

## Constraint Problems and Solution Alternatives for Potentially Available Integrated Geothermal Energy Utilization in Turkey

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### ABSTRACT

From enthalpy point of view there are eleven geothermal fields in Turkey, which are apparently available for integrated geothermal energy uses. Namely, they are Kizildere, Tekkehamam, Aydın-Germencik, Salavatlı, Seferihisar, Balcova, Yılmazkoy, Canakkale-Tuzla, Simav, Manisa-Caferbeyli and Manisa-Göbekli. The temperatures of the prospective fields are in the range of 100 to 242 °C. The potential of those fields is of great importance. The expected potential is as much as 75 MWe for single flash, 71 MWe for binary cycle and 1609 MWt for district heating applications.

For achieving the continuous development in both direct and indirect geothermal energy utilization, beside technological innovation the solution alternatives to corresponding operational and environmental restrictions have become necessary.

The chemical nature of the geothermal areas generally poses some technical constraints to developments. The fluids produced from the geothermal areas subjected to this presentation contain various quantities of soluble species and dissolved gases. The scaling of calcite and silica minerals is often associated with the utilization of geothermal fluid.

The objective of this paper is to put down the potential and problems associated with the utilization and offers a general description of the geothermal fields for achieving the continuous development in Turkey

### 1. INTRODUCTION

Prior to discussing the specifics of geothermal constraint problems, it is useful to examine the available potential of those field subjected into this study. Turkey has a high geothermal potential as a result of its suitable geological situation: the presence of young volcanism, extensional tectonics (horst-graben systems) and hydrothermal altered areas (Simsek 1997).

There are approximately a total of 1000 thermal and mineral water spring groups throughout the country. Geothermal resources in Turkey vary in temperature from 30-242 °C, and are either in the form of a mixture of steam and water or just liquid water (Simsek et al 2000). The high (<240 °C) and moderate-low geothermal fields are found in the western part of the country (Figure 1).

The utilization of geothermal energy in the form of electricity generation has been realized only in Kizildere geothermal field of Turkey. The total potential of all the fields, which are suitable for electricity generation is approximately, is 1610 MWt.

A combination of conventional flash and binary cycle technology is becoming increasingly popular in the world and in Turkey. In flash power plant, after the steam and water is separated in a pressure separator, with the steam piped to the power station where it drives one or more steam turbines to produce electric power, the separated geothermal water can be utilized in a binary cycle type plant to produce more power. Aydın-Germencik and Kizildere Geothermal fields are two geothermal fields in Turkey, which can be used in combination of conventional flash and binary cycle technology. A single flash power plant with 20.4 MWe installed capacity has been working since 1984 in the Kizildere geothermal field. 1000 kg/s wastewater with temperature of 147 °C is being disposed from the power plant. This amount of water can be utilized efficiently to produce more power from that field. Investigation on the thermal waste fluids after separator was carried out as well as analysis of scaling in this field. Another high temperature geothermal field, Aydın- Germencik which has 231 °C reservoirs temperature can also be used in combination way. The other nine moderate-low temperature geothermal fields can be utilized only in binary and/or hybrid cycle systems or in district heating.



Figure 1. Distribution of high and moderate geothermal fields in Turkey

### 2. POSSIBLE BINARY CYCLE POTENTIAL OF THE 11 FIELDS

In reservoirs where temperatures are typically less than 220 °C, but greater than 100 °C, binary cycle plants are often utilized. The illustration below shows the principal elements of this type of plant (Figure 2) (World Bank Group). The reservoir fluid (either steam or water or both) is passed through a heat exchanger, which heats a secondary working fluid, which has a boiling point lower than 100 °C. These are typically organic hydrocarbon fluids such as isobutene, isopentane or isopropane, which are vaporized and are used to drive the turbine (Maghiar et al, 2001).

As discussed in the previous section, there are only two geothermal fields in Turkey that can be used to generate electricity by direct drive steam turbines. From these, Kizildere has been in utilization since 1984 with 20.0 MWe

single flash installed capacities. Since the separation pressure of the steam is 4.5 kg/cm, the outlet of discharged wastewater from the separators at Kizildere is 147 °C. The steam ratio of the fluid at this separation pressure is changeable from 10 % to 18 % depending on inlet pressure and temperature. In average, 85 tons/h of wastewater with 147 °C temperatures is discharged from separators to produce each hour MW of electrical power. The present operational capacity of the Kizildere power plant is 14.5 MWe. The discharged water which corresponding to this power generation capacity is approximately, 1293 tons/hour. When the problems, which arise from lowering the outlet temperature, are solved, from this amount of disposed water at least, 16 MWe additional electrical powers can be produced in a binary cycle power plant (Yildirim et al, 2003). The estimated capacity of the Aydin-Germencik geothermal field is 55 MWe within flash power. It has not been any power plant installed on this field yet. Supposing that Aydin-Germencik is also operated with the same condition as in Kizildere, the amount of the electricity that can be generated by binary system from the Germencik will be approximately 21 MWe.

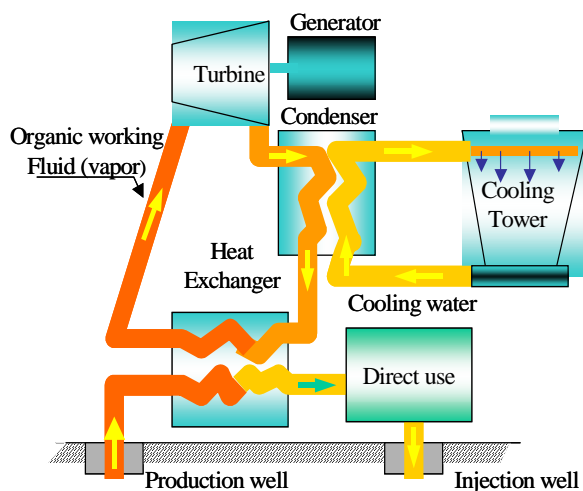


Figure 2: Simplified binary cycle power plant

The curves in Figure 3 give an indication of the electrical power output from the binary plant systems over a range of flows and geothermal reservoir temperatures of the moderate geothermal fields in Turkey.

Prospective total 'Binary Cycle' electricity production capacity of Turkey from the Kizildere and Aydin-Germencik fields with flash power plants discharges, together with that of the other moderate- low geothermal fields potential, is shown in the Table 1. Binary cycle type plants are usually between 7 and 12 % efficient depending on the temperature of the primary (geothermal) fluid. The higher the temperature of the fluid becomes, the more efficiently the electricity can be generated. The electricity that can be generated is proportional to temperatures and flow rate. This can be seen clearly in figure 3.

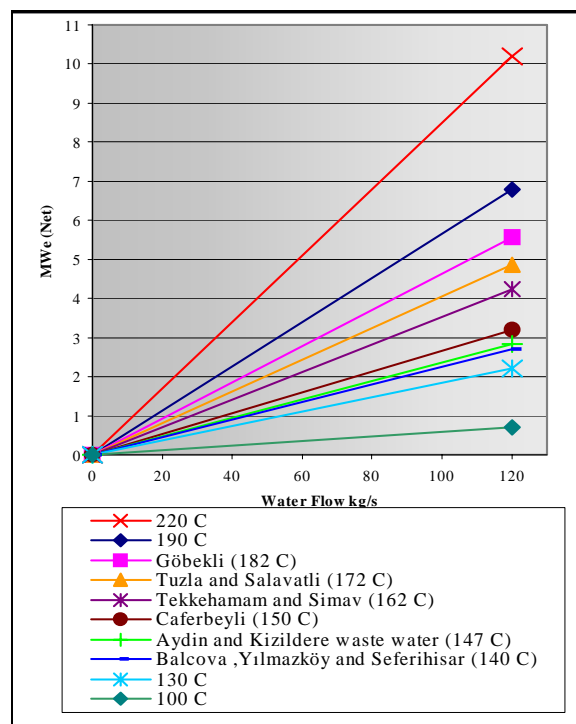


Figure 3: Net power versus flow rate from known temperature geothermal fluids

Table 1: Measured temperature, present flow rate and total thermal potential of the fields

Name of Fields	Number of Wells	Depth of Wells (m)	Temperature Range (°C)	Total Flow Rate (kg/s)	Possible Potential	
					MWe	MWt
D-Kizildere	10	510-2261	190-242	666.20	16.0	485.2
D-Tekkehamam	2	615,5-2001	116-162	26.60	1.0	11.6
A.Germencik	9	285-2000	203-231	907.90	21.0	699.1
A.-Salavatli	2	960-1500	167-172	185.40	7.5	104.4
A.Yılmazkoy	1	1501.00	142	30.00	0.7	13.4
I.Balçova	27	100-1000	91-140	297.75	6.7	116.5
I.Seferihisar	3	1232-2009	56-145	10.15	0.5	4.6
M.Göbekli	1	1447.1	182	15.00	1.0	9.2
M.Caferbeyli	1	1189.00	150	2.00	0.2	0.9
K.Simav	12	65,80-958	51-162	354.13	12.5	126.4
Canakkale	2	81-814	90-174	101.70	4.0	38.5
Total	73			2596.8	71.0	1609.5

### 3. FLUID CHEMISTRY

The chemistry of the geothermal fluid is very complicated. A resource with high salinity fluids, high silica concentrations, high gas content, or acidic fluids can pose technical problems, which may be costly to overcome. The main analysis results of the selected fields for integrated uses in Turkey are illustrated in (Table 2). Water in the most fields is a dilute solution, containing mostly sodium, potassium, lithium, bicarbonate, sulfate, chloride, borate and silica. Boron (B), which is harmful for the crops in the agriculture activities, is contained in the geothermal west in high concentration.

Four primary types of water were identified for the fields (Yildirim and Guner 2003). In particular, except as in Canakkale Tuzla and Izmir-Seferihisar field's water is of Na-Cl type, the end member of other geothermal field's

water tapped from the geothermal reservoirs is of Na-HCO<sub>3</sub> type. Mixing phenomena between this end member and shallow (which is of Ca-HCO<sub>3</sub> and Ca-SO<sub>4</sub>) are found in some places. Before we examine the different sides of the constraints problems, it appears useful to recall the chemical composition of low temperature geothermal fluids in general. General considerations show that such geothermal fluids have the following general characteristic:

-Most of low temperature resources contain from 500 to 15000 mg/l of TDS

-Minor constituent (Li, Sr, Fe, Al, Mn, Br, I, F) ranges between 0.000005 and 5 ppm

-Trace constituent (Ge, Ga, Mo, Hg, Cd, Cu, Zn) is less than 0.000005 ppm

-The pH ranges from 6.0 to 9.0 in unlashd fluid

-Bicarbonate constitutes at least 40 percent of the total dissolved solids

-Non-condensable gas is less than 3% in the aquifer fluid. Most of the gas is CO<sub>2</sub>

-H<sub>2</sub>S and NH<sub>3</sub> are present in low percentage

**Table 2: Chemical analysis of the geothermal fluids**

Place	Kizil dere	Tekke Hamam	Ger- mencik	Sal- vatli	Yılmaz- köy	Çanakkale Tuzla
Reserv.(°C)	242	162	231	172	140	173
Sampling(°C)	98	97.2	98	97	97	100
µS/25°C	5500	4000	7100	4600	5150	70000
pH/25°C	9.25	8.07	8.3	7.67	6.7	7.0
Na mg/l	1400	750	1775	1100	1200	22250
K mg/l	138	75	170	90	105	2125
NH <sub>4</sub> mg/l	14	17	4.8	0.67	3.7	2.6
Ca mg/l	1.2	12	1.6	14	40	5715
Mg mg/l	0.6	12	0.5	1.2	32	101
As mg/l	0.72	0.28	0.9	<0.1	<0.1	-
B mg/l	26	12.1	68	42	67	35
Li mg/l	-	-	3.5	6.0	1.7	74
SiO <sub>2</sub> mg/l	450	210	475	210	252	123
HCO <sub>3</sub> mg/l	1342	446	1342	2831	1900	55
CO <sub>3</sub> mg/l	720	-	0.0	0.0	0.0	0.0
SO <sub>4</sub> mg/l	735	1350	74	170	98	176
Cl mg/l	136	76	1818	223	170	44140
F mg/l	21.7	8.3	8.0	0.8	2.8	-
Chemical Properties	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	Na-Cl	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	Na-Cl
Place	İzmir Balçova	İ.Seferi- hisar	Simav Eynal	Manisa Göbekli	Manisa Caferbey	
Reserv.(°C)	140	137	162	182	150	
Sampling(°C)	98	96	96	98	86	
µS/25°C	1518	33500	2075	5260	2025	
pH/25°C	8.7	6.8	8.7	8.6	7.25	
Na mg/l	395	6558	600	1520	320	
K mg/l	24	734	61	86	40	
NH <sub>4</sub> mg/l	1.5	3.9	0.1	<1.0	3.4	
Ca mg/l	27	1120	5.5	5.4	54	
Mg mg/l	2.7	150	1.3	<0.1	25	
As mg/l	<0.01	0.1	1.0	-	<0.1	
B mg/l	13	20	5.4	116	30	
Li mg/l	1.5	10.8	1.0	4.8	1.2	
SiO <sub>2</sub> mg/l	270	198	218	274	267	
HCO <sub>3</sub> mg/l	622	454	460	2723	1031	
CO <sub>3</sub> mg/l	0.0	0.0	130	698	0.0	
SO <sub>4</sub> mg/l	143	606	483	27	98	
Cl mg/l	176	11698	73	170	64	
F mg/l	14	38.7	18	3.9	1.7	
Chemical Properties	NaHCO <sub>3</sub>	Na-Cl	NaSO <sub>4</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	

#### 4. TROUBLES ENCOUNTERED DURING UTILIZATION

Future geothermal development in Turkey largely depends on the progresses of constraints solution technologies. As in most high enthalpy water dominated geothermal fluid, also low-moderate temperatures geothermal fluids of Turkey contain dissolved gases and solids whose thermodynamic behavior during utilization cycle cause troublesome either corroding the metal surfaces or causing scaling. The chemical composition of the geofluids varies almost from pure water to hot brine containing 60.000 ppm of dissolved solids. Turkey has more than 600 hot springs, which their dissolved solids range between 500 and 60000 ppm (Simsek 1986). Steam from the major geothermal fields of Turkey has a content of non-condensable gases that ranges from 10 % to 20 % of steam in volume. Carbon dioxide is the major component, but its emission into the atmosphere is below the figures for natural gas, oil or coal-fired power stations per kWh generated.

From what has been said, it can be concluded that knowledge of the chemical composition of the geothermal fluid is essential to predict the behavior of materials in the low temperature geothermal environment (Yildirim 1997).

Furthermore the geothermal fluid, which comes into contact with atmospheric air in pumping station and surface flow lines, may contain some amount of dissolved oxygen.

In this case, the concentration of oxygen may reach approximately 10 ppm. The water having chemical characteristics shown in Table 1 may cause both corrosion and scaling problems. In both cases the thermodynamic conditions of the geothermal fluid during utilization play important role (Yildirim et al, 2003). The type of solid, which precipitates during the geothermal cycle, depends on the chemical composition of the fluids, temperature and pressure. Naturally, low temperature geothermal fluids are saturated with scale forming material under equilibrium conditions. So any changes in thermodynamic conditions of geothermal water result in carbonates sulfate and silicate scaling.

When hot waters discharge from hot springs or geothermal wells, chemical reactions and evaporations occur with changing temperature, pressure etc. Then, suspended or muddy materials are formed by chemical reactions and microorganism's activities.

Low temperature geothermal deposits are not similar to hydrothermal deposit under high temperature condition. In general, the deposits are amorphous and mixture, because they are formed from complex solution composition and mechanism. The scale deposited from discharging geothermal fluid from a well is not complicate such as hot spring deposit. Deposits from the discharging well are mainly constituted of carbonates, while deposit from hot spring is formed from variety of compounds.

Wells drilled in Marble sector intersected rocks with abundant calcite formation was detected during their initial-medium term discharge testing prior to their utilization. The flushing within the well bores induces the formation of calcite. Calculation of calcite saturation index of the fluid from these field wells showed highly supersaturated levels in the flushed state. Considering the chemical analyses of the fluids from prospective fields for the binary cycle uses in Turkey, the below result has obtained for scaling and

corrosion tendencies of water according to "Langelier Saturation Index " (Table 3).

**Table 3: Saturation index for the geothermal fields**

Fields Name	pH	pHs	SI	Characteristics
Denizli- Kizildere	9.25	7.75	+ 1.50	Incrustative
Denizli-Tekkehamam	8.07	7.90	+ 0.17	Incrustative
Aydin-Germencik	8.3	7.3	+0.90	Incrustative
Aydin-Salavatli	7.71	6.75	+0.96	Incrustative
Aydin- Yilmazkoy	6.70	6.25	+0.40	Incrustative
Izmir Balcova	8.7	7.8	+1.10	Incrustative
Izmir- Seferihisar	6.8	6.8	±0.00	Neutral
Kutahya-Simav	8.7	8.1	+0.60	Incrustative
Manisa -Gobekli	8.6	7.25	+1.35	Incrustative
Manisa-Caferbeyli	7.25	7.0	+0.25	Incrustative

Workover operations were conducted in all of the Kizildere wells to clear the calcite blockages that had significantly reduced the output of the field. Calcite formation also has had a negative impact in other examined geothermal fields, that have been considered for integrated utilization. Calculation of The most frequent non-condensable gases that emitted along with geothermal vapor of the studied fields are CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub>. The percentage of the CO<sub>2</sub> among these gases almost reaches to % 99. Despite the fact that carbon dioxide forms a greater portion compared to other gases, it does not create negative environmental effects. But, during the up-flow of the water in the well bores, fluid pressure decreases, CO<sub>2</sub> separates from the liquid phase and pH increases. Consequently, CaCO<sub>3</sub> deposition occurs inside the well bores and in surface equipments and separators.

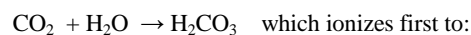
As can be seen, all of the fluids that are the subjects of this study are incrustative. It means they are liable to cause CaCO<sub>3</sub> deposition during up-flow in the well bores, in the separators and in the heat exchangers of the binary cycle plants.

#### 4.1. Corrosive agents in the geothermal fluids

Oxygen (O<sub>2</sub>), hydrogen (H<sup>+</sup>), carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloride (HCl) are the main corrosive species in geothermal fluids. These species involve in the major processes of the corrosion by the ways of redox reactions, hydrolysis and formations of complex components. In some cases, scaling prevents corrosion and corrosion yields active surfaces for scaling to start nucleation. But mostly mineral depositions promote the corrosion by causing local passive anodic regions on metal. Here is some of the components involve in corrosion processes in geothermal applications:

##### 4.1.1 Carbon dioxide (CO<sub>2</sub>)

CO<sub>2</sub> is a stronger acid than H<sub>2</sub>S. It combines with water to form carbonic acid:



The contribution of  $\text{CO}_2$  in corrosion of equipments is increasing acidity by  $\text{H}^+$  ion generation. Its product  $\text{FeCO}_3$  is often found on the geothermal pipe systems.

#### 4.1.2 Hydrogen ion (pH)

In most oxygen-free geothermal environments, the corrosion of carbon and low alloy steel is largely controlled by the reduction in hydrogen ions. The corrosion rates of the steel equipments decrease rapidly as pH increases.

#### 4.1.3 Chloride ion (Cl)

Major effect of chloride in the geothermal fluids is the breakdown of passivity of passivated alloys. Rapid pitting, crevice corrosion and stress corrosion cracking of some stainless steels can occur even in dilute chloride solutions if oxygen is present.

#### 4.1.4 Sulfate ion ( $\text{SO}_4$ )

Sulfate plays a minor role in most geothermal fluids. In some low-chloride geothermal fluids, sulfate may be the main aggressive anion.

#### 4.1.5 The contribution of dissolved salts

Saline geothermal water is usually considered to be more corrosive than low salinity or fresh water. However, neutral dissolved salts such as sodium chloride ( $\text{NaCl}$ ) or calcium chloride ( $\text{CaCl}_2$ ) are not the primary corroding species. They promote or accelerate corrosion if one or more of the three corrosive gases ( $\text{O}_2$ ,  $\text{CO}_2$  or  $\text{H}_2\text{S}$ ) are present in the solution.

Dissolved salts also have other effects that can be either good or bad. While they increase the electrical conductivity of the electrolyte, the salts reduce solubility of dissolved gases such as  $\text{O}_2$ .

#### 4.1.6 Ammonia species

Ammonia is known for its ability to cause SSC (stress corrosion cracking) of many copper alloys in geothermal brines. Ammonia species concentration is not high in our geothermal fields.

#### 4.1.7 Effects of microorganisms

In geothermal water flow lines, accumulations of bacterial slime and molds contribute to corrosion of steel equipment. In oil and geothermal producing operations, the major bacteria-related corrosion problem is attack by hydrogen sulfide that generated by metabolic processes of certain organisms. Bacterial accumulation or heavy slime deposits can promote corrosion by creating differential oxygen cells on steel in aerated geothermal water.

#### 4.1.8 Relative corrosiveness of dissolved gases

Figure 4 shows a comparison of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$  relative corrosiveness under specific conditions. Corrosiveness is defined as measure of corrosion damage at certain concentration of corrosive dissolved gases in water. From the Figure 4, it can be noted that 1 ppm of  $\text{O}_2$  is as corrosive as 100 ppm of  $\text{H}_2\text{S}$  or 50 pip of  $\text{CO}_2$  under the test conditions. Note also that corrosion rates are virtually proportional to dissolved gases concentration.

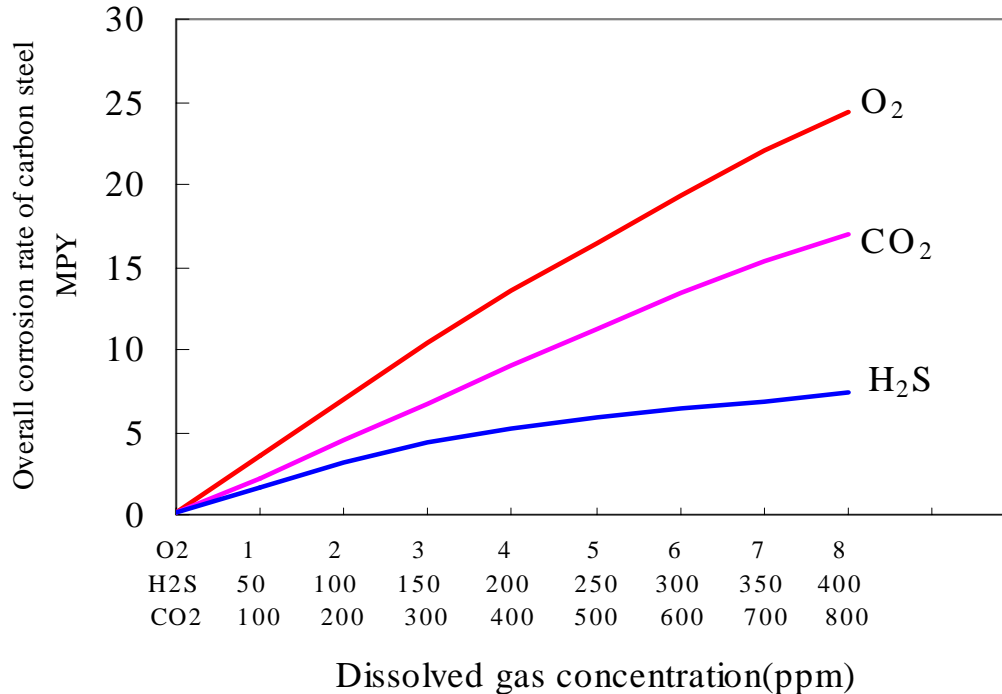


Figure 4: Relative corrosiveness of three common gases in geothermal fluids

#### 4.2. Corrosion protection in geothermal application

Corrosion of metallic materials can be reduced by various methods (Hayashi 1993):

- Protection by change of metal and design.
- Protection by change in the corrosive medium.
- Protection by change of the electrode potential.
- Protection by means of using inhibitors and surface coatings.

Using inhibitors seems to be more convenient than other protection ways in the geothermal operations. In low-temperature geothermal applications, the corrosive medium can be changed by the removal of corrosive constituents such as:

- (i) Elimination of oxygen from water by evacuation, by saturation with nitrogen or by addition of oxygen scavengers.
- (ii) Elimination of acid from water by neutralization.
- (iii) Elimination of salts from water by ion exchange.
- (iv) Elimination of water from air by dehumidifying.
- (v) Elimination of solid particles from water by filtration.
- (iv) Lowering of relative humidity.

The corrosive medium can also be changed by addition of corrosion inhibitors. Inhibitors are added to the corrosive medium to retard the anode or cathode process of corrosion. Double-acting adsorption inhibitors retard simultaneously both anode and cathode processes. The inhibitors can be grouped as inorganic, organic, anionic and cationic. Crystalline salts such as sodium chromate, sodium silicate, sodium phosphate or sodium molybdate are some examples to inorganic inhibitors. Amine structure and organic phosphate groups fall into organic class corrosion inhibitors.

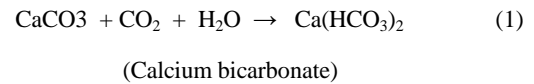
It was discovered that complex salts such as sodium chromate ( $\text{Na}_2\text{CrO}_4$ ), sodium phosphates ( $\text{Na}_3\text{PO}_4$ ) and sodium nitrite ( $\text{NaNO}_2$ ) arrest oxygen corrosion especially when the alkalinity of geothermal fluid increased with NaOH. Complex phosphates such as sodium hexametaphosphate ( $\text{Na}_2\text{P}_6\text{O}_{18}$ ) are found to be useful in preventing corrosiveness at geothermal applications. It is found that Chromate, nitrites and molybdates inhibitors apparently act by promoting formation of stable iron oxide on steel

#### 4.3. Calcium carbonate precipitation mechanism and protective methods

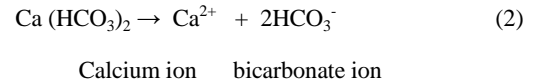
Well logging measurements show that calcium carbonate scale starts to deposit at the flashing part in high enthalpy wells and at "gas bubbling point" in low temperature wells. The point where  $\text{CO}_2$  begins to release from the solution is called "gas bubbling point".

Releasing of  $\text{CO}_2$  gas either by flushing or bubbling causes a shift in chemical equilibrium from bicarbonate to insoluble carbonate according to following reaction (Yildirim 1989). But, first let's see how the bicarbonate comes into the geothermal brines:

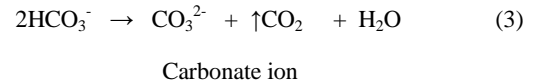
- i) Solution of  $\text{CaCO}_3$  by  $\text{CO}_2$  at elevated pressure



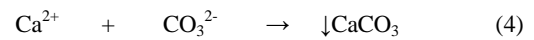
- ii) Ionization of soluble bicarbonate in water



- iii) Release of  $\text{CO}_2$  and equilibration of  $\text{HCO}_3^-$  to insoluble  $\text{CO}_3^{2-}$  ions



- iv) Precipitation of insoluble calcium carbonate



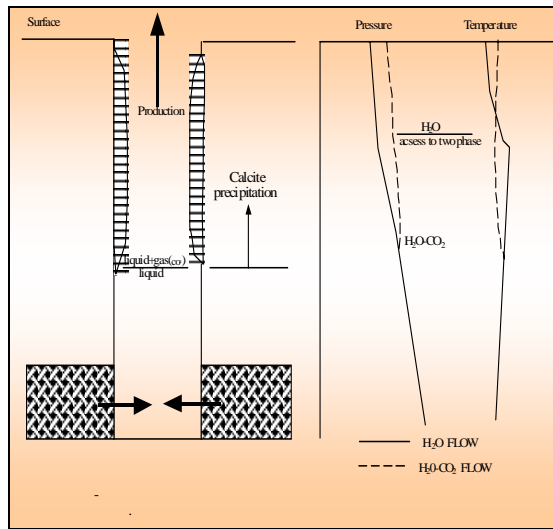
Normally all of the studied geothermal waters are close to saturation with calcite. The decrease of pressure, namely flash, causes loss of carbon dioxide and hence increase in pH accordingly, reaction (3) shifts to the right and carbonate ion concentration in hot water increases. The solubility of  $\text{CaCO}_3$  increases in proportion to partial pressure of  $\text{CO}_2$  (Ellis et al, 1963). Water such as geothermal one, which was originally close to saturation with calcite rapidly, becomes supersaturated and the reaction between the carbonate ion and calcium ion takes place to form insoluble calcium carbonate.

Calcium precipitation in flow lines can be summarized as follows (Figure 5):

1. As the water rises up in the well bore, the pressure drops,
2.  $\text{CO}_2$  release the liquid phase and forms gas phase
3. The pH of liquid increases,
4.  $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ , ( $\text{CO}_3^{2-}$  formed)
5.  $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \downarrow\text{CaCO}_3$

Calcium sulfate,  $\text{CaSO}_4$ , is another salt causing troublesome deposits or scales in geothermal operations. Many producing formations contain anhydride crystals or anhydrous  $\text{CaSO}_4$ . Formation water dissolves some amount of anhydride depending on temperature, pressure and concentration of other salt such as NaCl. Solubility varies from about 1500 to 6000 mg/l.



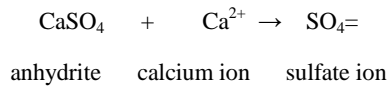


**Figure 5: Scaling formation during production due to pressure drop and gas releases**

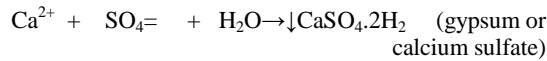
Both pressure and NaCl increase the amount of anhydrite that dissolves. When pressure declines as the formation water moves into a rock fracture or the wellbore, the concentration of  $\text{CaSO}_4$  exceeds the solubility limit and solid phase  $\text{CaSO}_4$  scale is formed.

The reaction may be written as follows:

Solution under pressure



Precipitation at reduced pressure

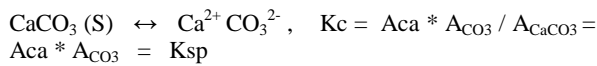


#### 4.4. Prediction of calcium carbonate scale

There are several methods to predict calcium carbonate scale formation from chemical components in water. Here are two of them:

##### 4.4.1 Activity Product (saturation index)

This method depends on the comparing the product of calcium ion activity ( $A_{\text{Ca}}$ ) and carbonate ion activity ( $A_{\text{CO}_3}$ ) with the thermodynamic activity product ( $K_{\text{osp}} = A_{\text{Ca}} \cdot A_{\text{CO}_3}$ ).



$$A_{\text{Ca}} \cdot A_{\text{CO}_3} > K_{\text{sp}} \quad (\text{SIC} > 0) \quad : \text{CaCO}_3 \text{ deposition}$$

$$A_{\text{Ca}} \cdot A_{\text{CO}_3} = K_{\text{sp}} \quad (\text{SIC} = 0) \quad : \text{solubility equilibrium (solubility limit)}$$

$$A_{\text{Ca}} \cdot A_{\text{CO}_3} < K_{\text{sp}} \quad (\text{SIC} < 0) \quad : \text{no deposition}$$

##### 4.4.2 Langelier Saturation Index

The Langelier saturation index is a method to predict scale formation from comparing measured pH of discharged hot water with calculated pH of water equilibrated calcium carbonate by using Ca concentration, alkalinity, temperature

and total solid. The pH calculated (pHs), is expressed as follows (Langelier 1936):

$$\text{pHs} = \text{p}(\text{Ca}) + \text{p}(\text{Alk}) + C$$

$$\text{pCa} = -\log(\text{Ca})$$

$$\text{pAlk} = -\log(\text{Alk})$$

C is a constant depending on the content of total solid and temperature. This can be read from Langelier saturation-index charts.

The Langelier saturation index (S) is the discrepancy between the actually measured pH and the calculated saturation pH;  $S = \text{pH}(\text{actual}) - \text{pH}(\text{calculated})$ .

If saturation index:  $S > 0$ , the water tends to deposit  $\text{CaCO}_3$

$S = 0$ , the  $\text{CaCO}_3$  equilibrated in water and there is no scale and corrosion

$S < 0$ , the water is corrosive

#### 4.5. Removal and preventative methods of calcium carbonate scale

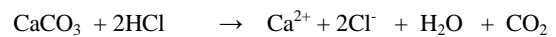
If  $\text{CaCO}_3$  scale clarified in a geothermal well the following methods can be applied to remove it:

##### 4.5.1 Mechanical method

A casing spear is introduced to the well with  $\text{CaCO}_3$  scale to break the scale mechanically. This method is convenient for low temperature geothermal wells. The troublesome scaling of Kizildere geothermal has been overcome by this way.

##### 4.5.2 Chemical method

$\text{CaCO}_3$  scale is removed by pumping a solution of hydrochloric acid plus a corrosion inhibitor into the wells. Calcium carbonate and most corrosion products can be dissolved and removed with 15% HCl acid. Iron chelating agents such as HEDTA or citric acid are added when iron corrosion product are present (Yildirim 1989). The calcium carbonate is dissolved by the following reaction.



The use of an acid plus corrosion inhibitor for removing calcite from cooler surface equipments has been reasonably satisfactory.

#### 4.6. Preventative methods

There are several methods in use to control  $\text{CaCO}_3$  scale in geothermal applications. The most common measures are the proper design of the utilization plant and selection of operating conditions, such as pH adjustment, use of chemical additives and the removal of deposition by mechanical or chemical means (Yildirim 1997). The scale formation in the Kizildere well bores has been removed by mechanical reaming. In the other utilized fields the chemical additives (Inhibitor) have been used.

Calcite precipitation can not be completely prevented by any of the methods. However, calcium carbonate scaling in low temperature fields can be prevented to a great extent.

(1) by acting on pH of hot water

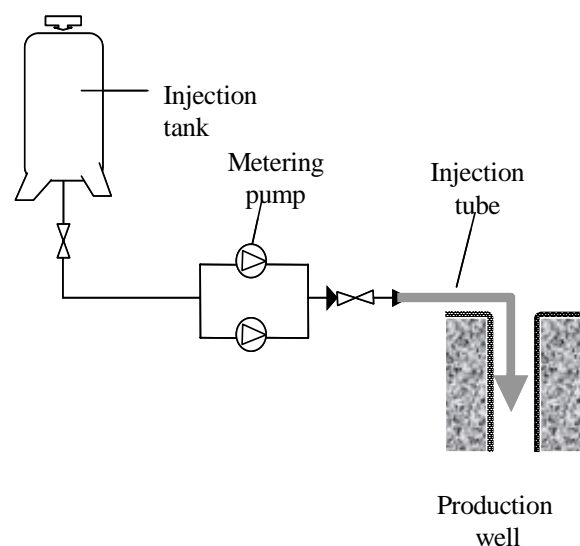
(2) by adding chemical additives (scale inhibitor)

#### 4.6.1 pH manipulations

The pH manipulation of the geothermal water is valuable way to avoid the formation of scale. However, excessively large amounts of HCl acid are required to obtain even a small decrease of the pH value (Corsi et al. 1986). The cost of treatment may be much higher than the price for the energy produced from the system.

#### 4.6.2 Adding scale inhibitor

The most promising method to prevent carbonate scale is the use of chemical inhibitors (Yildirim 1989). The most widely



**Figure 6: Simplified inhibitor injection system**

The importance of this method is to inject the chemicals into the depth below flashing or bubbling point. Well size and injection equipment such as pump and injection tube have to be given attention (Yildirim 1989).

### 5. ENVIRONMENTAL IMPACT

Environmental constraints on the siting, construction and operation of the geothermal power station can often result in increased development cost. A typical example may be the requirement for minimal discharge of geothermal gases (in particular hydrogen sulphide) to the environment. This may require the gases to be either reinjected into the reservoir or costly hydrogen sulphide abatement systems to be installed

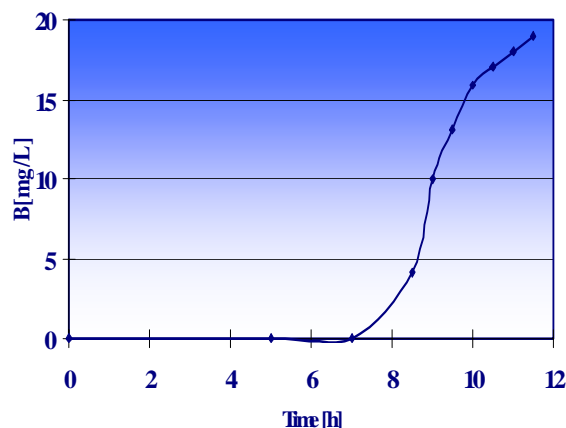
Environmental constraints have forced the geothermal industry to reduce their emission to water systems, otherwise several contaminants such as boron could cause environmental problems. Conventional wastewater cleaning technology does not meet all the new regulations for releases from the geothermal application plants. The reinjection is one of the ways to overcome the releases. But there should be other methods beside reinjection, in case the reinjection is not applicable. With this respect boron selective ion exchange experiment carried out in the one of eleven geothermal fields in Turkey which produce 1000 m<sup>3</sup> per hour. Removing boron from water, especially extremely high levels, is difficult, and can be prohibitively expensive and non-practical. However, depending on the actual levels of reduction required, water treatment may be an available option if treatment water does not contain high concentration of ions induce plugging the purification system and especially resins.

used classes of scale inhibitors are: (a) amino-phosphonates, (b) phosphate esters of amino-alcohols, (c) sodium polyacrylate polymers, (d) polycarboxylic acid, and (e) organophosphate.

The chemicals are usually sold as water solutions (20 to 30% active). The inhibitor chemical should be prediluted with water before injection to a final concentration of 1 to 2 vol %. Simplified scheme of downhole inhibitor injection system is represented in Figure

What follows is a brief discussion of the possible methods available to reduce or remove boron from water. The first method discussed is ion exchange but it is not particularly practical for great flow rates. There are new technologies being developed that one day may make boron removal from any given water source both easy and economical.

Diaion CRB 02 resin was found to be promising for the removal of boron from geothermal wastewaters of Kizildere geothermal power station. This selective exchanger removed more than 99% B from the wastewater for 7 hours before breakthrough. (Figure 7). Cheaper ion exchange resins with a higher capacity and other alternative technologies combined with IX technology should be considered for future studies.



**Figure 7: Boron removal with chelating Diaion CRB 02 resin. The concentration of the boron in KD-6 Geothermal fluid has been reduced from 19 ppm to 1 ppm for 7 hours Cycle time.**

### 6. CONCLUSION

All the high and moderate-low temperature geothermal resources of Turkey lie along western part of the country. The most widespread application in Turkey is concentrated on district heating. In district heating application moderate-low temperature geothermal field fluids (<200°C) have to be flashed to atmosphere before introducing to the heat exchanger. This means big energy loss for nowadays-available binary cycle technologies. It is calculated that present prospective potential of the high and moderate-low temperature geothermal fields is 75 MWe for single flash, 71 MWe for binary cycle and 1609 MWt for district heating applications. Of this potential only Izmir-Balcova potential in half capacity is being used in district heating. The amount of electricity that is being generated by single flash power plant is 14 MWe (Kizildere). This consists approximately only 1/5 of available capacity.



Unfortunately, binary cycle technology has not been yet put into practice on the potentially big Turkey's geothermal fields.

CaCO<sub>3</sub> scaling, corrosion, gases emissions and environmental impact are some of the constraints to developments of geothermal energy utilization. Thanks to studies carried out in those fields, the constraints problems have been solved. Recently, carbonate scaling has been overcome by means of chemical additives and environmental impact has been achieved by reinjection

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