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Effect of Ultrasonic Irradiation on Behavior of Silica Polymerization in Geothermal Water

地熱水中のシリカ重合挙動に及ぼす超音波照射の影響

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1. Introduction

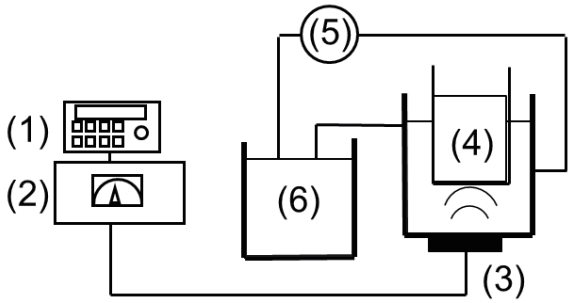
Japan has the third-largest geothermal resource in the world. Geothermal power generation is unaffected by weather. However, a serious problem encountered in geothermal power plant is deposition of silica scales at undesired locations of solid surfaces in a heat exchanger and a conveyance system. This deteriorates heat transfer efficiency of the heat exchanger and leads to blockage of water flow in the conveyance system.

The deposition of silica scales is due to polymerization of silicic acid on the solid surface which touch to cooling fluid. Prior reduction of silica monomer concentration from silica rich process-water is effective to prevent scaling at undesirable locations. One of the ways for prior reduction of silica monomer concentration is that polymerization rate of silica monomer is accelerated in solution and the resulting silica particles are removed. In this study, ultrasound is irradiated to silicic acid solution and concentration changes of silica monomer and total silica was measured. Effects of ultrasonic frequency and the solution pH were investigated.

2. Experimental

Fig. 1 shows the outline of the experimental appratus for ultrasonic irradiation at 500 kHz. A transducer were driven by a power amplifier and a signal generator. Sample temperature was maintained at 308 ± 1 K by a constant temperature bath and a pump. Sample volume was 200 mL. For a comparison, an ultrasonic horn at 28 kHz and a stirrer were used. Ultrasonic intensities at 500 and 28 kHz measured by a calorimetric method were 3.6 and 15.3 W, respectively. Liquid glass aqueous solution was used as a sample. The initial concentration of silica was 1.1 g/L. The solution pH was adjusted by the addition of HCl or NaOH.

The concentrations of silica monomer and total silica in the filtrate were measured by the molybdate yellow method. For the measurement of total silica, to make silica polymer depolymerize, sodium bicarbonate and distilled water added to the filtrate and boiled for 30 min. The filtrate was cooled to room temperature, and the silica concentration was measured.



(1) Signal generator
(2) Power amplifier
(3) Transducer
(4) Sample
(5) Liquid pump
(6) Const. temp. bath

Fig. 1 Outline of experimental apparatus for ultrasonic irradiation at 500 kHz.

3. Results and Discussions

Fig. 2 shows the change in silica monomer concentration with time for ultrasonic irradiation, stirrer and addition of chemical substance. The silica monomer concentration decreases to quasi-stable concentration because of silica polymerization. The quasi-stable concentration was close to amorphous silica solubility.[1)] Compared with stirring, the reduction rate of silica monomer concentration for ultrasonic irradiation at 500 kHz increases. An addition of H_2O_2 is accompanied by an additional increase in the reduction rate.

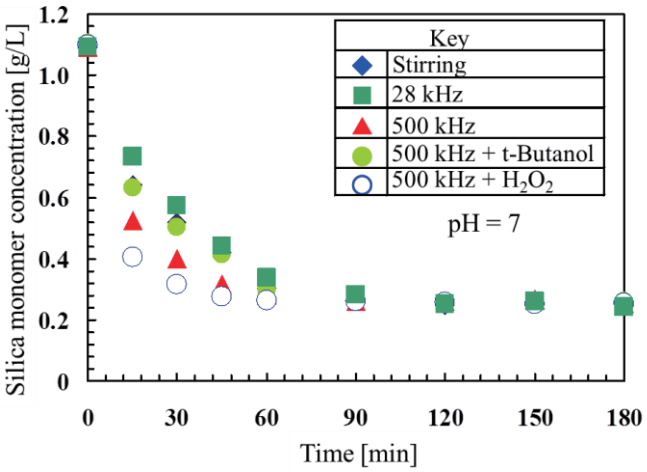


Fig. 2 Change in silica monomer concentration with time for ultrasonic irradiation, stirring and addition of chemical substances.

The formation rate of OH radical is enhanced by addition of H_2O_2. On the other hand, the reduction rates for irradiation at 28 kHz and the addition of t-butanol under irradiation at 500 kHz are almost the same as that for stirring. t-Butanol is radical trap agent. From these results, it is clear that the formation of OH radical due to pyrolysis of water accelerates polymerization of silica monomer. The rates of reduction from initial monomer concentration to quasi-stable one are obeyed a pseudo-first order kinetics given by Eq. (1).

$$(C - C_e) / (C_0 - C_e) = \exp(-k\,t) \qquad (1)$$

Here, C is the silica monomer concentration, C_e is the quasi-stable concentration of silica monomer, C_0 is the initial silica monomer concentration, k is the apparent reaction constant, and t is time.

Fig. 3 shows the effect of the solution pH on the apparent reaction rate constant of silica monomer. The reaction rate constant for irradiation at 500 kHz is higher than those for stirring and irradiation at 28 kHz. For all cases, the reaction rate constants are maximum at about the solution pH of 8. This is because the reaction rate between monosilicic and polysilicic acids is maximum at the solution pH of 8.5.[2)]

Fig. 4 shows the change in total silica concentration in solution with time for ultrasonic irradiation and stirring. The total silica concentrations for stirring and ultrasonic irradiation at 28 kHz are almost constant. However, for irradiation at 500 kHz, large silica particles were formed and the total silica concentration decreased. The formation ratio of large silica particles was estimated from Eq. (2).

$$\eta = (C_0 - C_T) / (C_0 - C_e) \qquad (2)$$

Here, C_T is the total silica concentration after 90 min.

Fig. 5 shows the effect of the solution pH on the formation ratio of large silica particles. Regardless of the solution pH, in the cases of stirring and irradiation at 28 kHz, large silica particles are little formed. On the other side, the case of irradiation at 500 kHz, the formation ratio of large silica particles becomes larger below the solution pH of 7. It is considered that the zeta potential of silica particle are close to zero as the solution pH becomes lower and the electrostatic repulsive force between silica particles decreases.

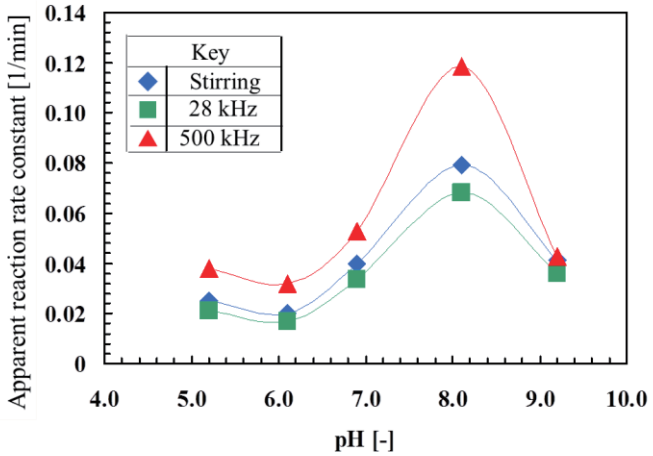


Fig. 3 Effect of solution pH on apparent reaction rate constant of silica monomer for ultrasonic irradiation and stirring.

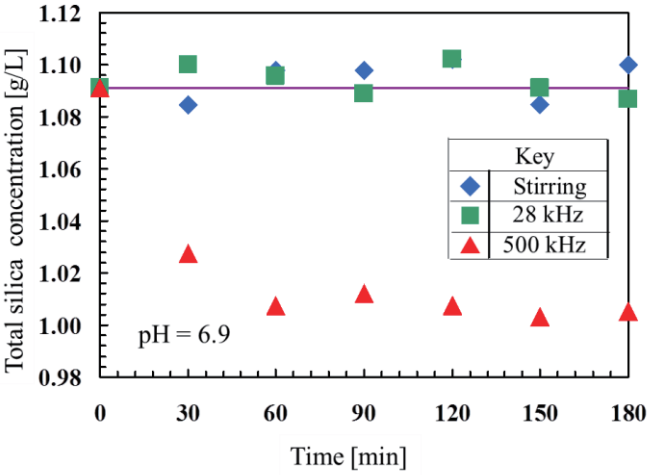


Fig. 4 Change in total silica concentration with time for ultrasonic irradiation and stirring.

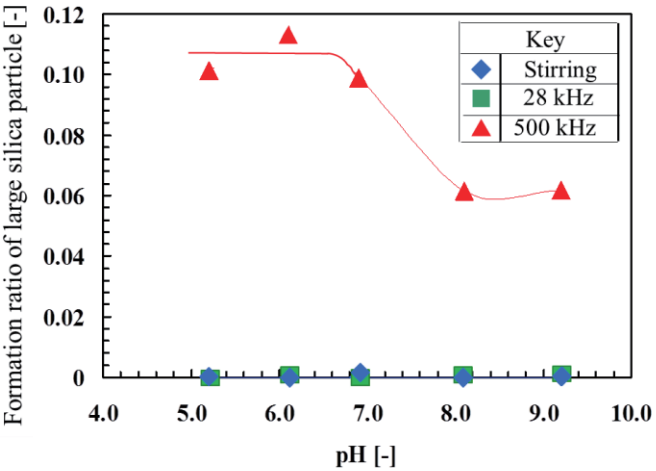


Fig. 5 Effect of solution pH on formation ratio of large silica particles for ultrasonic irradiation and stirring.

References

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