LETTER

Analysis of the electrolytic precipitation rate of calcite

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A high-frequency electrolysis method was used to reduce the calcium in circulating water by precipitating CaCO_3 on the electrodes. The oxidation-reduction potential, pH, and chemical composition were measured during the precipitation of the CaCO_3 . The calcite precipitated on the electrode cover. The concentration of calcium ions in the solution decreased under reducing conditions, and the precipitation rate of calcite depended on the pH. For initial Ca and HCO_3 concentrations of 200 ppm, the maximum precipitation rate of CaCO_3 was 2.4 $\text{mg/m}^2/\text{s}$ at pH = 6.8, and the precipitation rate decreased linearly as the pH decreased to pH = 4.6. The precipitation rate depended on the initial concentrations of calcium and HCO_3 , rather than being regulated by the initial pH using citric acid.

Keywords: Calcite, Electrolysis process, Precipitation rate, pH, ORP

INTRODUCTION

Calcium carbonate (calcite or aragonite) is a common mineral found in sedimentary rock, ore deposits, and fossils. There have been many examinations of water-rock interactions involving CaCO_3 , as summarized in Morse (1983). On the other hand, CaCO_3 frequently precipitates in pipes as scale in hydraulic systems that are subject to changes in temperature, such as in geothermal power plants, hot springs, and the cooling towers of factories. 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, and methods have been developed to prevent the precipitation of scale by using chemicals and electrolysis (Gabrielli et al., 1999; Morizot et al., 1999; Neville and Morizot, 2000; Rinat et al., 2005).

The concept of the electrolysis methods is as follows. The concentration of Ca and HCO_3 ions is reduced by the forced precipitation of CaCO_3 on the electrodes, which prevents the precipitation of CaCO_3 in other sections of the pipeline.

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 determined the dependence of the precipitation rate on factors such as the ratio of the

Ca and HCO_3 ion concentrations and the pH.

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. The electrode is 50 mm wide and 200 mm high, with many holes, and has a cylindrical electrode cover that is 130 mm in diameter and 220 mm high and also has many holes, as shown in Figure 1. The control unit provides a high-frequency current up to 30 kHz to the three electrodes, and the precipitation of scale on the electrodes is prevented by periodically altering the polarity of the three electrodes. Then, any scale precipitated on only an electrode cover that surrounds the electrodes.

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. The pH was measured at a distance of 10 mm from the electrode cover on the surface of the water tank. The solutions were sampled from two locations: one near the electrode cover and the other on the surface of the experimental water tank. The pH and calcium ion concen-

Figure 2. (1) ORP, (2) pH, and (3) Ca and HCO₃ ion concentrations in an experiment with initial HCO₃ and Ca ion concentrations of 200 ppm.

equation:

Consequently, the deposition of CaCO₃ is facilitated by the higher concentration of Ca, HCO₃ and OH⁻ ions.

The pH near the electrode cover increased rapidly immediately after the transmission of an electric current and decreased rapidly after a period of 1 h, showing a similar value to that on the surface of the water tank, as shown in Figure 3. The Ca ion concentration near the electrode cover usually exceeded the concentration observed at other sites. This indicates that the deposition of

Figure 3. The pH distribution in an aqueous solution.

Figure 4. The pH dependence of the calcite precipitation rate (for equal concentrations of Ca and HCO₃ ions).

CaCO₃ readily occurs near the electrode cover. The OH⁻ ions are then used up as the deposition of CaCO₃ proceeds, and the pH of the solution decreases, since the H⁺ ions generated from the anode remain in solution.

We did not observe any precipitation of CaCO₃ in the water tank except that observed on the electrode cover. In addition, in a test where no electrical power was supplied, we did not observe any precipitation of CaCO₃ in the water tank and the concentration of Ca ions was constant. We supposed that CaCO₃ nucleation and precipitation occurred only on the electrode cover in this experiment.

Dependence of pH on the CaCO₃ precipitation rate

We observed delayed changes in the calcium concentration in the solution as the pH decreased. Thus, from the changes in calcium ion concentration, we calculated the precipitation rate of CaCO₃ per square meter of electrode cover, and determined the relationship between the precipitation rate and the pH.

Figure 4 shows the relationship between the pH and

Figure 5. The pH dependence of the calcite precipitation rate (regulation of the initial pH).

the precipitation rate of the scale. At a calcium ion concentration of 200 ppm, the precipitation rate increased rapidly when the pH decreased from pH ~ 8 to pH ~ 6.8 , and reached $2.4 \text{ mg/m}^2/\text{s}$ at pH ~ 6.8 . Thereafter, the precipitation rate decreased linearly with decreasing pH, and it virtually ceased at pH ~ 4.6 . Conversely, at a calcium ion concentration of 100 ppm, the precipitation rate was $1.1 \text{ mg/m}^2/\text{s}$ at pH ~ 7.1 , which was half the rate observed when the calcium ion concentration was 200 ppm. The precipitation rate decreased linearly with decreasing pH, but, in general, the precipitation rate was proportional to the calcium ion concentration and reached a value of zero at pH ~ 4.6 , which is similar to the case where the calcium ion concentration was 200 ppm.

Figure 5 shows data from a comparative experiment, in which the initial concentration of calcium and HCO_3^- ions was 200 ppm, and the pH was set to pH 6, 7, and 8 using citric acid. The initial pH was pH ~ 7 , and the precipitation rate was $2.4 \text{ mg/m}^2/\text{s}$ at pH ~ 6.8 . Subsequently, the overall precipitation rate decreased linearly with decreasing pH. A similar trend was observed when the initial pH was pH ~ 8 . When the initial pH was pH ~ 6 , the precipitation rate reached $1.9 \text{ mg/m}^2/\text{s}$ at pH ~ 5.9 , and tended to show somewhat higher values compared with the precipitation rates for an initial pH of pH ~ 7 or ~ 8 , but it decreased linearly and reached a value of zero near pH ~ 4.8 . This indicates that the precipitation rate decreased linearly with decreasing pH, even when the initial pH of the solution was altered. The precipitation rate reached zero in the pH range of pH ~ 4.6 – ~ 4.8 .

Figure 6 shows the relationship between the pH and the precipitation rate of the scale when the initial HCO_3^- concentration was set to 100, 200, and 300 ppm. At an HCO_3^- ion concentration of 100 ppm, the reaction was initiated at pH ~ 8.5 , at which point the initial rate was $1.5 \text{ mg/m}^2/\text{s}$. The precipitation rate decreased linearly

Figure 6. The pH dependence of the calcite precipitation rate (change in HCO_3^- ion concentration).

with decreasing pH, and reached a value of zero at pH ~ 5.5 . The precipitation rate increased in the range pH ~ 7.7 – ~ 7.2 at an HCO_3^- ion concentration of 300 ppm and exceeded $3.0 \text{ mg/m}^2/\text{s}$ at pH ~ 7.2 , but the rate decreased rapidly with decreasing pH and reached a value of zero at pH ~ 5.5 .

In this way, the precipitation rate increased rapidly on initiation of the electrolytic current, and reached a peak at pH ~ 7 with an initial HCO_3^- ion concentration of 200 ppm, after which, the precipitation rate decreased in a linear manner. The precipitation rate depended on the initial concentration of calcium and HCO_3^- ions, rather than being regulated by the initial pH using citric acid. The precipitation rate for Ca/ HCO_3^- ratios that deviated from the ratio of 1:1 was lower than that when the initial concentrations were equal at the same pH.

CONCLUSIONS

1. Calcium carbonate was precipitated on the electrode cover of the Dynakleen-D150T system from the following reaction:

The pH of the aqueous solution decreased as this reaction progressed. In addition, the pH in the vicinity of the electrode cover was higher than at other sites, and the calcium ion concentration was also confirmed to be higher.

2. With progressive precipitation of scale and decrease in pH, the precipitation rate of the scale decreased linearly and was accompanied by a decrease in the pH to pH < 7 , regardless of the initial pH and calcium and HCO_3^- ion concentrations. The precipitation rate depended on the initial concentrations of calcium and HCO_3^- ions, rather

than being regulated by the initial pH using citric acid.

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