TWO VIEWPOINTS FOR REMOVAL OF SILICIC ACID FROM GEOTHERMAL WATER TO PREVENT SILICA SCALING

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ABSTRACT

As a prevention method of silica scales at geothermal power plants, removal of silicic acid from geothermal water was studied from two chemical viewpoints: removal of supersaturated polysilicic acid and removal of all monosilicic acid by the addition of cethyltrimethylammonium bromide (CTAB) and calcium chloride accompanying pH adjustment, respectively. As the polymerization of silicic acid proceeds and polysilicic acid grows, the removal efficiency of polysilicic acid is higher. At the addition of 10^{-4} M CTAB, most of the polysilicic acid was removed. For removal of monosilicic acid, the addition of the same amount of Ca^{2+} as monosilicic acid and the following adjustment to pH 12 around 90°C is the best condition to precipitate all of silicic acid as a calcium silicate hydrate from geothermal water. In addition, aluminum, which affects the formation of silica scale, is also removed by the both methods.

1. INTRODUCTION

In order to accelerate useful use of geothermal energy, it is essential to retard the formation of silica scales from geothermal water. In many geothermal power plants, to avoid the problem of the silica scale formation, reinjection of geothermal water with high temperature and/or addition of sulfuric acid to geothermal water to adjust pH 5 ~ 6 have been conducted. The two ideas are based on chemical thermodynamics and chemical kinetics: lower silicic acid concentration than the solubility of amorphous silica and kinetic retardation of silica scale formation. Although silica scaling has been retarded on the surface of ground facilities at geothermal power plants, decrease in the injection ability of reinjection wells of geothermal water has been continued. It may be due to deposition of silica scales in the formation around reinjection wells. Therefore, we have set the work on development of removal method of silicic acid, which can cause the formation of silica scales, based on a chemical viewpoint.

As geothermal water from which silicic acid is removed, we selected two geothermal waters with different properties: (1) the polymerization of silicic acid occurs rapidly (Geothermal water A) and (2) no polymerization occurs for a certain period (Geothermal water B) after the water/vapor separation. As the polymerization of silicic acid proceeds, polysilicic acid particles are formed and grow. Polysilicic acid particle has negative charges of Si-O- sites on the surface. Therefore, organic ammonium ion with a positive charge is considered to electrostatically react with polysilicic acid particles. Due to the reaction, the polysilicic acid particle is destabilized and the reaction between polysilicic acid particles is accelerated to precipitate silica. Recently, Hanajima and Ueda (2017) reported the effective precipitation of silicic acid by the addition of DADMAC (an organic ammonium). On the other hand, calcium ion can react with silicate ion to precipitate a calcium silicate hydrate (C-S-H) under alkaline condition.

In this study, cethyltrimethylammonium bromide (CTAB), which is a detergent that hydrophobic interaction occurs in addition with electrostatic interaction, and calcium chloride solutions were applied to precipitate polysilicic acid particle and monosilicic acid to geothermal water A and geothermal water B, respectively and the effective condition for the precipitation was examined. In addition, the behavior of aluminum during the precipitation reaction of silicic acid, which affects the formation of silica scales, was also examined.

2. EXPERIMENTAL

2.1 Polymerization of silicic acid

The polymerization of silicic acid in geothermal waters A and B was examined for 2 h. The geothermal waters used in this study were collected under 1 atom using a small size separator connected with a two-phase pipe line of geothermal liquid. The geothermal water was collected in a polyethylene bottle as a reaction vessel and the temperature of the geothermal water was maintained at 90℃ in a water bath. At adequate intervals, a part of the geothermal water was taken out and filtered with a 0.45μm membrane filter. The filtrate was adjusted to pH 2 with hydrochloric acid immediately after the filtration to retard the polymerization of silicic acid. Monosilicic acid (Si(M)) concentration in the filtrates was spectrophotometrically determined on the site. Total silicic acid (Si(T)) concentration was determined by ICP-AES in Department of Earth Resources Engineering, Kyushu University. Size of poly silicic acid particle was measured by Dynamic light scattering (DLS, Malvern, zeta sizer nano ZSP).

2.2 Removal of polysilicic acid by the addition of CTAB

Geothermal water A (one liter) was collected in a polyethylene bottle. The temperature of the geothermal water was maintained at 90°C in a water bath. After 0, 15, 30 and 60 min. from the sampling of the geothermal water, CTAB (cethyltrimethylammonium bromide) solution was added. The CTAB concentrations in the geothermal waters after the addition were 10^{-4} M, 10^{-5} M, and 10^{-6} M. The reaction time was 5 min. After the reaction, the sample solution was filtrated with a 0.45 μm membrane filter and the filtrate was adjusted to pH 2 with HCl to retard the reaction of silicic acid. Si(T) concentration and aluminum (Al) concentration were determined by using ICP-AES.

2.3 Removal of monosilicic acid by the addition of Ca^{2+} and pH adjustment

Geothermal water B (one liter) was collected in a polyethylene bottle. The temperature of the geothermal water was maintained at 90°C in a water bath. $CaCl_2$ solutions were added just after sampling of the geothermal water. The Ca^{2+} ion concentrations added in this study were 200ppm (5mM), 400ppm (10mM), 800ppm (20mM) and 1600ppm (40mM). Then NaOH solution was added to adjust pH. The target pH was 10, 11 and 12. The reaction time was 5 min. After the reaction, the sample solutions were filtrated with a 0.45 μm membrane filter and the filtrate was adjusted to pH 2 with HCl to retard the reaction of silicic acid. Si(T) concentration, Al concentration and Ca concentration were determined by using ICP-AES.

2.4 Characterization of precipitates

XRD analysis was conducted to identify the mineral composition in precipitates. ^{27}Al and ^{29}Si MAS NMR spectra was also measured to examine the local structures of Al and Si atoms (coordination state of Al and polymerization mode of silicate structure). The NMR measurement was conducted by a JEOL ECA 400 spectrometer.

3. RESULTS AND DISCUSSION

3.1 Polymerization of silicic acid in geothermal waters A and B

Table 1 represents the analytical results of geothermal waters A and B used in this study. When geothermal waters A and B were collected, the temperatures were 89 and 86 °C, respectively and the both geothermal waters were weak alkaline. The silicic acid concentration was significantly different between geothermal waters A and B. For the both geothermal waters, the salt concentration was not high. Aluminum (Al) concentrations in the geothermal waters A and B, which affect deposition of silica scales, were 1.0 and 0.4 ppm, respectively. Calcium (Ca) concentrations were low in the both geothermal waters.

Figure 1 shows the changes in monosilicic acid (Si(M)) and total silicic acid (Si(T)) concentrations with time in geothermal waters A (a) and B (b). In the geothermal water A, the Si(T) concentration was higher than the Si(M) concentration at 0 min, indicating that the polymerization of silicic acid had already occurred when it was collected. Although the Si(M) concentration decreased with time, the Si(T) concentration was almost constant during the reaction time. It indicates that although the polymerization of silicic acid occurred, larger polysilicic acid particle than 0.45μm was not formed. In the geothermal water B, while, the Si(M) concentration was close to the Si(T) concentration, indicating that no polymerization occurred in the geothermal water B.

Figure 2 shows the change in particle size of polysilicic acid with time after the collection of the geothermal water B. In Fig. 1(b), polysilicic acid particle existed immediately after the collection, however, the polysilicic acid particle was not detected by DLS, suggesting that the hydrodynamic diameter of the polysilicic acid particle may be smaller than 1 nm because of the sensitivity. After 5 min, the hydrodynamic diameter was about 2 nm and grew rapidly to 10 nm for 60 min. After 60 min, the polysilicic acid grew slowly. The diameter was 11 nm after 2 h.

Table 1: Analytical result of geothermal waters A and B

	A	B
	ppm	ppm
Si(T)*	638	456
Cl	820	740
Ca	10	20
Al	1.0	0.4
pH(temperature)	8.3 (89°C)	8.9 (72°C)
Temperature	89°C	86°C

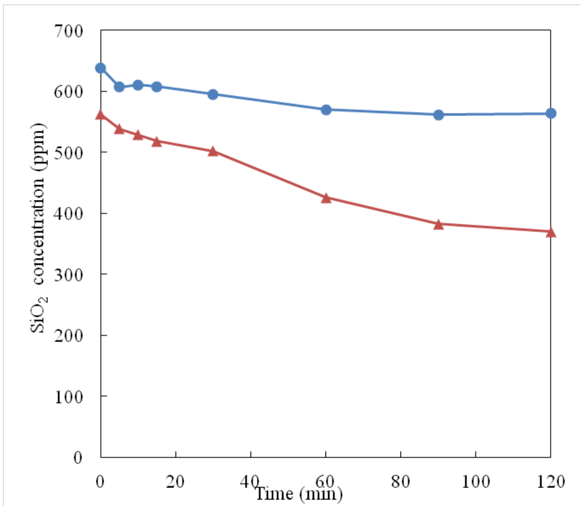

Figure 1a: Changes in Si(M) (●) and Si(T)(▲) concentrations in geothermal water A with time.

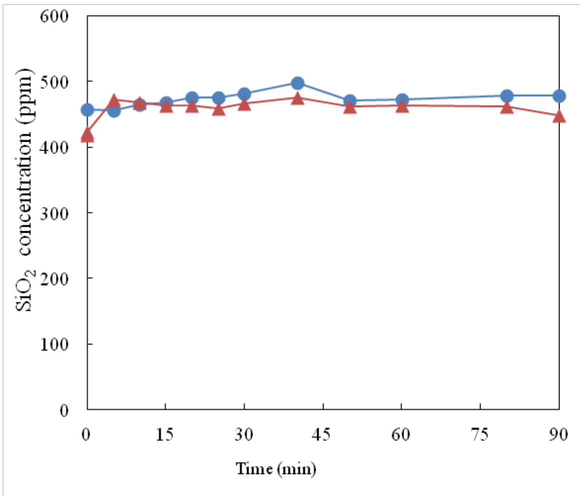

Figure1b: Changes in Si(M) (●) and Si(T) (▲) concentrations in geothermal water B with time.

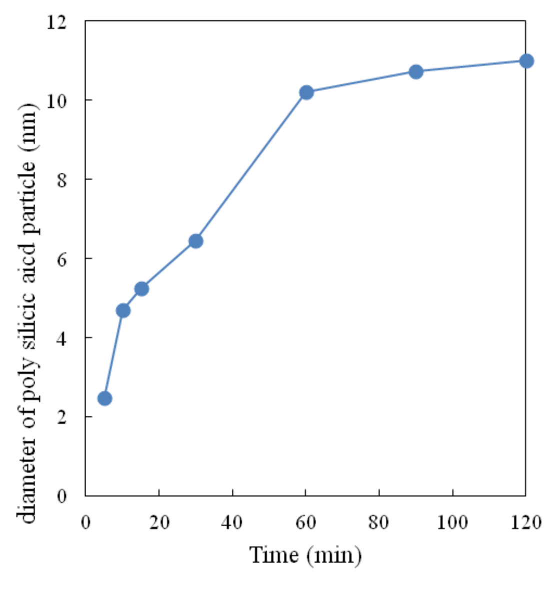

Figure 2: Change in hydrodynamic diameter of polysilicic acid particles in geothermal water A with time.

3.2. Removal of polysilicic acid by addition of CTAB

The cetyltrimethylammonium ion (CTA$^+$) is a detergent with hydrophilic ammonium part and hydrophobic hydrocarbon part. The CTA$^+$ ion can adsorb to Si-O$^-$ group on the surface of silica gel by the electrostatic interaction (Iler, 1979) .

The CTA$^+$ also adsorb to the surface of polysilicic acid particle to destabilize the polysilicic acid particle and the reaction between polysilicic acids is accelerated to precipitate silica (Kitsuki el., 1986). This method is considered to be useful to remove the supersaturated silicic acid. In principle, monosilicic acid molecule cannot react with the CTA$^+$ because of electric neutral. Therefore, CTAB was added to only the geothermal water A

In Fig. 1, the polymerization of silicic acid occurred in the geothermal water A. The Si(M) concentration attained near the solubility of amorphous silica around 90℃ after 2 h. In Fig. 2, the polysilicic acid particles grew rapidly with time until 60 min. The CTAB was added by changing the timing of addition. It was added at 0, 15, 30, 60 min after the sampling of the geothermal water A. The CTAB concentration in the geothermal water A was 10^{-4}, 10^{-5}, 10^{-6} M after the addition. The Si(M) concentration in geothermal water A decreased from 634 ppm (SiO_2) to about 400 ppm, which is close to the solubility of amorphous silica at 90℃. In Fig. 3, a relationship between the timing of addition of CTAB and the Si(T) concentration in filtrates is shown. In the CTA$^+$ addition of 10^{-6} M at 0 and 15 min, silicic acid was hard to precipitate but the Si(T) concentration decreased to 550 and 525 ppm at 30 and 60 min, respectively. In the addition of 10^{-5} M, the silica precipitation behavior was similar to that of 10^{-6} M but much silicic acid precipitated compared with that in the addition of 10^{-6} M. The Si(T) concentration decreased to be 510 and 460 ppm at 30 and 60 min, respectively. In the addition of 10^{-4} M, the Si(T) concentration decreased linearly and the Si(T) concentration decreased to the solubility of amorphous silica, suggesting that almost all of polysilicic acid particles were precipitated. Consequently, larger polysilicic acid particle than around 5 nm can probably react with CTA$^+$ to effectively precipitate.

The removal efficiency of polysilicic acid particle greatly depends on the timing of addition of CTAB.

As the polymerization of silicic acid proceeds, aluminum is taken up into polysilicic acid particles (Yokoyama et al., 1991). Therefore, the aluminum taken up into polysilicic acid particle is also removed at the same time.

As aluminum affect the formation of silica scale (Ichikuni, 1970, Yokoyama et al., 1993 and 1999, Gallup, 1997 and 1998, Carroll et al, 1998, Nishida et al., 2000,), this removal method of silicic acid from geothermal water maybe more effective to prevent the formation of silica scales. Figure 4 shows a relationship between the timing of addition of CTAB and the aluminum (Al) concentration. In Figure. 4, the Al concentration was measured in the same experiment as that shown in Figure. 2. The initial Al concentration was 1 ppm in the geothermal water A. In the addition of 10^{-6} M, the Al concentration decreased to 0.8 ppm at 15, 30 and 60 min. In the addition of 10^{-5} M, the Al concentration decreased to 0.3 and 0.2 ppm at 15 and 60 min. The decrease tendency of the Al concentration was similar to that of the Si(T) concentration. On the other hand, most of aluminum was removed by the addition of 10^{-4} M. All of polysilicic acid particles incorporating aluminum can be considered to be removed.

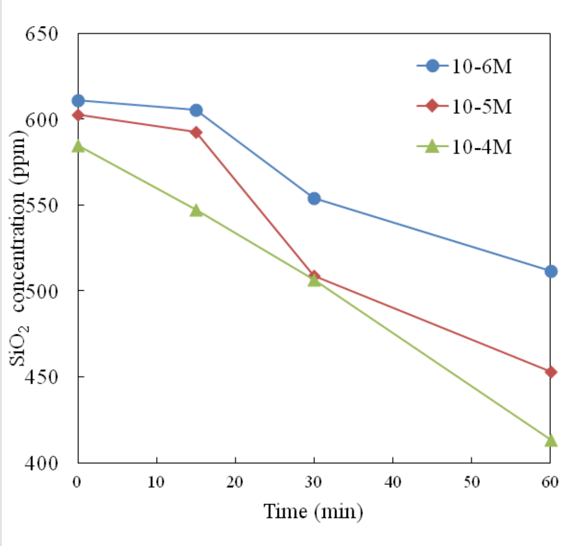

Figure 3: A relationship between the timing of addition of CTAB and the Si(T) concentration in filtrate. Added CTAB concentration: 10^{-4}, 10^{-5} and 10^{-6} M.

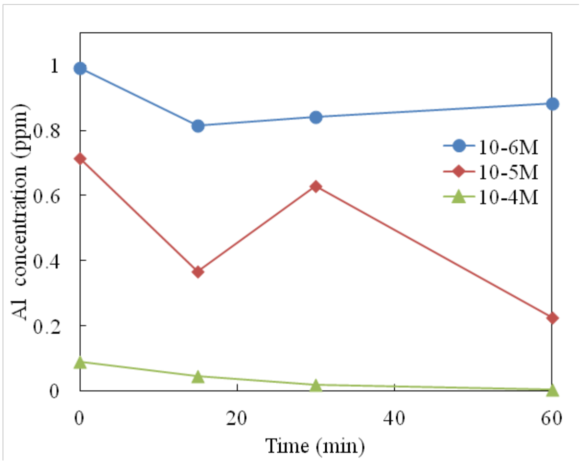

Figure 4: A relationship between the timing of addition of CTAB and the aluminum concentration in filtrate. Added CTAB concentration: 10^{-4}, 10^{-5} and 10^{-6} M.

3.3. Removal of monosilicic acid by addition of Ca^{2+} and pH adjustment

In Fig. 2, no polymerization of silicic acid occurred in the geothermal water B because of lower Si(T) concentration and higher pH than those of the geothermal water A. However, the Si(M) is in the range 450 ~ 500 ppm which is still higher than the solubility of amorphous silica, suggesting that silica scale may be deposited in the formation around the reinjection well of geothermal water. To prevent the formation of silica scale, the removal of monosilicic acid is a possible way. It is well known that hydroxides of Fe^{3+}, Al^{3+} and Mg^{2+} can effectively coprecipitate/adsorb monosilicic acid (Yokoyama et al., 1980, 1982. However, the remaining metal ions may induce the formation of silica scales (Gallup, 1991, Manceau et al., 1995, Morita et al., 2017). In this study, the addition of calcium (Ca) ion was applied to remove all silicic acid from geothermal water, which is a method described by Rothbaum et al. (1975) and by Kato et al. (2003). They used CaO and $Ca(OH)_2$ as a calcium source because it is cheap. But, CaO is insoluble. The reaction of CaO with silicic acid is slow and it remained in precipitate. Therefore, $CaCl_2$ was used as source of Ca^{2+} and then pH was adjusted to desired value.

Figure 5 shows a relationship between the added Ca concentration and Si(T) concentration in filtrate at desired pH which is adjusted with sodium hydroxide solution. As pH increased and Ca^{2+} concentration increased, the Si(T) concentration decreased. When the addition concentration of Ca^{2+} exceeded 400 ppm at pH 12, silicic acid was completely removed. Figure 6 shows a relationship between the added Ca^{2+} concentration and Ca/Si atomic ratio of precipitate. As the added Ca^{2+} concentration increased, the Ca/Si atomic ratio increased apparently (a part of Ca^{2+} formed $CaCO_3$). According to powder X-ray diffraction analyses, the precipitates were X-ray amorphous, suggesting that calcium silicate hydrates (C-S-H) may be formed. Figure 7 shows some ^{29}Si CP MAS NMR spectra for the precipitates formed at pH 11 (a) and pH12 (b) under the addition of 10 mM Ca^{2+} (400 ppm). The Ca/Si atomic ratio of the both C-S-H was about 1.1. From the chemical composition, the C-S-H is deduced to be a precursor of $CaSiO_3$ and tobermorite ($5CaO \cdot 6SiO_2 \cdot 5H_2O$)which consists of Q^2 and Q^3 structures (Q: connecting mode of silicate ion (Matsui et al., 2013). At pH 11, the chemical shift values (relative to TMS) were -80.8 (Q^1), -85.7 (Q^2) and -95.0 (Q^3) ppm, on the other hand, pH 12, were -85.4 (Q^2), -99.6 (Q^3) and 108.4 (Q^4), respectively. The strongest intensity peaks were -85.7 and 99.6 ppm at pH 11 and pH 12, respectively. It suggests that the polymerization degree of silicate ion in the C-S-H formed at pH 12 is higher than that at pH 11, deducing that the higher pH, the faster formation rate of C-S-H.

When silicic acid was completely removed, Al concentration in filtrate approached to zero. According to the ^{27}Al MAS NMR spectra of precipitates, the chemical shift values were around 52~53 ppm (relative to $[Al(H_2O)_6]^{3+}$), suggesting that the Al is present as 4-coordinated species and taken up into the C-S-H by the substitution with Si atom.

Judging from the removal efficiency of silicic acid from geothermal water, the addition of the same amount of Ca^{2+} as monosilicic acid and the following adjustment to pH 12 around 90°C is the best condition to precipitate silicic acid as C-S-H from geothermal water.

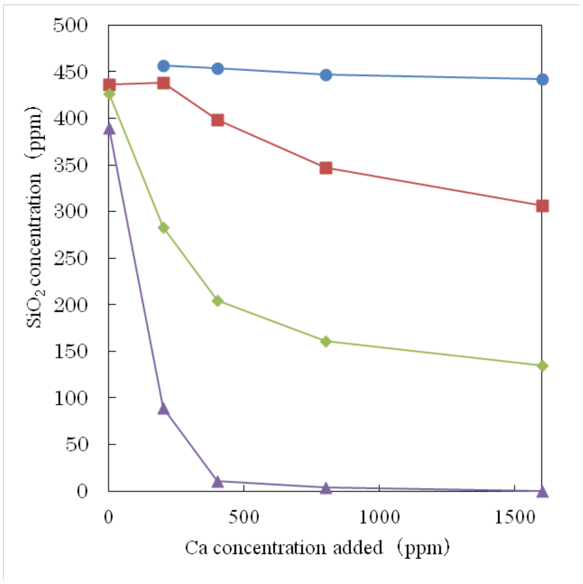

Figure 5: A relationship between the added calcium concentration and the Si(T) concentration in filtrate; pH: 9 (●), 10 (■), 11(◆), 12 (▲)

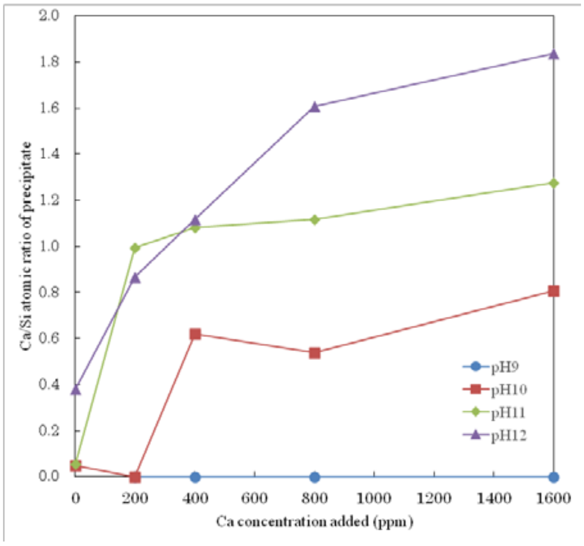

Figure 6: A relationship between the added calcium concentration and the Ca/Si atomic ratio of precipitates.

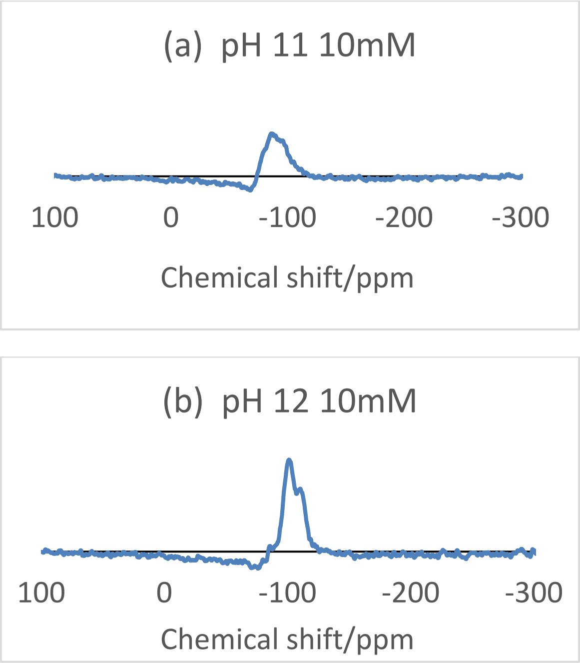

Figure 7: ^{29}Si CP MAS NMR spectra for precipitate formed at pH 11 and pH 12.

4. CONCLUSION

Removal method of polysilicic acid was established using cetyltrimethylammonium (CTA$^+$). The removing efficiency depends on the reaction time of the polymerization of silicic acid (the size of polysilicic acid particle). At the addition of 10^{-4} M CTA$^+$, most of polysilicic acid was removed. Large polysilicic acid particles were precipitated even by the addition of 10^{-6} M CTA$^+$. In case of removal of monosilicic acid, the addition of 10 mM calcium ion (Ca^{2+}) and the following pH adjustment to pH 12 is the best condition and all of the monosilicic acid was removed as a calcium silicate hydrate. In the both methods, aluminum is also removed effectively.

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