$ precipitation rate using the change in Ca ion concentration in the solution during continuous sampling of two samples and from the 0.1 m2 surface area of the electrode cover. And we measured the weight change of the stainless plate in the flow line or water tank and calculated rate of weight change, dissolution or precipitation.

3. RESULT AND DEISCUSSION

3.1 Chemical changes in the solution

Figure 2 shows the changes in the ORP, pH, and the concentration of Ca and HCO_3 ions from the initial experimental period to a period of 72 h, with the initial Ca and HCO_3 ion concentrations set at 100 mg/l each. First, the ORP value decreased rapidly after the commencement of the experiment, and reached 0 mV after about 20 min. It reached the minimum reduced value of –250 mV after approximately 3 h. During this period, the pH also began to change: foam developed from the electrodes, and the Ca and HCO_3 ion concentrations began to decrease. This shows that the Ca and HCO_3 ions reacted as the solution entered the reduced state, and that $CaCO_3$ precipitated as scale. The precipitation of white calcite scale on the electrode cover was observed.

The ORP value increased slightly, reaching zero after a period of 30 h. During this period, the pH decreased to pH = 4.8, and the HCO_3 ion concentration decreased to 20 mg/l and the Ca ion concentration decreased to 50mg/l. Subsequently, these values reached a virtually constant level. We concluded that the precipitation rate of the scale had declined after an experimental period of 42 h. About 10.9 g of white scale had adhered to the electrode cover, and this was identified as calcite from X-ray powder diffraction data.

3.2 Mechanism of the precipitation of scale

The electron transfer due to the transfer of current is as follows:

Anode (+) side: $2H_2O \rightarrow 4H^+ + 4e^- + O_2$
Cathode (–) side: $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$.

The precipitation of $CaCO_3$ on the electrode cover in contact with cathode was confirmed in our experiments. The precipitation reaction is represented by the following equation:

$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O$.

Consequently, the deposition of $CaCO_3$ is facilitated by the higher concentration of Ca, HCO_3 and OH^- ions.

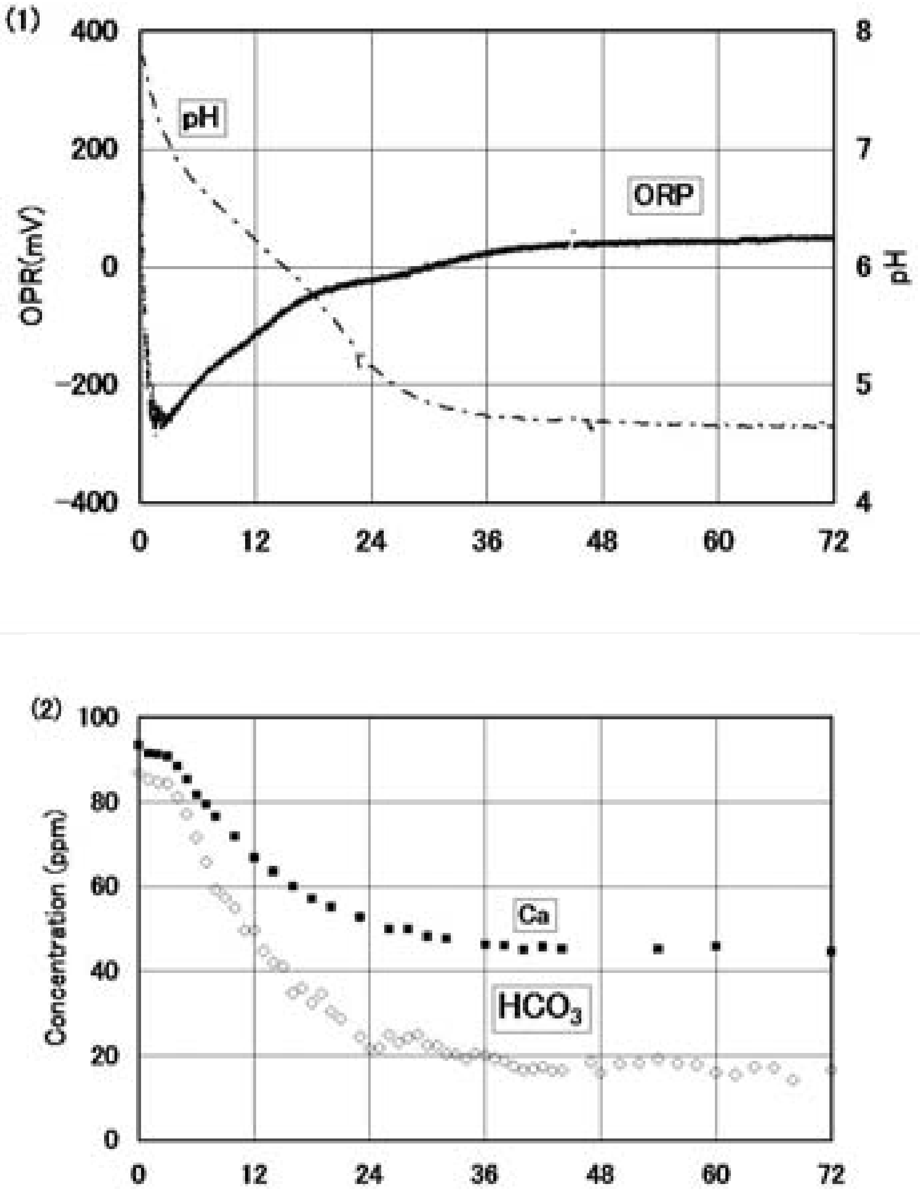

Figure 2: (1) ORP and pH (2) Ca and HCO_3 ion concentrations in an experiment with initial HCO_3 and Ca ion concentrations of 100mg/l.

3.3 Precipitation and Dissolution in super-saturation conditions of the flow line test

Table 1 shows the weight change of stainless plate, $CaCO_3$ dissolution or precipitation rate on the stainless plate and $CaCO_3$ precipitation weight and rate on the electrode cover. Initial HCO_3 concentration was 100 mg/l and Ca concentration were 50, 100 and 200 mg/l.

In the case of no electric power supply, the weight of the electrode cover did not change. And the weight of the stainless plate increased. This precipitation of $CaCO_3$ was due to super-saturation. The $CaCO_3$ precipitation rate on the stainless plate was from 0.01 to 0.025 mg/m^2/sec and highest at Ca 200mg/l solution.

However, in the case of electric power supply, $CaCO_3$ precipitated on the electrode cover on the cathode side. And the weight of stainless plate with $CaCO_3$ scale was decreased and the adhesion area of $CaCO_3$ was decreased. Ca and HCO_3 concentration in solution were decreased. The $CaCO_3$ precipitation rate on the electrode cover of Dynakleen-D150T increased with Ca concentration from 0.15 to 0.35 mg/m^2/sec due to electrical conductivity increasing. However, the $CaCO_3$ dissolution rate on stainless plate decreased with Ca concentration from 0.1 to 0.05 mg/m^2/sec.

Then, in high Ca conditions, $CaCO_3$ precipitated easily on the electrode cover and the stainless plate due to the degree of super saturation. And this degree of super saturation made it difficult for the $CaCO_3$ on the stainless plate to dissolve, with the initial Ca increased.

And in the electric power supply test, the pH decreased from 8.0 to 4.7 at 36 h. after the test started and became constant as shown in Figure 2. Difference of the minimum pH during test affected the $CaCO_3$ dissolution weight because $CaCO_3$ dissolves easily under low pH condition as follows;

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

Table 1: Weight change and precipitation or dissolution rate of stainless plate and electrode cover at initial HCO_3 concentration was 100 mg/l for super-saturation solution of $CaCO_3$.

Ca	CaCO3 adhesion stainless plate				Electrode cover	
(mg/l)		weight change(mg)	precipitation rate (mg/m2/s)	dissolution rate (mg/m2/s)	precipitation weight (mg)	precipitation rate (mg/m2/s)
50	ON	-870		0.1067	6570	0.1547
	OFF	157	0.0192		0	0
100	ON	-569		0.0698	10900	0.2566
	OFF	73	0.0090		0	0
200	ON	-419		0.0514	15100	0.3555
	OFF	196	0.0240		0	0

4. CONCLUSIONS

(1) Under $CaCO_3$ super-saturation conditions, calcite on the stainless plate dissolved by electric power supply due to precipitation on electrode cover and the pH decreased. At lower Ca or HCO_3 conditions, the dissolution rate was higher. But, with no electric power supply test, calcite

precipitated more on the stainless plate from high Ca or HCO_3 solution with pH gradually increasing.

(2) This electrolysis method is useful for removing calcite scaling on pipeline and has potential for use for geothermal systems in the future.

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