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Formation Mechanism and Control Techniques of Calcium Carbonate Scale in the Langjiu Geothermal Field Tibet

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ABSTRACT

Calcium carbonate scale is one of the challenges which must to be solved during the process of mass production in middle to high temperature geothermal fields. The formation trend of the calcium carbonate scale in the Langjiu Geothermal Field of Tibet is apparent. The speed of the scaling is 2 mm/d. In this paper, based on the research of geothermal geologic conditions in the area and formation characteristics of the geothermal fluids, the authors concluded that the inherent mechanism for calcium carbonate scale formation is the catalyst precursor formation of supersaturated solutions—the transformation of solubility between aragonite-calcite. The external condition is the mixture of the deep geothermal fluids and the cold surface water, which occur after the pressure decreases.

According to the scaling control and scaling removal in the discharge-spray tests, the authors proposed that the first choice of scale control is the combination of compression and the addition of a resistance scale agent, which is from the series of phosphate molybdenum. Moreover, the preferred methods for scale removal are mechanical scale removal and chemical scale removal.

1. INTRODUCTION

Geothermal water scaling is a widespread phenomenon that occurs in geothermal heating stations and high-temperature geothermal power plants. Geothermal scaling mostly happens within geothermal wells (with high-temperature water running), piping, and plate heat exchangers. Scaling in producing wells will block well casings. When the problem becomes worse, it will form a blockage in the well which could lead to well abandonment. Meanwhile, scaling in heat exchangers will totally or partially block off tiny heat exchange channels, which will increase the pump consumption and decrease the heat exchange efficiency. If the problem becomes more serious, it can even affect the normal operation of a geothermal energy application system.

1.1 The judgment of scaling trend

Although there are many kinds of geothermal scale, the most common one is calcium carbonate scale. The formation mechanism of calcium carbonate scale is that the calcium carbonate in geothermal water is in the supersaturated state. The definition of calcium carbonate saturation index (SI) is:

$$SI = \log(Q/K) = \log Q - \log K \tag{1}$$

where, K is the solubility of calcium carbonate in geothermal water (mol/L), Q is the ion activity product of calcium carbonate which actually dissolves in geothermal water (mol/L).

When SI < 0 or Q / K <1, the actual dissolution of calcium carbonate in the ground water is less than the amount of calcium carbonate that can be dissolved in ground water. This indicates that calcium carbonate deposition will not occur. When SI > 0 or Q / K> 1, the amount of calcium carbonate dissolved in hot water is more than the actual amount of calcium carbonate that can be dissolved in ground water. Thus, the ground water will have a tendency for calcium carbonate deposition (Plummer and Busenberg, 1982). It should be noted that Equation 3 is a reversible reaction.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{2}$$

$$Ca^{2+} + 2(HCO_3^-) \leftrightarrow CaCO_3 + CO_2 - H_2O \tag{3}$$

From the perspective of thermodynamics, the precipitation of calcium carbonate depends on the amount of CO_2 partial pressure, temperature and water composition. In normal operating conditions, the only variables from the bottom to the scaling point are pressure (P) and temperature (T). When the exploitation of water increases, the temperature change is generally negligible. Therefore the main factor affecting the formation of calcium carbonate scale is the change of voltage (Zhang, 1995). The starting point of scaling is usually the flash point, because the release of CO_2 leads to the rise of pH value and degree of superheat. It forces calcium carbonate scales to drop out (Xu and Li, 2004).

From the perspective of the processes for calcium carbonates formation and transformation, the crystallization is divided into three steps. The first step is the formation of a catalyst precursor in the supersaturated solution. The second step is the the nucleation and growth of vaterite, which is transformed from the catalyst precursor. The third step is the vaterite transformation into calcite (Marcus V.E.). The fact that the process of transformation includes the following: solubility of catalyst precursor, solubility of vaterite (aragonite), and the solubility of calcite. There is often a supersaturated region that appears before the supersaturated solution of geothermal fluid produces calcium carbonate scale. This supersaturation ratio is generally two to three times the original value, which means that the ground water may contain this much of the theoretical amount of calcium carbonate without scaling.

2. DISTRIBUTION OF BOREHOLES AND THE CHARACTERISTICS OF GEOTHERMAL FLUID

2.1 The distribution of boreholes at present

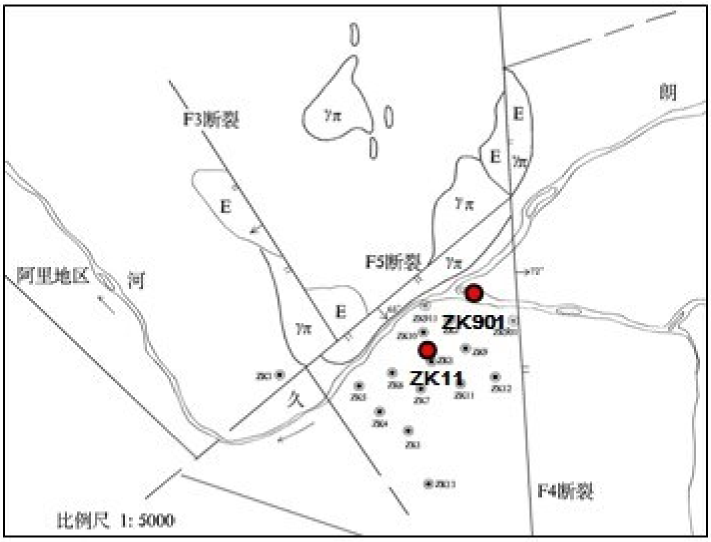

Figure 1: Distribution of boreholes

According to the geophysical data information, the Langjiu geothermal field has two thermal reservoirs: a shallow one located at 20 to 150 m depth and a deep one at 700 to 900 m depth. There are 15 producing wells in this field, of which three wells are drilled in the shallow reservoir. The highest temperature section of these wells is at 20 to 110 m. Although the completion depth of borehole ZK901 is deeper than the depth of borehole ZK11, the highest temperature point is similar. It shows that ZK901 also belongs to the shallow thermal reservoir. The geothermal energy, which developed at present in this region, belongs to the shallow geothermal reservoir.

2.2 The characteristics of geothermal fluid

In order to study the relationship between the geothermal fluid in the field and Langjiu River, four water samples were collected from the following locations: Langjiu River water upstream of the geothermal field; Langjiu River water downstream of the geothermal field; ZK11 (spray well); and ZK901 (the deepest well). The chemical analyses are shown in Table 1.

Table 1: Water quality analysis results of Langjiu geothermal field list

Samples ‘location			Sample (1)	Sample (2)	Sample (3)	Sample (4)
Depth(m)			-	-	69	455
The highest temperature of water in well （℃）			12	14	110 (Depth 63 m)	101 (Depth 20 m）
Positive ion (mg/l)	K+		1.06	2.69	44.17	39.2
	Na+		6.88	26.78	585	540
	Ca2+		41.19	39.77	30.64	32.38
	Mg2+		4.43	4.82	1.58	3.63
	Li+		0.004	0.18	6.22	5.08
Negative ion (mg/l)	Cl-		1.48	39.42	367.63	368.07
	SO42-		10	10	340	360
	HCO3		127.57	147.75	557.42	599.66
	F		0.3	0.48	7.41	6.65

Samples 'location			Sample (1)	Sample (2)	Sample (3)	Sample (4)
Special components (mg/l)	HBO2		0.828	10.77	253.47	215.34
	SiO2		11.4	14.4	136	290
	corrosive carbon dioxide		48.01	51.01	220.53	193.57
TDS(mg/l)			152.63	216.38	1881.24	2000.3
pH			8.09	7.92	8.11	6.9
hydrochemical co-position type			HCO_3-Ca	HCO_3·CI-Ca·Na	CI·HCO_3·SO_4-Na	CI·HCO_3·SO_4-Na

The Langjiu River water location, which is upstream from the geothermal field, is a typical cold surface water source. However, flowing through the geothermal field had changed the hydrochemical composition type of the Langjiu River. It significantly increased the concentration of K^+ , Na^+, Li^+, Cl^-, HCO_3^- , HBO_2, SiO_2, CO_2, TDS and the water temperature. All the results show clearly that the chemical composition of water has been affected by flowing through the geothermal field.

3. THE REASON OF LANGJIU GEOTHERMAL FLUID SCALING

3.1 Pressure drop

By using the PHREEQC software, the tendency of calcium carbonate scaling to ZK11 could be predicted at different temperatures and different partial pressure of CO_2 (Table 2）.

Table 2: Evaluation of scaling potential in well ZK11 well and the water of Langjiu River which flowing through the geothermal field

PCO_2	Temperature (℃)	Calcite (SI)	Aragonite (SI)	Conclusion
Calculated partial pressure 10-1.97bar	107	1.36	1.26	Calcite and aragonite is in the supersaturated state with a tendency to forming scale
Calculated partial pressure 10-2.19bar	69	1.06	0.94	When fluid temperature down to 69 ℃, there is a tendency that fluid produces calcite, aragonite scale. Scaling trend increases when the partial pressure of carbon dioxide approaches the partial pressure value of Tibet Ali
Turn partial pressure into 10-3.7bar*	69	1.47	1.35	
Calculated partial pressure 10-2.49bar	16	0.51	0.36	When fluid temperature down to 16 ℃, there is a tendency that fluid produces calcite, aragonite scale. Scaling trend is more serious when the partial pressure of carbon dioxide approaches the partial

Turn partial pressure into 10-3.7bar*	16	1.28	1.13	pressure value of Tibet Ali

Calculations show that, when PCO2 is less than 10-2.19 bars with temperatures below 69 °C, the calcium carbonate scaling tendency of the fluid increases, as confirmed by tests. Five days' worth of calcium carbonate scaling speed tests were carried out with and without pressurization in spray tests for the ZK11 geothermal well. A less than 1 mm thick scale occurred when the pressure was 0.5 relative to atmospheric conditions. Meanwhile, a 10 mm thick scale on the discharge port, was observed for the run with no pressure adjustment. Accordingly, the scaling speed is 2 mm/day in the latter case (Figure 2).

3.2 The mixture of deep geothermal fluids and cold surface water

The shallow thermal reservoir of the Langjiu Geothermal Field is formed by the mixture of deep rising geothermal fluids and cold infiltrating surface water. The temperature of the deep thermal reservoir is 150 to 180 °C, as predicted by geochemical geothermometers. According to the data from the 15 developed exploration wells at present, the average temperature of the geothermal reservoir is 110 °C. The lower reservoir temperature can be explained by the mixing of distant cold surface water (1 °C) and hot water with a ratio of 26.8% (150 °C) and 39%（180 °C).

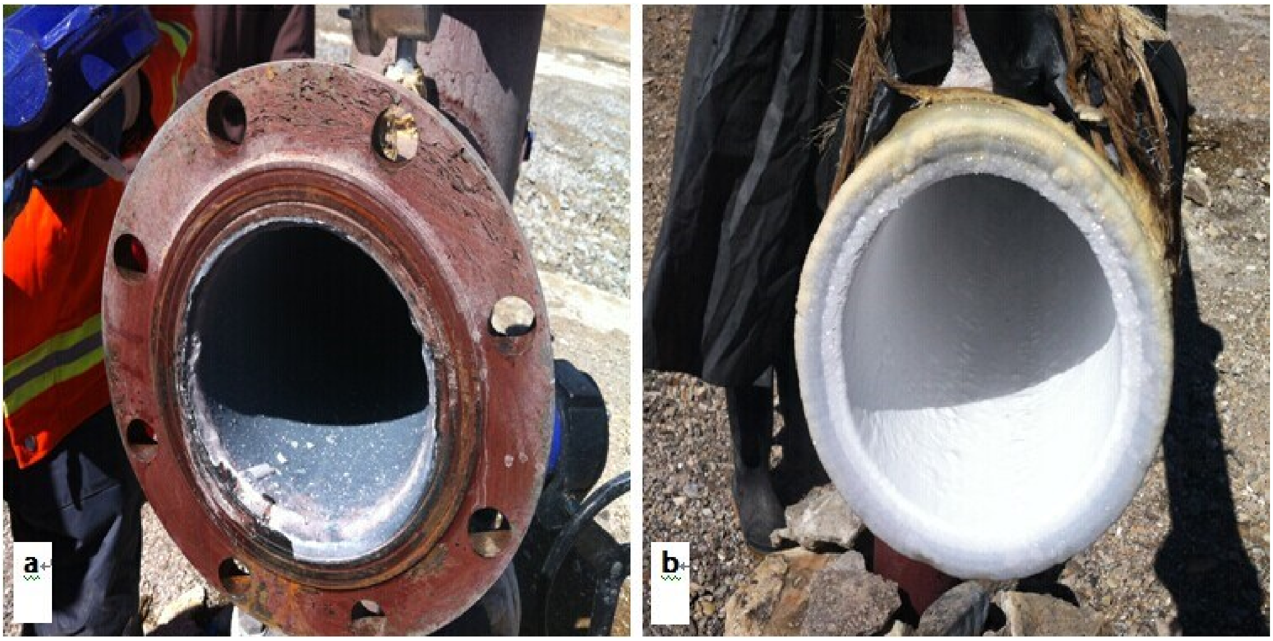

Figure 2: Effects comparison chart of spray tests in ZK11 geothermal well. (a) Under the condition of pressurizing 0.5 relative to the atmosphere, the scale thickness is less than 1 mm after five days. (b) At the same time, under the condition of non-pressurization, the scale thickness is 10 mm.

The Ca^{2+} ion, which has a strong trend in mixed geothermal fluids, mainly comes from cold surface waters (argillaceous components in glutenite) and secondary minerals from the alteration of granite (mica thermal alteration of mud) with HCO_3^-. The CO_3^{2-} mainly transforms from HCO_3^-, which comes from the low salinity surface water, and geothermal fluids, when the partial pressure of carbon dioxide has changed.

3.3 The prediction of the starting point of scaling

By using the forecasting software program HOLA and combining it with the structure of the geothermal wells and geothermal fluid parameters (Table 3), the position of flashing point has been located between wellhead and 2 m depth.

Table3 the structure of geothermal well and geothermal fluid parameters about ZK11

Parameters	Values
Depth (m）	62
Nodal value (m）	2
Well radius(m)	0.17
Annulus(mm)	0.09

Wellhead pressure(bar)	1.6
Enthalpy(KJ/kg)	476.94
Flux (kg/s）	32.2

4. PREVENTION AND CONTROL MEASURES

Many methods have been developed to remove and control $CaCO_3$ scale, such as the additive method, electromagnetic and acoustic methods, coating anti-scaling methods, inducing scale vector methods, system pressure methods and others (Liu and Zhu, 2012). However, these are not desirable solutions. The anti-scaling coating tends to fall off, the descaling effect of magnetic and electric ion stick water processor will not work if the water flow is greater than 100 m^3/h, and the fluid temperature is higher than 100 °C. In addition, the equipment usage is shortened and it is technically difficult to adapt these to production requirements. Based on the characteristics of geothermal resources in the Langjiu Geothermal Field and past industry experiences in anti-scaling and descaling practices in high temperature geothermal fluids, the recommended methods are outline below.

4.1 Prevention scaling in operation system

4.1.1 Pressurization

Installing a deep well pump is an excellent pressurized descaling method. It is widely used in geothermal wells. The selected pump should be high temperature resistant, have multistage series operations, light weight, and be effective on descaling.

The closed wellhead pressure of ZK11 is 0.72×10^5 Pa. The average atmospheric pressure of Langjiu Geothermal Field is 433 mmHg = 0.57×10^5 Pa. Thus, the absolute pressure on the wellhead is 1.29×10^5 Pa. Inspection shows that there is only a small amount of calcium carbonate scale on the wall of the well. Combined with the prediction results from the HOLA program, it can be calculated that the wellhead pressure at an absolute pressure of 1.3×10^5 Pa (i.e. increasing 0.73×10^5 Pa relative to the atmospheric pressure in a geothermal well) will prevent scaling.

4.1.2 Addition of scale inhibitors

The series of phosphate molybdenum could expand the supersaturated region of calcium carbonate scaling. The current developing technology already makes sure that the scale will be prevented and decreased by adding a low concentration (ppm). It will allow operation of the system that can run for several months or even several years without stopping to remove fouling.

4.2 Developing deep geothermal fluids

Drilling for the deep reservoir is ongoing in the Langjiu Geothermal Field. Its first section has been drilled down to 200 m with 339.7 mm surface casing. Its second section has been drilled down to 1100 m with the purpose of exploring the 800 m deep geothermal resources. So far, five faults have been intersected.

It is suggested that the first choice of scale control in the new well be the combination of compression and the addition of a resistance scale agent, which is from the phosphate molybdenum series. The main options for scale removal are: mechanical scale removal and chemical scale removal.

4.3 Cleaning scaling in operation system

The normal cleaning procedure is to use a drifting hammer to do mechanical scale removal in the wellbore. It is necessary to use chemical methods (HCl), when the drifting hammer cannot completely remove the scale. Using chemical methods (HCl) can be necessary especially when the drifting hammer has to be changed to a smaller one. The advantage of this method is that it is cheap and effective (Yang and Tang, 1995). The following are recommended:

(1) Adopt a mechanical descaling system in the spare pipes of the primary pipe network.

(2) Depending on expansion and contraction, which is caused by the changes of pressure and wellhead flow, eliminate the scale layer.

(3) Acid picking for the features of calcium carbonate scale, includes using hydrochloric acid as a cleaning agent. It is low cost and has fast dissolution characteristics. At the same time, it is useful to add corrosion inhibitors in the cleaning liquid.

REFERENCES

Liu, M.Y., and Zhu, J.L.: Progress of corrosion and fouling prevention in utilization of geothermal energy. *Geothermal Energy*，6 (2011), 11-12

Plummer L.N., and Busenberg E: The solubilities of calcite, aragonite and vaterite in CO2-H2O solutions between 0 and 90℃, and an evaluation of the aqueous model for the system CaCO3-CO2-H2O. *Geochim Cosmochim Acta*，46 (1982), 1011-1040

Zhang, H.X.: The formation and prevention of calcium carbonate scale in the process of recovering gas by discharging water in gas wells. *Chemical Engineering of Oil & Gas*,22(1993), 29-32

Xu, J., Li J.,: The influence of CO2 releasing to the crystallization progress of saturated solution of calcium carbonate .*Journal of Tongji University (Natural Science)*, 9(2004), 1176-1177

Marcus V.E., Geothermal *Resources Council Bulletin*, l9, Vo1.18，№8， 8-11

Liu M.Y., Zhu J.L: Research on new technology of anti-corrosion and fouling prevention in geothermal utilization, *Project of Tianjin science and technology Committee of Tianjin University*．2012

Yang D.F., and Tang L.D.,: Scales removal of a Tibet geothermal producing well. *Sichuan electric power technology*, 4(1995), 8-10