SILICA SEPARATION FROM REINJECTION BRINES HAVING DIFFERENT COMPOSITION AT MONTE AMIATA GEOTHERMAL PLANT

Sandra Vitolo and **Maria Luisa Cialdella**

Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali
Università di Pisa, Via Diotisalvi 2, 56126 PISA, Italy

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Abstract

A process for the separation of silica from Monte Amiata reinjection geothermal brines, whose scaling effect causes serious problems in the operation and maintenance of reinjection facilities, is reported, in which the phases of coagulation, sedimentation, and filtration of silica are involved Brines discharged from three different wells were studied, in order to investigate the influence of the brine composition on the effectiveness of the separation treatment. The addition of different amounts of lime, calcium chloride and sodium hydroxide at different temperatures were investigated and the separating operations were determined. The brine pH was revealed to be a fundamental factor in affecting the process of coagulation of the silica present

Introduction

Exploitation of the Monte Amiata water-dominated geothermal reservoir yields a two phase flow, which is flashed and separated on the surface This produces steam for the generation of electric power, and waste brine at atmospheric pressure at about 100°C, which is reinjected into shallow wells to solve the brine disposal problem During flashing, volatile substances transfer to the vapour phase, whereas the non-volatile salts and silica remain in the liquid Evaporation losses and temperature decrease cause a concentration and supersaturation of the constituents of the brine The high degree of silica supersaturation promotes a rapid conversion of the excess silica in solution to suspended colloidal silica, which adheres to the surfaces and forms a solid deposit that obstructs the reinjection pipelines The scale is very hard and can be removed by mechanical or other means only in a few cases. A study on the behaviour of Monte Amiata waste brines were conducted. in order to investigate the possibility of removing the suspended colloidal silica by coagulation and subsequent sedimentation and filtration, prior to reinjection These brines are characterized by a high silica content and a rather high salinity Table I reports chemical analysis, pH, and conductivity of the three brines used in these tests

The mechanism of aggregation of colloidal silica is controlled by surface charge effects Factors affecting surface charge. and therefore, silica precipitation rate are pH, and metal cations present' in the brine Coagulating agents are predominantly multiple-charged cations, which serve as bridges between the surfaces of the colloidal silica particles. These factors have been exhaustively reviewed by Iler (1979) and Chan (1989) in their publications on the chemistry of silica Silica scaling in waste brine reinjection facilities has been encountered in many geothermal fields but, owing to their different composition, brines discharged from various fields behave differently, each requiring a specific solution (Weres and Tsao, 1981; Dahlstrom et al., 1982, Henley, 1983; Axtmann and Grant-Taylor, 1986; Gudmundsson and Einarsson 1989; Hibara et al , 1989; Hurtado et al . 1989; Lindal, 1989; Thordarson and Tomasson, 1989). The experiments reported for the Cerro Prieto field (Weres and Tsao, 1981; Hurtado et al , 1989), where lime was used as the coagulating agent, have been very helpful Referring to the great amount of information available in the above mentioned literature, three brines representative of the range of variation of composition of Monte Amiata field reinjection streams were examined in order to investigate the influence of composition and pH of the brines on the working conditions of the separation treatment Lime and calcium chloride were used as coagulating agents The separation treatment was studied at room temperature and 90°C to investigate the influence of the temperature on the process

Table 1 Chemical composition, pH and conductivity of Monte Amiata field brines

	PC-33 well	PC-34 well	PC-35 well
	ppm	ppm	ppm
Ca^{++}	128	16 9	0 96
Mg^{++}	< 0 5	< 0.5	0019
Na^+	1977	1684	1070
K^+	558	430	101
Cl^-	4135	3498	1160
SO_4^{--}	25 8	3 2	5 6
H_3BO_3	31904	9082	3920
NH_4^+	439	99	123
SiO_2	700	1040	820
Li^+	21 9	26 8	11
Rb^+	2.06	2 2	0 35
Cs	071	1 19	0 7
Sr^{++}	2.4	0 6	0 25
Br^-	8.4	9 2	2
I^-	4.1	3 6	1 4
As tot	114	34 4	3 4
Al tot	0 31	1	1.1
Fe tot	1.6	< 0 05	0 01
Sb tot	10 3	34	11 3
pH (20°C)	601	7 32	8.53
Conductivity (μS/cm)	8000	7210	5060

Experimental

The different phases of the brine silica removal treatment. consisting of coagulation, sedimentation and filtration, were carried out using the experimental apparatus shown in Fig 1 Preparation of the untreated brine and the coagulation test were both conducted in a jacketed heatable pyres stirred reactor with a reflux condenser to minimize evaporation losses. Temperature in the reactor was be maintained at the set point by a temperature controller that regulates the electrical resistance heater heating the water circulating in the jacket After treatment, the brine was discharged from the reactor into an Imhoff cone dipped in a water bath, whose temperature was maintained at a constant value by a second thermostat After sedimentation of the precipitate, the brine was transferred from the cone into a second stirred and heatable tank, from which it was fed to the filtration device There, the sludge was separated by vacuum filtration in a ceramic filter with a cellulose acetate membrane (0 45μm pore diameter), obtaining a solid filter cake and a clear filtrate The filtrate was collected and measured in a

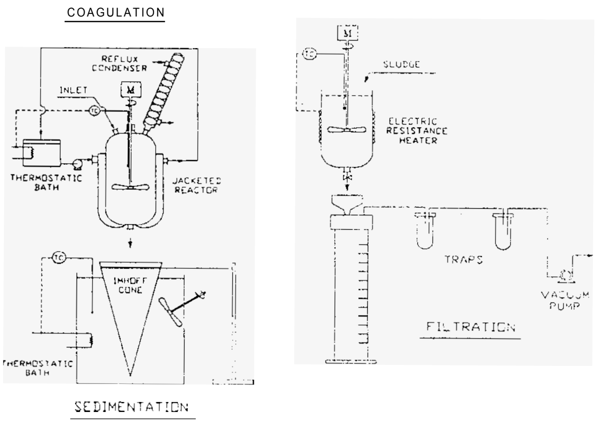

Fig 1 Diagram of the experimental apparatus (M is the motor of the stirrer, TC is the temperature controller)

cylinder. The vacuum was created by a vacuum pump and measured by a mercury vacuum meter The vacuum was manually controlled and maintained at about 170 mm Hg, and the level of the liquid on the filter was mantained at a constant value by controlling the dropping rate of the sludge from the feeding tank Dissolved (nionomeric) silicic acid was determined in accordance with the molybdate yellow method recommended by Iler (Iler. 1979) and slightly modified for the total (nionomeric plus colloidal) silica *as* described by Weres et al (1981) The method is based upon the formation of a yellow complex of silica and molybdate, which can be measured in a spectrophotometer at 410 nm The spectrophotometer used was a Perkin Elmer Hitachi mod 200 The brine samples were taken from the reinjection tanks of wells PC-33, PC-34, and PC-35 downstream of the atmospheric separator at about 90°C, transported to the laboratory and stored at room temperature The equilibrium at room temperature between monomeric and colloidal silica was reached in a very short time No sedimentation was observed in the storage tanks during the testing period, and the colloidal silica remaining suspended Preliminary thermostated brine ageing tests were carried out on 1000 ml brine samples at 90°C, in order to test the possibility of re-attaining equilibrium between nionomeric and colloidal silica, which characterizes the brines as they are discharged in the reinjection pipelines With time, the monomeric silica content in the samples increased until a constant concentration was obtained in about 3 hours The final monomeric silica content measured in the brine was in agreement with the values reported in the literature for the equilibrium solubility of amorphous silica at observed temperatures (Fournier and Rowe, 1977, Marshall, 1980) The sample should therefore be conditioned at constant temperature to allow the brine *to* reach equilibrium of momomeric and colloidal silica, prior to performing the treatment process at 90°C The ageing period was obviously not necessary in the tests at room temperature, where the samples were taken from the storage tanks and submitted directly to the treatment. The brine was stirred for about 10 minutes after the addition of the coagulating agent The sample was then transferred to the Imhoff cone, where the sedimentation was observed for a period of 150 minutes The total silica content in the clear liquid was also measured at fixed times during the sedimentation phase The sludge was then transferred to a stirred and heatable feed tank, from which it was passed to the filtration device, in which the times of fixed filtrate volumes were recorded After filtration, the filtercake height was recorded and, once dryed, the cake was weighed and the monomeric and total silica concentration in the filtrate were determined

Results

In Figs. 2 and *3* the total residual silica in the clear liquid after the coagulation and settling treatment at room temperature and 90°C using lime and calcium chloride, respectively, are reported for the three samples. The total silica content of the three samples before treatment are also reponed for comparison The experimental points reported begin from the minimum amount of additive which proved to have an effective coagulating action The coagulating action was fixed *to* be effective if the coagulation and sedimentation of the precipitate started no later than 30 minutes after the sample was discharged into the Imhoff cone

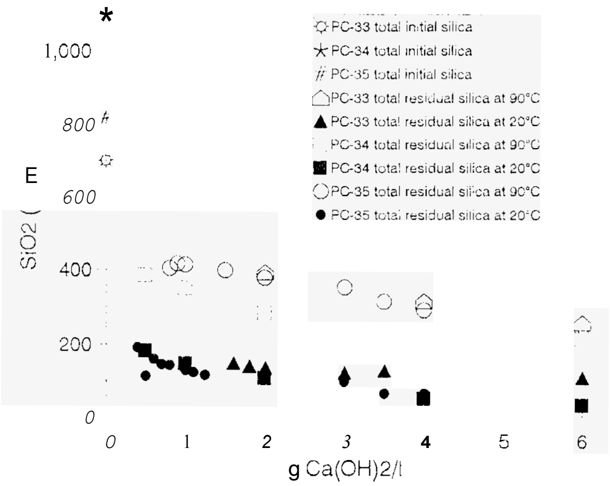

Fig 2 Residual total silica after treatment with lime at different temperatures and dosages

Lime proved to be effective in the coagulation of the colloidal silica for all the three brines The residual silica content in the supernatant liquid corresponded tu the solubility concentration of silica at the given temperature at the lower dosages (up to about 2-3 g/l of lime), and lower than the solubility concentration at the higher dosages Lime additions up to 7 g/l caused only the coagulation and separation of the already-present equilibrium colloidal silica fraction at the working temperature They had no influence on the soluble component With higher lime additions. the total silicn content began to fall significantly below the equilibrium concentration of monomeric silica, showing an additional removal of a fraction of the monomeric silica. The different behaviour of lime when high amounts are added can be attributed either to the formation of calcium silicate species or to the influence of the pH increase It is interesting to note that a higher amount of lime was necessary to reveal an effective coagulating action in PC-33 brine, compared *to* the other two samples In fact, while for PC-34 and PC-35 brines the coagulating action was effective starting from about 0 5 g/l, higher dosages of lime (about 2 g/l) were necessary to obtain the coagulation of silica in the IT-33 sample This behaviour may be attributed to the lower value of pH of PC-33 brine The calcium ions-bridging mechanism is, in fact, more effective *at* relatively high values of pH, when the colloidal particles surfaces are negatively charged by the adsorption of hydroxyl ions In the case of PC-33 brine, at lower dosages of lime, the value of pH was still too low and the bridging effect of calcium was inhibited When about 2 g/l of lime were added, the pH increased to about 6 S and the calcium ions could perform the coagulating action The coagulation in this case was obtained by the combined action of raising the pH and the calcium-bridging mechanism In the case of PC-34 and PC-35 brines, characterized respectively by a natural pH of 7.30 and 8.53, lime caused the coagulation by means of the addition of calcium-bridging ions, while the effect of the pH increase was less significant

A different behaviour was displayed in the tests of coagulation using calcium chloride, which promoted the coagulation and settling of the equilibrium colloidal silica fraction only, leaving in the brine the soluble part present before treatment, at all temperatures and amounts added PC-35 brine colloidal silica was coagulated by using the lowest amount of calcium chloride, while higher amounts were necessary for PC-34 brine. **As** far as PC-33 brine is concerned, the coagulation was effective only at 90°C, while at room temperature no coagulation was observed even at the highest dosages. This behaviour may be attributed to the pH increase effect due to the addition of calcium

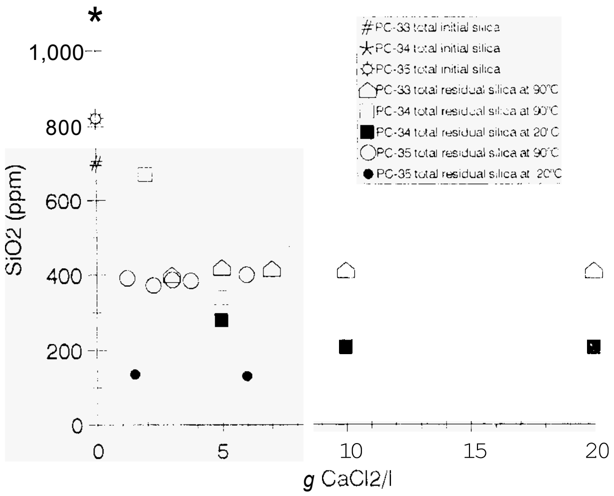

Fig 3 Residual total silica after treatment with calcium chloride at different temperatures and dosages

chloride While the coagulating action was possible for the brine having a relatively high natural pH, the bridging effect of calcium was inhibited for the low pH brine of PC-33 well, and was possible only at 90°C, probably due to the lower content of colloidal silica at this temperature.

Fig 4 reports the results of the tests of coagulation, at room temperature and 90°C, conducted on PC-33 brine by increasing the pH with different amounts of sodium hydroxide prior to adding lime as coagulating agent The experimental results obtained by using only lime are reported for comparison

As the pH was increased prior to coagulation, less lime was required to cause the coagulation of the colloidal silica fraction and, as was observed in the treatment with lime, an additional removal of a fraction of the soluble silica was displayed at the higher dosages

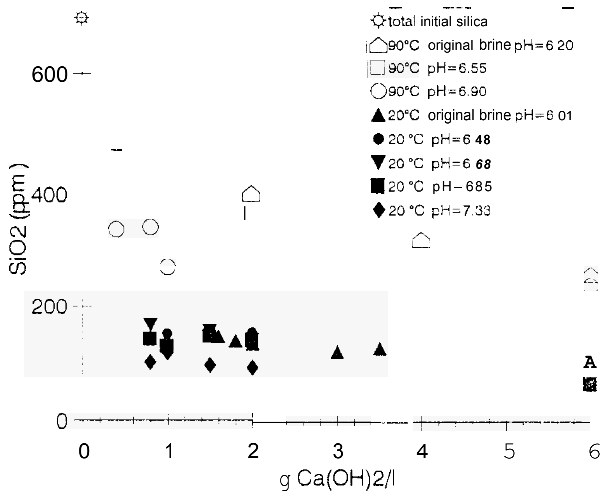

Fig 4 PC-33 residual total silica by modifying the pH before treatment with lime at different temperature and dosages

Fig. 5 reports the results of the tests of coagulation at room temperature conducted on PC-33 brine by increasing the pH with different amounts of sodium hydroxide prior to adding calcium chloride as the coagulating agent. While the addition of calcium chloride at room temperature did not succeed in causing the coagulation, this effect was obtained by increasing the pH.

Likewise, as reported in Fig 6, an increase of pH favoured the coagulating action of calcium chloride on PC-34 brine, expecially at room temperature

These tests confirm the effectiveness of calcium ions as coagulating agents and the significance of the pH in the mechanism of bridging by means of cations, as reported in the literature (Goodman, 1966; O'Melia and Stumm, 1967, Tadros and Lyklema, 1969; Iler, 1979; Hurtado et al , 1989; Weres et al 1981; Yokoyama et al , 1989)

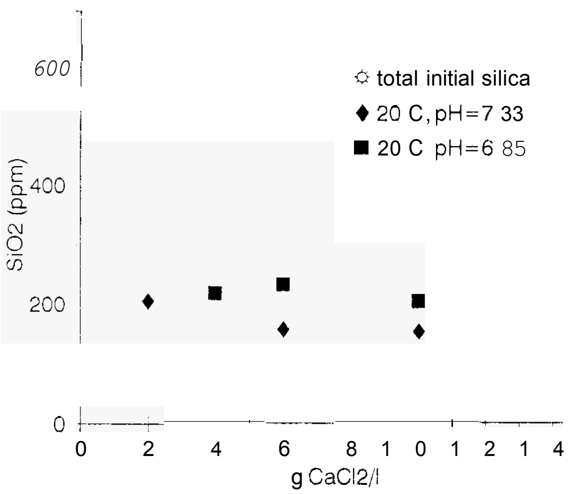

Fig 5 PC-33 residual total silica by modifying the pH before treatment with calcium chloride at room temperature and different dosages

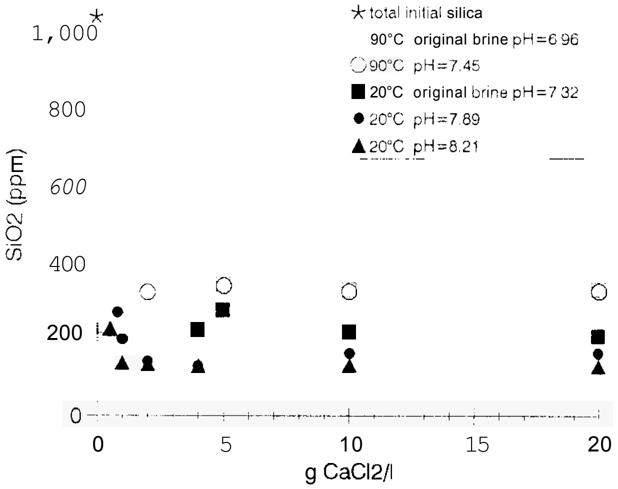

Fig 6 PC-34 residual total silica by modifying the pH before treatment with calcium chloride at different temperatures and dosages

Table 2 Initial sedimentation velocity of coagulated silica

		Sedimentation velocity (cm/min)		
Temperature	Coagulant	PC-33	PC-34	PC-35
20°C	Ca(OH)2	1.65	1.24	1.22
	CaCl2	-----	3 97	0.91
90°C	Ca(OH)2	4 33	4 33	4.11
	CaCl2	3.97	3.97	4.04

The settling rate of the coagulated silica was unaffected by the amount of coagulant added, in the range of dosages studied As reported in Table 2, the settling rate generally increased with temperature, and was in the same range both using lime and calcium chloride This behaviour may be attributed to (a) the influence of Brownian motion which, at higher temperatures, favours aggregation towards larger particle diameters, and (b) to the decrease in the viscosity of the brine as the temperature rises

The equation for filtration at constant pressure drop (Coulson et al.. 1985) was used to investigate the filtration behaviour of the brines:

$$\frac{t}{V} = \frac{r\mu\upsilon}{2A^2(-\Delta P)}V \qquad (1)$$

where t is time (s), V the volume of filtrate (m^3), υ the volume of cake deposited by unit volume of filtrate (dimensionless) μ the viscosity of the filtrate (Ns/m^2), **A** the total cross sectional area of the cake (m^2), ΔP the applied pressure drop (N m^2), and r the specific resistance of the cake (m^{-2}), which decreases with the void fraction of the aggregates in the cake and increases with their specific surface area.

Through the slope of t/V versus V curves, obtained from the experimental filtration data, it is possible to obtain the specific resistance of the cake for each filtration test, as reported in Fig. 7, at the different temperatures and for the different amounts of coagulant added A lower specific resistance was displayed in the filtrations conducted at 90°C, compared with the filtrations at room temperature, for both coagulants used As the void fraction is only slightly affected by a variation of the diameter of the aggregates, the decrease of the specific resistance must be attributed to a decrease of the specific surface area of the aggregates, thus confirming the supposition of the coagulation of aggregates with larger diameter at higher temperature

Furthermore, the specific resistance of the samples coagulated with calcium chloride was much higher in comparison with lime, both at room temperature and 90°C

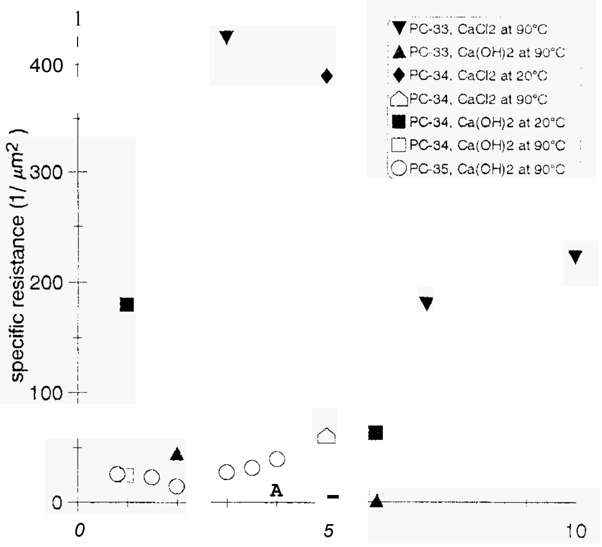

Fig 7 Specific resistance of the cakes in the filtration of the brines treated with lime and calcium chloride at different temperatures and dosages

Conclusions

The effectiveness of lime and calcium chloride as coagulating agents of the silica present in suspension in Monte Amiata reinjection brines has been investigated The aggregation by means of calcium ions, which act as bridges between the silica surfaces, was found to be influenced by the brine composition and pH It is, in fact, more effective at relatively high values of pH, when the colloidal particles surfaces are negatively charged by the adsorption of hydroxyl ions Lime, whose addition causes an increase of the brine pH, proved to be effective for all the three brines studied, promoting a rapid coagulation of the suspended colloidal silica at the temperatures investigated (room temperature and 90°C) The minimum dosage necessary to cause the coagulation, dependent upon the brine, was lower for the brines having higher pH While the minimum dosage of lime caused the coagulation of the suspended colloidal silica, higher dosages allowed the removal of an additional fraction of the monomeric dissolved silica, thus reducing to a very low value the silica content in the brine Calcium chloride, whose addition causes a decrease of the brine pH, was effective only if added to the brines having a higher pH, and an increase of its addition did not cause the removal of dissolved silica While the most effective removal was obtained at room temperature, the subsequent sedimentation and filtration phases improved at higher temperature, due to the lower viscosity of the suspension and to the larger diameters of the coagulated aggregates. Since the degree of silica removal was the most important design specification, the working temperature to be chosen for real treatment is that at which the residual content in the reinjected brine is too low for scaling effects The maximum allowable silica concentration should be verified by further experimental work, taking into account the real operating conditions of Monte Amiata reinjection pipelines

Finally, the results obtained in this preliminary laboratory study could be used to test the brine treatment process concept in a pilot plant installed in the field, and to estimate the size of an industrial plant and its corresponding capital and operating costs

These costs should be compared to those spent at present for the maintenance of the reinjection lines (cleaning by mechanical means, substitution of obstructed piping), in order to determine the economical effectiveness of the silica separation treatment.

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