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RECOVERY OF SILICA FROM THE SUMIKAWA GEOTHERMAL FLUIDS BY ADDITION OF CATIONIC NITROGEN-BEARING REAGENTS.

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ABSTRACT

In order to recover excess silica in fluids for prevention of silica scale deposition, two types (aril and estel) of cationic nitrogen-bearing reagents were examined at the Sumikawa geothermal plant, Japan. The total silica concentration in the fluid studied is 0.76kg/m^3 after flashing under an atmospheric pressure where that of dissolved silica decreased quickly(within 15 minutes) from 0.76 to 0.39 kg/m^3 due to polymerization. From this, two different procedures were examined; The cationic reagents were mixed into fluids at 90ºC with no residence time(NRT; immediately after flashing or mixed into fluids with residence time of 15 minutes(RT; keeping at 90ºC). The concentrations of total and dissolved silica in the fluids with both RT and NRT quickly decrease with increasing reaction time (5 minutes) after addition of the reagents. The degree of silica recovery is higher in the fluids with RT than fluids with NRT. These results mean that the reagent mainly reacts with the polymerized silica. The suitable concentration of the reagent added is around 0.05kg/m^3 where the total concentration becomes almost constant to be 0.34kg/m^3 similar to the solubility of amorphous silica at 90ºC. There are no clear differences in the two types of reagents as for their degrees of silica recovery. After the reaction, the fluids become transparent. The deposited silica is amorphous and is composed of SiO_2 and H_2O with a minor amount of other elements. From their zeta potential data, one atom of cationic nitrogen seems to react with 30 atoms of silica.

1. INTRODUCTION

Silica concentration in reservoir fluids is generally controlled by solubility of quartz. On the surface, the fluid is separated into fluid and steam due to pressure and temperature decline, where silica is concentrated into the fluid. In such environment, the fluid becomes supersaturated with respect to silica and a part of silica deposits as silica scale in pipelines and in reinjection wells. This results in the reduction of the reinjection capability, generation of electricity and exchange rate of heat exchanger. To prevent the silica deposition, many methods have been applied such as hot reinjection, pH adjustment (ex. Hirowatari et al., 1996; Hirowatari,1998; Gallup and Kilz,1997; Gallup,1997) and dilution with condensed water(Abe,1997). However, problems on reprecipitation of silica in the reservoir and decreasing reservoir temperature are still encountered. In the pH adjustment, pH 6.5 is enough for fluid containing about 0.5kg/m^3 of silica but it is needed to be less than 5.0 for fluids containing silica of more than 0.7kg/m^3 (Miyauchi et al., in prep.).

To prevent the silica scale problems, it is better to remove excess silica before injection. Many chemical reagents have been examined in the world (Yoshinaga et al., 1984, 1987; Vitolo and Cialdella,1995) . Such reagents contain cation ions such as Al, Mg, Ca and so on, because silica in fluids is charged in nagative ion. However, industrial application of this method becomes impractical due to high cost. Another method, a seed circulation method (Hurukawa et al.,1995; Sugita et al.,1998a,1998b) has been also applied to remove the excess silica. This method is suitable for fluids with high salinity but cannot directly be applied for fluids with low salinity as observed at Sumikawa.

This report summarizes the results of two types (aril and estel) of cationic nitrogen-bearing reagents for recovery of excess silica in fluids at the Sumikawa geothermal field. These reagents do not contain metallic ions. Such non-metallic reagents have been similarly studied by using BTBA (Yokoyama, 1991). These reagents may be more suitable to industrial applications for prevention of silica deposition because the recovered silica can be used for industry such as a silica-fume.

2. EXPERIMENTAL

2.1 Cationic Nitrogen-bearing Reagent

Two types of cationic nitrogen-bearing reagents were used in this study an aril-type (dimethyl aril ammonium chloride) and an estel-type (dimethyl amino rhyle methyle chloride methacryliate). Figure 1 shows their molecule structure and characteristics. The main characteristic of these reagents is to contain a cationic nitrogen element ionized in their molecule structures. As for the aril-type, three reagents with different molecule weights (EC, EC-40 and EC-004; molecule quantity 162, 5,000 and 500,000, respectively) were polymerized at the various rates.

2.2 Experimental Procedures

Geothermal fluids used in this study were collected from fluid transportation pipe at C-Base in the Sumikawa geothermal plant. The chemical compositions are shown in Table 1. The fluids is of a neutral Na-Cl type and is characterized by their low salinity (<3kg/m^3) compared to other geothermal fluids in the world(Ueda et al.,1991).

In this study, two types of cationic-nitrogen bearing reagents were examined as mentioned above. The effects of these reagents were studied on the concentration of silica in fluids by their different molecule weights and with/without residence time. The residence time means time for keeping the fluid at 90ºC after flashing under an atmospheric pressure. That is, the fluid was immediately put into a Teflon vessel after flashing, and was mixed with the reagents after keeping for 0 minute (defined as NRT) and 15 minutes(RT) at 90ºC. In the latter, the concentration of dissolved silica (silica monomer) decreased quickly due to polymerization, whereas that of total silica is constant (Figure 2).

The cationic-nitrogen bearing reagent was once diluted to 1% concentration with distilled water, and mixed with fluid in the concentration of 0.01-0.2kg/m^3. Then the fluid was stirred for 1 to 30 minutes with a magnetic stirrer (200rpm) and was filtrated through a filter with 0.22 micron meter in pore size.

The concentrations of dissolved and total silica in the filtrate were measured colormetrically by a molybdate yellow method using a spectrophotometer, Shimazu UV-2500PC. The wave length used was 420nm. During these experiments, silica concentrations of fluids collected from the pipeline were monitored every day. The uncertainty of the silica concentration was +/-1 % for dissolved silica and +/-2 % for the total silica.

Zeta potential measurement used Zetamaster and Malvern Instruments Ltd.. Possible size of measurement is 0.01 to 30 micron meter.

3. RESULTS

The experimental results in this study are shown in Figures 3 to 9. The results are summarized as follows;

(1) The concentrations of the total silica in the fluid decreased quickly almost within 5 minutes after addition of cationic-nitrogen bearing reagents(Figure 3 and 4).
(2) There was no clear difference in the silica concentrations by addition of reagent between aril and estel types (Figure 7).
(3) At the same concentration of the reagent, the ability of silica recovery is higher for fluid with RT than that with NRT (Figure 5). This means cationic nitrogen favors to react with polymerized silica than monomer silica.
(4) Silica concentrations in fluids decrease with increase in the concentration of reagent and become uniform with reagent concentration of more than 0.050kg/m^3 (Figures 6 and 7).
(5) Zeta potential of the deposited silica changes from negative value (-40mV) to positive one with increased concentration of the reagent (Figure 8). The zero potential point is observed at the reagent concentration of 0.050kg/m^3.

4. DISCUSSION

In this experiment, no clear differences were observed in the degree of recovery of silica not only between aril-type and estel-type but also between different molecule weights of each type. In other words, the reaction of silica in the fluid with the cationic nitrogen bearing reagent is independent on the reagent structure. What is paramount is that the cationic nitrogen ion is reacted with anionic silica acid. It is also noted that only the starting material of the aril-type reagent did not react with silica.

Figures 3 and 4 show the change of the silica concentration in the fluid with addition of aril-type reagent. The reaction of silica quickly proceeded in a short time (2 minutes) and after that, the reaction continued slowly. The final silica concentration is still higher than the solubility of amorphous silica at 90ºC (0.32kg/m^3; Fournier and Marshall, 1983, 0.36kg/m^3;Marshall, 1980). In the fluid with NRT, silica is polymerized after flashing and the concentration of dissolved silica decreased to 0.395kg/m^3 even for 60 minutes (Figure 2). From this result, the solubility of amorphous silica is estimated to be about 0.38kg/m^3 and the difference from the literature values at 90ºC is caused by the difference in the brine concentration. Therefore, in this report, this value is used as the solubility of amorphous silica at 90ºC.

Initial total silica concentration in fluid at Sumikawa was almost constant to be 0.78kg/m^3 during this study (Table 1). The fluids have excess silica of around 0.46kg/m^3 at 90ºC. In such a condition, silica monomers (analyzed as dissolved silica in this study) in the fluid are rapidly polymerized after flashing and are converted into silica polymer. Within 15 minutes after flashing under an atmospheric pressure, more than 70 % of the excess silica was polymerized. The polymerization rate of silica is depended on the initial silica concentration, pH, temperature and brine concentration (Rothbaum and Rohde,1979). This polymerization rate reaches maximum when 25 % of the excess silica is polymerized (ex. Sugita et al., 1998, Mroczek and Reeves,1994). It is equivalent to about 8 minutes after flashing at Sumikawa.

Figure 4 shows the relationship between concentration of the reagent added and the total silica concentration after reaction. At the same concentration of the reagent, the silica concentration in fluid with RT is approximately 80% less than that in fluid with NRT. This strongly indicates that the reagent reacts with silica polymer rather than silica monomer. The concentration of total silica decreases with increase of concentration of the reagent and gets almost constant at the reagent concentration of more than 0.050kg/m^3. Figure 9 also shows the concentration of dissolved silica versus the concentration of the reagent. From these results, silica monomer does not react with the reagent under the condition with not enough concentration of the reagent. In contrast, it starts to react with the reagent when concentration level reaches 0.050kg/m^3.

Figure 6 shows total silica concentration at the reaction time of 2 minutes in fluids with RT (15 minutes) after flashing. A straight line in this figure shows concentration of silica monomer at 17 minutes after flashing (calculated from Table 1). From this figure, the stoichiometrical concentration of reagent (EC-004) for recovery of silica in fluid is 0.05kg/m^3, where zeta potential value is zero, e.g., electrically neutralized (Figure 8). The absolute quantity of silica atoms reacted in this case is 3.67x10^{-4}kg(6.1x10^{-3}mol) for each 1kg of the fluid. For the reagent, the quantity reacted is also calculated to be 3.0x10^{-3}kg by the following equation:

$$Q_{SAR}=W_M/W_{UM}xW_{RR}/W_{1MR}$$

Q_{SAR}:quantity of silica atoms reacted
W_M:molecule weight(100,000)
W_{UM}:unit molecule weight(161.5)
W_{RR}:weight of reagent reacted(5x10^{-5}kg)
W_{1MR}:weight of 1 mol of reagent(100,000x10^{-3}kg)

From these results, cationic nitrogen and silica atoms reacted in fluids is estimated to be about 20 :1 atomic ratios.

5. CONCLUSION

Two types (aril and estel) of cationic nitrogen-bearing reagents were examined to prevent silica deposition in the Sumikawa geothermal plant and to industrially recover excess silica. The concentrations of total and dissolved silica in the fluids with both RT (keeping at 90ºC after flashing) and NRT (immediately mixed with the reagent after flashing) quickly decrease with increasing reaction time (5 minutes) after addition of the reagents. The degree of silica recovery is higher in the fluids with RT than fluids with NRT. These results mean that the reagent mainly reacts with the polymerized silica. The suitable concentration of the reagent added is around 0.05kg/m^3 where the total concentration become almost constant to be 0.34kg/m^3 similar to the solubility of amorphous silica at 90ºC. There are no clear differences in the two types of reagents as for their degrees of silica recovery. After the reaction, the fluids become transparent. The deposited silica is amorphous and is composed of SiO_2 and H_2O with a minor amount of other elements.

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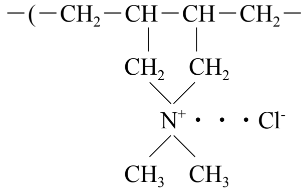
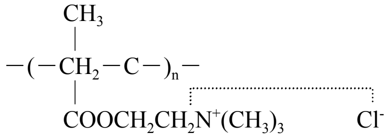
(1) Aril-type



reagent	moleculer quantity	pH	viscosity (cP/25°C)	specific gravity(20°C)
EC starting material	162	-	-	-
EC	5,000	2.6	4	1.02
EC-40	40,000	6.5	9	1.02
EC-004	100,000	6.1	17	1.02

(2) Estel-type



reagent	pH	viscosity (cP/25°C)	color
D-1114	8.2	134	red brown
D-1115	8.4	40	red brown
D-1116	8.5	108	light brown

Figure 1 Molecule structures of cationic cohesions used in the experiments.

Table 1 Chemical compositions of geothermal water used in the experiments

component	unit	concentration	
		1997	1998
pH	-	7.5	7.5
EC	mS/m	205	218
Na	kg/m^3	348	371
K	kg/m^3	70	67.6
Ca	kg/m^3	5.1	3.9
Mg	kg/m^3	<0.1	<0.1
Al	kg/m^3	2.4	1.9
Fe	kg/m^3	0.03	0.05
Cl	kg/m^3	550	552
SO_4	kg/m^3	106	144
HCO_3	kg/m^3	46	50.4
B	kg/m^3	237	238
SiO_2	kg/m^3	860	772
As	kg/m^3	14	13.5
TSM	kg/m^3	3100	2740

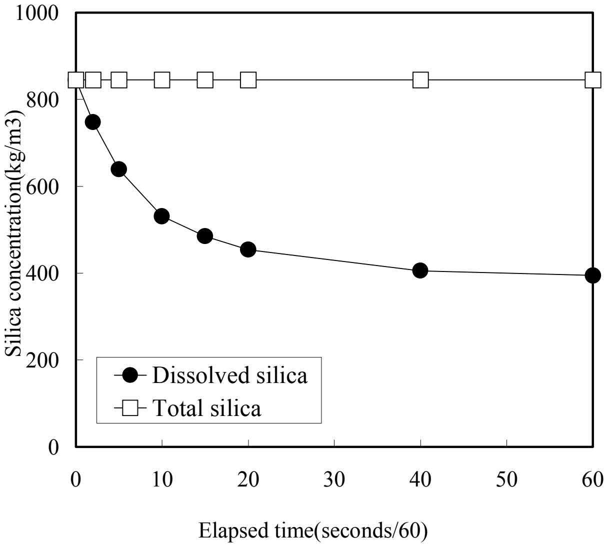


Figure 2 Silica concentration after flashing.

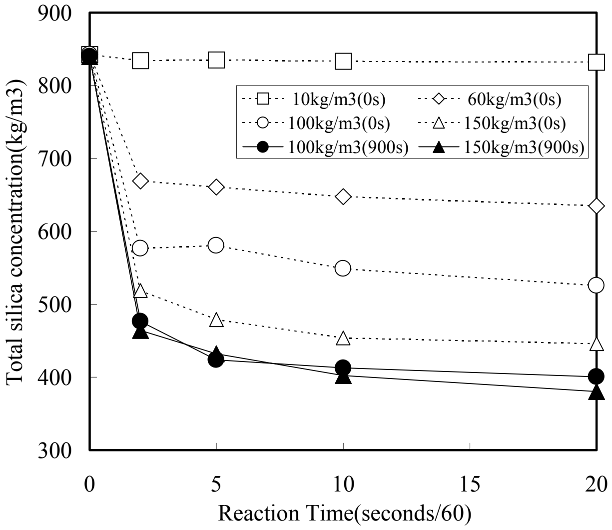


Figure 3 Total silica concentration in fluid mixed with EC-40 reagent.

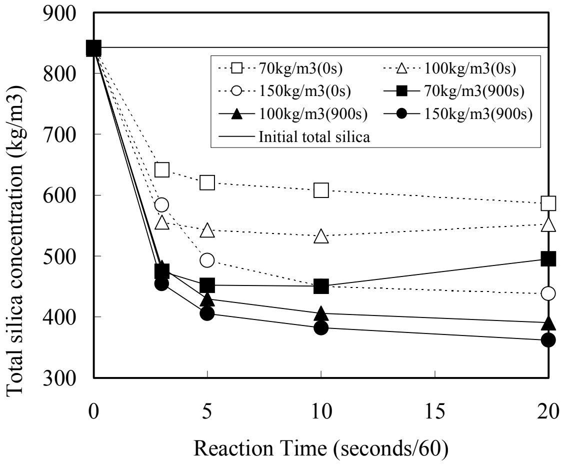


Figure 4 Total silica concentrations in fluids with EC-004 cohesion.

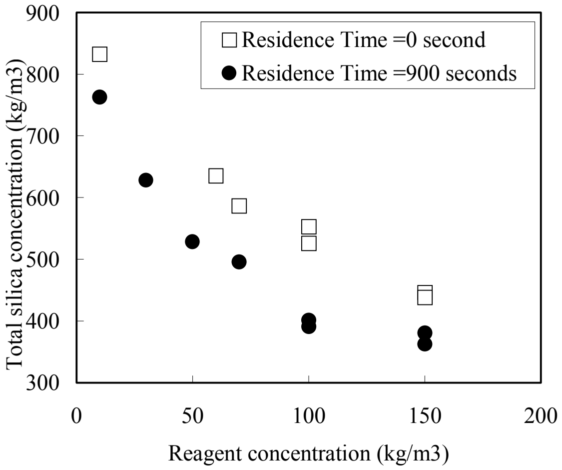


Figure 5 Total silica concentration in fluids with/without residence time.

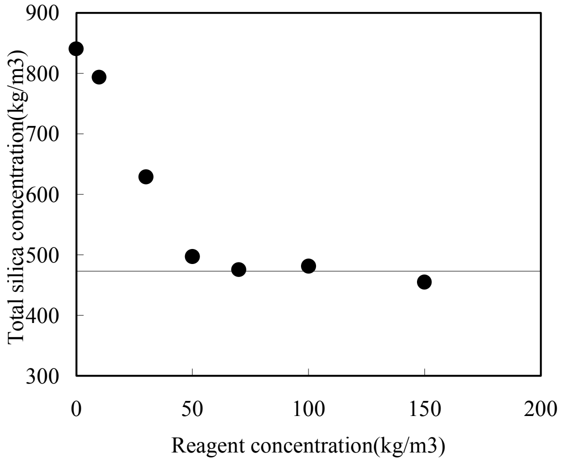


Figure 6 Total silica concentration at reaction time of 120 seconds after 900 seconds residence.

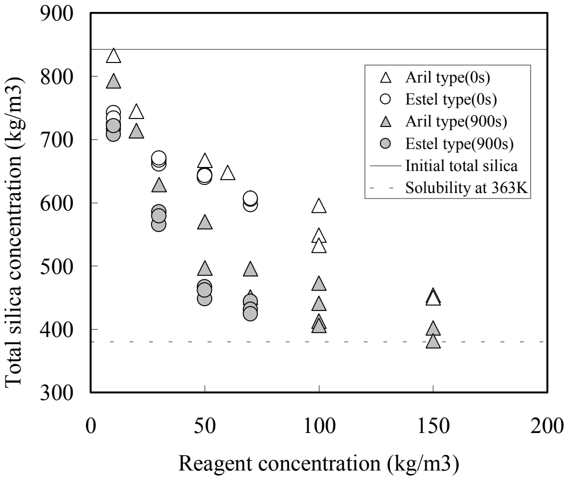


Figure 7 Total sulica concentration in fluids with cationic cohesions.

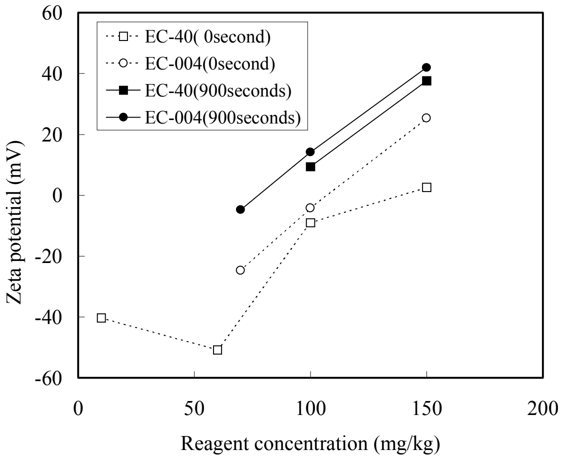


Figure 8 Zeta potential of silica deposits in fluids with cationic cohesions.

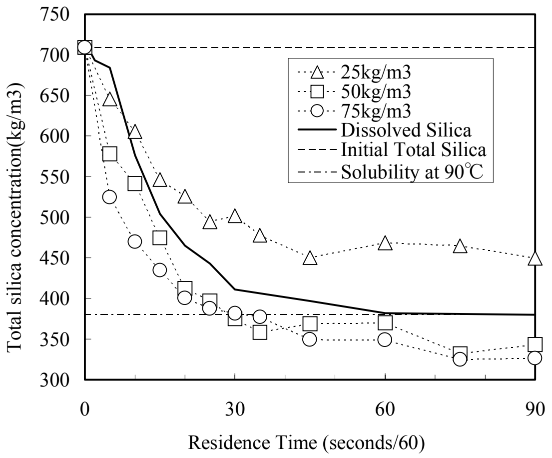


Figure 9 Total silica concentration in fluids with EC-004 cohesions of various residence times.