Proceedings World Geothermal Congress 2000
Kyushu - Tohoku, Japan, May 28 - June 10, 2000

SILICA SCALE PREVENTION METHOD USING SEED MADE FROM GEOTHERMAL BRINE

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Key Words: silica scale, seeding method, silica removal, silica precipitation, Onuma geothermal area

ABSTRACT

Silica scale formation from geothermal brine causes various problems. We have proposed a silica scale prevention method: the seeding method using silica gels. In this work, the seeds are made from silica scale or geothermal brine and evaluated on the silica removal performance. Tests were conducted at the Onuma geothermal field. The experiments were conducted using three kinds of seeds: (1) colloidal silica solution, (2) silica scale and (3) colloidal amorphous silica precipitate.

The colloidal silica solution and the silica scale seeds could not remove the excess silica in the geothermal brine. On the other hand, the colloidal amorphous silica seeds showed silica removal-ability and could decrease the silica concentration in the brine close to the amorphous silica solubility. The silica precipitation rate on the colloidal amorphous silica seeds is correlated with the excess silica above pre-equilibrium silica concentrations. Since the colloidal amorphous silica obtained in this work has high silica purity of 98 wt%, there are good possibilities to have a good resource of silica.

1. INTRODUCTION

Geothermal utilization plants have serious problems such as decline of performance by plugging of pipelines and permeable layers due to silica scale. It is therefore desirable to solve the silica scale problems. We have proposed a silica scale prevention method: the seeding method using silica gels (Sugita *et al.*, 1998a). This method removes the excess silica in geothermal brine by precipitating it on seeds. The seeds are silica gels with high specific surface area (about 350×10^3 m_S^2/kg) normally used for column chromatography. Though the method is effectively inhibits of silica scale formation, the silica gel seeds are relatively costly. Inexpensive seeds are desired for field uses.

In this work, the seeds are made from silica scale or geothermal brine, in order to be self-sufficient at geothermal facilities. A series of field tests were conducted in a heat exchange facility at the Onuma geothermal field.

2. FIELD EXPERIMENT AT ONUMA GEOTHERMAL FIELD

2.1 Characteristics of geothermal brine

The pH and electric conductivity of the Onuma geothermal brine were 7.0～7.3 and 2.3 mS/cm, respectively. The chemical composition of the brine is shown in **Table 1**. As seen in this table, the brine has low salinity relative to other geothermal brines in Japan.

2.2 Preparation of colloidal silica solution and seeds

The colloidal silica solution and the silica scale and colloidal amorphous silica seeds were prepared and examined on the silica removal efficiency. The preparation of the solution and seeds are described below

<u>(1) Colloidal Silica Solution</u>

For polymerize, the monomeric silica in the geothermal brine, the brine was aged at ambient temperature (10-15℃) for about 3 days. The total silica concentration in the brine after 3 days was the same as that in fresh Onuma geothermal brine (0.50 $kg\text{-}SiO_2 \cdot m_L^{-3}$). On the other hand, the concentration of monomeric silica in the brine after 3 days （0.15 $kg\text{-}SiO_2 \cdot m_L^{-3}$） was lower than that in fresh brine（0.50 $kg\text{-}SiO_2 \cdot m_L^{-3}$）. Therefore, after 3 days, the excess monomeric silica have polymerized and formed the colloidal silica. The particle size of the colloidal silica is smaller than 0.2 μm because the pore size of the filter used for sampling was 0.2 μm. Also, the values of pH and electric conductivity of the colloidal silica solution were the same as those of the fresh brine respectively. After 3 days, the aged brine was used as the colloidal silica solution.

<u>(2) Silica scale seed</u>

Silica scale formed on the surface of pipelines feeding the heat exchanger at the Onuma heat exchange facility. The silica scale was taken and pulverized to about 100 μm. The silica scale pulverized was then washed with hydrochloric acid (6N) or distilled water in an ultrasonic bath and dried at 110℃. After treatment, the silica powder was used as the seed. The specific surface area of silica scale seeds is 0.88×10^3 m_S^2/kg. The chemical components of the silica scale seeds are shown in **Table 2**.

(3) Colloidal amorphous silica seed

Onuma brine was concentrated by heating and finally evaporated. The residues were pulverized to about 100 μ m and washed with distilled water under ultrasound and dried at 110℃. The residues after treatment were used as the colloidal amorphous silica seed. X-ray diffraction analysis showed, the purity of silica in the colloidal amorphous silica is about 98 wt%. The initial values of particle diameter (as the median) and specific surface area of colloidal amorphous silica seeds were 188×10^3 m_S^2/kg and 90 μ m, respectively. The chemical components of the colloidal amorphous silica seeds are shown in Table 2.

2.3 Experimental procedure

We carried out the following experiments to evaluate the seeds silica removal–ability,.

(1) Mixing with colloidal silica solution

In Onuma geothermal heat exchange plant, the actual geothermal brines were spouted out through the pipeline from underground to earth surface. After flashing at atmospheric pressure, 0.500×10^{-3} m^3 of the brine was taken into a Teflon vessel and put into a hot water bath thermostated at a specified temperature (90℃). The brine was stirred by a magnetic stirrer during the experiment. Then 0.500×10^{-3} m^3 of the above colloidal silica solution was added to the vessel. Part of the mixed brine was sampled and filtered through 0.2 μ m at 0, 30 and 60 minutes after brine mixing. Also, the brine temperature was measured at sampling.

(2) Adding of silica scale seeds

Flashed brine of 1.00×10^{-3} m^3 of the brine was taken into a Teflon vessel and put into a water bath thermostated at a given temperature (90℃). The brine was stirred as in (1). Within two minutes after the brine was taken into the vessel, the silica scale seeds (10.0 g) were added to the brine. Part of the brine was sampled and filtered by 0.2 μ m filter in pore size before the seeds were added and after 30 and 60 minutes. Also, the temperature of the brine was measured at sampling. The temperature of the brine was 82～85℃ during the experiment.

(3) Adding of colloidal amorphous silica seeds

The experimental procedure was similar to (2) above except for adding the colloidal amorphous silica seeds instead of the silica scale seeds. The amount of colloidal amorphous silica seeds added was 0.500, 1.00 and 5.00 g. The experimental period for each was 120 minutes and part of the brine was periodically sampled and filtered by 0.2 μ m filter.

2.4 Measurement method

Measurement methods for silica concentration, specific surface area and particle diameter of the seeds are described as follows:

(1) Silica concentration

Part of the brine was sampled and filtered by 0.2 μ m filter. Concentrations of dissolved silica (mostly monomeric silica) and total silica in the filtrate were measured by the molybdate yellow method (JIS K 0101) using a spectrophotometer (Shimazu, Type UV-1600). The wave length was set to be 420 nm.

(2) Specific surface area

The specific surface area per unit mass of the seeds was measured using the BET surface area analyzer（Horiba, SA-6201）. The adsorbed gases used were mixed gas ($N_2$30%、He70%) or nitrogen gas (99.99%).

(3) Particle diameter

The particle diameter of the seeds was measured using the laser scattering particle size distribution analyzer（Horiba, LA-910）.

(4) SEM observation and X-ray analysis

The surface of the seeds was observed using a scanning electron microscope (S-570 Scanning Electron Microscope, HITACHI Co.). The composition of the samples was examined using an energy dispersive X ray spectrometer (Electron Micro Analyser Xray-5570, HORIBA Co.)

3. RESULTS AND DISCUSSION

3.1 Colloidal silica solution mixing

Figure 1 shows the change of the silica concentrations C with reaction time t on mixing colloidal silica solution. C_M and C_T denote the monomeric silica and total silica concentrations, respectively. The value of C_T did not change for 60 minutes after mixed. On the other hand, the value of C_M slightly increased with time. The value of C_M directly after mixing (t=0) was 0.317 kg-SiO_2・m_L^{-3}, which is equivalent to the value calculated from the mixing ratio (0.325 kg-SiO_2・m_L^{-3}), and C_M at t=60 minutes is 0.336 kg-SiO_2・m_L^{-3}. The increase in C_M is caused by re-dissolution of the colloidal silica. The temperatures of the mixed brine were measured to be 52, 72 and 80℃ at 0, 30 and 60 minutes, respectively. This increase in temperature with time is considered to cause the re-dissolution of the colloidal silica. The value of C_M at t=60 minutes (0.336 kg-SiO_2・m_L^{-3}) is higher than the solubility of amorphous silica (0.320 kg-SiO_2・m_L^{-3}). The amorphous silica solubility was calculated using Marshall's equation (Marshall, 1980).

$$\log s^0 = -0.1185 - 1.1260\times10^3/T + 2.3305\times10^5/T^2 - 3.6784\times10^7/T^3 \qquad (1)$$

where s^0 is the amorphous silica solubility [mol/kg] and T is the absolute temperature [K]. Sugita *et al.* (1998 b) has reported the following. In a supersaturated silica solution without precipitates or seeds, the concentration of monomeric silica rapidly decrease to a constant value and then is apparently stable. This value is slightly higher than the amorphous silica solubility and is defined as the pre-stable concentration. In mixing with colloidal silica solution, the concentration of monomeric silica is considered to proceed toward the pre-stable concentration.

3.2 Silica scale seed addition

Figure 2 shows C_T and C_M with time t when added with the silica scale seed. Both silica concentrations did not change during the experiment. From the result, it is clear that the silica scale seeds affect nothing on the polymerization of silica in the brine in spite of the silica scale is the material forming naturally in the brine. This reason may be that the surface of the silica scale seeds are covered with siloxane bonds （—Si—O—Si—）and do not have any silanol group（—Si—OH）. Though silica scale seed acts as a nucleus and grows, the growth of silica scale seeds was not verified. This may be because that the reaction time in this work (60 minutes) is shorter relatively to the period taken to grow the silica scale (several weeks to months) and the specific surface area of the silica scale seeds is much lower than the colloidal amorphous silica.

3.3 Colloidal amorphous silica seed addition

Figure 3 shows C_T and C_M with time t when added the colloidal amorphous silica seed. Both silica concentrations in the brine quickly decrease. Though there was initially a small amount of colloidal silica (t=0), new colloidal silica was not produced after seed addition because the difference between C_T and C_M hardly changed with time. Therefore the decrease in both silica concentrations are regarded to precipitation of monomeric silica on the colloidal amorphous silica seeds. Then the silica removal quantity is represented as the decrease in total silica $C_{T0}-C_T$ or the decrease in monomeric silica $C_{M0}-C_M$. From this result, the colloidal amorphous silica seeds is shown to be effective in removing silica from geothermal brine.

Figure 4 shows C_T with t for different initial seed concentration in the case of the colloidal amorphous silica seeds addition. As the initial seed concentration C_{s0} is higher, the value of C_T is lower. Amorphous silica solubilities from 82 to 85℃ are 0.328～0.340 kg・m_L^{-3}. (calculated using Eq.(1)). In C_{s0} =0.500 kg・m_L^{-3}, the silica precipitation is nearly finished at t=90 minutes and then mo further silica removal could be achieved. On the other hand, in C_{s0} =5.00 kg・m_L^{-3}, C_T decreased to the value equivalent to amorphous silica solubility at t=30 minutes, so that all the excess silica in the brine was removed. In C_{s0}=1.00 kg・m_L^{-3}, though C_T is not decreased to amorphous silica solubility at t=120 minutes, but silica removal may be achieved at longer reaction time.

3.4 Silica precipitation rate on colloidal amorphous silica seeds

For the silica precipitation on the silica gel seeds, the results are examined with following equation (Sugita *et al.*, 1998c)
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$$R_T = -\mathrm{d}C_T/\mathrm{d}t = K(C_M - C_X) \qquad (C_X > C_e) \qquad (2)$$

$$K = kC_S S_W = kA_s \qquad (3)$$

where R_T is the silica precipitation rate (silica removal rate) [kg・m_L^{-3}・s^{-1}] and K is the overall silica precipitation rate coefficient [s^{-1}]. C_X is the concentration value slightly higher than amorphous silica solubility, which is called the pre-equilibrium silica concentration [kg・m_L^{-3}] (Fleming, 1986). K is represented as Eq. (3). k is a constant [m_L^{3}・s^{-1}・m_S^{-2}], C_S is the seed concentration [kg・m_L^{-3}], S_W is the surface area per unit mass of seeds [m_S^2/kg]and A_S is the surface area per unit liquid volume [m_S^2・m_L^{-3}]. The values of C_S and S_W change with silica precipitation : C_S increases and S_W decreases. However, A_S , the product of C_S and S_W, does not change and remains at the initial value $A_{S0}=C_{S0}S_{W0}$ in the case of relatively small amount of precipitated silica (Sugita *et al.*, 1998c).

In order to examine the kinetics of silica precipitation on the colloidal amorphous silica seeds, the silica removal rate R_T is plotted against C_M in **Figure 5**. The data used are those in C_{s0}=5.00 kg・m_L^{-3}. There is a linear relationship in this figure and the relationship between monomeric silica and the removal rate is represented by Eq. (2). The values of C_X and K obtained from Eq. (2) are 0.36 kg・m_L^{-3} and 5.5×10^{-3} s^{-1}, respectively. Also, the value of k obtained from Eq. (3) is 5.8×10^{-9} m_L^{3}・s^{-1}・m_S^{-2}. However the values of k obtained for C_{s0}=0.500 and 1.00 kg・m_L^{-3} were 4.3 and 3.98×10^{-9} m_L^{3}・s

$^{-1}\cdot m_S^{-2}$, respectively. For the latter two *k*, the correlation constants are less than 0.89. On the other hand, the correlation constant for C_{s0}=5.0 kg$\cdot m_L^{-3}$ is 0.98. Therefore the results where C_{s0}=5.00 kg$\cdot m_L^{-3}$ is judged to reflect most closely the kinetic characteristics of the colloidal amorphous silica seeds. The colloidal amorphous silica seeds were found to be effective on silica removal because those values of *k* for the colloidal amorphous silica seeds are comparable to the for silica gel seeds previously studied (2.3～5.8×10^{-9} $m_L^{\ 3}\cdot s^{-1}\cdot m_S^{-2}$) (Sugita *et al.*, 1998 c).

3.5 Characteristics on extracted colloidal amorphous silica seeds

The colloidal amorphous silica seeds extracted after the silica removal experiment were analyzed. The values of particle diameter (as the median) and specific surface of extracted colloidal amorphous silica seeds were 83 μm and 178×10^3 m_S^2/kg, respectively. These values are slightly lower than those of initial ones.

The chemical components of extracted colloidal amorphous silica seeds are shown in **Table 3**. Compared with the initial values, the aluminum concentration increased, the silica and the sodium concentrations decreased and calcium was not detected. These results imply that the colloidal amorphous silica seeds enhance precipitation not only of silica but also aluminum. Over long time period, the aluminum content may be higher. The aluminum may be easily removed from the colloidal amorphous silica seeds by using acid such as HCl. Therefore there are good possibilities that the silica removed from geothermal brine will became a resource of good quality silica.

4. CONCLUSIONS

In order to prevent silica scale formation in geothermal brine, adding three kinds of seeds were examined. Colloidal silica solution made from the brine, seeds made of silica scale or the colloidal amorphous silica seeds made from the brine were added into the geothermal brine. The both of the colloidal silica solution and the silica scale seeds could not remove the excess silica from the brine. On the other hand, the colloidal amorphous silica seeds could remove the excess silica. The silica removal performance using the colloidal amorphous silica seeds is similar to that of the silica gel seeds. In addition to their silica removal efficiency, the colloidal amorphous silica seeds a source of high quality silica. The purity of silica in colloidal amorphous silica seeds made from Onuma geothermal brine was about 98 wt%.

ACKOWLEDGMENT

We thank Central Research Institute, Mitsubishi Materials Corporation for using Onuma geothermal heat exchange facility. We also thank A. Ueda and H. Watanabe for help and discussion.

NOMENCLATURE

A_s = surface area per unit liquid volume [$m_S^2\cdot m_L^{-3}$]
A_{s0} = initial surface area per unit liquid volume [$m_S^{\ 2}\cdot m_L^{-3}$]
C = C_M or C_T [kg$\cdot m_L^{-3}$]
C_M = monomeric silica concentration [kg$\cdot m_L^{-3}$]
C_{M0} = initial monomeric silica concentration [kg$\cdot m_L^{-3}$]
C_s = seed concentration [kg$\cdot m_L^{-3}$]
C_{s0} = initial seed concentration [kg$\cdot m_L^{-3}$]
C_T = total silica concentration [kg$\cdot m_L^{-3}$]
C_{T0} = initial total silica concentration [kg$\cdot m_L^{-3}$]
K = overall rate coefficient of silica precipitation [s^{-1}]
k = constant [$m_L^{\ 3}\cdot s^{-1}\cdot m_S^{-2}$]
R_T = silica precipitation rate (silica removal rate) [kg$\cdot m_L^{-3}\cdot s^{-1}$]
S_W = surface area per unit mass of seed [$m_S^{\ 2}\cdot kg^{-1}$]
S_{W0} = initial surface area per unit mass of seed [$m_S^{\ 2}\cdot kg^{-1}$]
s^0 = amorphous silica solubility [mol/kg]
T = absolute temperature [K]
t = reaction time [s]

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Table 1 Chemical composition of Onuma geothermal brine

Na	391	B	566
K	54.6	Cl	10.3
Mg	0.77	SO_4	205
Ca	1.3	HCO_3	31.7
Al	0.03	SiO_2	512
Fe	3.4		

unit [kg·m_L^{-3}]

Table 2 Chemical components of seeds before experiments

	Silica scale	UCAS *	WCAS **
SiO_2	94.6	32.5	98.2
Na_2O	0.1	30.6	0.6
K_2O	0.3	3.0	0.0
MgO	0.3	0.0	0.0
CaO	0.5	0.0	0.5
Al_2O_3	4.1	0.0	0.2
SO_3	0.0	5.7	0.5
Cl	0.0	28.3	0.0

unit [wt%]

* unwashed colloidal amorphous silica seeds

** washed colloidal amorphous silica seeds

Table 3 Chemical components of colloidal amorphous silica seeds extracted after silica removal experiments

SiO_2	97.8	Na_2O	0.2
Al_2O_3	1.7	K_2O	0.0
SO_3	0.3	MgO	0.0
Cl	0.0	CaO	0.0

unit [wt%]

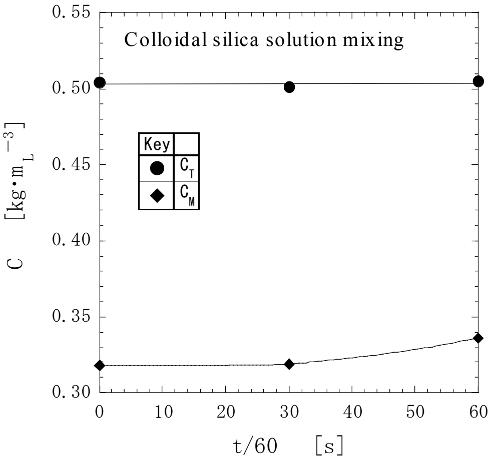

Figure 1 Change of silica concentrations with time when mixed with colloidal silica solution

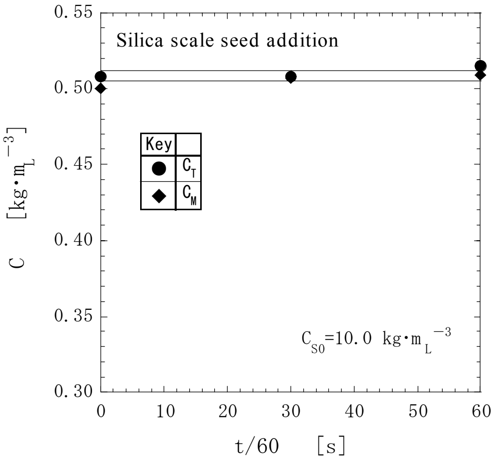

Figure 2 Change of silica concentrations with time when added silica scale seeds

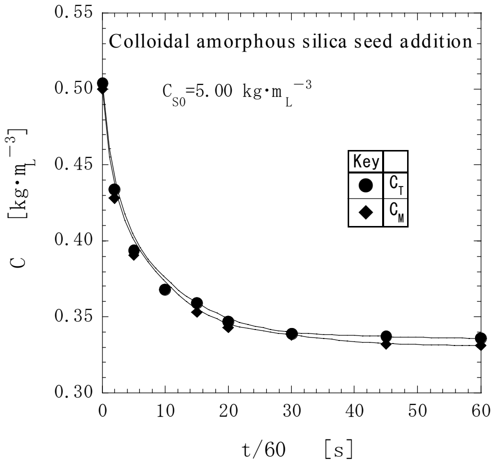

Figure 3 Change of silica concentrations with time when added colloidal amorphous silica seeds

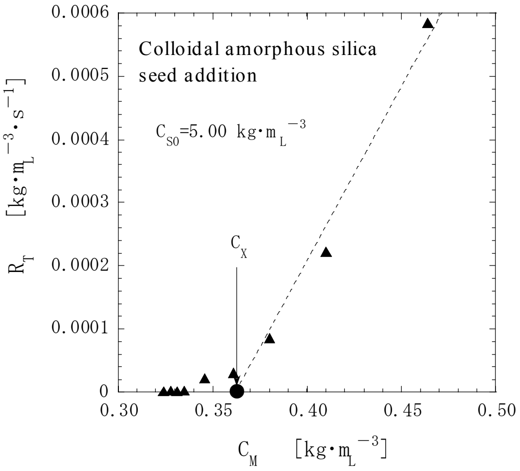

Figure 5 Plot of silica removal rate against monomeric silica concentration

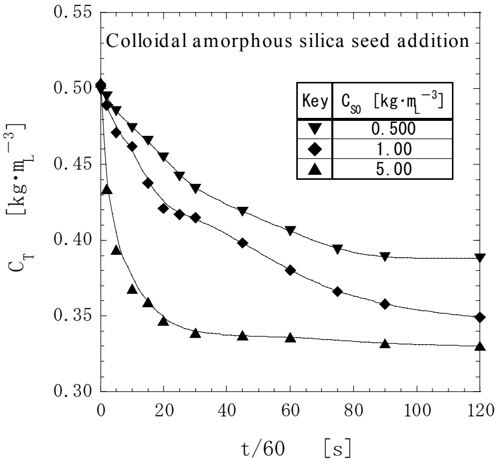

Figure 4 Effect of seed concentrations on silica removal when added colloidal amorphous silica seeds