

The effect of polyacrylic acid (PAA) as an inhibitor of calcium carbonate scales on the formation of silica scales at geothermal power plants

川本, 幸

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氏 名 : 川本 幸

論文題名 : The effect of polyacrylic acid (PAA) as an inhibitor of calcium carbonate scales on the formation of silica scales at geothermal power plants
(炭酸カルシウムスケール抑制剤としてのポリアクリル酸(PAA)が地熱発電所におけるシリカスケール生成に及ぼす影響)

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論 文 内 容 の 要 旨

Precipitation of calcium carbonate and silica, which is formed from geothermal water at geothermal power plants, often causes serious problems from the viewpoint of efficient stable power plant operation. In Takigami geothermal power plant, polyacrylic acid (PAA) is added to inhibit the formation of calcium carbonate scale in production wells. The addition of PAA succeeded in inhibiting calcium carbonate scale formation, on the other hand, the amount of silica scale formed in the separator of the production wells increased. Although chemical properties of geothermal water was not changed apparently and whether PAA accelerates the silica scale precipitation or not has never been elucidated, silica scale precipitation was in fact accelerated. Aluminum ion (Al^{3+}), which induces deposition of silica scales, is a hard metal ion and can interact strongly with PAA to form Al^{3+} -PAA complexes. Some studies on the interaction between Al^{3+} and PAA have been published. PAA can be adsorbed on the surface of aluminum oxide (Al_2O_3) by weak hydrogen bond formation. If aluminum interacts with PAA in aqueous solution, the compound of Al and PAA has a potentially harmful effect on the growth of silica scale. In this study, the following research was conducted to elucidate the adverse effect of PAA for the silica scale acceleration. Therefore, the purpose of this investigation is to elucidate the effect of PAA addition into geothermal water on the formation of silica scales at geothermal power plants. The contents in each chapter of this thesis are as follows.

Chapter I describes the general introduction and the research background about the effect of PAA addition into geothermal water on the formation of silica scales.

Chapter II describes the effect of pH on the interaction between Al^{3+} and PAA to clearly understand the stability of Al^{3+} -PAA complexes. PAA can interact with Al^{3+} in a wide pH range and can form stable Al^{3+} -PAA complexes not only in the liquid phase but also in the solid phase. The complexation mechanism depends on the chemical state of Al^{3+} and COOH in PAA, that is, hydrolysis of Al^{3+} and deprotonation of COOH group in PAA. The chemical reaction between Al^{3+} and PAA is the displacement of H^+ of COOH group and three COOH groups can combine with one Al^{3+} on average at pH 3. On the other hands, above pH 4.5, the bond formation between Al hydrolyzed species, especially $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$ and COO^- group in PAA occurs.

Chapter III describes a model experiment using sodium silicate solution with the purpose to examine the effect of Al^{3+} -PAA complex on the precipitation of silicic acid. PAA can interact with Al^{3+} in the sodium silicate solution at pH 8.5 and can form a stable Al^{3+} -PAA complex. In the sodium silicate solution including Al and PAA, the M-P (monomer-polymer) reaction is retarded, and the dissolution of silica gel was simultaneously inhibited. The formation of silica scale is considered as an equilibrium reaction between polymerization of monosilicic acid in solution to solid phase and dissolution of silica from a solid phase. From the experimental results, it can be reasonably concluded that the addition of PAA into geothermal water causes both the retardation in dissolution of silica

scales, and the acceleration in deposition of monosilicic acid.

Chapter IV describes the investigation of polymerization of silicic acid and precipitation of aluminum and silicic acid from geothermal waters, with or without PAA, at Takigami geothermal power plant. The purpose is to elucidate the effect of PAA on the formation of silica scales through an on-site experiment. The polymerization of silicic acid based on the changes in monosilicic acid concentration in geothermal water with time, and hydrodynamic size of polysilicic acid particles, was not affected by PAA. On the other hand, the adsorption behavior of aluminum was considerably different between in the absence and presence of PAA. Only a small amount of aluminum was adsorbed in the absence of PAA, however most of aluminum was adsorbed in the presence of PAA. The amount of silicic acid adsorbed in the presence of PAA was significantly larger than that in the absence of PAA. Consequently, the Al^{3+} -PAA complex may accelerate the formation of silica scales from geothermal water.

Chapter V describes the conclusions from Chapter I to Chapter IV. PAA added into geothermal water can interact with Al^{3+} in a wide pH range, and can form a stable Al^{3+} -PAA complex. This complex in geothermal water can be adsorbed on the pre-formed silica scale, to which causes both the retardation in dissolution of silica scales, and the acceleration in deposition of monosilicic acid on the surface of silica scale. Aluminum in Al^{3+} -PAA complexes acts as an adsorption site for monosilicic acid. Consequently, the Al^{3+} -PAA complex accelerates the formation of silica scales from geothermal water.