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Chemical Cleaning and Rejuvenation of Geothermal and Oil Wells

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ABSTRACT

The paper presents the method and the results for increasing recovery of geothermal production well, injection well, surface equipment, and oil wells. The deposits located within any part of the geothermal system such as production well, surface equipment, or injection well can reduce the production of steam and thus impact power production. The technology reported here is able to clean the wells and surface equipment both online and offline. The method is based on a systematic laboratory study using either a complete deposit analysis or predicting the composition of the deposit based on system parameters and using Geomizer as the predicting tool. The results from the rejuvenation of an injection well at a geothermal plant are also discussed in this paper. The injectability of the injection well was improved by 73% resulting in the plant gaining 1MW power.

1. Introduction

Proper maintenance and operation of geothermal wells (Thorhallsson, 2003) and surface equipment is vitally important in achieving objectives of any geothermal project whether it is power production or district heating. The harsh conditions of temperature, brine chemistry, non-condensable gasses, and sediments can cause either corrosion or corrosion products or deposits in any part of the plant, which make the geothermal projects less efficient. These operational conditions can lead to a premature shut down of the project or curtail production. The same is

true within the petroleum industry, when crude oil production declines; there are a number of causes for the decline in production. Two reasons for a decline in oil production are

1. A reduction in the permeability of the oil "reservoir"
2. The invasion of this reservoir by the water contained in a lower layer.

A reduction in permeability is typically due to the entrainment of fines or scale formation by the flow of the oil towards the production well. Around this well, these particles accumulate and gradually plug the natural pores in the rock. The oil can then no longer flow out at an efficient rate through this well. These particles can be of various origins (e.g., type of rock, damage to the formation, progressive deterioration of the rock, mineral scales, etc.).

These problems can accumulate with aging of the production and the injection wells. The production of high enthalpy fluids (steam, mixture of steam and hot brine, and just hot brine) from geothermal wells and oil production from the oil wells has many similarities and many times the rejuvenation of the wells to restore capacity, requires similar procedures such as work-over, hydro blasting, alkaline, and acid washing. Most of the deposits in the geothermal systems are associated with injection wells and surface equipment, although the production wells are also prone to fouling with calcium carbonate and calcium sulfate. Injection wells are generally, plugged-up with silica based minerals and some of the sulfides of antimony, arsenic, lead, copper and iron.

Acids perform many functions, i.e. removing inorganic and organic scales, decarbonation, pH adjustment, general cleaning, and disinfecting; however, some of these mineral acids can be highly dangerous to handle and transport, highly corrosive to metal surfaces, and can lead to the formation of mineral scales. In geothermal systems most commonly used acid to clean up the wells and surface equipment are mixtures of hydrochloric acid and hydrofluoric acids. This blend is especially used for removing calcium carbonate and silica based deposits. In oil wells, the acid job is often carried out using inhibited hydrochloric acid in order to remove the particles (deposits and rocks) and improve the mobility of the oil in the formation, where some of the deposit and the rock in the formation are partially soluble in this acidic fluid. Thus, this well stimulation method can cause these particles and rock to partially dissolve, and make the formation more porous thereby increasing the mobility of the oil in the formation and increasing

well production. These acids, however, can be very corrosive to the casing and surface equipment materials. Acid treatment can help remove scale or similar deposits from perforations and well completion components as well. Conventionally, inhibited acids are used to reduce the corrosion rate; however, the corrosion rate can still be unacceptable. The technology described in this paper can remove the scale and similar deposits while exhibiting less corrosion than conventional acids, thus protecting the well. As detailed above, these methods can rejuvenate geothermal wells, oil wells, water wells, deep injection wells, and production wells.

There is always a chance of marginal success or hit and miss with chemical cleaning such as acid injections or caustic chelation additions, so a continuing need exists for a systematic approach to chemical cleaning and alternative agents that are easier to handle, more environmentally benign, more versatile, and have reduced corrosiveness. This paper presents such an approach to remove the guesswork and alternate chemical-cleaning agents. Field results are also included as a case study to demonstrate the application of the laboratory results.

2. Laboratory Studies

The method for cleaning the surface in contact with liquid containing silica or silicates can be performed at a temperature from about 0°C to about 374°C. Initially several deposit samples were collected from various industrial sites including geothermal power plant, and analyzed using X-ray fluorescence (XRF) and X-ray scattering (XRD) methods. The chemical composition of these deposits is summarized in Tables 1 and 2. In the laboratory, we used two methods to determine the dissolution of various deposits and minerals.

1. Jar Test.

The dissolution test method consisted of weighing several grams (~3 g) of a standard solid into a 4 oz. plastic jar, followed by the addition of 100 mL of distilled water. The deposit dissolver solutions were made at 5, 10, or 15 wt. percentage product in distilled water. The cap to the jar was attached and the jar was shaken vigorously several times to completely wet the solids. If necessary, the cap was loosened to vent the build-up of pressure. During room temperature tests, the jars were shaken ~three times per week (Method 1). During higher temperature tests, the jars were stored in a circulating water bath with an integral shaker (Method 2). Periodically, aliquots (3 mL) were removed at least one hour after shaking and then syringe filtered through a 0.45 μ filter. This type of the data can be used to determine the

kinetics of dissolution. Since the rate of dissolution is a function of the concentration of the scale dissolver, temperature and the hydrodynamics, a large amount of the data will be needed predict the kinetics of dissolution. The filtrates (2 gram) were then diluted with 98 mL of distilled water and submitted for elemental analysis using ICP. Sometimes the remaining solids were analyzed using X-ray fluorescence (XRF) and X-ray scattering (XRD) methods. Elemental analysis is presented in Tables 1 and 2.

2. Flow through Cell.

A flow through cell was designed to determine the dissolution of various deposits where the deposit was placed between the two finely perforated Teflon™ plugs enclosed in a high-density plastic cell shown in Figures 1 and 2. Pre weighed 2-3 grams of the deposit sample is placed in the bottom half of the cell, which is mounted vertically on to a holder and then the entire cell is immersed into a water bath. A circulating loop is made using a peristaltic pump and a small reservoir tank. The circulation loops mimics the online cleaning. The dissolution progress is monitored using the similar analysis as for the Jar test.



Figure 1: The inside of the cell where the deposit is placed at the bottom of the right side section



Figure 2: The recirculation-flow cell, which is placed vertically in the water bath, 60-80°C

3. Results and Discussion

The most common procedure to workover operation or remove the deposit from the well is to drill with the same type of bit with which the well was originally drilled. This is not only very expensive but sometime damages the well-casing as well. Another common method is to ream the well with well flowing. A trailer mounted drilling rig with top drive is used and the casing is not stressed due to killing the well with cold water and the cuttings are swept out of the hole and the well is quickly put in service in couple of days. High pressure jetting has also been successfully used in cleaning wells and surface equipment. Coil-tube rig fitted with jetting nozzle at the end uses water at 200-300 bar at a rate of 2-3 gallons per second. For surface pipes and separators, the water pressure can be as high as 700-900 bar. Acid cleaning is also common where hydrochloric acid can clean calcium carbonate and a mixture of hydrochloric acid and hydrofluoric acid can clean silica-based deposits. Caustic EDTA has also been used to clean some deposits.

Chemical well rejuvenation and surface equipment cleaning of geothermal systems have been hit and miss due to variability of deposits in different systems even using the same reservoir. The scaling problem is very specific to the chemistry and well profile of individual wells, which can vary a lot even between wells within the same field. In this work, the authors have developed a

matrix to take the guesswork out and significantly improve the cleaning success. The following parameter are used in developing a systematic approach to cleaning deposits

1. Collect deposit sample from the system that need to be cleaned
2. Complete analysis of the deposit using X-ray fluorescence (XRF) and X-ray scattering (XRD)
3. If the deposit sample is not available, predict the deposit composition by using a predictive modeling tool (Gill, 2015, 2017) that uses brine chemistry, NCG, steam chemistry and well characteristic including temperature, enthalpy or pressure
4. Use the laboratory and the field data bank to select the right cleaner based on the composition of the deposit.
5. If the deposit sample is available, verify the cleaner choice by doing a laboratory study.

A large amount of cleaning data (Gill, 2017 and Sommesse, 2017) was produced using the laboratory procedures described above for well-characterized deposit samples from the field and some known mineral samples. The chemical composition of several deposits was determined by a standard composition analysis using X-ray fluorescence (XRF) for elemental composition, organics concentration by C/H/N/S elemental analysis, and the concentrations of organics/water of hydration and other volatile substances by heating to 925°C for defined period of time. The results are shown in Tables 1 and 2. In addition to the field samples, several other minerals were studied for dissolution. These minerals are talc, amorphous magnesium silicate, aluminum oxide, magnesium oxide, calcium metasilicate, calcium fluoride, aluminum silicate, magnesium aluminum silicate, magnetite, manganese dioxide, calcium carbonate, barium carbonate, strontium carbonate, barium sulfate, and strontium sulfate.

This focus of this study was to use commercially available alternate scale dissolvers for the dissolution of the field deposits and the minerals listed above. These alternate scale dissolvers are less corrosive compared to HCL and HF (Table 5). The corrosion study was done for 1010 carbon steel at 130°C, 200 PPM Calcium and 2000PPM of Cl ions (from sodium chloride and calcium chloride) and the cleaning solution concentration was 15%.

Table 1: Chemical composition of deposits from various Industrial systems, such as evaporators and steam team generators.

Chemistry	Deposit #1	Deposit #2	Deposit #3	Deposit #4
Silica (as SiO ₂)	56%	49%	56%	51%
Calcium (as CaO)	15%	41%	11%	5%
Sodium (as Na ₂ O)	4%	5%	7%	3%
Aluminum (Al ₂ O ₃)	<0.5%	<0.5%	1%	3%
Chlorine (as Cl)	3%	<0.5%	2%	not detected
Magnesium (as MgO)	2%	1%	1%	8%
Potassium (as K ₂ O)	<0.5%	<0.5%	4%	2%
Sulfur (as SO ₃)	<0.5%	<0.5%	<0.5%	2%
Iron (as Fe ₂ O ₃)	<0.5%	<0.5%	1%	<0.5%
Organics	<0.5%	<0.5%	5%	14%
Loss at 925°C ^a	20%	2%	17%	25%

^a Likely due to water of hydration and also includes organics

Table 2: Analysis of the deposits from a geothermal power plant in the Imperial Valley, CA

Analysis	Injection Head ND048483	Hoch Brine outlet ND048484	Injection ND048485	Cooling tower Fill ND048487	2 nd Injection ND 048486
Major	Amorphous silica	Amorphous silica	Amorphous silica	α Quartz	Amorphous Silica
Minor	Barium sulfate	Metallic Silver	Metallic silver, Silver antimony	Iron Oxide Fe ₃ O ₄	Metallic silver, silver antimony
Minor	Sodium Chloride	Silver Chloride	Cu ₃ As, Cu ₂ Sb	(Ca,Na)(Al, Si) ₂ Si ₂ O ₈	Cu ₃ As, Cu ₂ Sb
Minor				KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	

The results of the dissolution studies for these deposits and various other minerals are tabulated in Table 3-4. The composition of the scale dissolvers is described as compositions A, B, C, D,

and E is disclosed in reference (Gill, 2017) as proprietary, containing both inorganic and organic components. These scale dissolvers can be obtained from Nalco Water as various geothermal products. The study was done by contacting 2.5 Gms of the deposit sample with 100 mL of the 15% cleaning solution A, commercially available from Nalco water as product GEO991. The water matrix of this study also contained 200 mg/L of Ca and 2000 mg/L chloride ions from sodium chloride and calcium chloride.

Table 3: Results of dissolution of the field samples

Sample ID	% Dissolution with the alternate acids				
	A	B	C	D	E
Deposit #1	93	56	15	11	17
Deposit #2	89	87	24	14	20
Deposit #3	96	45	34	8	6
Deposit #4	87	31	36	15	49
ND048483	98	92	45	31	66
ND048484	40	38	11	7	5
ND 048486	74	63	71	56	18
ND048487	24	44	21	50	10

Table 4: Dissolution of some of the selected minerals by using alternate scale dissolvers

Mineral	% Dissolution for each component (element) of the mineral					
	A	B	C	D	E	
Talc	Mg	62	81	76	6	6
	SiO ₂	33	21	34	2	2
Amorphous magnesium silicate	Mg	100	100	100	100	100
	SiO ₂	37	2	39	2	2
Aluminum oxide		56	22	40	11	2
Calcium Metasilicate	Ca	85	19	90	100	93
	SiO ₂	55	6	52	4	5
Al silicate	Al	80	5	100	2	2
	SiO ₂	29	4	32	2	2
CaCO ₃	Ca	80	78	62	90	23
Hematite		78	65	72	89	15

Mg	Al	SiO ₃	Al	89	45	45	65	34
	Mg			100	100	89	11	7
	SiO ₂			48	15	6	5	5

Table 5: Corrosion with cleaning products

Temperature °C	Cleaning product	Corrosion Inhibitor	Corrosion Rate MPY
130	15% product A	None	37
130	15% HCl	None	123
130	15% product A	100 PPM substituted Azole	7.8
130	15% HCl	100 PPM substituted Azole	78

The composition of the scale dissolvers developed in this study comprise of a salt of a nitrogen base having a fluoro inorganic anion. These compositions are advantageous because these are capable of dissolving a variety of inorganic and organic deposits, reducing the pH in an aqueous environment, and is easier to handle than conventional acid compositions. On Heating up to 130°C, these scale dissolvers do not generate any free HF. As shown in Table 5, there is significant reduction in the corrosion rate compared to commercially available inhibited HCl. Using the composition in this study, the use of HCl and HF have been eliminated which are highly known corrosive acids. The corrosion rate can be further reduced by formulating these scale dissolvers with corrosion inhibitors (Gill, 2010, 2016). The cleaning of the wells can also be done by using online some of the scale inhibitors (Muller, 2015) at higher dose, over a longer time.

4. Field case study:

The field trial was done in a Power plant located in the Salton Sea field, which is a three-stage flash geothermal plant with an installed capacity of ~50 MW. As shown in Figure 3, injection-well flow-rate decreased by 22% to 0.78 million lbs. / hour, restricting plant throughput resulting in lost power production capacity. The injectability of the injection-well decreased by 75% (Mass Flow/ pressure). Due to the reduced injectability of the injection well, the plant had to throttle back production well capacity resulting in loss of steam and thus power production. During this time, the injection pump pressure increased by 45% to 112 psi, thus increasing the parasitic load. The plant was losing revenue ~1MW (~\$2400/day @\$100/MW).

We followed the process developed in this paper and requested samples from the injection well. After receiving the deposit sample, the deposit was analyzed. The deposit analysis showed 83% Silica, 7% black iron silicate, 6% calcium 2% sulfate and 2 % aluminum. Laboratory dissolution study was completed using one of the alternate acids (GEO991) selected from this study. Customer previously tried HCl/HF 6/1 blend but did not get good results with HCl/HF 6/1 blend. The study was also done to determine the impact of the cleaning product that was selected on well cuttings, which showed significant improvement of HCl/HF. There was significant less dissolution/damage of the cuttings with GEO991 in comparison to HCl/HF blend.

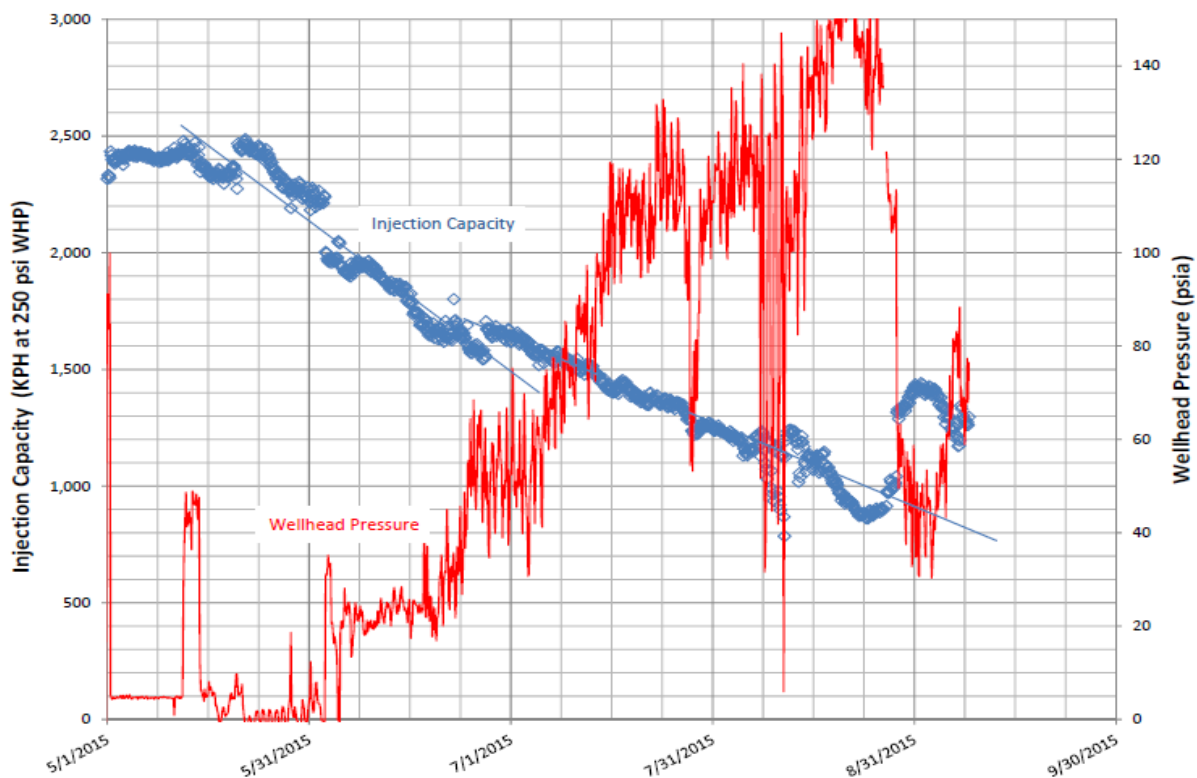


Figure 3: Injection well #2 injection performance

Program recommendations were developed for an on-line cleaning procedure. The plant ordered 2450 Kilograms (540 US gallons) of the product GEO991 for the trial. The trial started by feeding the product to the suction side of the injection well pump, at 100 PPM of the neat product for 2-3 hours, then the product feed rate was reduced to 50PPM for 2-3 hours and finally reduced to 20 PPM for the remainder of the trial (total ~48 hours. Dosage fed to target a pH of 4.5-5.0 in the brine normal brine pH 5.5. Chemical feed started on August 27th and finished on September 1st. During this time, the plant was running as normal generating power, the injection

well pressure was monitored. As the trial progressed restoring the injectability, the production well was throttled up and the net power production capacity restored. The wellhead pressure and injection capacity plotted as a function of time in Figure 3 clearly shows that during three months prior to the trial period, injection capacity was coming down while the wellhead pressure was going up. The trend of injection capacity and wellhead pressure was reversed immediately, after start of the GEO991 feed.

By feeding GEO991 to the injection brine online for three days, over all injectivity improved by 73% by experiencing flow rate increased from 0.78 million lbs. /hour to 0.94 million lbs. /hour. A 20% improvement in flow and the Injection pressure reduced from 112 PSI to 78 psi, a 43% improvement that amounted to decreased parasitic load by 0.5 MW. The plant gained 1.0 MW (0.5 from Parasitic and 0.5 from plant).

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