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A STUDY ON MESOPOROUS SILICA RECOVERY FROM GEOTHERMAL BRINE

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ABSTRACT

The produced brine from production wells tends to deposit siliceous scale at the surface facilities such as brine transportation lines, because of high silica concentration in the brine. Then, research and development to extract supersaturated silica as a starting substance of a kind of zeolite groups was undertaken. Unlike a commonly used zeolite, mesoporous silica has large pore size between 12-100Å, so it can be used as carrier materials introducing new functional characteristics. In a newly developed process, the brine with a temperature of 91° C and a SiO_2 concentration of 850 ppm(w/w) is flowed into moving bed packed with γ-alumina after adding cationic surfactant of 10ppm so that the silica-surfactant compound is grown efficiently with occurrence of polymerization. The treated brine is stored at a holding tank and filtered to recover the white silica precipitate. An alkaline reagent is added into the silica powder (SiO_2;65.4w%,Al_2O_3; 24.5w%, specific surface area; 23 m^2/g) as raw material, and normal cationic surfactant and HCl are added with constant stirring for three hours at room temperature. A precipitate is filtered and it is calcined at 450° C for one hour to remove cationic surfactant. The calcined precipitate was identified as a mesoporous silica by X-ray diffraction analysis (XRD). The final silica product has a 861 m^2/g of specific surface area that is a relatively higher value than about 500-600 m^2/g of other zeolite crystals.

We considered that the benefits of this process are to adopt an efficient separation systems and to eliminate minor chemical disturbance in the brine.

1. INTRODUCTION

When the temperature of brine is decreased, the saturation concentration of silicic acid is decreased and it becomes the cause of plugging of brine transportaioin lines and pressure loss of a water permeable layer increased by silica deposition at reinjection wells. Conventional countermeasures of silica deposition reduction, have been studied such as 1) pH modification to acidic medium by mineral acid, 2) silicic acid polymerization by high polymer coagulant, 3) silica removal by filtration, 4)decrease of high mono-silicic acid concentration by retaining tank system, and 5) others. However, it cannot be asserted that those countermeasures reach the practicable stage from the points of view of effectiveness and treatment cost.

The authors found that normal cationic active surfactant acceralate mono-silicic acid polymerization on γ-alumina surface even at high temperatures, its polymerized silicic acid could be filtered easily, and it could be used as a silica source of mesoporous silica which had a large specific surface area in the zeolite group. With this reaction, it becomes practicable not only to decrease the concentration of mono-silicic acid for the reduction of deposition, but also to recover a silica that is a valuable source of mesoporous silica.

For that purpose, 1) the polymerization of mono-silicic acid from a branched brine (Kitsumi et al., 1985), the polymerization under the condensation temperature of more than 80° C, 2) recovery of silicic acid polymer by a micro-filter (Hirowatari et al., 1986) and 3) a synthesis of mesoporous silica with a recovered silicic acid polymer as a silica source (Teroaka et al., 1996) were experimented. A synthesized mesoporous silica was evaluated with 1) XRD (X-ray diffraction) to determine its structure and 2) BET method to measure a specific surface area.

2. POLYMERIZATION OF MONO-SILICIC ACID

2.1 Apparatus and Experimental Procedure

The schematic illustration of the experimental apparatus is shown in Fig. 1. The brine exhausted from Ohtake Geothermal Power Station were sampled and then the cationic surfactant, pH control chemicals (HCl or NaOH) and γ- alumina beads were added to 700ml of brine while it was being stirred with a motor driven stirrer. The mono-silicic acid and total silicic acid concentration were measured for 120 minutes to determine the polymerization rate. The experimental conditions are shown in Table 1 and the procedure of mono- silicic acid and total silicic acid analysis is shown in Fig. 2.

2.2 Results and Discussions

Time dependencies of mono-silicic acid concentration under several polymerization conditions is shown in Fig. 3a). When brine, of which the total silicic acid concentration was 800ppm and that of mono-silicic acid was and 800ppm, a temperature was 85° C, and pH value was 7, had been stirred without addition of alumina beads for two hours, the mono- silicic acid concentration decreased to 480ppm. And then when the same experiment with addition of 80 grams of γ- alumina beads was undertaken, the mono-silicic acid concentration decreased to 420ppm. Fig. 3a) showed that the γ-alumina beads had a nature to acceralate the mono- silicic acid polymerization. When 80 grams of silica-gel was used as a packed material, there was no difference between brine without beads and with silica-gel beads. In this experiment, a fresh alumina showed a large adsorbed amount of mono-silicic, when mono-silicic acid concentration decreased and the adsorption or the polymerization of mono- silicic acid could not be distinguished. For this reason, only the γ-alumina, which adsorbed mono-silicic acid at the saturation level, was used.

When n-dodecyl tri-methyl ammonium chloride of 10ppm was added to brine with γ-beads, the mono-silicic acid concentration decreased to 300ppm. (Fig. 3b)) With this result, it was confirmed that cationic surfactant also acceralates the mono-silicic acid polymerization.

When the concentration of surfactant was altered between 1 and 50ppm, the polymerization proceeded more rapidly at the higher concentration region. However, from the economical point of view, the lower concentration region was favorable and it was evaluated that even 10ppm addition was effective for the mono-silicic acid polymerization.

When the amount of γ-alumina beads was increased from 80 grams to 160 grams, the mono-silicic acid concentration decreased from 300ppm to 250ppm. (Fig. 3c)) It showed that this polymerization seemed to proceed on the surface of γ-alumina.

The mono-silicic acid is considered to exit as $H_3SiO_4^-$ and on the other hand, cationic surfactant exists as cation and it seems that these two ions are associated easily in the brine.
If a packed material such as γ-alumina provides adsorption surface for associated materials, it can be speculated that adsorbed material is enriched on the surface and the polymerization is accelerated.

3. SILICA RECOVERY

3.1 Experimental Apparatus and Experimental Conditions

When the polymer diameter distribution was measured, it was found that the particle grew more than 0.1μm and this particle can be separated with a micro-filter module. Fig. 4 shows the schematic illustration of this silicic polymer recovery unit and its specification is shown in Table 2.

The branched brine from the brine transportation line was supplied to a moving bed packed with 1kg of γ-alumina with flow rate of 500ml/min. At the inlet of the moving bed, the cationic surfactant and pH control agent were injected.

The packed γ-alumina was stirred with a motor driven stirrer and mono-silicic acid was partially polymerized to poly-silicic acid. The brine, which contained the poly-silicic acid, was stored once at the holding tank and it was supplied to a micro-filter module by a pump. At the micro-filter, only the smaller mono-silicic acid can be permeable through the module to the outlet and the rest of the larger poly-silicic acid could be refluxed to the holding tank.

With this filtration, the holding tank - the micro-filter - the reflux line was formed as closed cycle and the polymer could be enriched for the recovery.

3.2 Results and Discussions

Results for an experiment where the pH value of the brine was adjusted to 7.5 and the temperature was 85° C, and the polymer was refluxed from the micro-filter module to the holding tank are described in Fig. 4. Since the pH value was changed to the alkali side, the strong polymerization and the high enrichment could be expected, a total silicic acid concentration of 719ppm was maintained in the exit of the holding tank.

It was considered that the saturation concentration of the complex material between silicic acid and surfactant was 700-800ppm and the super saturation amount was deposited at the holding tank. The tank was opened, to confirm this and a white fine particle deposited at the bottom was observed. As it was also found that only mono-silicic acid could be permeated through the micro-filter, the poly-silicic acid could be recovered by the micro-filter efficiently.

4. MESOPOROUS SILICA SYNTHESIS WITH THE RECOVERED SILICIC ACID AS A STARTING SUBSTANCE

4.1 Mesoporous Silica Synthesis

The recovered silica precipitate was dissolved with NaOH and 5 w% of colloidal silica was prepared and it was used as a silica source. Then, n-dodecyl tri-methyl chloride ammonium chloride (SiO_2/surfactant=8/1) was added and it was adjusted at pH value of 0-1 to yield a white precipitate. After three hours of aging, the white precipitate was filtered, washed and dried. As this material contained a large amount of surfactant, it was calcined to remove surfactant and mesoporous silica of 30Å micro-pore could be prepared.

Fig. 5 shows a synthesis procedure of mesoporous silica and its XRD pattern is shown in Fig. 6. A space distance of 35.1Å was observed and this is the typical pattern of mesoporous silica. In addition, the specific surface area was measured using BET, as 946 m^2/g. When the hydrate of TEOS (Tetra Ethoxy Ortho Silicate) and low polymerized colloidal silica, which do not contain Q4 bond, are used as a silica source, the specific surface area reaches 1,600 m^2/g. As that of this material is smaller, a more precise optimization is required.

Experiments of mesoporous silica synthesis confirmed that, if the silica source contained even an extremely small amount of Q4 bond, that the mesoporous silica synthesis, at room temperature under an acidic medium, does not proceed at all. Concerning this point, this silica product recovered from the geothermal brine transportation line can be used for the mesoporous silica and it is expected to have a great advantageous point.

5. CONCLUSION

For the reduction of silica deposit in geothermal recirculating hot water, we studied 1) polymerization of mono-silicic acid with normal cationic active surfactant on the surface of γ-alumina bead, 2) recovery of poly-silicic acid using a micro-filter, and 3) mesoporous silica synthesis with recovered silica as a starting substance. A synthesized mesoporous silica showed a specific surface area of 1,000 m^2/g and a micro diameter of 40Å and it can be expected to use as a high performance adsorbent. With this silica recovery unit, it has a great potential to realize both the reduction of silica concentration to avoid the silica deposition at the recirculation line and to produce a starting substance for mesoporous silica.

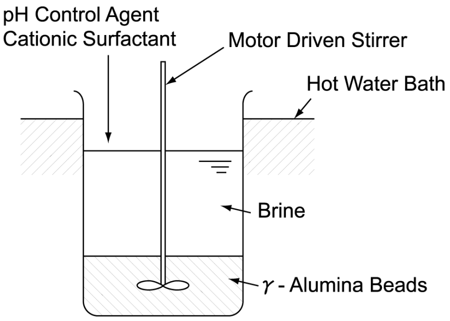

Figure-1 Schematic illustration of mono-silicic acid polymerization apparatus

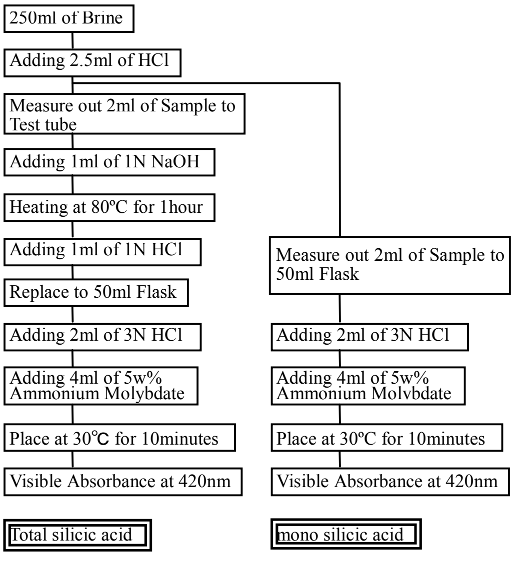

Figure-2 Chemical analysis of total and mono silicic acid

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Table-1 Experimental conditions of mono-silicic acid polymerization

Brine Temp. (℃)	pH	Surfactant and its Conc. (ppm)	Packed Material Shape and Amount (grams)
85	7	No Addition	No Addition
85	7	No Addition	γ -Alumina Beads, 83
85	7	No Addition	Silica-Gel Beads, 83
85	7	Tertiary Amine, 10	γ -Alumina Beads, 83
85	7	Tertiary Amine, 1	γ -Alumina Beads, 83
85	7	Tertiary Amine, 50	γ -Alumina Beads, 83
85	7	Tertiary Amine, 10	γ -Alumina Beads, 83

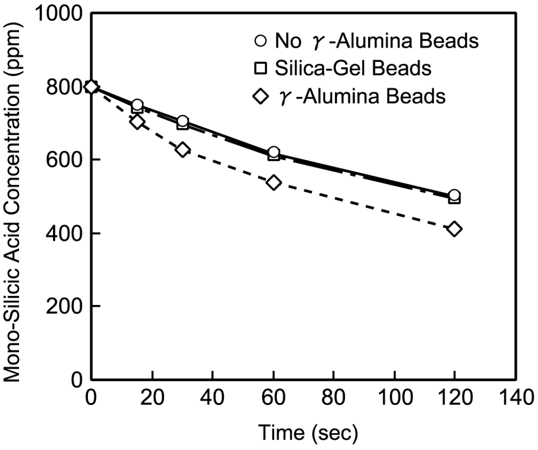


Figure-3a) Time dependency of mono-silicic acid concentration with packed material

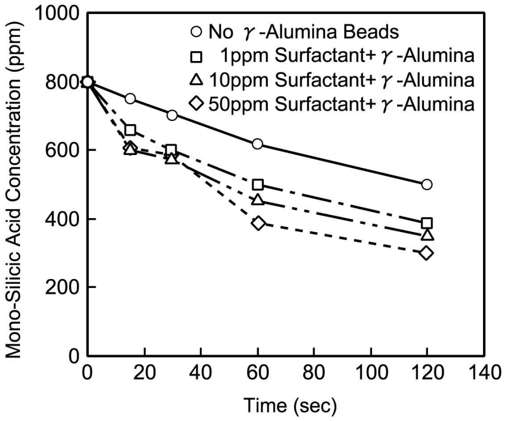


Figure-3b) Time dependency of mono-silicic acid concentration at different surfactant concentration

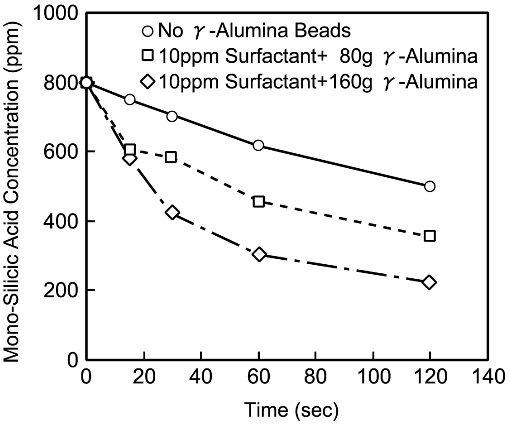
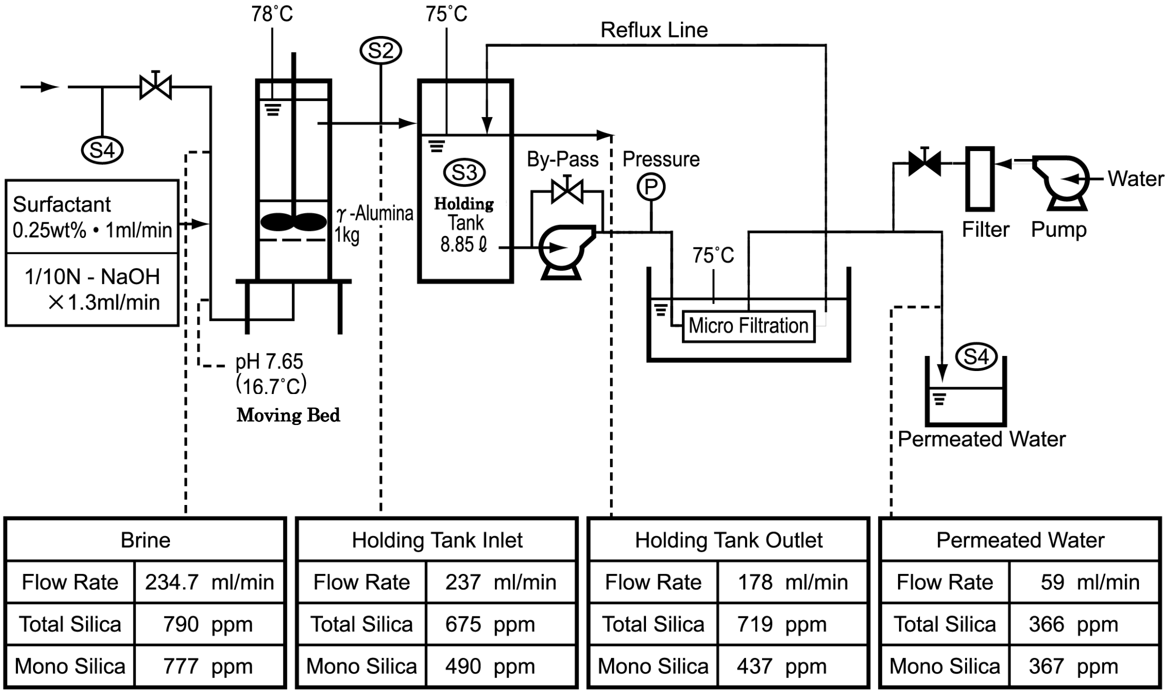


Figure-3c) Time dependency of mono-silicic acid concentration at different packed material amount



Brine	
Flow Rate	234.7 ml/min
Total Silica	790 ppm
Mono Silica	777 ppm

Holding Tank Inlet	
Flow Rate	237 ml/min
Total Silica	675 ppm
Mono Silica	490 ppm

Holding Tank Outlet	
Flow Rate	178 ml/min
Total Silica	719 ppm
Mono Silica	437 ppm

Permeated Water	
Flow Rate	59 ml/min
Total Silica	366 ppm
Mono Silica	367 ppm

Figure-4 Schematic illustration of silica polymer recovery unit

Table-2 Specification of polymerized silica recovery unit

Item	Element	Capacity
1	Injection Pump	60*l*/hour
2	Moving Bed	3 *l*
3	Stirrer (Motor Driven)	1 set
4	Holding Tank	5 *l*
5	Chemical Pump	1 set
6	Injection Pump for Filter	600*l*/hour
7	Micro Filter Module	1 set, 60*l*/h
8	Maximum Available Temp. of Filter	85℃

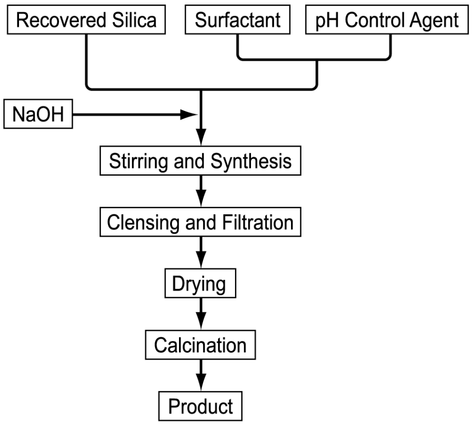


Figure-5 Procedure of mesoporous silica synthesis

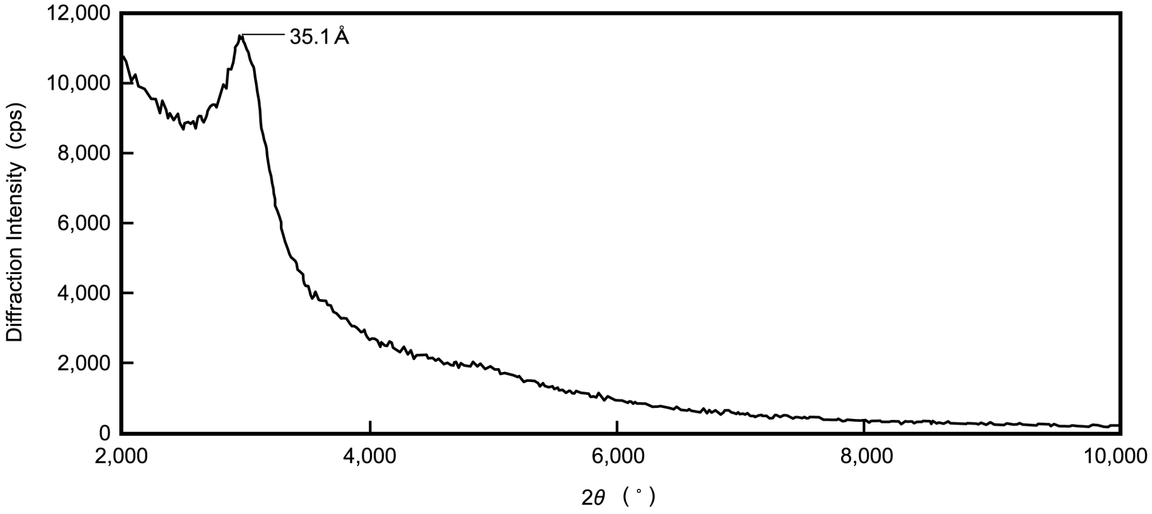


Figure-6 XRD pattern of mesoporous silica with recovered silica