Metal Silicate Formation at Tuzla Geothermal Brine Lines

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ABSTRACT

Tuzla Geothermal Power Plant is an Ormat manufactured ORC binary plant that is located in Northwestern part of Turkiye, in the city of Canakkale. The plant has been in operation since January 2010. The two-phase geothermal fluid coming from two production wells by artesian flow is separated as steam and brine at the wellhead horizontal separators and brine is pumped to the ORC Plant by booster pumps, while steam reaches the plant naturally. Separation pressure is 3bar.g and temperature of separated brine is 143Cdeg.

Tuzla Geothermal brine is highly saline, with 32.000ppm Cl and 22.400ppm Na content, and has a conductivity of almost 100.000 µs, with the total hardness around 9.000ppm. Although the hardness is high, Calcium Carbonate Scale has been successfully prevented in the wells by commercial inhibitors.

The focus of this paper is mostly the metal silicate scale which precipitated in the *separated brine* lines and in the heat exchanger (Vaporizer & Preheater) tubes, where the brine is passing through (Brine Pressure at Vaporizer inlet is 3,5 – 4,25 bar.g, brine temperature is 142 Cdeg). The scale formation at the binary plant Vaporizer tubes not only decrease the heat transfer from the brine to the motive fluid n-pentane, but also decrease the volume of the brine flow passing through the Vaporizer, causing reduction in the energy output of the power plant. The scale analysis shows that the composition of the scale is mostly silis, iron and magnesium. To mitigate the silicate scaling problem various chemical inhibitors were tested. Effectiveness was evaluated both by the analysis of accumulated scale on coupons distributed in many locations along the brine line from Wellheads to the Vaporizer inlet, and analysis of PH, silis, iron and hardness levels at site laboratory. We also monitored the process parameters such as "brine inlet pressure" and "Vaporizer Motive Fluid Pressure" to get an indication on the effectiveness of the inhibitors.

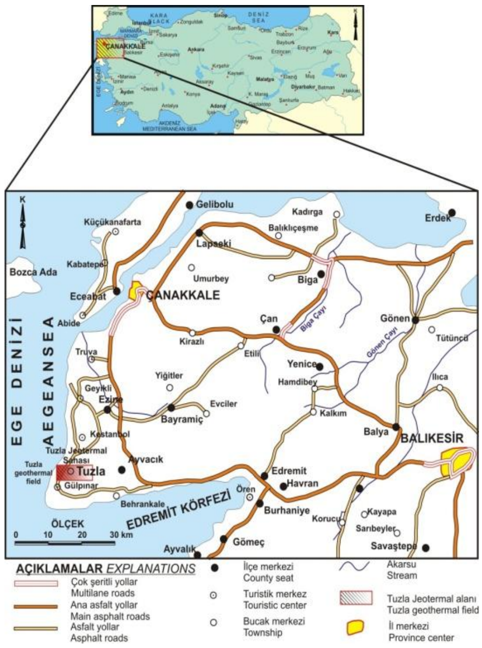
In search of the solution to the Scaling Problem, we continued in 4 lanes.

1. Testing local and international commercial inhibitors and dispersants that are not hazardous to the environment.
2. Studying the process (e.g. BOP design) and its effect on scaling such as Changing Separation Pressure, PH Adjustment with acid injection, Employing Lineshaft pumps in the production wells, Rerouting condensate in brine line upstream the Vaporizer inlet.
3. Keep on producing energy, by periodically cleaning HX tubes, pipe spools, pumps, valves, filters etc. Taking mechanical measures such as installing filtration systems upstream of the Vaporizer, and scale traps along the brine pipeline.
4. Ongoing research on the net, fairs, university visits etc.

One year after the commissioning of the power plant, the Mg/Fe Metal Silicate scale formation rate has been reduced almost 6 times by using inhibitor. Further studies will be focused on the process and/or applications to go beyond the point that has been reached by inhibitors, so that we can start the investment of new modular units for bottoming cycle option, and later the second power plant.

1. INTRODUCTION

Tuzla GEPP Project is located at Çanakkale, Turkiye – Tuzla geothermal area, 5 km west of Gurpınar town of Ayvacik. *Tuzla* means salty area in Turkish language.



Geothermal research and development Works at site were initially started by MTA General Directorate in 1966, these studies continued till 1993 sporadically. During these years geophysical, geochemical, and geological studies had been made at the area resulting by 8 gradient and 4 research wells. Existing volcanic rocks at site, high temperature springs (35-102 Cdeg), up to 176 Cdeg reservoir temperatures at the drilled wells, and common hydrothermal alteration at site manifests that this area has high geothermal potential.

During Tuzla Geothermal Power Plant Project, 8 new wells were drilled in the area. Today two of these wells (T9 & T16) are used as Production wells and two of them are used as Reinjection wells (T15 & T10).

Tuzla Geothermal Binary Power Plant's installed capacity is 7,5MW. The geothermal fluid which comes from underground cools down to 80-95 Cdeg after the power plant circulation. This temperature still permits the use of the Water's energy, at bottoming cycle, greenhouse heating, and after that at shrimp farm and fish cultivating farm etc. All the fluid exiting the power house and this kind of integrated facilities will be reinjected back to the reservoir.

At Tuzla site, it has been noted that there has been scaling problem like in any other geothermal field. At previous capacity tests right after well completions, scaling had been observed at horizantal production pipe attached to the wellhead. The cause of the scaling in the well is due to the attachment of the Ca ions to the Bicarbonate ions in the geothermal fluid. Calcite scaling has been succesfully prevented by dosing inhibitors down the well.

A black scale had been found to accumulate on the wellhead scaling coupons during testing of calcite inhibitors. It was mainly iron, silica and sulfur.

1.1 ORC Binary Plant

Tuzla Geothermal Power Plant is a binary plant with Organic Rankine Cycle.

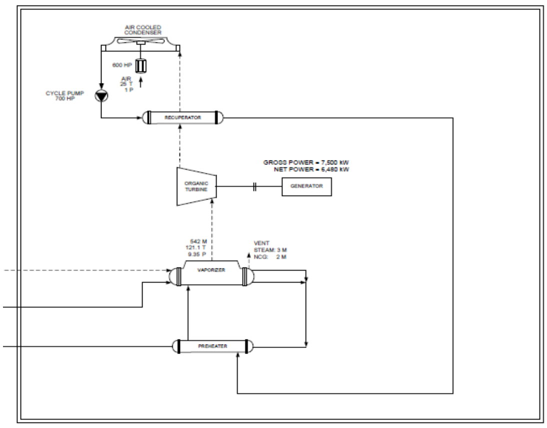


Figure 1: Heat & Mass Diagram

The motive fluid is N-Pentan.

The heat source (brine, and steam) passes through main heat exchanger (Vaporizer) and a secondary heat exchanger (Preheater) to transfer the heat to the motive fluid. Tubing material for both Heat Exchangers was selected as dublex stainless steel A789 SAF2205 considering the highly saline brine.

Figure 2: Tuzla Power Plant situated right next to Tuzla Dome.

NCG is vented into the atmosphere, a third HX called Recuperator was also employed at Pentan side. Cooling of the fluid is realized by Air Cooled Condenser.

1.2 BOP – Balance of Plant

Two phased flow (Brine & steam mixture) from wellheads of T-9 & T-16 is directed to Horizantal Separators located close to each Wellhead and separated to steam, and brine. Steam, and brine are carried via aboveground pipelines to plant area where they are going through Tube Type Heat Exchangers (Vaporizer and Preheater respectively) transferring the heat to Pentane. After Preheater, brine, and condensate mixture is pumped to T-10 and T-15 for reinjection, back to the reservoir, concluding the first cycle.

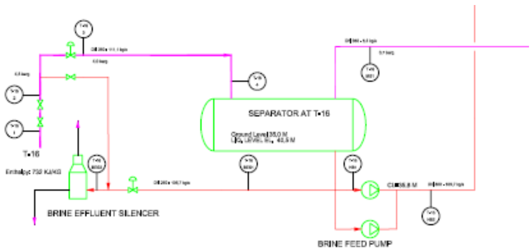


Figure 3: Wellhead Flow Diagram

1.3 Brine Composition

Sampling campaign was conducted by Icelandic Chemist Trausti Hauksson on each well separately according to a stated sampling procedure. Tuzla Geothermal separated brine characteristics is as follows:

Main Components		
CL	33000	mg/lt
pH	6,8	
T-pH	25	°C
CO2	88,3	mg/kg
H2S	0	mg/kg
SiO2	186	mg/kg
Li	28	mg/kg
Na	22409	mg/kg
K	2005	mg/kg
Ca	2166	mg/kg
Mg	53	mg/kg
Fe	0,76	mg/kg
Mn	4,7	mg/kg
Ba	13,4	mg/kg
Sr	155	mg/kg
Al	0,07	mg/kg
F	3,81	mg/kg
Cl	32798	mg/kg
Br	55	mg/kg
SO4	105	mg/kg
B	32	mg/kg
PO4	6,6	mg/kg
Sum Parameters		
Salinity	6,14	w%
Density (143 °C)	970	kg/m3
Density (100 °C)	1001	kg/m3

1.4 Black Scale & Pilot Plant Test

The wells in Tuzla geothermal field discharge hot brine and steam. Calcite scaling occurred in the wells and discharge piping. This was controlled by inhibitors.

A black scale had been found to accumulate on wellhead scaling coupons during testing of calcite inhibitors. This black scale had been analyzed to be mainly iron, silica and sulfur. To confirm this and to study the rate of this scale formation a scaling test was conducted before the construction of the plant.

A sampling separator was used for separating the well fluid into steam and brine. The brine was cooled down in experimental coolers to simulate operation of the plant. The brine flowed through steel pipe before and after cooling to simulate time delay in brine transfer and reinjection pipes.

Current Metal Silicate Scale problem was not realized during this pilot plant test. Therefore silicate scaling was not foreseen before the construction of the plant.

1.5 Gas Content and Analysis

Gas flow from Production Wells T9 and T16 are as follows;

Well	WHP	Vol.	CO2	N2	CH4	NH3
	bar.a	l/kg	vol%	vol%	vol%	vol%
T-09	5,1	43,8	91,2	4,9	2,7	1,3
T-16	5,3	40,2	92,5	4,1	2,3	1,2

H2S flow from both wells is %0. CO2 release from these two wells is 0,625 kg/s, Hauksson (2009).

1.6 Suspended Solids filtered from the brine sample taken from T15 Weir Box

These yellow colored suspended solids are coming from the production zone. Relation of these suspended solids to Andesit formations at the production zone is being investigated. Composition of this material is mostly; 25,35% Si, 28,61% O2, 10,37% Na, and 19,68% Cl.

2. SCALE CHARACTERIZATION

In this section composition of the Metal Silicate Scale is given.

Figure 4: Photo of Thick scale formation at separator brine outlet.

2.1 Scale

In below figure, photo of the grey/green deposit sample from brine pipeline is seen

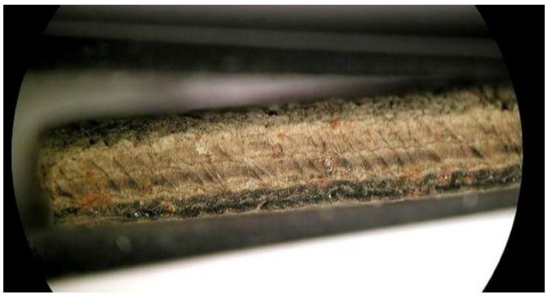


Figure 5: Photo of the sample (stereoscopic enlargement)

Such sample appears as flakes with thickness around 2mm; the surfaces are smooth and, it is easy to see stratifications with different chromatic intensity.

2.2 Composition

Every layer has been submitted to EDAX microanalysis, technique that allows a qualitative evaluation of the constituent elements, with a substantial uniformity of results.

The elements that constitute the different layers of the alteration are silicon, oxygen, iron, magnesium, chlorine, manganese and calcium.

In the following table you can find the results.

ELEMENT	U.M.	Value
Magnesium	% p/p as MgO	14.4
Silicon	% p/p as SiO_2	50.4
Calcium	% p/p as CaO	1.58
Iron	% p/p as Fe_2O_3	22.7
Chlorine	% p/p as Cl	2.30
Aluminum	% p/p as Al_3O_3	0.39
Phosphor	% p/p as P_2O_5	0.13
Sulphur	% p/p as SO_3	0.21
Zinc	%p/p as ZnO	0.57

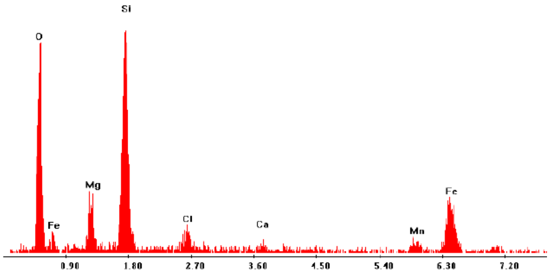


Figure 6: Representative EDAX spectra of the different layers composition.

Analysis say us that every layer is characterized by the same principal elements, therefore silicon, oxygen, iron, magnesium, chlorine, manganese and calcium: the different coloration of the bands seems to be due to crystallization of the constituent.

2.3 Location

Scale occurs wherever the geothermal fluid or brine is in contact: On the capillary tubing, pump sections, valve seats, thermowells, PT and Orifice tubings, Separator walls, level colons, Vaporizer tubings, Preheater tubings etc.

Scaling occurs on the Production side, from the wells to the Power Plant. On the reinjection side we do not see scaling at all. The brine temperature at the plant outlet is 97Cdeg and it is around 95Cdeg at the reinjection wellhead. Scaling composition in the heat exchanger tubings is different than the one in the brine pipeline.

3. UTILIZATION OF INHIBITORS

First inhibitor tests were conducted at T10 Well in January 2009, right before the Capacity & Interference tests of the wells. Succesful inhibitors for calcite scaling were selected.

After the discovery of the silicate scaling in the brine line, 3 days after the start-up date January 14th, 2010 inhibitor manufacturers were informed about the situation immediately. The year of 2010 passed with almost continuous inhibitor tests.

Around 30 inhibitors from 12 companies were tested at different dosing rates and locations. Inhibitors were dosed down the well, at the wellhead, after the wellhead control valves, before the wellhead separator, right after the separator, halfway between the separator and the plant, right before the Vaporizer inlet at the plant area etc.

Acidic inhibitors were avoided to protect the dosing equipment and well casing at the dosing depth. Prescreening tests were conducted at the plant laboratory to avoid clogging of the capillary tube due to gelling, clouding of the chemical etc. Other visual and experimental tests were done to check the specs of the incoming chemicals.

Finally it was found to be more effective by following the below format, which was suggested by the manufacturer of the current inhibitor.

3-5 ppm Scale Inhibitor down the well

8-10 ppm iron dispersant into the brine, right after separation.

With this final dosing format, scaling rate was decreased almost 6 times within a year from the initial rate during the start-up time.

3.1 Dosing Applications

Dosing of the chemical was realized by redundant heavy duty simplex dosing pumps, located on a stainless steel pump skid. Home made pump skid was used to keep together the pumps, fittings, valves, check valves, filters, pressure transmitters, level transmitters, metering column etc.

Inhibitor was pumped below the flash point down the well.

Figure 7: Photo of Inhibitor Dosing System

On the otherhand, an iron dispersant was dosed into the separated brine on the ground. At the below photo the dosing location underneath the horizontal separator is shown.

Figure 7: Photo of dosage point for iron dispersant.

3.2 Evaluation of the Inhibitor Performance

Inhibitor performance was followed and reported by the accumulation rate on the coupons inserted into the brine pipe along the pipeline. Judgement was done not only by the accumulation rate on sample coupons but also the water analysis results, and plant process parameters.

3.2.1 Coupons

Coupons are stainless steel metallic rods used with a stuffing box and a ball valve to insert in and take out the rod from the flowing brine inside the pipe.

Figure 8: Photo of physical coupon

The tip of the coupons are screwed to the shaft. This tip that is around 8cm long is unscrewed and weighed at a 4 digit scale every 24 hour, 48 hour and 72 hour periods. Although some of the scale may fall of during taking out and inserting in, it is still a very powerful indication on scaling rate. It is physical, visual and measurable.

Caution should be given to ensure that the diameter and length of the coupon tips are standard, and coupon is chained at each location for personel protection.

In Tuzla 8 coupons were monitored. One on each wellhead (T9 & T16 Production Wells), one on each separated brine line after the horizontal separator (T9 & T16 Wellhead Separators), three before the plant inlet and one before the tie point of the two well flows.

Figure 9: Photo of coupon at location.

The coupon weight differences in a 24 hour period are given at the below table. Weights are in grams.

DATE	22.01.2011
Duration	24 hrs
Coupon No and Location	Inhibitor XXXXXX into the Well 3ppm + Inhibitor YYYYYY separator brine outlet 10ppm
1 (T16 Wellhead)	0,1995
2 (T16 Sep. Brine Outlet)	0,2653
3 (T16 – T9 Line)	0,1211
4 (T9 Wellhead)	0,2087
5 (T9 Sep. Brine Outlet)	0,1819
6 (Muffler Area)	0,1661
7 (Before Vaporizer)	0,1016
8 (Before Filter Group)	0,1049

3.2.2 Water Analysis

Site laboratory was set up at the Tuzla Geothermal Power Plant and a chemical technician was employed to conduct the daily and test measurements. PH, Conductivity, Alcalinity, Iron, Silis, Ca Hardness, Total hardness measurements of the brine is done daily by spectrophotometer, titration and related equipments. During these measurements we mainly focus on the difference of a parameter value between the separator outlet and plant Vaporizer inlet. For example if the average of iron readings at the separator brine outlets is much greater than the iron reading at the Vaporizer inlet than it is stated that there is a settlement of iron on the way.

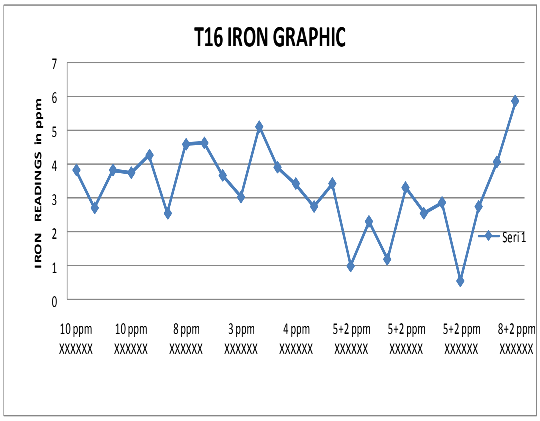
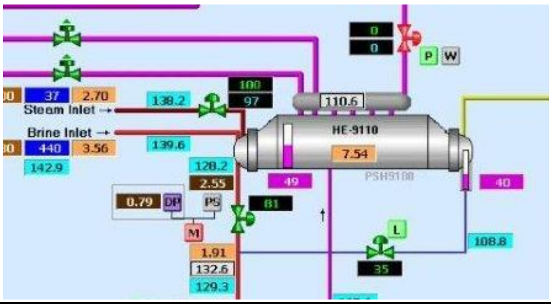


Figure 9: Graph of iron readings at the samples taken from the T16 Separator brine outlet.

Above graph stipulates the iron readings (ppm) at separator outlet according to the dosage rates of the dispersant. When the dosage rates is decreased also the iron readings fall down. The readings were back to normal when the dosage rate was pulled back to 8ppm.

<u>3.2.3 Power Plant Process Parameters</u>

The brine inlet pressure (3,56 bar.g below) and also the Vaporizer Pentan Pressure (7,54 bar.g below) were continuously monitored during the tests of an inhibitor. Brine inlet pressure is the brine pressure at the Vaporizer inlet, where as Vaporizer Pentan Pressure shows the heat transfer efficiency of the Heat Exchanger from the heat source to the pentan fluid. This pressure value is very sensitive to the accumulation rate inside the tubings, a non-promising inhibitors causes a downward trend at this value in a certain time e.g. 24hrs.



4. OTHER METHODS TESTED FOR THE MITIGATION OF SCALING

4.1 PH Adjustment Tests

Adusting PH by injecting sulphuric acid (H2SO4) into the brine at wellhead separator outlet was tested. Dosing acid through stainless steel and titanium tubings were unsuccessful due to the deterioration of the tubing end. An exotermic reaction occurring at the end of the tube where the acid gets into contact with the brine damaged the tubing end causing the creeping of acid to the pipe wall and giving additional damage. Installing a Teflon injection head at the end of the tube did not fully solve the problem due to the clogging of the injection holes at the teflon head, but enabled the run of the test at least for a 12hr period. It was possible to see the effects of the acid injection at least for 24 hours by replacing the teflon heads.

Figure 9: Photo of damaged acid injection tube.

By injecting 30ppm Sulphuric acid into the brine for 48hrs, it was managed to decrease the PH 0,4 – 0,5 units at the separator brine outlets, and the accumulation rate on the sampling coupons at the plant area were equal to a 24hr non acid test.

Study is ongoing to find out a safe and more effective way to mix the acid into the brine.

4.2 Higher Separation Pressure

Tuzla GEPP Wellhead separator pressure is set at 3 bar.g as the power plant requirement for steam pressure at the inlet is 4bar.a and brine temperature at the inlet is 143Cdeg. At maximum flow the Wellhead pressures of T16 and T9 production wells are 4.2 bar.g (When T16 flow control valve is 80% open, and T9 flow control valve is 70% open) with 350 ton/hour and 340 ton/hour total well flows respectively.

In July 2010, An experiment was conducted by increasing the separation pressure up to 4.0 bar.g. The duration of the test was limited to 24 hours as 1bar.g increase at the separation pressure causes more than 1 MW decrease at the energy output per hour at the gross 7.5 MW capacity plant.

Coupon at 3bar.g separation pressure

Coupon at 4bar.g separation pressure

On above coupon you can see the coupon no:5 which is located underneath the T9 horizontal separator on the brine outlet boom. This coupon was obviously cleaner at 4bar.g separation pressure than the coupon at 3bar.g separation pressure. This clear improvement was not seen at the coupon which is located at similar location on T16 horizantal separator.

Higher separation pressure may greatly help scale control performance. It is not sure where the best pressure will be to ensure optimal power output. Steam output of the separator decreases from 6,4% of total well flow to 4,8% of the total well flow according to the steam table. Therefore energy transfer from steam to the pentan will decrease. On the otherhand if scale control performance increases at the brine lines and vaporizer tubes, there will be better heat transfer at brine side of the heat exchanger, and less downtime for cleaning.

5. LIVING WITH THE SCALE

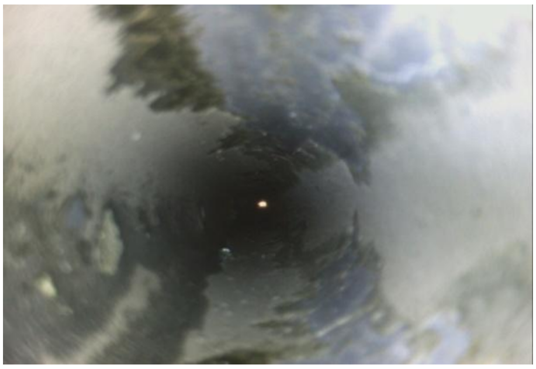
Tuzla Geothermal Power Plant had to keep on producing as much energy as possible during all these tests. Power plant personel learned how to live with the scale. These measures can be listed as;

5.1 Periodical Cleaning of the HXs

Periodical cleaning of the Heat Exchangers were performed almost every month by Hydroblast cleaning. Water jetting pressures were limited to 1250 bar, as higher pressures left dentures inside the tubings. Hot NaOH circulation was tried, as it was reported that heated caustic can dissolve the scale into tiny particles by breaking bonds. Hydrofluoric Acid solution (%2,5 – 5) was also recorded to be very effective on dissolving scale samples completely at lab experiments. HF solution has not been circulated yet through the heat exchangers for cleaning fearing the possible effects of the acid solution on tubings and wetted parts of the HXs.

5.2 Quality Control of the Cleaning

To control the cleaning performance of the tubings; tubing inspection camera, water test (filling randomly selected tubes with water and recording the water volume filled), and pigs (small pigs attached behind water jet nozzle, or long rods with certain diameters)



5.3 Filters and Traps

During plant shut down periods the brine pipeline cools and shrinks in length after the drainage of the pipes. During restart hot brine and the extension of the pipes causes the scale particles to fall of from the walls of the pipe interior and move with the flow towards the power plant inlet. These particles were clogging the tubes at the vaporizer brine inlet pass. By-pass filters installed before the Vaporizer inlet ,and traps installed on the brine pipeline helped prevent the reach of these particles to the Vaporizer.

5.4 Equipment and Spools

Pipe spool connections before the Power plant inlet, at filter group, around the wellhead separators and booster pump groups were changed from welded connection to flanged connection in order to easily dismantle and clean the interiors with water jets.

6. CONCLUSION & DISCUSSIONS

At latest dosage format, it has been possible to see below 0,10 gr/24hr accumulation rate on coupons before the Vaporizer Inlet.

Further studies will concentrate on

a. PH Adjustment by acid injection or CO2 injection,

b. Dosage rate optimization of existing inhibitors

c. Installing a simulation balance of plant, to test the effects of Cyclones, Vertical Separators, inhibitors, CO2 Injection, and Acid Injection.

REFERENCES

Hauksson, T.: Tuzla Geothermal Power Project, Procedures for Well Sampling and Field Analysis, Kemia Iceland (2009), 15p.

Hauksson, T.: Tuzla Geothermal Power Project, Chemistry of Steam and Brine in Wells, Results of Chemical Sampling in March 2009, Landsvirkjun Power (2009), 25p.

Giovanni Bozzetto S.p.A.: Test Report 10/000534405, Analytical Results of the Scale Composition Test, (2010).

Hauksson, T.: Summary of Gas Analysis of Steam from Wells, Kemia Iceland (2009), 8p.

Cevre Arge: Chemical Analyse Results for the Tuzla Wells, IYTE (2009), Excel Table.

ORMAT: Tuzla Project, Heat & Mass Diagram, (2008).

Rodriguez, A.: Amorphous Iron Silicate Scales In Surface Pipelines, Proceedings World Geothermal Congress, Bali, Indonesia (2010)

Gallup, D.L.: Iron Silicate Scale Formation and Inhibition at the Salton Sea Geothermal Field, Unocal Corporation, Unocal Science and Technology Division, Brea, CA, USA