LABORATORY AND FIELD TESTING OF POLYMERIC COMPOUNDS AS POTENTIAL SILICA SCALE INHIBITORS

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ABSTRACT

Silica deposition presents significant constraints in the design and operation of geothermal steam fields. To improve the efficiency of geothermal exploitation, silica precipitation must be controlled or avoided.

Referring to ENEL geothermal fields at Piancastagnaio (Tuscany, Italy), a brief analysis of the different techniques for silica scaling prevention is reported.

We intend to examine the possibility of using chemical inhibitors for silica scale prevention. The development of antiscaling products is reviewed, samples of commercially available scale inhibitors have **been** acquired and a technique for preliminar screening for laboratory tests is defined.

We intend also to investigate how shear stresses influence silica scale deposition

1. INTRODUCTION

Corrosion and silica scaling problems can seriously affect the operation and electric power production from geothermal plants. A high concentration of silica in many geothermal brines causes the solution to become supersaturated when flashed. Silica deposition may occur in plant equipment pipelines and injection wells. Siliceous scales are typically inert to most chemicals and, once deposited, are very resistant to mechanical removal. Hence the most desiderable treatment methods focus on prevention of silica deposition or on controlling the morphology of deposits.

Siliceous scale are formed by reactions between silanol radicals and the speed of reaction is controlled by various factors such as pH, temperature and salt concentration.

The concentration of aqueous silica in reservoir brine is determined by the solubility of quartz which is directly related to reservoir temperature. At wellhead, aqueous silica levels are controlled by equilibrium with amorphous silica.

In steam field design, the common practice for controlling silica deposition in reinjection pipelines is to set flash separator pressure sufficiently high so that the temperature of separated brines is higher then the saturation temperature of amorphous silica. The setting of higher pressure causes the reinjection of brine at higher temperatures, increasing thermal inefficiencies and reducing the amount of flashed steam.

A number of potentially effective techniques for controlling silica deposition have been proposed and field tested, including pH modification, chemical addition and aging of the effluent waters in ponds.

Until recently, no treatment has shown significant precipitation inhibition of deposition at different geothermal fields.

One of the developed techniques is the aging tank method proposed by Yanagase *et al.* (1970). Ponding geothermal waters into an aging tank proved effective in delaying the deposition of silica scales and, consequently, in prolonging reinjection well life. This method is based on the assumption that only active silica (polysilicic acid, smaller then 0.3μm) creates scale, so active silica is made unreactive during ponding in the aging tank. A reduction of 10% has been obtained in field tests at the Hachobaru power station in Japan.

Silica deposition can be prevented by controlling the pH of the brine by maintaining it in an acid condition (about 5.0). Lowering the pH of the brine decreases the rate of siloxane bond formation and consequently increases the time before supersaturated silica deposits. In 1977 Greens and Owen demonstrated effective control of the siliceous scales by acidification of the brine with hydrochloric acid. This technique has been verified in New Zealand by Rothbaum *et al.* (1979). At the Hatchobaru power station, the scale deposition rate has been significantly reduced by lowering the pH from 7.5 to 5. Even if useful, control of silica deposition through pH modification has several disadvantages, high costs of acid (concentration > 300ppm of HCl are required) and a sharp increase of corrosion rates.

One of the other possible solutions to reducing silica scaling is to dilute the brine with a secondary fluid which is low in silica, for example turbine condensate. The temperature of the diluant must remain high enough to avoid a temperature drop which could result in saturation of the solution. If silica content is high, the amount of diluant required to keep the geothermal solution under the concentration corresponding to saturation pH and temperature values of the brine may greatly increase the reinjection volume of the plant. Therefore, this method appears suitable only for low-medium silica content brines.

During the past ten years crystallisation-clarification technology has proven to be a solution for the exploitation of Imperial Valley geothermal fields. De-supersaturation of silica is accomplished in the crystallizer-clarifier process by seeding brine with recycled iron silicate particles. Brine resulting from the clarifiers exhibits very little tendency to form scale deposits. (Newell *et al.*, 1989).

This technique involves the formation of a great amount of solid material which can be difficult to dispose.

2. THE PIANCASTAGNAIO GEOTHERMAL FIELD

The Piancastagnaio geothermal field produces a vapor dominant fluid, characterized by a low content of volatile compounds in the vapor phase and by a high salinity liquid phase, the latter being the result of the interaction between the hot fluid and sedimentary rocks.

In the exploitation cycle (Figure 1), a supersaturated silica solution results as a consequence of the temperature and pressure decrease upon flashing and the pH rising due to the release of CO_2 and H_2S. Silica concentration in the exhausted brines sent to the reinjection wells is about **800-1000ppm.** This value is very high when compared to the amorphous silica solubility at the same temperature and pH.

Though the liquid phase composition and the pipeline layout may be appreciably different from one well to another, a general deposition phenomenon is present in the pipeline connecting the flash pool to the reinjection well (ENEL-VDAG, 1992).

The rate of deposition is so high that mechanical cleaning of pipelines is required at least every three-four months. More over when the total occlusion of pipelines occurs, the scale is such a hard material that a mechanical removal is unfeasible. Such pipelines can't be used again and are difficult to remove.

In order to minimize plant shutdowns, pipeline diameters have been oversized, so that channelling flow is obtained. Since it is necessary to know the amount of scale formation in the pipelines, parts of each line can be opened for visual inspection even if the exposure of geothermal waters to air is known to have an accelerating effect on silica deposition).

One of the reinjection section of Piancastagnaio field consists of 60-70m^3/h of a brine with pH 8.2, temperature 90°C and silica concentration of 900ppm. Lowering the pH of this brine with hydrochloric acid is not proposable because a complete control means large amounts of acid to be employed to reduce the pH. This would increase corrosion rates and the probability of environmental pollution.

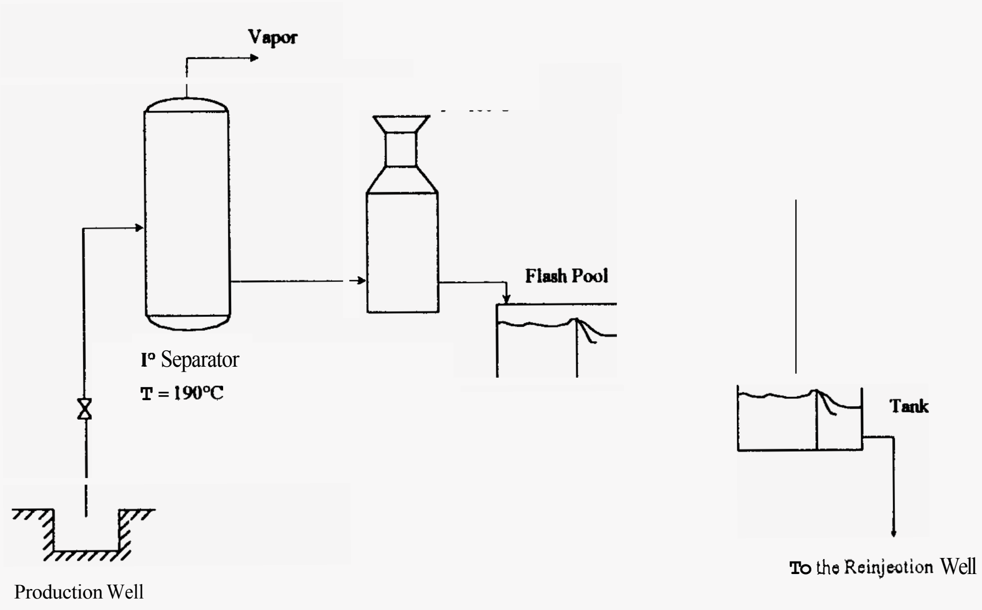

Fig. 1. Schematic separation and reinjection layout at Piancastagnaio

Another method to be considered consists of precipitating salts present in the solution by chemical and physical processes, followed by their separation and disposal.

Using this approach several possible solutions have been developed in our Department.

In calm conditions, silica separation and scaling is not appreciable for brines in which silica concentration is two or three times the monomeric silica value which correspond to the solubility of amorphous silica. On the other hand, when the same brine flows inside pipelines scaling occurs readily. Chemical analysis on resting geothermal brines collected at Piancastagnaio do not show any time dependence, so that one must presume that stable equilibrium conditions exist between monomeric and polymeric silica. On the contrary, in flow conditions the same solution shows appreciable scaling phenomena without remarkable variations of pH and temperature. This fact supports the hypothesis that the fluid flow behaviour of the system may modify existing monomeric-polymeric silica equilibrium. Previous research in our Department demonstrated that shear stress was able to promote degradation of low polymeric silica so that the new derived oligomeric portion could adhere more easily to the solid surfaces. Indeed, the derived polymeric portion is more active at the breaking point and has a higher probability of adherence, but it is also well known that high fluid velocity in the pipelines exerts a favourable effect against scaling involving scaling removal.

There are only a few studies concerning the effect of fluid velocities on deposition rates. Rothbaum and Rohde (1979) investigated the rotating effect on silica deposition. They found that, while only a small effect was present on the single phase aqueous polymerisation reaction (thus suggesting that it was not diffusion controlled), once some silica had been deposited further deposition was substantially accelerated by rocking.

Arnorsson (1981) also found that the deposition rata of amorphous silica from supersaturated solutions is accelerated by turbulent flow. A different point of view is expressed by Mroczek and McDowell (1990) who maintain that the deposition rate in pipes seems to be independent of flow rate. Another approach is proposed by Clian *et al.* (1988). Their result of two runs with different Reynolds numbers demonstrate that a lower Reynolds number increases fouling rate in term of asymptotic the fouling resistance. The lack of agreement on the fluid flow effect underlines the need of a systematic series of experiments to widen the knowledge about this aspect.

In addition to the effect of turbulence, we intend to evaluate the possibility of using chemical inhibitors. Unfortunately there is much disagreement and poor understanding concerning the effectiveness of these inhibitors, their dosage, and the reaction mechanisms involved. In some previous experiments encouraging results have been obtained so that chemical inhibition seems to be a promising method in preventing silica scales(Harrar *et* al., 1980).

Chemical treatments involves the adsorption of organic molecules on the surface of colloidal particles to retard their agglomeration and flocculation. It is generally thought that the deformation of permanent chemical bonding does not occur *so* that the stabilised suspension and precipitation reactions are sensitive to environmental factors such as temperature and fluid motion. Harrar *et* a/. (1982) reported the results obtained from field and laboratory testswhich showed the dependence of silica scale formation on several factors: pH, temperature, silica content. presence of electrolytes, and fluid motion.

Through a series of experiments carried out at Lawerence Livermore Laboratories (Harrar et *al.*, 1982), a group of compounds was selected. Among these compounds a certain activity towards silica was exhibited by many cationic substances, while classes which apparently don't react with silica were anionic in character: polyacrylates, polymaleic acid, phosphonates and sulfonates. It appears that electrostatic attraction involving the negatively charged colloidal silica and the cationic additives play an important role in the interaction. In particular, the most active were those containing polymeric nitrogen compounds. The stronger the cationic character the stronger the interaction with silica.

The probable mechanism is steric colloidal stabilisation rather then electrostatic stabilisation. The term "steric stabilisation" was used by Heller and Pugh (1954) to describe a phenomenon of stabilisation of a dispersion without electrostatic contribution, based on the adsorption of polymers on the surface of particles of dispersed solutions.

The experiments performed at Lawrence Livermore Laboratories show that the additives retard neither the polymerisation nor the formation of nuclei of discrete particles of silica, They act on the formed particles to decrease their rate of aggregation and the rate of deposition of silica particles on a substrate surface.

Steric stabilisation depends on the solubility of the surfactant in the dispersant and is not related to the ionic strength of the solution. A typical aspect of steric stabilizated systems is a dependence on temperature. The intent of a silica scaling control system is to arrest or retard, at the earliest possible stage, the development of colloidal particles of silica from the supersaturated brine: for steric stabilisation to occur, the particles must interact with the inhibitor when they are about 0.1μm in *size*.

The ideal antiscaling product would be a dual function molecule in which one portion is a group anchored firmly to the silica particle, while the other is highly soluble in the brine.

The behaviour of each compound depends on the relative concentration of the additive and colloidal silica, the *size* of the particles, and the salinity of the solution. Silica precipitation rates increase with salt content due tu the decrease of silica equilibrium solubility. A careful design of the experiments for the evaluation of the activity of inhibitors involves a comparison on an equal salinity basis.

Corrosion and morphology alteration of the substrate influence the initial stage of the deposition process. From the tests performed by Harrar et a/. it was found that the scaling rate on mild steel was greater than on more inert materials such as Teflon and Hastelloy. These tests were carried out over quite short exposures times (2-4 h).

Due to the complexity of the scaling phenomenon, our experiments have been planned in two phases. The first phase of the program consists of two principal efforts:

- field tests to study the effect of flow rate arid substrate material on silica scale deposition, with scale formation and characterization at various Reynolds number.

- laboratory tests for a preliminary screening of chemical products which prove to be to be effective at inhibiting silica deposition in simulated silica brines at the same conditions of field brines (pH, temperature, SiO_2 content).The rate of formation, the chemical constitution, and morphology have to be examined as a function of temperature, brine salinity, substrate material, and inhibitor activity.

In the second phase of the program, potential antiscaling compounds will be tested with geothermal brine at the pilot plant, Our search of products for the prevention of silica deposition is quite empirical in nature. We have acquired no direct evidence of the detailed mechanism of how the inhibitors are able to retard the precipitation reaction.

3. EXPERIMENTAL TESTS:

APPARATUS AND PROCEDURE

Initial studies have been performed with artificial and real silica solutions at our Department laboratories to investigate the Reynolds number effects on silica scale formation. Experiments have been carried out in a glass atmospheric vessel with an internal capacity of 1000cc, provided with a jacket for the controlof temperature. Vessel agitation is accomplished by a top entering turbine (Rushton-type, AISI 316).

The impeller speed is 200m/min corresponding to a Reynolds number of 46000. The impeller frequency (maximum value of 29 Hz) is controlled by a magnetic frequency meter (Fig. 2).

A preliminary experiment was done with an artificial solution (850 ppm SiO_2 from Na_2SiO_3, pH 8.5, and NaCI 0.3 N): the stirred test prouved very effective in accelerating the formation of a gel-type deposition with respect to the resting solution test.

The following tests were carried out at different Reynolds numbers with fluid samples collected from the Piancastagnaio geothermal field. Test results at high Reynolds numbers (20,000 to 30,000) pointed out the formation of deposits in the turbine. Removing these deposits was very difficult. Neither hot caustic soda solutions or hydrochloric acid solutions succeed in eliminating the deposit. A difficult mechanical removal was performed by a special micro grinding-wheel.

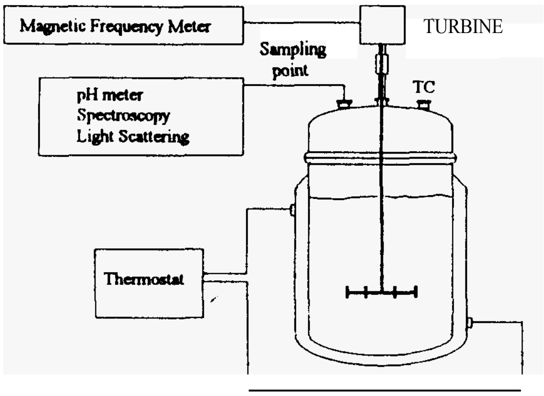

Figure 2 Laboratory test apparatus

In Table 1, the results obtained from a 40,000 Reynolds number (25Hz) test are shown. The difference in silica content exceeds turbine weight increase. This is probably due to the solution sprinkling on the top of the vessel. The increase in temperature is caused by stirring dissipation. Other tests in jacket vessels are planned to investigate simultaneous temperature effect on silica deposition. In Table 2 the deposit composition is shown.

Due to the fact that even small traces of contaminants can strongly influence the rate of silica polymerisation and deposition, a systematic field test series is proposed. At Piancastagnaio field, a dynamic loop facility for studying scaling tendency in geothermal brines has been designed. The intent is to provide for movement of real geothermal brines in simulated geothermal layout in order to study silica deposition in relation to turbulence effects. The pilot plant consists of 60m of a 2 inches pipeline. The brine is fed by a centrifugal pump and its flowrate ranges between 0.5 and 2.5 m/s. The flow is measured by a magnetic flowmeter. Pipelines consists of extractable sections connecting different sections of the pipe. Scaling rates will be determined by visual inspection at different sections of the pipes. Scale samples will be characterisad by crystallography. scanning electron microscopy, and X-ray diffraction.

This program should allow the correct evaluation of turbulence effects (effect of different Reynolds numbers and pulsed flow on silica deposition along pipes) and the possibility of treating the brine with chemical additives.

To gain more information on turbulence and wall shear stress effects, test sections of various shape will be inserted in connecting sections joining the pipelines.

Table 1. Results of the deposition test

	Silica content in the solution (mg)	Turbine weight (mg)	Temperature (°C)
Start	**614.18**	**14,715**	**23.3**
After 24hr	**586.76**	**14,728**	**31.7**
Difference	**27.42**	**13**	**8.4**

Table 2. Elementary composition of deposits formed during laboratory tests

Si	present	Mn	not found
S	present	Fe	present
Cl	present	Ni	not found
K	present	Zn	present
Cu	present	As	present
Ca	present	Pb	present
Cd	present	Cr	not found

As a result of a wide industry solicitation, various chemicals from different companies (Betz, Nalco, Nadar, Norso Haas, Union Carbide) have been submitted to us (Table 3).

Table 3. Potential silica deposition inhibitors

Company	Name
BETZ	**2023 - 465**
NALCO	**A-2**
NADAR	**4091/C - 4091/D** -4097
UNION CARBIDE	UCARFLOC **300 - 302 - 304**

By preliminary laboratory experiments we will test the effectiveness of these compounds. Different techniques such as chemical analyses (active and total SiO_2), density and viscosity measurements at various temperature and SiO_2 concentrations will be employed.

On the basis of the activity as silica antiscalant showed in these tests, the initial group of compounds will be narrowed for the following field experiments.

The scaling behaviour of the brine has been measured at two different temperatures (60 and 85°C). To better simulate the actual conditions of the reinjection line, we intend to perform tests with progressive cooling from 85 to 60°C.

The SiO_2 content will be set at 600 and 1000ppm. The higher represents the case of a typical separated geothermal brine from the Piancastagnaio field, while the lower represents the case of separated brine together with turbine condenses. Preliminary experiments will be performed with an artificial solution (600-1000ppm of SiO_2 from Na_2SiO_3, pH 8.2-8.3 with HCl).

According to other researchers, silica precipitation is helped by the addition of Ca^{2+} (Dubin, 1985). A content of 400-2000 ppm of $CaCl_2$ is set for the four runs and replicable procedures for the experiments are defined. The scaling behaviour of the brine is characterisad by an increase in turbidity. Silica precipitation will be followed by chemical analyses Periodically small amounts of solution will be withdrawn, filtered and analysed.

Total silica concentration will be measured by atomic absorption spectroscopy, while monomeric silica content is determined spectrophotometrically using the molybdate method.

In this way it will be possible to define a characteristic behaviour of the brine without the additives. These results (Table 4) will allow for the evaluation of inhibitors activity. A deposition time is defined on the basis of the time required by the silica content in the solution to decrease to corresponding monomeric silica values.

Temperature, pH, salinity, concentration and floudynamic effects must be considered to improve the comprehension of silica precipitation inhibition.

Table 4. Deposition time of the brine without additives

SiO_2 ppm	$CaCl_2$ ppm	pH	Temperature (°C)	Deposition time
600	2000	8.2	60	2h 30'
1000	2000	8.2	60	2h
600	400	8.2	85	2h
1000	400	8.2	85	1h 30'

CONCLUSIONS

Potential benefits foreseen in silica scaling control for geothermal exploitation at Piancastagnaio are substantially:

- -the reduction of redundant pipelines and tanks of the reinjection section
- -the reduction of brine line occlusion, dismantling and replacement and consequently their discharge rate
- -the reduction of pumps and line instrumentation replacement

The debate concerning the effects of different flowdynamic regimes and the use of chemical additives for silica scaling precipitation is still open. A research project concerning these potential antiscalant techniques has been launched by ENEU DPT-VDAG and our Department.

A preliminary laboratory investigation is programmed and a geothermal brine loop has been designed for the study of silica behaviour in actual conditions.

By inhibiting silica precipitate formation, the quantity of solid wastes requiring disposal can be reduced, thus decreasing significantly the costs related to solid handling and plant components replacement. These advantages have to be compared with chemical costs due to inhibitor dosages.

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