

Mitigation of Silicate-Stibnite Deposits in Reinjection Wells of Geothermal Power Plants

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Abstract: Geothermal energy is an important resource for power and heat generation. The main operational handicap of geothermal power generation is scaling. As the mineral-rich underground waters rise to the well-head, the solubility of silica and minerals in the water decreases and precipitation occurs as the pressure and temperature decrease. In geothermal systems, an inorganic layer is formed on the inner surface of the pipe due to precipitation, called scale or deposit. This structure reduces the efficiency of energy harvesting as it reduces the internal diameter of the plant's piping systems. Silica is one of the most frequently observed deposits encountered in geothermal systems. In addition, Stibnite (antimony sulfide) has been recently observed along with silica deposit in power plants located in the west coast of Turkey. In order to reduce the undesirable effect of the formation of both deposits as mixture (in fact this is the case in Kubilay geothermal system in Turkey), antiscalants need to be applied to the system to manage the scaling. The effect of antiscalants (A: acrylic homopolymer, B: carboxylic sulfone copolymer, C: carboxylic sulfone nonionic terpolymer), and the antiscalant composition (10 different mixtures) at 6.5 ppm has been examined in order to maintain the continuity of the efficiency of the power plants and to minimize the cleaning need of the system.

Key words: antiscalants, scale, stibnite, silica.

1. Introduction

The usage of geothermal resources has attracted great attention in Turkey in the last two decades for heating and modern thermal tourism facilities [1]. Following the first geothermal electricity production in

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1984, the first privately funded geothermal power plant was established in 2006, and this development was followed by governmental investment for the establishment of new geothermal power plants in Western Turkey [1]. Following the drilling and test studies carried out within the scope of investment studies in geothermal fields, the changes in the reservoir parameters that should be monitored during the operation, as well as the cooling tower performance that affects the energy production performance in the power plants and the heat centers. The prevention of precipitation due to mineral saturation in the fluid phase is of great importance in terms of continuation of fluid production [1].

Geothermal fluids contain varying amounts of dissolved gases and solids. If the conditions such as temperature, pressure and/or pH in the reservoir change, the minerals tend to dissolve or precipitate depending on the instantaneous thermodynamic conditions [2]. The scaling inevitably occurs as a result of the saturation and precipitation of some minerals in the geothermal fluid and poses a significant risk for the geothermal fields. Scaling causes contractions and/or blockages in underground and above-ground equipment during the use of geothermal resources, causing operating problems and therefore economic losses [2].

Antimony rich deposits have become very popular in recent years. This type of deposit has been frequently observed in New Zealand, Italy, and west of Turkey [3]. A variety of polymeric macromolecules are used to mitigate the formation scale as antiscalants. It is the costliest and tediously to try potential antiscalants in field conditions [4]. Artificial synthesis of geothermal deposits under laboratory conditions is more practical and economical to test the performance of antiscalants. Çiftçi et al. in their study, obtained a Sb-rich deposit by refluxing SbCl_3 and $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ in 18 h [4]. It has been determined that the product is a mixture of Sb_2O_3 and Sb_2S_3 [4]. The performance of antiscalants such as poly (ethylene glycol), poly (vinyl pyrrolidone), Gelatin, and poly (vinyl alcohol) of various molecular weights at 5 to 100 ppm were investigated [4]. Sb_2S_3 is suppressed in the presence of polymeric antiscalants. It has been determined that the dosage is critical for the dissolution of Sb-rich deposits and that the performance of antiscalants depends largely on the dose [4]. A low dosage of polymeric antiscalant helped to increase the concentration of antimony ions in the decantate, while higher doses improved the solubility of sulfur ions. The amount of precipitation increased in high doses, most likely due to the appearance of flocculation [4].

Metal silicate is one of the most abundant deposit observed in high enthalpy fields. Inhibition of silica / metal silicate has been attempted using antiscalants with functional groups, particularly $-\text{NH}_2$; however, metal silicates are widely available in the fields and antiscalants developed so far are not effective against

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these compounds [5]. In this study, Topçu et al. developed polymeric antiscalants for metal cations by combining two or more functional comonomers consisting of various chelating groups [5]. Homo- and copolymers of acrylamide (AM), the sodium salt of vinyl sulfonic acid (VSA), and vinyl phosphonic acid (VPA) were synthesized to examine their antiscaling performance against metal silicate scaling, lab-scale metal silicates were obtained in a pressured autoclave reactor [5]. The antiscalants were tested at various dosages (25, 50 and 100 ppm) to investigate the effects of decantate remaining after isolation of solid precipitates [5]. It was determined that polymeric antiscalants were particularly effective against metal silicates but were ineffective against simple silica precipitates [5]. Acidic groups may be coordinating metal cations, which prevents the formation of sediment. Among the acidic comonomers, especially polymers containing VSA increase the solubility of metal silicates [5]. The synthesis of VSA-rich copolymers shows promising antiscalant performance for silicate precipitates, as the polymers offer remarkable performance against metal silicates (Fe, Mg) [5]. The polymeric molecules presented here could potentially be used as antiscalants in combination with a complementary dispersing agent, since the mechanism of action may be based on the inhibition (chelation) of silicate rather than the dispersion of colloids [5].

The effect of various environmentally friendly chemical additives on the dissolution of colloidal silica has been systematically investigated [6]. Polycarboxylates, mixed polycarboxylates/phosphonates, and amino acids with one to five $-\text{COOH}$ groups can be counted as silica scale dissolvers [6]. The principle findings are summarized as follows:

- (i) Among the effective silica scale dissolvers, anionic additives having at least one $-\text{COOH}$ group are at dosage levels of >2500 ppm.
- (ii) Chemical structures affect dissolution performance.
- (iii) In some cases, increasing the dose improves performance.
- (iv) Additional groups in the dissolver molecule (eg $-\text{PO}_3\text{H}_2$, $-\text{NH}_2$ or $-\text{OH}$) are known to increase the dissolution process.
- (v) Surface complexation, the first step in silica dissolution, can be significantly inhibited by suitable cationic reagents [6].

The inhibitory performance of three synthetic amine/ammonium-containing cationic polymers on colloidal silica particle growth has been reported [7]. The three additives are compared with the control that is silicate polymerization under identical conditions in the absence of the additives. Polyethyleneimine (PEI),

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polyallylamine hydrochloride (PALAM) and poly (acrylamide-co-diallyl dimethylammonium chloride) (PAMALAM) were investigated in two sets of experiments, long (24-72 hours) and short duration (0-8 hours) [7]. The potential to inhibit silica formation is largely dependent on the polymeric additive dosage [7]. The most effective dosages were 10 ppm for PEI, 20 ppm for PALAM and 80-100 ppm for PAMALAM [7]. The inhibitory activity of PEI (at 10 ppm dosage) reaches 55% in 24 h, while PALAM reaches 65% inhibitory activity at 20 ppm after 24 h [7]. PAMALAM at 80 ppm dosage shows 60% inhibition [7]. The inhibitory activity decreases at longer silicate polymerization times (48 and 72 hours) [7]. All three inhibitors show higher activity than the control during the first 8 hours, with minor differences in performance [7].

A grafted co-polymer PEGPHOS-LOW (polyethylene glycol and phosphonate grafted) with methacrylate structure was used to control inorganic precipitation in four artificial geothermal brines with variable scaling tendency in the presence of common geothermal scale such as amorphous silica, magnesium, aluminum and iron silicates, zinc, lead and iron sulfides, and calcium carbonate has been studied in a systematic attempt to examine its effect [8]. It displays a dosage-dependent scale inhibition and dispersion; however, very high concentrations are necessary for satisfactory effectiveness due to the high scaling propensity of the brines [8]. This study suggested a systematic study about the inhibition effect of methacrylate-based polymer chains with various morphology having phosphonate and PEG grafts [9]. The four inhibitors are individual scales tested with amorphous silica, magnesium silicate, aluminum silicate, iron (III) silicate, zinc sulfide, lead sulfide, iron (II) sulfide and calcium carbonate. According to studies, the most effective inhibitor is PEGPHOS-LOW [9]. Existing problems become more difficult when the following items are considered: (a) supersaturation, (b) very low solubility products of potential scaling salts, (c) high temperatures, (d) complex water chemistry, (e) potential for composite fouling, (f) under deposit corrosion [9]. Not unexpectedly, scale deposits that form in geothermal brines vary considerably in composition, depending on their location and their respective surrounding environments [9]. The precipitation of minerals and other scales from geothermal fluids commonly takes place as the temperature decreases, dilution, increasing pH, reaction with sulfides and redox reactions. All deposit types can present challenging operational problems for geothermal plants. Geothermal waters are very complex and problematic because they pose a risk of composite fouling, which is rare in reverse osmosis and cooling systems [9].

The purpose of the employment of antiscalants is to surround the newly born particles, which tend to precipitate in the well, and to prevent them from becoming scale [1]. Antiscalant applications can be made in the field by determining the most suitable product after the determination of the appropriate dosages after the well antiscalant optimization tests [1]. However, although they are successful applications, it should be

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foreseen in geothermal investments that it may be necessary to perform well cleaning applications in several years by following well production [1].

Determining and controlling the performance of the antiscalant sent into the well by using antiscalant system is important to determine whether the appropriate dosages are applied, and scaling is prevented at the highest level [1]. Within the scope of well operation plans, detailed geochemical analysis are required. Daily monitoring of wellhead pressures and changes in separator pressures and temperatures in power generation plants, pH, electrical conductivity measurements of the fluid in daily/two-day periods, and total hardness analyzes are needed [1].

In this study, various composition of three raw materials were prepared and tested in the field conditions. These raw materials are acrylic homopolymer for chelation of cations, carboxylic sulfone copolymer for dispersion of newly born colloidal particles, and carboxylic sulfone nonionic terpolymer for both chelation and dispersion.

The prevention of Stibnite-Silica scale formation achieved in the preheater heat exchanger unit of a geothermal power plant by the application of chemical antiscalant. The best composition was found to be (A %50, B %25, C %25) at 6.5 ppm dosage. The performance of the antiscaling was determined visually by observing the changes in the heat exchanger output coupon.

2. Materials and Methods

The potential antiscalant products prepared in this study were tested in a field. Beştepeliler Kubilay GPP geothermal site is a binary power plant located in western Turkey. Wellhead temperature is 135-160 °C, reservoir temperature is 150-175 °C. The last preheater heat exchanger was followed, and this investigation pointed out that the decrease of temperature causes the formation of Silica-Stibnite scaling. The occurrence of deposit that is always a mixture of Silica and Stibnite is the main handicap of the system since it reduces the energy harvesting. All pipes, separators, accumulators, filters, etc. equipment were examined, and photographs were taken. Geothermal fluid and scale samples were subjected to detailed analysis. Figure 1 shows representative electron micrographs and XRD of the deposit obtained from the field.

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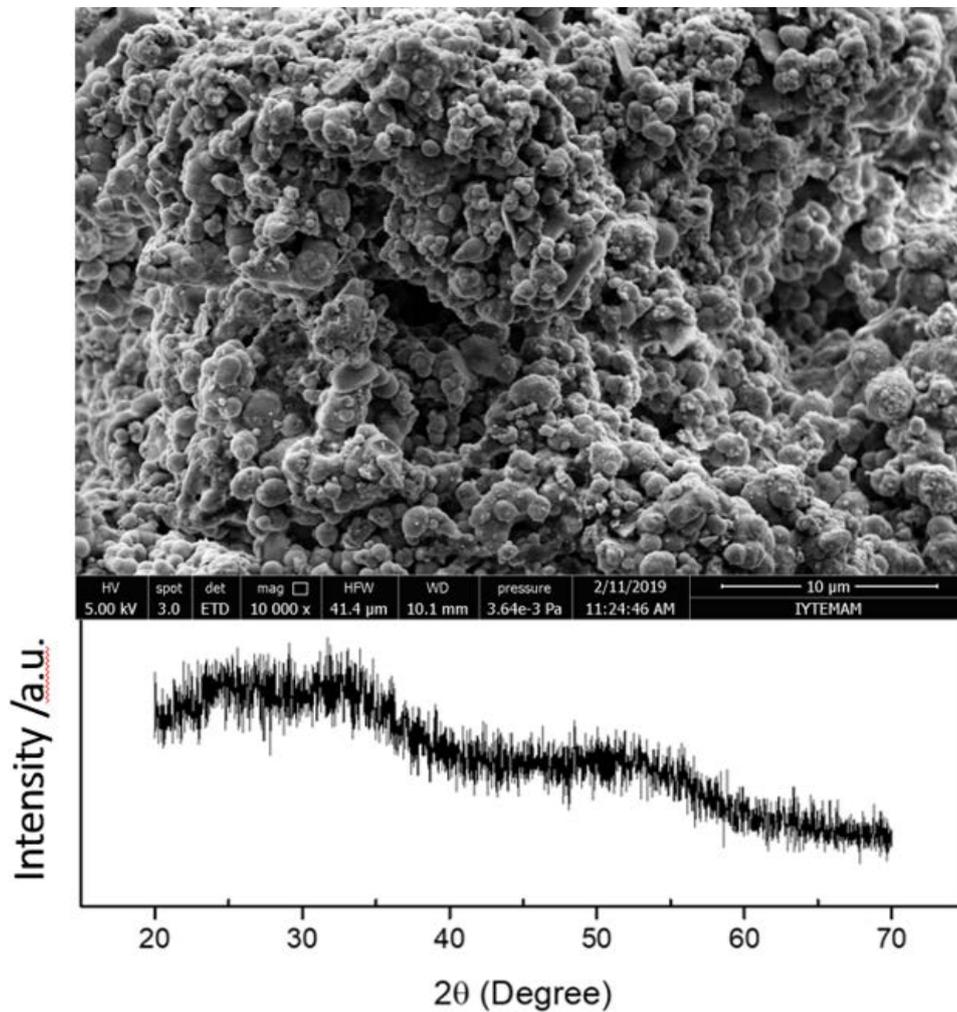


Figure 1. SEM image and XRD result of the scale sample taken from the field

Elemental composition suggests the presence of mainly Stibnite (>75%) and trace amounts of calcium-magnesium silicate (>10%) and calcium carbonate (<1%) in the last preheater (2nd Preheater) tube wall. The formation placements of the deposits were determined in the system. The potential antiscalants were attempted to be applied before just before these placements of the Silica-Stibnite deposits. The Vaporizer (Evaporator) outlet line before the unit was found to be the most effective placement for dosing of the antiscalants. The effect of the application on the system was evaluated by visually following the deposit coupon placed at the preheater outlet and monitoring the pressure-temperature values at the preheater input and output points.

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Table 1. Scale XRF Elemental Composition Result

Z	Symbol	Element	Concentration, %
51	Sb	Antimony	46,34
16	S	Sulfur	29,70
12	Mg	Magnesium	2,54
13	Al	Aluminum	0,92
20	Ca	Calcium	0,39
52	Te	Tellurium	0,23
50	Sn	Tin	0,20

Formulations trials

Ten different formulations were prepared and tested in this study. The raw materials are abbreviated as A, B and C referring to acrylic homopolymer, carboxylic sulfone copolymer, and carboxylic sulfone non-ionic terpolymer, respectively. The properties of raw materials are shown in Table 2. The polymeric raw materials are usually short chains, molecular weight is lower than 12.000 g/mol. The mechanism of mitigation varies depending on the functional groups of the molecules. For instance, acrylic homopolymer are used for chelation of the metal cations via carbonyl groups. Moreover, carboxylic sulfone work for the stabilization of colloidal Silicate and/or Stibnite particles. The dispersion of the colloids is needed because individual particles are considered to be the main component of the deposit.

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Table 2. Molecular weight and working principle of the raw materials

RAW MATERIAL	PRODUCT TYPE	MOLECULER WEIGHT (Mw)	WORKING MECHANISM
A	Acrylic homopolymer	2.000	Carbonate inhibition
B	Carboxylic sulfone copolymer	11.000	Metal and silt dispersant
C	Carboxylic sulfone non-ionic terpolymer	5.000	Metal and silt dispersant

Table 3. Formulation Studies with Different Raw Materials, % by mass (w/w) composition

Raw Materials	A	B	C
Trial Number			
1	30	50	20
2	25	25	50
3	25	50	25
4	50	25	25
5	30	45	25
6	45	30	25
7	40	35	25
8	20	55	25
9	30	15	55
10	15	30	55

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As a result of formulation trials, Trials 4, 6 and 7 were found as stable product, and trial number 4 was determined as the most stable trial among others. The physical property of the resulting product regarding with the trial 4 is given Table 4. Moreover, the optimum storage conditions for the product were determined as 5-38 °C.

Table 4. Analysis Results of Formulation No. 4

Physical Appearance	Liquid
Density (20 °C 1.15 ± 0.05)	1.13 g/cm ³
pH (20 °C 4.00 - 6.00)	5.17
Viscosity (<100)	30 cP
Freezing Point	<5 °C

3. Results and Discussion

Testing of the potential products was carried out to prevent the formation of Silica-Stibnite (antimony sulfide). This deposit causes differential-pressure formation and thus loss of efficiency, especially in the LP (Low Pressure) Preheater heat exchanger in a Geothermal Electricity Production facility. The existing dosing point and dosing system in the plant were seen on site, information was obtained from the plant and information was given about product dilution-preparation. The same dosage setting, and similar dilution ratio were chosen (1/4 dilution ratio) with a competitor chemical applied at the same point. As a result of the studies carried out in the plant, the product developed before the HP (High Pressure) Preheater was applied as 6.5 ppm. The dosage amount was calculated by measuring how much the liquid was dosed in the scaled cylinder with a stopwatch. The products used in the experiment were diluted with the water used in the dilution of the existing product in the plant. The density of water was accepted as 1.0 g/cm³. The data kept fixed during the trial period are shown in Table 5.

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Table 5. Data Kept Fixed During the Trial Period

Input Flow	2200 t/h (In the 4 days period followed, Avg. 2147 t/h)
Inlet Temperature	135 °C
HP Vap. Input Flow	7.99 bar
Reinjection Pressure	19.8 bar
Reinjection Temperature	70 °C
Chemicals Used	($d = 1.15 \text{ g/cm}^3$)

During the application, the change of HP Preheater and LP Preheater inlet-outlet differential pressures was followed. In addition, the control was provided with the coupons attached to the LP Preheater inlet line and the reinjection line. A significant improvement was observed in the inlet-outlet differential pressure values of the Preheater plant within the first 24 h following the initiation of the recommended chemical conditioning program for the system (Fig. 3).

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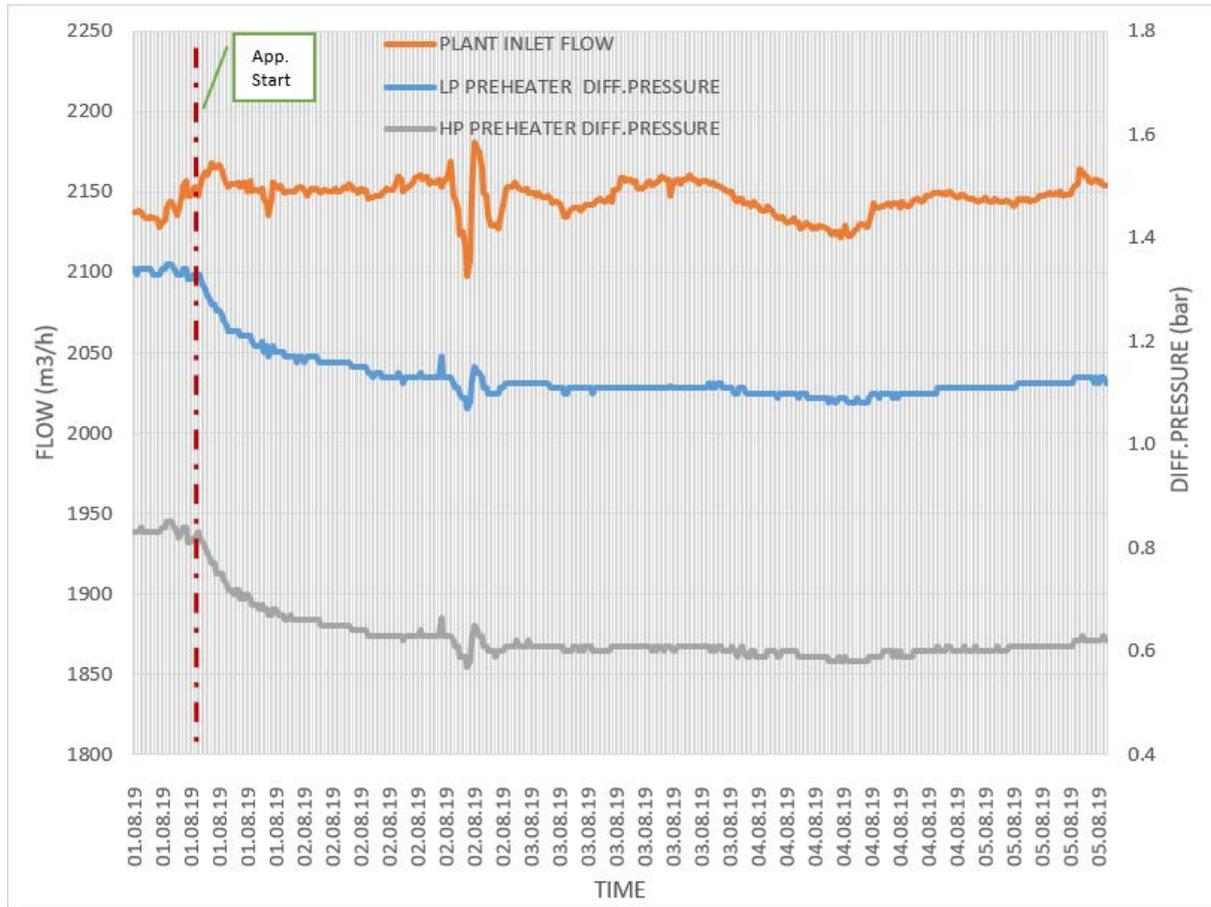


Figure 3. Preheater Input-Output Differential Pressure Variation

The performance of the testing has also been visually observed by the deposit coupon. Figure 4 shows three sets of coupons: the ones as they are without any treatment with brine; the one treated with brine; and the ones treated with brine including chemicals we tested in this study. In the case of no chemical application, stibnite deposits with a brick red appearance and soft structure were observed on the coupons, while clean coupon images were detected in case of simultaneous chemical application. This visual testing is an established test method for potential antiscalant products.

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Figure 4. Preheater Output Coupons

Pressure of the brine is followed at two different points in the system. A significant decrease was observed in HP and LP Preheater inlet-outlet differential pressures. The LP Preheater differential pressure, which was at the level of 1.30 bar at the beginning of the application, decreased to the levels of 1.20 bar 4 hours after the start of the application and then stabilized at the level of 1.10 bar after about 24 h. HP Preheater differential pressure in the same process; it decreased from 0.80 bar to 0.60 bar and continued as unchanged. As indicated in Figure 1, 15-min flow rate and the differential pressure values of the preheaters were taken as standard during the entire trials. As an indicator of the intended Stibnite-Silica antiscalant effect in the trial application; beyond the expectation that the differential pressure value will be fixed in the preheaters, the fact that there is a differential pressure drop of 0.2 bar in both preheaters shows that the application gives meaningful results, prevents the formation of deposits, and helps the soft precipitate to get away from the system. As of the beginning of the application, 96 h coupon control at the input of LP Preheater also supports the success of the application.

4. Conclusion

Composition of three antiscalant components (acrylic homopolymer, carboxylic sulfone copolymer, carboxylic sulfone non-ionic terpolymer) were combined with various compositions to obtain an effective antiscaling product against Stibnite-Silica deposit. Successful field results were obtained as a result of testing 6.5 ppm dosage (50%, 25%, 25%, respectively (formulation no. 4). The testing condition given the best

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result has been continued for 5 days. The deposit coupons were remained almost unchanged and no remarkable deposits were observed. Note that an approach is reported here in this study, where various compositions of the raw materials are prepared and tested to fine control over the mitigation of the deposits. This approach can be applied to any geothermal power plants suffering from rigorous scaling. Moreover, it can be more developed as follows. The dosing needs to be applied to the system before the Vaporizer; however, this application requires logistics investment. The application of the potential antiscalant products can be applied along with well antiscalant such that dosing can be applied once to well and another dosing location will not be needed (considering that the antiscalants were assumed to be resistant for high temperature and pressure).

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References

- [1] F.S.T. Haklıdır, Jeotermal Akışkan Kaynaklı Kabuklaşma Oluşumu ve Engellenmesinde Kontrol Parametrelerinin İzlenmesinin Önemi, Türkiye’ de Jeotermal Kaynaklar Arama Ve Uygulamalar Sempozyumu (İTÜ), 2012.
- [2] C. Başaran, A. Gökgöz, Heybeli Jeotermal Sahasında (Afyonkarahisar, Türkiye) Potansiyel Kabuklaşma Problemlerinin Jeokimyasal İrdelenmesi, Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi, 025803, 753-761, 2017.
- [3] J. S. Gill, L. Muller, D. Rodman, Inhibition of Antimony Sulfide (Stibnite) Scale in Geothermal Fields, GRC Transactions, Vol. 37, 2013.
- [4] C. Çiftçi, E. Karaburun, S. Tonkul, A. Baba, M. M. Demir, M.İ. Yeşilçınar, Testing the Performance of Various Polymeric Antiscalants for Mitigation of Sb-Rich Precipitates Mimicking Stibnite-Based Geothermal Deposits, Wiley, Paper No. 10, 2020.
- [5] G. Topçu, A. Çelik, A. Baba, M.M. Demir, Design of Polymeric Antiscalants Based on Functional Vinyl Monomers for (Fe, Mg) Silicates, Energy & Fuels, 31 (2017), 8489–8496.
- [6] K.D. Demadis, E. Mavredaki, Green Additives to Enhance Silica Dissolution During Water Treatment, Environ Chem Lett, 3 (2005), 127–131.
- [7] A. Stathouloupoulou, K.D. Demadis, Enhancement of Silicate Solubility by Use Of “Green” Additives: Linking Green Chemistry and Chemical Water Treatment, Desalination, 224 (2008), 223–230.

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- [8] A. Spinhaki, M. Kamaratou, G. Skordalou, G. Petratos, A. Tramaux, G. David, K. D. Demadis, A Universal Scale Inhibitor: A Dual Inhibition/Dispersion Performance Evaluation Under Difficult Brine Stresses, *Geothermics*, 89 (2021).
- [9] A. Spinhaki, M. Kamaratou, G. Skordalou, G. Petratos, I. Petrou, A. Tramaux, G. David, K.D. Demadis, Searching for A Universal Scale Inhibitor: A Multi-Scale Approach Towards Inhibitor Efficiency, *Geothermics*, 89 (2021).