Dieng Geothermal Field: Testing of the effectiveness of pH modification for the mitigation of silica and arsenic-sulfide scaling in heat extraction process using a pilot plant.

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ABSTRACT

A new mobile pilot plant unit was designed and built for Geo Dipa Energy in Indonesia. The unit's purpose was to test different process cycles and find the most effective method of scale mitigation for present and future power plants in the Dieng geothermal field. The pilot plant was constructed in Indonesia and transported to Dieng geothermal field in central Java and connected to well HCE-7C. Tests, conducted for demonstrating the operability of the pilot plant provided conclusive results about the suitability of the proposed mitigation methods for the Dieng brine. Of four process options tested only high-pressure separation and hot injection proved satisfactory. The tests demonstrated that the proposed pH modification is not effective for scale mitigation in an ORC process using the hot brine as the energy source. This is because of high scaling rate of arsenic sulfide and silica. Because of the low solubility of arsenic sulfide at low pH, acidification for mitigation of silica scale is not beneficial. The tests demonstrated that the proposed pH modification is neither sufficiently effective for scale mitigation in a dual flash process operated at low secondary separator pressure. Diluting the brine with the condensate is less effective than expected because of the high ammonia content, and high pH of the condensate. Testing of injectivity with packed bed was demonstrated but due to the short duration of the tests the significance of the packed bed experiments is somewhat limited.

1. INTRODUCTION

The Dieng geothermal power plant, located in the Dieng Volcanic Complex, was first commissioned in year 1998 and continuous operation started in year 2002. The brine from the Dieng wells is highly saline and with high silica content. This makes it very difficult to keep the silica in solution and to avoid scaling in pipes and reinjection wells after flashing to atmospheric pressure. Very high separator pressure is needed to avoid silicate and amorphous silica supersaturation. When the brine is flashed to atmospheric pressure, rapid precipitation of silicates and amorphous silica causes scale formation in wells, surface equipment and injection system. This has led to operational difficulties. Geo Dipa Energy (GDE) is expanding its operation in Dieng by installing two new power plants with 55 MW capacity each. As a preparation for the new power plants an extensive study of the scaling potential in the brine was initiated by GDE in order to find an optimal solution to this problem. The study was divided into three parts. First a theoretical study was conducted by Thermochem Inc (TCI), in which the scaling potential was analyzed, and five alternative process schemes recommended. Secondly GDE engaged Electroconsult (ELC) to study the feasibility of the proposed expansion at Dieng. ELC recommended some modifications of TCI approach. Finally, the proposed process schemes were be tested in a pilot unit. The objective was to select and proof the success of recommended options for operation of the planned Dieng power units.

MICK, a joint venture of Mannvit, ISOR, CBN and Kemía were assigned by Geo Dipa Energy (GDE) to design, build, install and operate the test of a pilot unit in the Dieng geothermal field in Indonesia. The purpose of the pilot plant study was to test different process cycles and find the most effective method of scale mitigation for Dieng power plants. The work commenced in June 2020 and was completed in May 2021. The Pilot unit was constructed in Cikarang in Indonesia and transported to Dieng in March 2021 where it was connected to well HCE-7C. After commissioning, two test runs were done and completed. The execution and results of the test in Dieng are described in this paper.

2. PILOT PLANT OPERATION

The principal design of the pilot plant was based on the experimental pilot units used in Reykjanes and Peistareykir in Iceland, for studying silica scaling in geothermal brine for bottoming plants (Hauksson 2011 and 2018). The pilot plant was designed with great flexibility with two parallel process lines for testing two process options simultaneously. The overall flow diagram for the pilot unit is shown in Figure 1.

Hauksson, Widianto, Mukti, Sigmarsson.

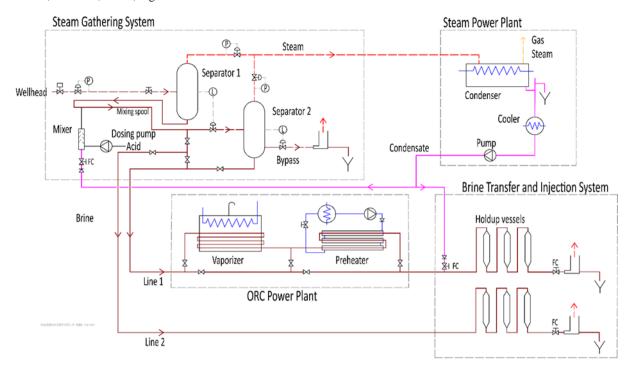


Figure 1: Dieng - Pilot Plant - Overall Flow Diagram (MICK 2021).

The design and construction are described in more detail in a paper presented in the 8th Indonesia International Geothermal Convention & Exhibition, (Sigmarsson et al. 2022).

The pH was measured after cooling the brine to 25 °C. The acid, prediluted for dosing, was pumped into an online mixer made of Hastelloy C-276 with a hydraulically actuated diaphragm pump where the acid is further diluted with condensate. The injection quill for injecting diluted acid into hot brine is made of Tantalum metal and the diluted acid is injected into the brine in a mixing spool made of Super Duplex Alloy 2507. The pH was monitored, and the dosing rate adjusted automatically and manually. The level in the acid holdup tank was monitored manually to determine acid dosing rate.

System pressure in the inline spool was controlled and kept higher than the pressure in separator 1. Pressure in the separators was controlled by automatic steam control valve. The two-phase inflow was controlled by orifice restriction in the flow line and automatic control of the pressure difference between inlet spool and separator thru combination of manual throttling and the automatic action of control valves.

The brine stream from the separator was divided into two streams for running of two parallel tests. In one stream the brine was not cooled for the testing of high-pressure separation and injection. In the other stream the brine was cooled in a vaporizer and a preheater simulating the brine side in an ORC process. The vaporizer has multiple cooling tubes allowing the study of fouling rate at different temperature. The fluid in the vaporizer boils and condenses internally so that no steam escapes. This ensures that no fouling will occur on the outside of the tubes and any scaling on the brine side can be detected by monitoring the heat transfer. From the vaporizer the brine enters the preheater which also has multiple cooling tubes and closed loop circulation on the cold side. The brine flow in the test lines was controlled by orifices and control valve at the outlet.

The steam from separators was throttled and condensed in a shell and tubes type of condenser at atmospheric pressure and excess steam and NCG released to air through an exhaust pipe muffler. The condensate was cooled and pumped at pressure of 32 bar and used for diluting the acid and for the mixing of condensate with the brine for simulating reinjection conditions.

Holdup vessels were used for increasing the residence time to 60 minutes like the proposed actual conditions in the injection lines of full-size plant. The holdup vessels consist of serially connected vertical pipes with narrow residence time and downward flow to avoid separation of suspended solids. The holdup vessels have sample taps for monitoring silica polymerization in the brine flowing through the process.

Finally, the suitability of brine for injection was tested in a packed be filled with rock cuttings. The flow through the bed is controlled by orifice in the outlet line.

3. BRINE CHEMISTRY

The brine discharged from Dieng wells is with high salinity with total dissolved solids (TDS) of 20,000 to 35,000 mg/kg at plant separator pressure. The reservoir temperature is from 305 and 330 °C and average production enthalpy around $1600 \, kJ/kg$. Well HCE-7C has historically produced the highest levels of silica in the flashed brine while the enthalpy has been around $1600 \, kJ/kg$, close to the average production enthalpy. Well HCE-7C was therefore chosen for the pilot tests.

The brine composition was analyzed during the tests and the typical concentration of the main components at Separator 1 pressure is shown in Table 1.

Table 1: Typical chemical composition of tested brine and condensate (MICK 2021).

Site name		Separator	Condensate
Temperature	°C	215	43
рН		6.2	8.2
Sodium, Na	mg/kg	6727	3
Potassium, K	mg/kg	1718	<0.1
Calcium, Ca	mg/kg	385	<0.1
Magnesium, Mg	mg/kg	<0.1	<0.1
Iron, Fe	mg/kg	0.43	<0.01
Ammonia, NH ₄	mg/kg	33	77
Chloride, Cl	mg/kg	12966	1
Sulfide, SO ₄	mg/kg	17	7
Fluoride, F	mg/kg	1.8	<0.1
Carbon dioxide, CO ₂ (total)	mg/kg	70	97
Hydrogen Sulfide, H₂S (total)	mg/kg	0.7	0.2
Manganese, Mn	mg/kg	4.4	<0.02
Antimony, Sb	mg/kg	<0.01	<0.01
Aluminum, Al	mg/kg	<0.01	<0.01
Silica, SiO ₂ (total)	mg/kg	1145	
Silica, SiO ₂ (monomer)	mg/kg	1062	
Arsenic, As	mg/kg	20	0.05
Total Dissolved Solids (TDS)	mg/kg	23092	

The untreated brine flowing from separator 1 at 215 °C had total silica concentration of 1145 mg/kg well above silica saturation concentration which is 1056 mg/kg at 215 °C (Fournier and Row 1977). The Arsenic concentration was 20 mg/kg but is believed to be somewhat higher because of precipitation in the sample cooler. This also applies to antimony which also precipitated upon cooling.

The rapid precipitation in the sample cooler contaminated the pH electrodes in short time, Figure 2. Continuous monitoring of the pH and automatic dosing of acid was therefore not possible. Instead, the pH was measured, and the dosing adjusted manually.



Figure 2: Dieng - Pilot Plant - Contaminated pH electrode, As₂S₃ 84%, Sb₂S₃ 16%. (MICK 2021).

During tests, samples were collected from various location in the pilot plant. Example of the measured concentration of silica is shown in Figure 2 along with the silica saturation index (SSI = Silica concentration / Silica solubility).

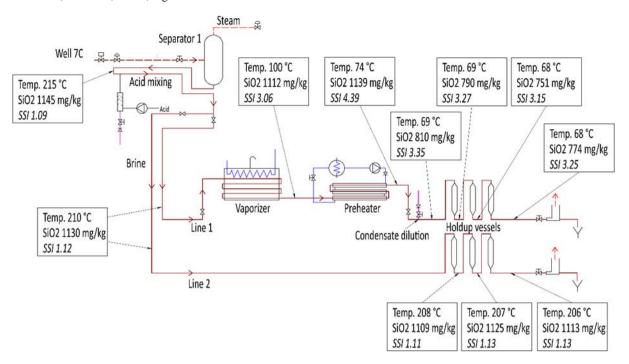


Figure 3: Dieng - Pilot Plant - Concentration of total silica and silica saturation index (SSI) (MICK 2021).

4. RESULTS OF TESTS

4.1 Deposition on Coupons

Scaling was determined by coupons inserted in the brine lines. Pictures of the coupons retrieved after 13 days test are shown in Figure 4. The calculated scaling rate based on thickness measurements and indicative analysis by SEM/EDS are also shown in the figure.

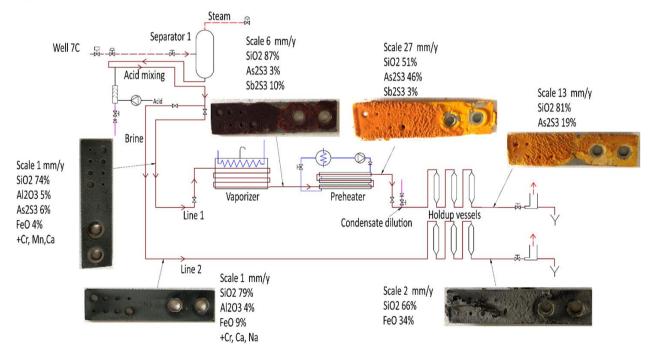


Figure 4: Dieng - Pilot Plant - Scaling coupons retrieved after 13 days (MICK 2021).

Heavy scaling was apparent in test which simulated ORC brine process by cooling the pH modified brine in the vaporizer and preheater. The scale was mostly silica but contained high concentration of arsenic sulfide (As_2S_3) which caused the orange color of the scale in the preheater and antimony sulfide (Sb_2S_3) apparent also as darker colored scale in the vaporizer. The scaling rate was estimated 6 mm/y in the vaporizer outlet and 27 mm/y in the preheater outlet. The scale is amorphous as demonstrated by the typical spheric form of amorphous precipitates, see Figure 5.

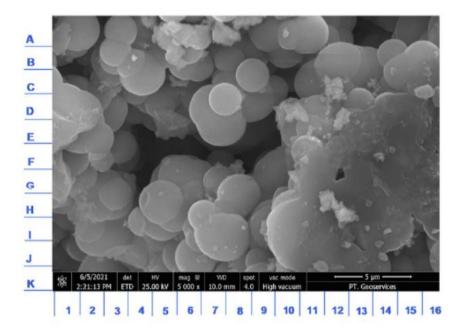


Figure 5: Dieng - Pilot Plant - Preheater coupon. SEM photomicrograph (MICK 2021).

In alkaline H2S rich solution the arsenic is dissolved as sulfide species. The solubility of amorphous arsenic sulfide decreases at low pH as can be seen in the following equilibrium for dissolution of arsenic-sulfide in H_2S rich solutions.

$$3/2 \text{ As}_2\text{S}_3 + 3/2 \text{ H}_2\text{S} \iff \text{H}_2\text{As}_3\text{S}_6^- + \text{H}^+$$

When the pH is lowered (H⁺ concentration increased) the equilibrium is shifted to the left and As2S3 is precipitated. The solubility of amorphous arsenic sulfide is prograde, see Figure 6 (Eary, 1992) and when the brine is cooled down the solubility product will become higher than the solubility product constant (Ksp) for arsenic sulfide.

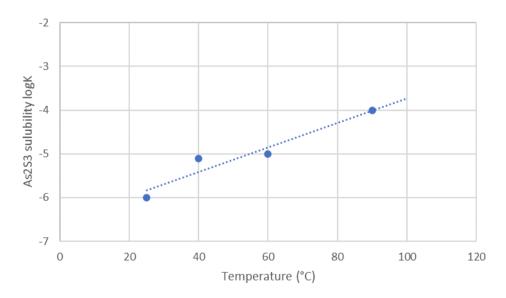


Figure 6: Solubility of amorphous As₂S₃ (Eary, 1992).

The solubility of antimony sulfide is also pH dependent according to the following equilibrium (Brown 2011).

$$Sb_2S_3 + H_2S \Leftrightarrow HSb_2S_4^- + H^+$$

Because of the low solubility of antimony and arsenic sulfide at low temperature and at low pH the pH modification is not optimal solution to mitigate silica scaling when the antimony and arsenic concentrations are high, as is the case in Dieng well HSE-7C. This comes as no surprise because of the unusually high arsenic concentration in the brine. This was pointed out in TCI's analysis as a possibility but needed to be tested experimentally. When the arsenic sulfide precipitates out of solution silica is coprecipitated and the benefit of the pH modification for silica mitigation is reduced. After holdup vessels the scaling rate was 13 mm/y which is far too high for injection into wells.

Hauksson, Widianto, Mukti, Sigmarsson.

Less scaling occurred in tests which simulated high pressure separation and hot injection process. The scaling rate was 1 mm/y in the inlet pipe at 210 °C and increased to 2 mm/y in the outlet pipe after 1 hour holdup in the holdup tanks. The scale was mostly silica but contained also aluminum and other metals, causing the grayish color of the scale. This scaling rate can be accounted for in operation of separators, but the rate is higher than expected at the low pH of 4.6 and the high temperature. Scaling rate of 2 mm/y is high for reinjection and is likely to considerably reduce the lifetime of injection wells.

High scaling rate was also the case in a test which simulated dual flash process. The second separator was operated at 137 °C and silica saturation index (SSI) of 2.48. The scaling rate was 27 mm/y in the inlet which is high considering the low pH of the brine. The scale was almost pure silica and light colored. The scaling rate was even higher or 49 mm/y in the brine diluted with condensate at a supersaturation of SSI 2.36. This is likely caused by the increase in pH when the ammonia mixes with the brine. These results are not satisfactory, and the pH modification seem not to work efficiently at these conditions.

4.2 Thermal transfer coefficient

The brine passed 5 times through the vaporizer and 3 times through the preheater and the temperature drop was measured after each pass. The overall thermal transfer coefficient was calculated for the vaporizer and preheater during the tests. The decrease in thermal transfer coefficient was 2.3% per day in the preheater while the decrease was insignificant in the vaporizer which demonstrates the difference in the effect of scaling on heat transfer in the vaporizer and preheater.

4.3 Packed beds

The brine from the tested process flowed through a packed bed with drill cuttings collected from Dieng injection wells. Orange-colored deposits were noticeable on the drill cuttings in the inlet sections of packed after cooling in vaporizer and preheater (ORC process) but little in the outlet section, Figure 7. Some deposits were also noticeable on the cuttings in the inlet section of from the hot injection simulation, packed bed 2, Figure 8. No restriction of flow could be detected during the tests and negligible changes in chemical composition of brine were detected before and after packed beds.



Figure 7: Dieng - Pilot Plant - Packed bed drill cuttings in inlet and outlet for ORC process (MICK 2021).



Figure 8: Dieng - Pilot Plant Packed bed drill cuttings in inlet and outlet for hot injection process (MICK 2021).

5. SUMMARY AND CONCLUSIONS

The pilot plant was constructed and transported to Dieng and installed and commissioned at site. Tests were conducted for demonstrating the operability of the pilot plant. The tests were successfully completed and provided conclusive results about the suitability of the proposed mitigation method by pH modification.

The tests were done with brine from well HCE-7C in Dieng and are specific for this well. Although well HCE-7C is considered reasonable representative for the Dieng wells, the results should be used with caution for judging the general operability of the Dieng geothermal field.

Of the process options tested only one proved satisfactory.

The scaling rate of 1-2 mm/y, at high separator pressure of 21 bar abs (hot injection process), is acceptable but the scaling may affect injectability of injection wells. This scaling occurs despite the pH modification of the brine to pH 4.6. Dilution of the hot brine with condensate may prove beneficial.

The tests demonstrated that the proposed pH modification at a pH of 4.6 is not effective for scale mitigation in an ORC process using the hot brine as the energy source. This is because of high scaling rate of arsenic sulfide and silica, especially in the preheater. The high scaling rate is caused by high concentration of arsenic in the brine which counteracts silica scale mitigation by pH modification at low temperature. Because of the low solubility of arsenic sulfide at low pH, further acidification will not be beneficial.

Diluting the brine with the condensate is less effective than expected because of the high ammonia content, and high pH of the condensate. Automatic monitoring of pH and control of acid dosing is difficult because the precipitation of arsenic sulfide in the sample cooler contaminates the pH sensor.

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