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Thermodynamic Effects on Scale Inhibitors Performance At Multi-flash and Advanced Geothermal Power Systems

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ABSTRACT

In water-dominated reservoirs, binary and single flash cycle geothermal power systems are widely used for power generation around the world and the reservoirs temperatures generally indicate moderate or moderate-high temperatures at depth. In these systems, controlling and understanding the effects of pressure and temperature changes on geothermal fluids much easier than advanced geothermal systems. Depending on geothermal reservoir rocks, water-rock interaction can be explained and expected scale types can be determined easily and suitable inhibitors may be determined with short-term field tests before start up process.

Although energy efficiency higher than binary and single flash systems, power generation from multi-flash (double or triple) and combine (flash systems + binary) systems are still limited in the world. In these systems, reservoir temperatures are observed quite high and water- steam (with gas) phases separated more than one time. It concludes that pressure and temperature dramatically drops after each separation system when geothermal fluids reach to surface. This time the types and compositions of scales may show differences beginning of the production; high-pressure separation to low pressure separation station. The power system may require that different scale inhibitors and different inhibitor dosage points to protect itself.

1. INTRODUCTION

Installed geothermal power production was declared near 12.6 Gwe around the world in 2015. The installed geo-power capacity is expected 21.5 Mwe with development of new medium-low temperature geothermal power projects for 2020 (Bertani, 2015).

The most common geothermal power plant types have been recorded as binary and single-flash systems and the others might be ordered; double-flash, dry steam, back pressure and triple-flash types for 2015 (Fig.1) and new geothermal power plants have been added each year.

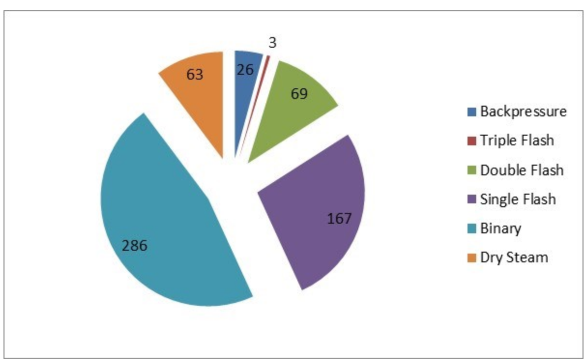

Figure 1: Number of geothermal power plants for each type (modified from Bertani, 2015)

The most important criteria for power cycle selection are reservoir temperature and energy conversion efficiency of a geothermal system. The resource assessment results indicates to a best cycle or cycles as flash, binary or advanced (flash+ binary) based on thermodynamic performance comparison in the feasibility study for water dominated systems (Lewis et al., 2015). For example; Lou and Gong (2015) have been studied to increase the energy efficiency of the geothermal resource for China. The researches have been thermodynamically compared to flash and flash + binary cycle systems at different geothermal reservoir temperatures and they says that if reservoir temperature is ranged from 130-150 ºC, the net power output of advanced (flash + binary) will be more than up to 5.5 % of double flash cycles but if the reservoir temperature higher than 130 ºC, the best solution will be multi-flash system (double-flash) because of high efficiency and low operation cost. Actually these numbers indicate low-medium reservoir temperatures, generally if the reservoir temperatures are less than 150 ºC, binary cycle has been selected for a geothermal system in the world. Flash cycles are more efficient and more economical option above this temperature for water-dominated systems (DiPippo, 2012). Multi-flash systems require higher temperatures because of multi-flash processes.

2. DESIGN OF MULTI-FLASH AND ADVANCED GEOPOWER SYSTEMS

2.1 Multi-flash Systems

If reservoir temperatures are enough high (based on the existing systems; it is higher than 200 ºC) geothermal fluids can be flashed twice or thrice in a geothermal systems. Actually the flashing process starts in the well and in different pressured separators on the surface in water-dominated systems. In these systems separated high-pressure (HP) steam is fed to the high-pressure stages of the steam turbine. The liquid phase from the HP separator is flashed again in the second (sometimes in the third) medium or low-pressure (MP or LP) separators. This additional steam is fed to low-pressure stage of the turbine and the last liquid phase is sent to reinjection lines after low-pressure separation station. Multi-flash systems can produce 15-25 % more power output than a single-flash system for a same reservoir conditions (DiPippo, 2012).

2.1.1 Double-flash Systems

Principally geothermal fluids from production well is sent to the first separator (HPS), the first separated steam enters the HP stage of turbine and the separated liquid flows into the LPS, the steam from the LPS enters the LP stage of turbine and the secondary flashing liquid is sent to injection well in double flash systems (Fig.2). Noncondensible gases and wet steam, which come from turbine, are send to cooling tower by a condenser system.

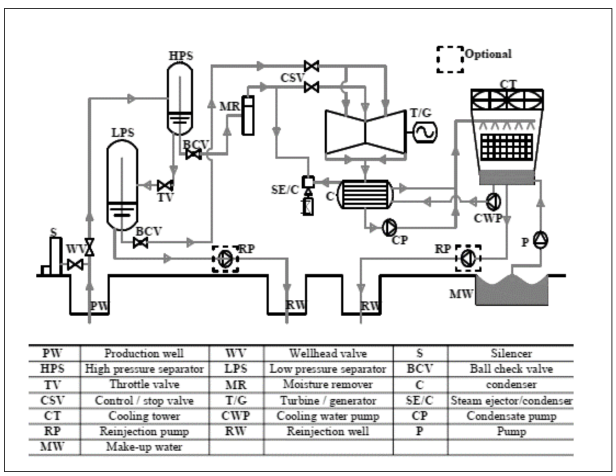

Figure 2: Basic process diagram for a double-flash plant (Zarrouck and Moon, 2014)

2.1.2 Triple-flash Systems

Triple-flash technology is quite new for geothermal power production and at the end of 2015, only three numbers triple-flash power plants are recorded (Table.1) in the world (Bertani, 2015; Haklidir Tut et al, 2015).

Table. 1 Existing Triple-flash Geothermal Power Plants (*reservoir temperature for Nga Awa Purua; Addison et al., 2015, for Hudson Rach I; US Dept.of the Interior, 1973; for Kizildere, Haklidir Tut et al., 2015)*

Plant Name	Location	Capacity	App. Reservoir Temperature	Turbine by	Operation Date
Nga Awa Purua	New Zealand	132 Mwe	above 300 º C	Fuji	2010
Hudson Rach I	Salton Sea-USA	50 Mwe	above 300 º C	Fuji	2012
Kızıldere II	TURKEY	80 Mwe (60 Mwe triple flash)	near 250 º C	Fuji	2013

Although the technology of a triple-flash system looks similar to double-flash system, the equipment used and operation issues of triple-flash cycle is more complex than double-flash system. At this system, to reduce one more time the pressure of the geothermal fluids after double-flash cycle to separate LP steam so, there are 3 different separators at a triple-flash cycle (Fig.3).

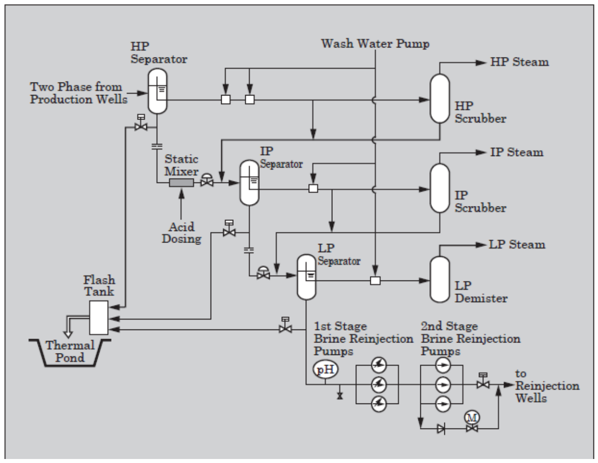

Figure 3: Basic process diagram for a Nga Awa Purua triple-flash system (Horie, 2009)

2.2 Advanced Geothermal Systems

In water-dominated systems, when reservoir temperatures increase, different energy conversion systems have developed to increase efficiency by integrating or combining different types of geothermal power plants. There are some options to combine or integrate two cycles for geopower industry. These options generally depend on technically reservoir temperature and noncondensible gas and project budget because of complex design engineering and equipment cost. Some alternatives are listed in literature such as; integrated single - double flash cycles, combined single-double flash cycles, integrated single-double flash cycles (DiPippo, 2012).

There are a few advanced geothermal systems such as single flash+ binary type in USA (Hawaii) and New Zealand (Mokai, Ngawla, Rotokawa) around the world. (DiPippo, 2012). One of the newest advanced geothermal power system was put into use in Turkey in 2013. The power plant; Kızıldere II, is located Denizli city in Western Anatolia and except this one, there is one old single-flash power plant (17.2 Mwe) has been operated since 1984 in the region (Kindap, et al. 2010).

Kizildere II plant has 9 production and 8 reinjection wells in the region (Haklidir et al, 2015). The system is quite interesting because Kizildere II geothermal power plant consists of 60 Mwe triple-flash cycle and 2x10 Mwe binary (ORC) unites and the system is combined with Kizildere-I plant at LPS part of the Kizildere-II plant. Kizildere-I plant's seperated liquid phase temperature is more than 140 °C. With this reason, before sending the waste fluid of Kizildere-I to reinjection line, it sends to Kizildere-II plant's low pressure seperator to produce more steam in this system (Fig.4). Kizildere II triple flash part consists of 3 seperator system as; HP, MP and LP and demister systems are used to provide higher quality steam to turbine in the system. The main system can be seen in Fig.5.

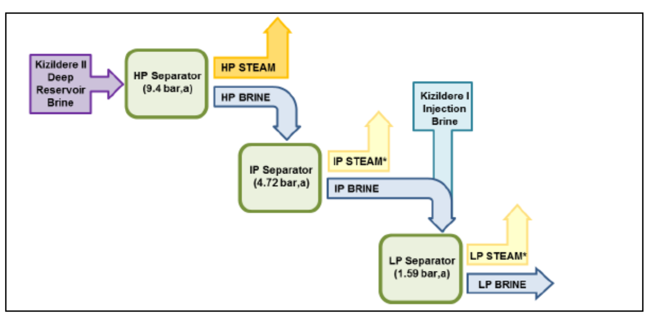

Figure 4: Basic flow diagram of Kizildere-II Geothermal Power System (Geologica, 2012)

During power cycle selection based on reservoir parameter, it was noticed that the HP turbine NCG steam exhaust was a potential heat source for a binary system (Fig.5). It looks good option for Kizildere field because the system has high concentration of noncondensible gases that dominant gas is CO_2 with almost 98% proportion in the reservoir (Photo.1).

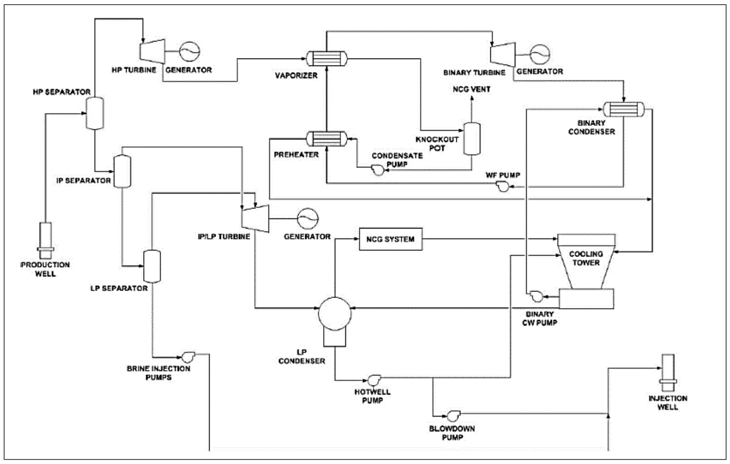

Figure 5: Basic process diagram for Kizildere (Turkey) triple-flash+binary system (Lewis et al., 2015)

Photo.1 : Kızıldere II triple-flash and binary system (Photo by Zorlu)

3. Monitoring Geofluids Behaviour at Multi-flash Systems

In this part, behavior of geofluid will be investigated for triple-flash + binary system based on Kizildere-II (Turkey), which has, consists of triple-flash + binary systems. Changing of pressure (P), temperature (T) and flow rate of geofluid is quite important to understand behavior of the geofluid and manage the geothermal system from production process to reinjection process.

3.1 The Path of Geothermal Fluids at Multi-flash Systems

After discharge of geothermal fluid, it moves to separator systems. These systems consist of different pressured separator systems at multi-flash systems. The flow rate is controlled by valves, while P, T parameters have been changed at different processes such as production, separation, reinjection. Changing of P, T is also changed mineral-equilibrium in the fluid and some minerals tend to precipitate of the different point of the system. To control scale occurrence, scale coupons are used in the system and chemical analysis and physical measurements of geofluid are performed at different part of the system.

As triple-flash system in Kizildere-II, 9 production wells are used for the feed to steam separators on 3 pressure stages (HP = 9,3 bara, IP = 4,2 bara and LP = 1,83 bara). The reservoir temperature fluid is up to 245 °C. Between wellhead and separator a control valve in the pipe reduces the pressure to a level of approx. 9,4 – 12 bara in the system. The temperature drops due to that pressure release to a level of approx. 175 °C before HPS. On that level the brines from the 9 wells are mixed and the mix is sent to the first stage of separators (2 HP separators). The residual brine is sent to the IP separators where further expansion takes place to 4,2 bara and 145 °C. After that the brine is sent to the LP separators from which it leaves at a pressure of 1,83 bar and 109 °C. Brine from phase I is also flashing LP pressure level. Before injection pumps, the brine, which comes from Kizildere-I and Kizildere -I are mixed in a pipeline which is called as collector. Total flow of the brine is around 3200 tph before the reinjection pump station. Pressured brine is injected at 108 C to reinjection line.

3.2 P, T Changes At Multi-flash and Combined Cycle Systems and Physical and Chemical Changes on Geofluids At Different P, T Conditions

Physical and chemical changes start in borehole with CO_2 and steam flashing. Concentration of some minerals and pH start to increase at that point and microcrystalline $CaCO_3$ begins to form. The second flashing point takes place after flow control valve, which is also working as pressure reducer for decreasing wellhead pressure to line pressure. Flashing for steam generation by using separators begins after these steps. The geofluid is flashed at least five times until injection pumps on the path at triple-flash system (Table.2). The chemical composition changes due to physical conditions of the systems and precipitation starts in the system. The solubility of minerals gradually decreases and the amount of microcrystalline particles increases. If these crystals don't dispersed sufficiently, the scale formation start to covers down-hole and surface facilities.

Table. 2 Pressure Changes at Triple-flash Geothermal Power Plants (Kizildere-II GPP)

Flashing No:	1		2		3		4		5	
	WHP (bara)	WHT (C)	LP (bara)	LT (C)	HP P (bara)	HP T (C)	IP P (bara)	IP T (C)	LP P (bara	LP T (C)
P& T Changes	20	203	12	182	9,3	172	4,2	145	1,83	109
Flashing Starts at:	Bore hole		After flow control valve		Inside Collector Line		After HP level Control Valve		After IP level Control Valve	

Due to the pressure reduction and the release of steam and CO_2, the pH and ion concentrations start to rise, while pH of brine is around 7 after control valve (wellhead), it is around 7.5 after the HP separators and 9.4 after the IP- and ≥ 9.6 after the LP-separators. If inhibitor treatment is not done efficiently, calcium carbonate and silicate deposition starts at first production point in Kizildere-II multi-flash system (Fig.6).9

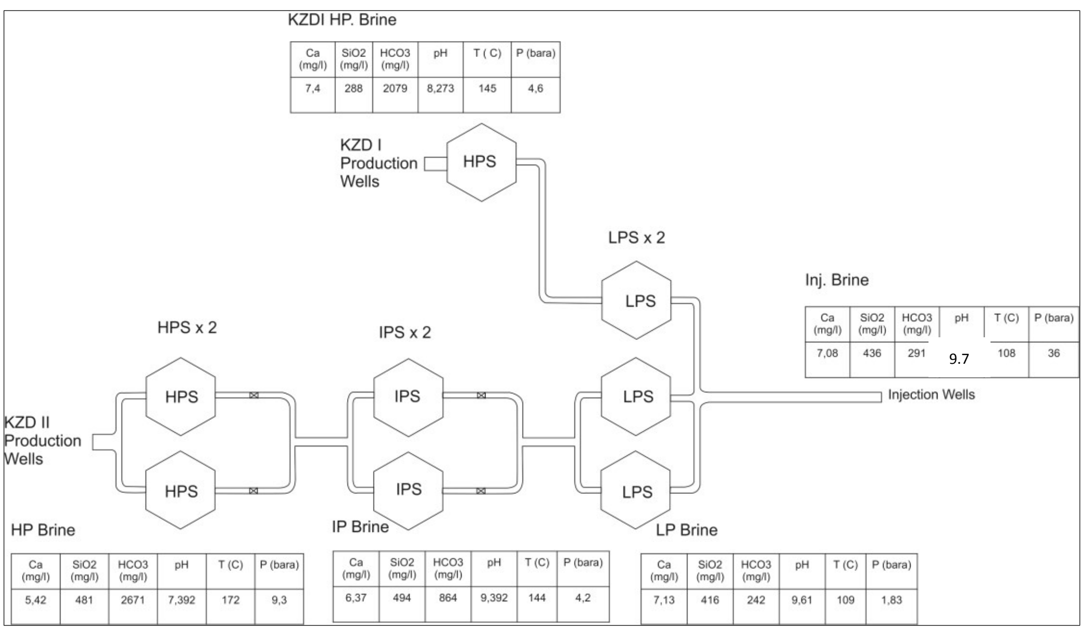

Figure 6: Mineral compositions at different separator systems and injection line for triple-flash system (Kizildere-II GPP)

Brine residence time is also important for transport the colloids or microcrystals. The fluid velocity per unit area is calculated as 2 mps for certain mass flow rates to transport micro particles. If flow rate of fluid is less than the design criteria values, the velocity also decreases .In this case, micro particles find to time to resonance of particles of the minerals in liquid phase. These particles start to merge and it causes scale occurrences. Especially after LPS, the pressure of brine is around 0.85 barg and the fluid move to injection pumps under this pressure in Kizildere-II. To prevent friction, the line diameter is designed widely that is allows little extent degassing with pumping of brine. After injection pump, the pressure dramatically increases to 35 barg and it causes slightly pH drops and increasing bicarbonate concentration in reinjection lines. The pumped brine starts to move to reinjection wells by reinjection lines. The pressure of line may be changed depends on the injectivity of reinjection well during reinjection process. The wellhead pressures of reinjection wells can be change between 25-28.5 barg in Kizildere-II. For binary units, only steam phase is used from HPS of triple-flash and scale occurrences is not expected at these units.

4. Potential Scaling Problems and Controlling and Prevention of Scaling at Multi-flash and Combined Cycle Systems

The geothermal fluid has different minerals and these minerals show different stabilities under different P, T conditions in water-dominated reservoirs. Changes of P, T conditions of the fluid cause different mineral accumulations at different points of a geothermal system.

Calcite, silica and some sulfide deposits are main scale types in a geothermal system. Calcite scaling can be seen in production wells and surface equipment, while silica can be often observed at reinjection lines and surface equipment also. In water-dominated systems, gas breakout or two-phase conditions occurs at the depth of borehole. Under dynamic conditions at depth, when measured total pressure lower than P_{gas} +P_{liquid}, flashing process starts (Haizlip Robinson et al, 2012). Calcite and silica stabilities are incompatible under same conditions in a geothermal system.

4.1 Potential Scaling Types and Scale Occurrence Points

Potential scaling types are directly depends on chemical compositions and P, T conditions in a geothermal system. Calcite, amorphous silica, different silicate minerals and some sulfide minerals such as stibnite (especially in heat exchangers) can be seen in geothermal systems.

As a case study, Kizildere geothermal system has multi-reservoirs. The main reservoir rocks are Paleozoic carbonates and Menderes Metamorphics. The average reservoir temperature is around 225 °C and the dominant gas is CO_2 with 98 %, average noncondensible gas concentration (ncg) in deep reservoir around 0.03 kg ncg/kg and 0.015 kg ncg/kg in intermediate reservoir in Kizildere (Haizlip et al, 2013). The main water chemistry is given Table. 3.

Table. 3 Water Chemistry in Kizildere Geothermal Wells (Haklidir et al, 2015)

Well ID	Unit	Sampling Date	WHP (barg)	ph (20-22 °C)	K	Na	Ca	Mg	Li	Fe	Bt	SiO2*	$NH4^+$	$CO3^{2-}$	$HCO3^-$	Cl^-	$SO4^{2-}$	F^-	Br^-	As	PO4	Hg
KD-23B	mg/l	05.01.2011	11,9	6,9	228	1304	1,33	<1	4,3	0,08	22,3	697	8,3	<10	2515	110	653	20,6	0,6	0,91		<0,005
KD-23D	mg/l	17.01.2010	13,9	6,7	209	1295	1,08	<1	4,1	0,05	24,1	503	11,3	<10	2487	104	591	18,2	0,9	0,98	<0,1	<0,005
KD-18A	mg/l	05.06.2011	12,5	7	220	1165	1,45	<1	3,8	<0,05	21	552	10,3	<10	2577	115	638	19,2	0,8	1,26	0,3	<0,005

At Multi-flash systems; especially at triple-flash systems, geofluid has been exposed different P conditions. Pressure and temperature differences in the system will directly affect the composition of geofluid and it may cause different scale types in the system (Table.4, Fig.7). The scale samples of different 12 points were taken from except from boreholes at Kizildere triple-flash systems (Table.4). CaO, Al_2O_3, SiO_2, MgO minerals are observed between HPS and brine injection line that indicate pressure drop points highly critical places to scale occurrences and need to eliminate of the system.

Table. 4a Some Scales Compositions in Kizildere Triple-flash System 4b. Sampling Points

Element	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	Cl	K2O	CaO
Dimension	%	%	%	%	%	%	ppm	%	%
1	0,077	14,55	2,068	27,78	0,104	0,05915	11,1	0,3826	11,41
2	< 0,014	6,012	1,182	12,46	0,7029	0,03284	5,6	0,1876	36,66
3	< 0,014	19,33	2,593	38,52	0,1619	0,00898	< 2,0	0,5412	12,66
4	< 0,014	18,83	2,413	37,34	0,4684	0,07548	33,3	0,3394	2
5	< 0,014	10,79	1,626	21,65	0,2876	0,02907	2,9	0,382	17,93
6	< 0,031	18,45	2,57	36,87	0,02047	< 0,00051	< 2,0	0,5908	1,805
7	< 0,031	18,12	2,569	36,58	0,02022	< 0,00051	< 2,0	0,6118	2,07
8	< 0,014	13,37	2,006	28,39	0,1344	0,04981	11,8	0,4737	12,29
9	< 0,014	11,88	1,644	23	0,2068	0,0126	0,8	0,369	14,61
10	< 0,014	10,18	1,397	19,85	0,2334	0,02614	< 2,0	0,2516	25,21
11	< 0,014	17,87	2,635	35,49	0,09957	0,00711	0,6	0,5005	4,742
12	< 0,014	16,98	2,341	32,58	0,06733	0,03976	16	0,478	4,506

Numbers	*Sampling Point*	*Numbers*	*Sampling Point*
1	Before P-LP Level Control Valve (LCV)	7	After HP-IP LCV
2	After HP-IP LCV	8	After P-LP LCV
3	After HP-IP LCV	9	Before P-LP LCV
4	Before HP-IP LCV	10	After P-LP LCV
5	Before P-LP LCV	11	On HP-IP LCV
6	On P-LP LCV	12	Before HP-IP LCV

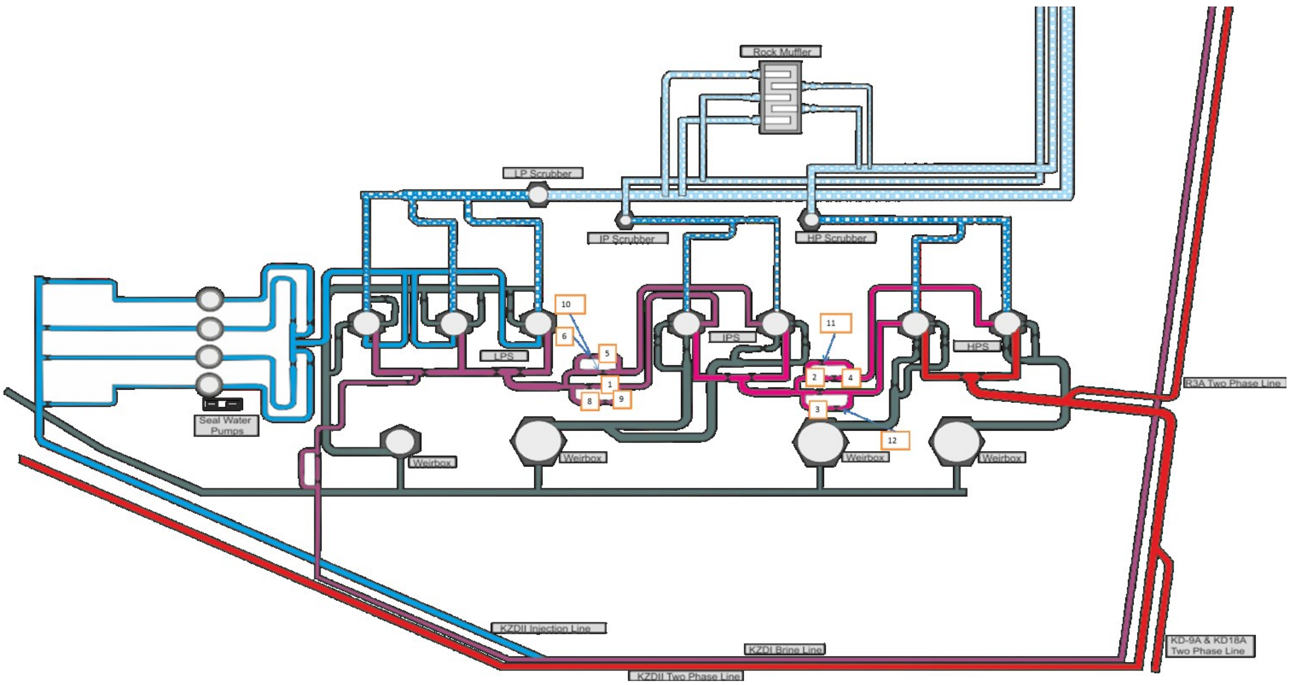

Figure 7: Possible scale points in the triple-flash System (Kizildere-II GPP)

4.2 Controlling of Scale Occurrences

There are limited methods to control of the scale occurrences in a water-dominated system. These are; pH control in of liquid phase, controlling of boiling point in borehole, mechanical and chemical cleaning and using chemical inhibitors. Except from using chemical inhibitors, these methods are hardly applicable and insufficient ways to treat of the complex systems.

4.3 Scale Prevention by Chemical Inhibitors

Firstly it is necessary to determine the expected deposition types for different points of the system. Saturation index calculations should be helpful to identify possible precipitation types in geothermal systems. Chemical inhibitors can be classified as; polymer type, phosphonate (acid or salts) type and polymer + phosphonate type. Reservoir temperatures, geothermal power type, water, gas compositions of geofluid, materials of equipment and field test are quite important to find correct inhibitor or inhibitors for a geothermal system. After selection of the correct inhibitor, dilution factor, dosage points and dosage amounts are critical parameters to correct scale inhibitor application in the system.

To prevent scaling in a production well, the chemical inhibitor must be injected into the flowing well through tubing at 10-50 m below the estimated gas-breakout depth. Sometimes one dosage point can be not enough to prevent scale to protect of surface equipment before separator systems. With this reason, after wellhead, before the valve the second dosage point set to the system at high temperature systems (Haklidir Tut and Haklidir, 2015). At multi-flash system, chemical dosage systems must be installed before high pressure drop points to protect the mechanical equipment also. To observe scaling conditions, control coupons can be set before and after critical pressure drop points in the multi-flash system. Calcite and silica minerals in water phase can be monitored by periodically chemical analysis for a geothermal system also.

4.4 Stability of Scale Inhibitors At Different P, T Conditions

Most scale inhibitors start to decompose while travelling inside capillary tubing. It's always recommended that the travelling time of inhibitor inside the tubing should be approximately one hour especially the temperature over 220 °C. Inhibitor inside the tubing starts to be gel form. If travelling time is long enough, inhibitor mixture burns and turns to powder like crystalline structure. Almost all types of inhibitors (phosphate salts or polymeric) may give the similar results during field tests at high temperatures. But it can be observed that polymer-based inhibitors are relatively more stable compared to phosphate salts at high temperatures.

High concentrated polymer and phosphate inhibitor mixtures may give more effective results instead of using them individually. Temperature resistance of phosphate salts is minimal. Polymer particles are dispersed them before practical size growth, if phosphate loose its stability and tends to create precipitate. Increasing the dilution rate with water mostly helps to minimize degrading.

Losing the stability of the inhibitors in down hole, surface facilities like flow control valves, separator's vessels and equipment requires extra dosage points. For double-flash systems, the secondary feed point can be set before the well-side flow control valve. However, brine chemistry may require another dosage point in the separation area at a triple-flash system. Based on field experiences, degrading starts at the first contact with geofluid at high concentration at the system and;

1. If the polymer type inhibitor degrades, it transforms to white or brownish a fragile, thick plastic covering,
2. If the phosphate salt degrades, it transforms to hard, low acid reacting, structured like rice or fish-scale, mostly white (If exposed to extreme temperatures, it shows black color) calcium phosphate scale,
3. If mixture degrades, it transforms to blackish green powder.

As a case study; 3 different inhibitor applications have been tried to prevent scale occurrence and find the best application at Kizildere multi-flash system in 3 years;

Case –I The First Inhibitor Application

Inhibitor a: For calcite dispersion (polymer type with 5.6 pH in borehole) ; *Inhibitor b:* For calcite inhibition (phosphonate type with 7.3 pH after wellhead before the valve); *Inhibitor c*: $CaSO4$, $CaPO4$, $SiO2$ dispersion; (different polymer type before LPS).

Result: Na + some organic scale was precipitated in borehole.

Case –II The Second Inhibitor Application

2 different type inhibitors have been used to prevent scale occurrence in the system.

Inhibitor a: For calcite dispersion; polymer (20%)+ phosphonate (30%) type used in borehole; *Inhibitor b*: For calcite inhibition; polymer (30%)+ phosphonate (20%) type used after wellhead before the valve .

Result: The scale occurred at the LPS flash point and inhibitor was solidified in the borehole.

Case-III Inhibitor Application:

2 different type inhibitors are being used to prevent scale occurrence in the system.

Inhibitor a: For calcite dispersion; polymer (45%) + phosphonate (25%) type inhibitor (ph of the solution is 8.8) used in borehole and before HPS, *Inhibitor b*: To prevent calcite; polymer+ phosphonate acid type (pH of inhibitor is around 1.3, the solution ph is around 6) used before IPS and LPS.

Result: This is the most effective inhibitor application for Kizildere Phase-II.

5. CONCLUSION

Operation and maintenance of multi-flash geothermal are more complex than other geothermal power plant. Different P, T conditions require different control and treatment applications at multi-flash systems. Especially a triple-flash system has 3 types steam separator systems such as HPS, IPS, LPS and it means high pressure drops will be recorded beginning of the fluid production process to reinjection process in this system. Each P, T changes cause mineral precipitation in the system and it is quite critical to control and prevent these deposits to provide interrupted power production in a power plant. These deposits can be occurred in borehole, in surface equipment (pipelines, separators, valves and even steam turbine blades), in reinjection lines and reinjection wells. Scale inhibitor application is generally the best solution to control and prevent different type deposits in a geothermal system. Selection of suitable chemical inhibitor, finding correct dosage points, after field tests finding optimum inhibitor dosages with correct dilutions can extend the lifetime of wells, equipment and a geothermal power plant. In some cases, polymer type inhibitors are not sufficient to prevent scaling and polymer+phosphonate types mixtures may show more effective results in high temperature geothermal systems.

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