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AN INTERPRETATION ON THE SILICA SCALING PHENOMENON IN GEOTHERMAL PLANTS

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ABSTRACT

Silica scaling phenomenon in reinjection pipelines of Piancastagnaio geothermal field (Monte Amiata, Tuscany) have been studied. The aim of this work is to gain insight into the nature of this problem, with regard to the possible effect of the near surface region. In particular we intend to focus our studies on the flow-dynamic aspect in order to understand how the fluid flow behavior could modify the existing monomeric - polymeric silica equilibrium. This analysis suggests that low brine velocity may be adopted as a mean to minimize silica scale deposition.

A preliminary qualitative silica deposition study was conducted using a laboratory unit; the purpose of this study was to establish an experimental technique for a series of more extensive silica deposition tests which aims to quantify the influence of shear stress on high silica content brine deposition in order to develop a way of controlling deposition.

INTRODUCTION

It is generally recognized that corrosion and scaling problems could seriously affect the operation and electric power production from geothermal plants. An important technical obstacle to the utilization of geothermal energy is the high salinity of fluids and the consequent precipitation of solids.

The high concentration of silica in most geothermal brines causes the solution to become supersaturated when extracted from the well and cooled deposition may occur in plant equipment, transmission pipelines and injection wells. Siliceous scales are typically inert to most chemicals and, once deposited, are very resistant to mechanical removal performed during periodic plant shut-downs. Hence most treatment methods must focus on prevention of silica deposition or on controlling the morphology of deposits.

Steam separation and reinjection of geothermal fluid at temperature higher than the amorphous silica saturation temperature could reduce deposition but could be wasteful in utilizing the available energy. Owen and co-workers[1] demonstrated effective control of the siliceous scale by acidification of the hot brine with hydrochloric acid, probably due to decrease of ionised silanol groups. However this method is not realizable at Piancastagnaio fields because brine pH must be lowered from 8.5 to 3 for complete control: that means a net increasing of corrosion rates in pipelines and reinjection wells besides high chemical costs and the possibility of environmental pollution. More over, though in the last years a number of systematic investigations[2] has been performed, until recently no chemical treatment has been shown to significantly delay precipitation of hot geothermal brines. An other technique developed is the aging tank method proposed by Yanagase et al. [3]: ponding geothermal waters into an aging tank proved to be effective to delay the deposition of silica scale and, consequently, to prolong reinjection well life time at Hatchobaru geothermal power station. Due to the considerable variation of geothermal fluid conditions along the different sections of the plant (pH, temperature, pressure, composition), the resultant scale morphology and composition can be quite different. Therefore it is necessary to carry out separate evaluations of the effects of different parameters involved.

In this work geothermal fluids of the Piancastagnaio area have been considered. In particular, scaling phenomena in the pipeline between the accumulation pool after the atmospheric flash and the injection well has been investigated. A mechanical approach has been proposed, that involves scale formation and growth mechanisms.

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 solubility action exerted by the hot fluid on the sedimentary rocks. In the utilization cycle (represented

in Figure 1), after steam separation, the additional flash produces a decrease in temperature causing an increase in silica supersaturation.
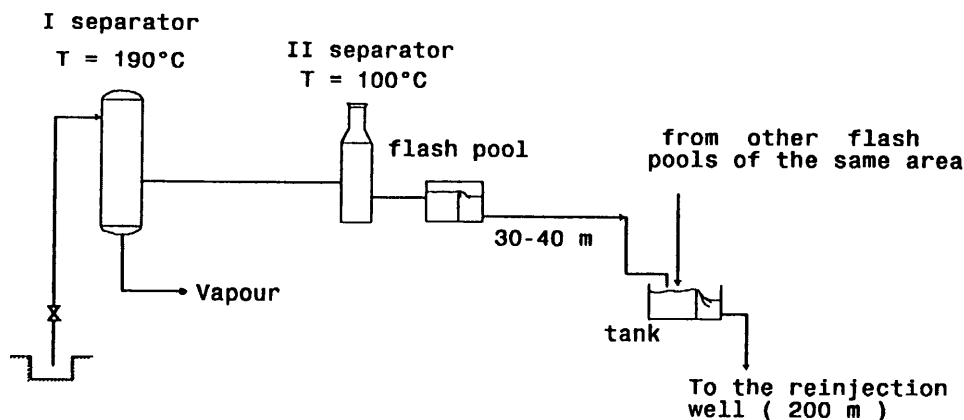

Figure 1 Schematic separation and reinjection layout.

More over, the effect due to concentration and the release of CO_2 and H_2S upon flashing induce an increase pH. Supersaturation effects and pH increase are thought to be the main factors in silica scale formation.

Though the liquid phase composition and pipeline layout may be appreciably different from one well to another, a general deposition phenomenon is present in the pipeline connecting the flash pool after atmospheric flash to the reinjection well (ENEL-VDAG, 1992) [4]. The rate of deposition is so high that the pipelines are blocked by deposits which consist of siliceous matter that tends to incorporate some of the brine. A typical analysis of the brine extracted from the well is shown in table 1. It is noteworthy that the total silica content is relatively high (- 1000 ppm).

After one of the unfortunate frequent shut-downs of the plant, an inspection of the facilities was conducted.

Exhaust brines, coming from the flash accumulation pools, are collected in a tank and then sent to reinjection wells. The connection between the pools and the tank and between the tank and the reinjection wells is accomplished through two or three parallel pipelines.

In order to minimize plant shut-downs, pipeline diameters have been oversized, so that channelling flow was obtained. Since it was desired to obtain an indication of the amount of scale formation in the pipelines, some parts of each duct were open for free inspection (It is noteworthy that exposure of geothermal waters to air is known to have an accelerating effect on silica deposition). A detailed

examination has been performed at PC34 and PC30 areas.

In the earlier part of PC34 pipelines we noticed an uneven deposition throughout the pipe length: approximately 17 mmpy inlet and 120 mmpy outlet deposition rates were observed. More over scales seemed to accumulate where fluid flow was slower.

Li^+	4-14	F^-	3-12
Na^+	564-1647	Cl^-	763-2670
K^+	93-342	Br^-	1-3
Rb^+	0-1	I^-	0.7-1.5
Cs^+	0-1	SO_4^{2-}	3-188
Ca^{2+}	1-28	H_2S	4-40
Mg^{2+}	0-4	H_3BO_3	1000-16000
Sr^{2+}	0-1	As	3-53
Ba^{2+}	0-0.1	Sb	8-72
Fe^{2+}	0-3	SiO_2	850-1500
Zn^{2+}	0-0.02	Al^{3+}	0.6-3
Pb^{2+}	0-0.6	NH_4^+	53-220

Table 1 Average exhaust brine composition (ppm)

Samples of fluid and scales have been collected. Scales , formed during a period of approximately six months over which shut-downs occurred, consisted of hard material with thickness in the range of 5 mm.

It was possible to distinguish three well defined layers, different in structure and color, which could not be separated. The upper one was grey and didn't present any layering, while the middle one was red and thin and the lower grey again and well layered. This fact suggests the existence of different mechanisms of deposition in the same pipeline.

Because of the great content of sulfur, every three or four months a large amount of sludge has to be cleared away from the tank and sent into a sedimentation tank in order to obtain the desired volume reduction before discharge.

Differences in pipeline layout and brine composition reflect different scale morphology and color: from hard and grey at PC34 to dark and crumbly at PC30.

Samples of fluid and scales have been collected.

TURBULENCE EFFECTS ON SCALING

To prevent or minimize the scale formation in hot water pipelines, one method must be considered: it consists of precipitating encrusting salt present in the solution by chemical and physical processes, followed by their separation and discharge and the injection of the encrusted free salt solution. Using this approach several research studies have been developed in our Department. Chemical analysis of geothermal brine have been obtained [4] for samples collected at different times (analysis performed after 9 days and after 4 months). The results show that monomeric silica values (110 + 120 ppm) correspond to solubility of amorphous silica at ambient temperature and account for solubility of amorphous silica at ambient temperature and account for between 9 to 11% of total silica content. It is clear that in calm conditions silica separation and scaling is not appreciable for solutions in which silica concentration corresponds to saturation at 10% of total silica content. On the other hand we observed that, when the same solution flows inside pipelines, scaling phenomena occur readily.

The results of chemical analysis on resting geothermal solutions doesn't 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 seems to support the hypothesis that the fluid flow behavior of the system may modify existing monomeric-polymeric silica equilibrium.

Previous researchers 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 wall surface. 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 an effect that makes scale removal more difficult.

There are only a few available papers concerning the effect of fluid velocities on deposition rates. Rothbaum and Rohde [5] investigated the rotating effect on silica deposition. They found that, while only a little 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. A similar conclusion is reached by Arnorsson [6], which asserts that deposition rate of amorphous silica from supersaturated solutions is accelerated by turbulent flow. A different point of view is expressed by Mroczek and McDowell [7], which maintain, on the basis of their experiments, that deposition rate in the pipes seems to be independent of flow rate. Another approach confirming Wahl's conclusions is proposed by Chan et al. [8]. Their result of two runs with different Reynolds numbers demonstrate that, for the brine chemistry they dealt, a lower Reynolds number increases fouling rate in terms of asymptotic fouling resistance.

The lack of any agreement on the fluid flow effect underlines the need of a systematic series of experiments to widen the knowledge about this aspect.

MONOMERIC AND POLYMERIC SILICA SCALE

When geothermal waters become amorphous-silica supersaturated, two chemical processes may occur: a "slow" deposition on surfaces and a "fast" polymerisation in the solution. However deposition of polymerised silica is slower than deposition of monomeric silica. If the concentration of dissolved silica is high, corresponding to large supersaturation factors (2.5 or higher), a homogeneous nucleation process occurs followed by rapid polymerisation and precipitation. Otherwise, relatively slow heterogeneous nucleation and deposition of dissolved silica directly on solid surfaces occurs.

Silica scaling in geothermal fields probably occurs by both deposition from monomeric silicic and from colloidal particles (polymeric silicic acid). A silica scaling analytical model has been developed by Chan et al. [6] In the case of deposition from monomeric silicic acid brines; the model accounts for salinity and pH effects and proposes a second order reaction for dissolved silica. Until recently, nothing has been done to model the particulate deposition of polymeric silicic acid.

A general model has been proposed for the

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particulate fouling under turbulent flow conditions [9]; this model is briefly outlined because we foresee the possibility to adapt it for the case of polymeric silicic acid deposition.

A PARTICULATE DEPOSITION MODEL

Particles in a fluid in turbulent flow are deposited on the wall according to the following mechanisms: the carrying of the particles to the surface, their adhesion to the surface and the re-entrainment as well as rolling of those particles which had only adhesion to the surface and the reentrainment as well as rolling of those particles which had only loosely adhered to the surface. Most particles deposition models have been developed by assuming a perfect stick ability, so that we can regard them as particle transport theories rather than particle deposition theories.

The sticking probability has been introduced or taken into account the nonperfect stickability, and is defined as the portion of particles reaching the wall which stay there. The adhesion, reentrainment and rolling steps need to be studied together since they are affected by both the kinetics of adhesion and the flow dynamics in the wall region.

Experimental studies regarding the fine structure in the wall region revealed the presence of organized motion [10]. These studies make it possible to assume that the deposited particles are affected by a variable wall shear stress. The adhesion of the particles on the wall surface is due to the attraction of the chemical bond forces, Van der Waals forces, electrostatic forces, etc. The kinetics of adhesion depend on the type of forces involved, as well as on the increase over time of the area of contact between the particle and the wall.

The introduction of the notion of adhesion time, demanded by the phenomena of non-instantaneous adhesion on the one hand and the removal or rolling of loosely adhered particles by turbulent bursts on the other, allows the combination of the adhesion, reentrainment and rolling process in a turbulent flow regimes. An analytical relationship of the sticking probability and the parameters of adhesion removal and rolling has been obtained [11].

INITIAL EXPERIMENTAL RESULTS

Initial studies have been performed with artificial and real silica solutions at our Department laboratories to investigate Reynolds number effect on silica scale formation. First experiments have been carried out in a glass atmospheric vessel with an internal capacity of 1000cc, provided with four vertical baffles in order to avoid dangerous vortexing. Vessel agitation is done with a top entering turbine (Ruse Ton-type, AISI 316). The higher impeller speed is 200 m/min corresponding to a Reynolds number of 46000;

the impeller frequency (maximum value of 29 Hz) is controlled by a magnetic frequency meter. Vessel dimensions, turbine diameter, baffles setting and rotating speed have been selected on the bases of available literature; turbine arrangement is shown in Figure 2.
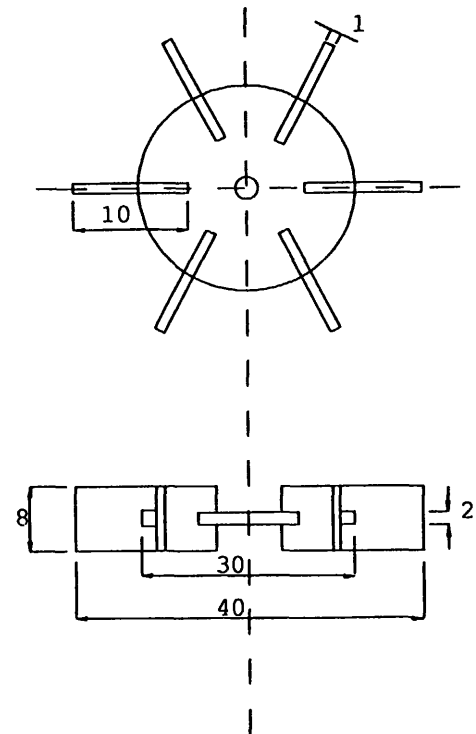

Fig.2 Schematic rapresentation of the reactor turbine

Periodically, small amounts of solution are withdrawn and analyzed: total silica concentration is measured by atomic absorption spectroscopy (according to the Weres and Tao method [12]), while monomeric silica content is determined spectrophotometrically using the molybdate method (according to the Iler method [13]). Since it is desired to obtain an indication of the relative sizes of silica polymers formed during these experiments, measurement of viscosity, density (DMA Anton Paar) and turbidity (Malvern particle sizer) are carried out.

A preliminary experiment was done with an artificial solution (850 ppm SiO_2 from Na_2SiO_3, pH 8.5 and NaCl 0.3 N): the sitrred test was very effective in accelerating the formation of a gel-type deposition with respect to the resting solution test. Following tests were carried out at different Reynolds numbers with fluid samples collected at PC30-35. Some test results at high Reynolds numbers (20000 + 30000) pointed out the formation of deposits in the supposed "resting" areas of the turbine. Clearing away these deposits are very difficult: neither hot caustic soda solutions or hydrochloric acid solutions succeed in

eliminating the whole deposit, so that a difficult mechanical removal was performed by a special micro grinding-wheel. In Table 2 the result obtained from a 40000 Reynolds number (25Hz) test is shown. The difference in silica content exceeds turbine weight increase; this is probably due to the loss of solution sprinkles on the bottom of the vessel. The increase in temperature is caused by stirring dissipation. Other tests in jacket vessels are planned to investigate simultaneous temperature effect. In Table 3 the deposit composition is shown.

The brine temperature gradient will be monitored by a Vortex flow meter. By installing scaling thermocouples inserted at pipeline inlets and outlets, it will be possible to estimate the contribution of deposits to heat transfer by comparison with clear conditions. If deposits grow up uniformly around the pipe diameter, the temperature gradient gives an indirect measurement of scale thickness. In order to gain more information on turbulence and wall shear stress effects, specimens of various shapes will be inserted in connecting sections joining the pipelines.

	Silica content in the solution (mg)	Turbine weight (mg)	Temperature (°C)
Start	614.18	14715	23.3
After 24hr	586.76	14728	31.7
Difference	27.42	13	8.4

Tab.2 Results of the deposition test

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

Table 3 Elementar composition of deposits formed on the turbine

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 program for studying scaling tendency in geothermal brines has been designed. The aim is to provide for motion of real geothermal brines in a real geothermal layout (two parallel pipelines connecting PC34 flash pool and PC34 tank have been designed) in order to study silica deposition in relation to turbulent effects. This program consists of two main efforts:
-evaluation of the effect of different Reynolds numbers on silica deposition along full cross section ducts, and
-evaluation of the effect of pulsed flow on silica scaling.

Pipelines consist of extractable sections which connect different sections of the pipe; the overall length is approximately 40 m with a slope of 8 to 10%. The flow through each of the pipes will be controlled by valves; liquid flowrate will be rates determined by director inspection at different sections of the pipes. Scale samples will be characterized by crystallography, scanning electron microscopy and X-ray diffraction.

CONCLUSIONS

The debate, concerning the effect of Reynolds number on Silica deposition is still open.

Previous researchers put in evidence that shear stress is able to cause deposition of low polymers present in solution.

We foresee the possibility of a particulate deposition model to account for wall shear stress effects.

Preliminary laboratory experiments on artificial and real solutions demonstrated that dynamic tests produced a massive deposition while resting tests didn't.

Recently, a geothermal brine loop has been designed for Monte Amiata geothermic field to investigate turbulence effects directly in actual conditions.

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