Proceedings International Workshop on Mineral Scaling 2011
Manila, Philippines, 25-27 May 2011

Precipitation mechanism of carbonate and sulfate scales in Enhanced Geothermal System (EGS) at Hijiori, Japan

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Keywords: EGS, calcite, anhydrite, inhibitor

ABSTRACT

Several kinds of scale precipitated in the pipelines and productions well during two years long circulation test in the Enhanced Geothermal System (EGS) of Hijiori, Yamagata, Japan.

The ratio of silica and calcium carbonate depends on fluid temperature and chemical composition. In the case of HDR-2a nearer to the injection well, wellhead temperature is about 120℃ after thermal breakthrough and the major scale is calcium carbonate. In the case of HDR-3 further from the injection well, wellhead temperature is kept about 160℃ during the circulation test and amorphous silica scale precipitated slightly.

At the deep zone of the production well, anhydrite scale precipitated at the reverse temperature zone. Injected water dissolved the anhydrite in the reservoir rock and anhydrite precipitated at the higher temperature zone because of the reverse solubility curve of anhydrite with temperature.

This anhydrite dissolution and precipitation behavior influences scaling in the pipeline. In the pipeline of HDR-2a, high content Ca reacted with CO_2. High content Ca came from dissolved anhydrite in the reservoir and kept during the lower temperature of production well.

Chemical scale inhibitor, sodium polyacrylate (C_2H_3COONa) injection trials into the reservoir were done to decrease scaling. After inhibitor was injected, production fluid chemistry changed. HCO_3 concentration increased with inhibitor suggesting that the inhibitor can be used and precipitation of calcite can be prevented in many geothermal fields. And inhibitor prevented to solve anhydrite as source of calcium at lower temperature. This suggests that this inhibitor effect for scale prevention in EGS.

1. INTRODUCTION

In many geothermal fields mineral scales tend to precipitate if there are changes in fluid temperature and/or pressure, leading to fluid flow problems. To overcome the operational problems associated with scaling, mechanical and chemical methods have been developed to eliminate and/or reduce the amount of mineral deposition. It is however important to further investigate and understand the mechanisms involved and the relation between mineral scaling and the physical and geochemical characteristics of the rocks and fluids in the geothermal system under exploitation.

Recently, research and development for EGS system are carried out especially in Australia, Europe and USA. For example, at Cooper Basin, Australia, circulation and tracer tests were carried out (Yanagisawa et al., 2009). However, after long -term circulation, scaling along pipelines and wells is the one of problems for EGS (NEDO, 2003). At Hijiori, Yamagata, Japan, a long-term circulation test (LTCT) was conducted from November 2000 to August 2002. After completion of the tests, scaling was also observed in the production wells and surface installations (Yanagisawa et al., 2008).

This paper presents the results of mineralogical and chemical analyses of the scales that precipitated in production wells and surface pipelines during the LTCT, discusses the mechanisms controlling scaling in the Hijiori HDR system and shows results using scale inhibitor (sodium polyacrylate) for decreasing the problem of anhydrite and calcite scaling.

2. LONG TERM CIRCULATION TEST (LTCT) IN HIJIORI EGS

The fluid circulation system at the Hijiori EGS site is shown schematically in Figure 1. A multi-stage centrifugal pump (ESP TJ9000) was used to inject the fluid at a constant flow rate of 16.66 kg/s.

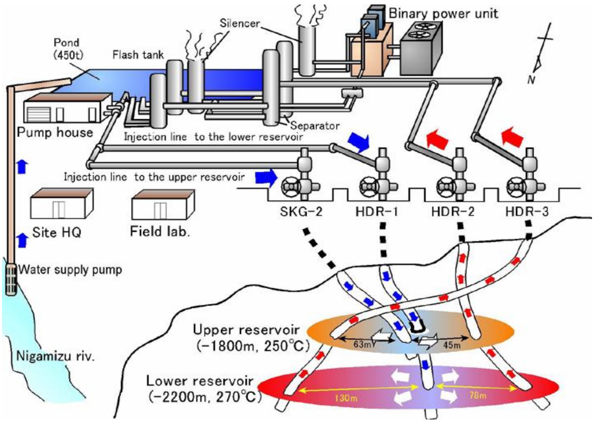

Figure 1: The sysem of Hijiori EGS test field

In the first stage of the LTCT, this fluid was directly injected into HDR-1. In the second stage, the injection fluid was separated into two lines after being pressurized by the pump. One was connected HDR-1, which was used as an injection well for the deep reservoir, and the other to SKG-2. On 8 April 2002, the injection ratio of HDR-1 to SKG-2 changed from 1:1 to 3:1. From 29 April to 31 May, injection was stopped to prepare for the power generation test. From 1 June to 31 August, 2002, the water injection ratio of HDR-1 to SKG-2 was kept 3:1.

The changes in production temperatures with time during the power generation test are shown in Figure 2.

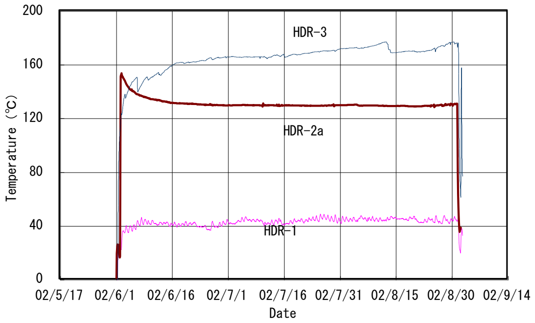

Figure 2: Wellhead temperature of production well (HDR-2a and HDR-3) and injection well (HDR-1) during power generation test from 1 June to 31 August, 2002

3. SCALE AND FLUID ANALYSIS

Scale sampling points are shown in Figure 3. Scale was collected at deep part of production well during the flow test in the production well by the PTS survey tools, and at various points in the surface equipment in September 2002, after the end of the flow test. Scale samples were also collected from the sampling pool at the downstream end of the hot water flow lines several times during the LTCT.

The bulk sample was powdered for X-ray diffraction and chemical analysis such as ICP-ES method, ion chromatography and high-frequency burning infrared absorption method.

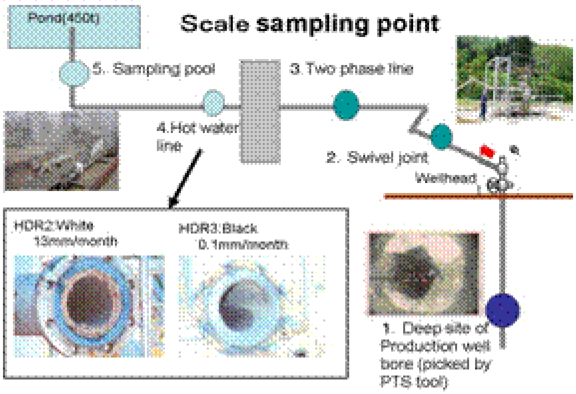

Figure 3: Scale sampling point in production well and pipeline of HDR-2a and HDR-3.

Fluid was corrected at sampling pool after scale precipitation at hot water line. Several fluid composition including Ca and SO_4 were measured by ion chromatography and HCO_3 concentration was measured using titration with H_2SO_4.

4. SCALE PROPERTIES

4.1 Scale analysis results

Figure 3 shows several photos of the pipeline in September 2002, after the end of the LTCT. The scale samples from well HDR-2a are white and thick, while those from well HDR-3 are black and thin. The scale precipitation rate of HDR-2a is about 13mm/month.

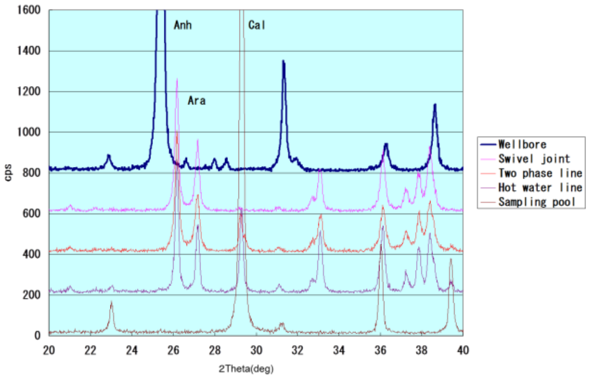

Figure 4: X-ray diffraction pattern of scale sample at several points in HDR-2a on September 2002

Figure 4 shows the chart of X-ray powder diffraction of samples from the deep site in the production well, the swivel joint near wellhead, the two phase line, the hot water line and the fluid sampling pool on September 2002 at HDR-2a. This figure shows the strong anhydrite peak from the production well sample. But anhydrite disappeared after the swivel joint. Instead of anhydrite, calcium carbonate minerals appeared. Near the swivel joint, aragonite, a calcium carbonate mineral, was the major part of the scale. At lower reaches of the pipeline, calcite became dominant instead of aragonite. At the fluid sampling pool, most of the scale is calcite with minor amorphous silica. Table 1 shows the results of chemical analysis. The main composition is calcium and carbonate with slight silica.

Table 1: Chemical composition and thickness of scale sample at several points in HDR-2a on September 2002 after power generation test

	Chemical ratio (%)			
	CaO	SO_4	CO_2	Thickness
Wellbore	40.6	53.8	4.0	
Swivel Joint	54.94	1.25	42.30	45mm
Two phase line	55.25	1.38	42.50	40-60mm
Hot water line	52.99	2.75	40.30	20mm
Sampling pool	51.2	3.7	38.6	

Figure 5 and Table 2 show the chart of X-ray powder diffraction and chemical composition of samples from the deep site in production well, water flow line and fluid sampling pool on September 2002 at HDR-3. At the swivel joint near wellhead and the two-phase flow line, samples cannot be collected because the scale is very thin. This figure shows the strong anhydrite and calcite peak of scale from the production well. But anhydrite disappeared at the hot water line, where calcite and amorphous silica were the major part of scale. This scale contained about 40% more silica than that of HDR-2a. At the fluid sampling pool, most of the scale is amorphous silica with a small amount of calcite.

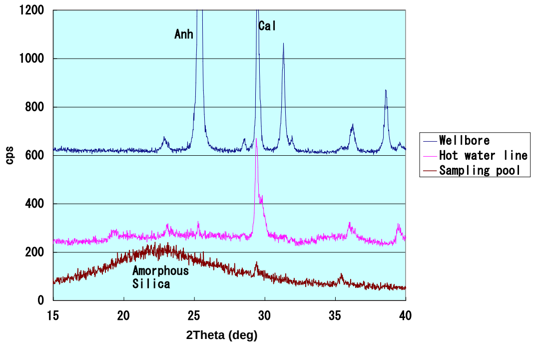

FIGURE 5: X-ray diffraction pattern of scale sample at several points in HDR-3 on September 2002

Table 2: Chemical composition and thickness of scale sample at several points in HDR-3 on September 2002 after power generation test

	SiO_2	Al_2O_3	FeO	CaO	SO_3	CO_2
Wellbore	2.0	0.7	1.0	42.5	30.9	17.8
Hot water line	39.6	6.8	4.5	13.6	1.7	7.8
Sampling pool	74.7	2.9	5.6	1.4	0.2	1.8

4.2 Scale precipitation and temperature profile

The scales precipitated at the deep part of the production well consisted mainly of anhydrite. Because the solubility of anhydrite decreases with higher temperature the reverse of usual scale compositions such as silica, anhydrite precipitates at higher temperature zones in the flow path. In the case of HDR, injection water is about 70°C when the water reached the reservoir. At the injection point, water dissolves anhydrite veins in the granite reservoir rock.

Dissolved anhydrite was transported with fluid flow in the reservoir to the production well, the water was then heated by granite around the reservoir, and the heated fluid became supersaturated with anhydrite. As shown in the temperature curve in Figure 6, high temperature exists at 500m depth, and a step change is seen at 2,000m. Anhydrite precipitated around this temperature and steep change zone was detected by the PTS logging tool.

The HDR-3 temperature is higher than at HDR-2a and gradually increases with depth until 1,950m where there is a slight decrease at the deeper zone. The PTS logging tool did not penetrate beyond 2,000m depth due to anhydrite scale at the high temperature zone. Anhydrite scaling at high temperature zones in production wells is found in other geothermal fields, for example, at Sumikawa geothermal field (Kato et al., 2002).

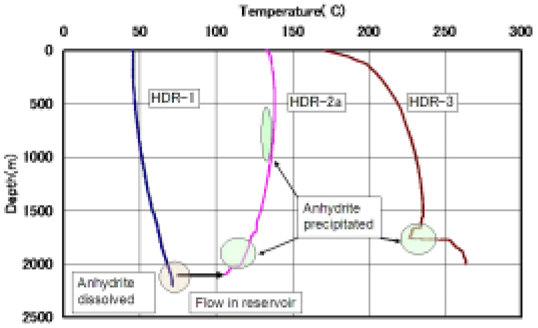

FIGURE 6: Temperature depth profiles of wells at July. 2002 with scaling process

The temperature in the production well and wellhead reflects the type of mineral scale in the pipeline. In HDR-2a, the lower temperature well, calcium carbonate is the major scale component. Ca and SO_4 content of the HDR-2a fluid were higher than HDR-3 due to higher anhydrite solubility at lower temperature. The high content of Ca reacted with CO_2 on ground to deposit calcium carbonate. On the other hand, in HDR-3, the higher temperature well, there was slight amorphous silica deposition. The Ca content of HDR-3 were too low to precipitate calcium carbonate. The SiO_2 content was higher than HDR-2a but lower than other geothermal fields and silica precipitated slightly.

4.3 Thermal breakthrough at HDR-2a

Figure 7 shows the change of the X-ray powder diffraction of scale samples with circulation progress at the fluid sampling pool of HDR-2a. These scales were collected May 2001 and October 2001 during the single well injection test and February 2002 and August 2002 during the dual injection test. Table 3 shows the chemical composition of these samples. The first two samples contain amorphous silica and calcite. During the single injection test, silica content decreased and calcium increased. The last two samples contain mainly calcium carbonate. Samples collected in February contain calcite and aragonite but those from August contain mostly calcite.

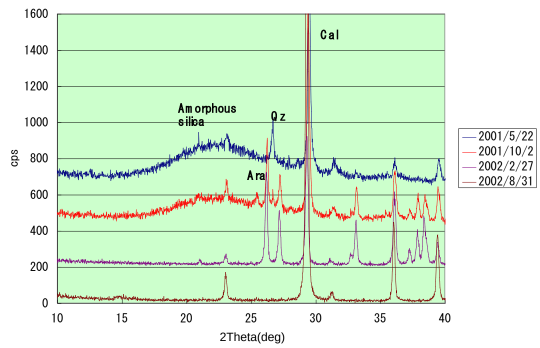

Figure 7: Change of X-ray diffraction pattern of scale sample at fluid sampling pool in HDR-2 at several times during Long time Circulation test

Table 3: Chemical composition of scale sample at fluid sampling pool in HDR-2 at several times during Long time Circulation test

	SiO_2	Al_2O_3	FeO	CaO	SO_4	CO_2
2001/5/22	68.2	1.9	3.2	10.4	1.6	9.1
2001/10/2	47.1	1.6	2.5	22.4	2.6	17.7
2002/2/27	0.8	0.2	0.0	53.8	2.1	42.1
2002/8/31	3.5	0.2	0.8	51.2	3.7	38.6

With circulation progress, scale species changed from amorphous silica to calcium carbonate at HDR-2a. This change was related with the temperature decrease and Ca and SO_4 increase as shown in Figure 8. At HDR-2a, thermal breakthrough occurred on June 2001 and temperature decreased, fluid composition changed and tracer response changed to quick and sharp (Yanagisawa et al., 2002) Scale species change corresponds with decreasing temperature.

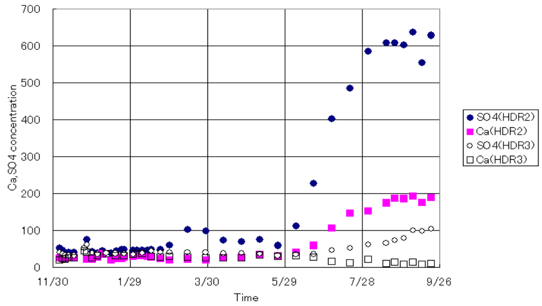

Figure 8 : Change of Ca and SO4 concentration of HDR-2 and HDR-3 during LTCT

Temperature depth profile at May 2001, prior to thermal breakthrough is shown in Figure 9 and the profile after breakthrough case at July 2002 is shown Figure 6. Compare with before thermal breakthrough, highest temperature of HDR-2a in well after thermal breakthrough is 100°C lower. This is caused by high Ca and SO_4 concentration due to less anhydrite precipitation in well and cause to calcite precipitation in pipeline.

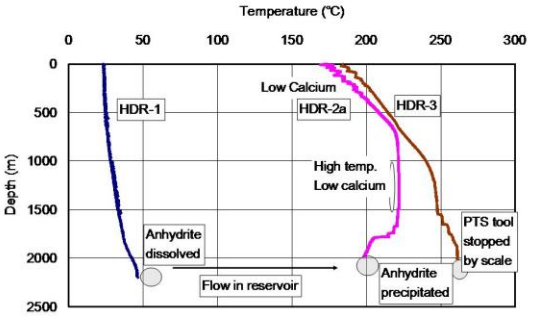

Figure 9: Temperature depth profile of HDR-1, injection well, HDR-2a and HDR-3, production well obtained by PTS survey at May 2001, before thermal breakthrough

5. PREVENTING SCALE

5.1 Scale inhibitor

Sodium polyacrylate, C_2H_3COONa, is common used scale inhibitor to prevent calcite precipitation (Ramos-Cardelaria et al., 2000). In Japan, sodium polyacrylate is used in several geothermal plants and hot spa, for example, Mori and Oku-aizu geothermal plants. At high fluid temperature, sodium polyacrylate reacts with calcium ion to produced calcium complex. Calcium complex cannot react with bicarbonate ion, HCO_3, to precipitate calcite.

This sodium polyacrylate inhibitor is effective in preventing calcite scaling. But it is not clear if it is effective for other kinds of scale, for example, anhydrite. We tried to use sodium polyacrylate for anhydrite, because other inhibitors have not been developed for anhydrite and sodium polyacrylate have possibility to affect calcium ion of anhydrite and is used in many calcite scaling geothermal fields.

5.2 On site test

First, about 10kg sodium polyacrylate was dissolved with 500 liter water in the 1000 liter tank used for tracer injection. This solution was pumped from tracer tank to fluid pond at 1 liter per minute rate. This fluid including inhibitor was pumped by a multi-stage centrifugal pump (ESP TJ9000) to injection well. The content of inhibitor was about 5 to 20 ppm.

The supply time of inhibitor was limited to about 12 hours due to the inhibitor solution volume in tracer tank. On this test, we pumped KBr as tracer with inhibitor to locate possible production zones.

The inhibitor injection test was carried out two times and condition of test, injection date and time, concentration of inhibitor are shown in Table.4 These tests are carried out several days after main tracer test.

Table 4: Chemical composition and thickness of scale sample at several points in HDR-2 on September 2002 after power generation test

TEST	Date	Injection		Inhibitor
		Start	End	(ppm)
1	2001/11/6	9:00	18:00	4.7
2	2002/3/2	9:00	21:00	18.2

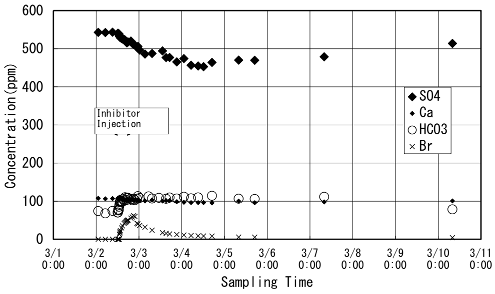

Figure 10: Change of Ca, SO_4, HCO_3 and Br concentration of HDR-2 after inhibitor injection

As shown in Figure 10, after about 6 hours from start of injection, Br appeared in fluid. Then, concentration of Ca, HCO_3 and SO_4 began to changes. HCO_3 concentration rapidly increased and SO_4 concentration gradually decreased with the arrival of inhibitor. Ca concentration slightly decreased.

After about 6 hours after injection was terminated, Br concentration decreased. But, SO_4 concentration was decreasing continuously and reached minimum value at 2 days after start of inhibitor injection. After that, SO_4 concentration gradually increased for 6 days. Therefore, HCO_3 concentration was the highest value in 2 days after start inhibitor injection. After that, HCO_3 concentration gradually decreased. This means that the effect of inhibitor, sodium polyacrylate lasted for several days in reservoir.

Table 5: Maximum and minimum concentration and change rate with inhibitor injection of Ca, HCO_3 and SO_4

TEST NO.	Inhibitor (ppm)	SO4(ppm)		Change	HCO3(ppm)		Change	Ca(ppm)		Change
		Max	Min	Rate(%)	Max	Min	Rate(%)	Max	Min	Rate(%)
1	4.7	765	715	−6.5	102	70	45.5	180	175	−3
2	18.2	540	450	−16.7	110	70	55.5	107	96	−10

Table 5 shows the maximum and minimum concentration and change rate with inhibitor injection of Ca, HCO_3 and SO_4 of two inhibitor injection tests. This table shows that the dependence of inhibitor concentration to Ca, HCO_3 and SO_4 concentration change. SO_4 concentration decreased 6.5%, from 765 to 715ppm, at 4.7ppm inhibitor, November 2001 test and the decreasing rate changed to 16.7%, from 540 to 450ppm at 18.2ppm inhibitor, March 2002 test.

HCO_3 increasing rate with inhibitor was lesser dependence than SO_4. HCO_3 concentration increased 45.5%, from 70 to 102ppm, at 4.7ppm inhibitor and 55.5%, from 70 to 100ppm, at 18.2ppm inhibitor. Ca decreased with inhibitor concentration similar to SO_4.

5.3 Discussion of on site test

Increasing HCO_3 concentration with inhibitor shows the effect in inhibitor to prevent precipitation of calcite such as many geothermal plants. But as SO_4 decreased in contrast to HCO_3, the effect for anhydrite by inhibitor is not same as for calcite to prevent precipitation.

However, the solubility of anhydrite becomes lower at higher temperature in contrast to common minerals, for example silica. SO_4 decrease suggests the prevention of dissolution anhydrite at lower temperature region, for example near HDR-1 and SKG-2, injection well.

To be clear the reason of SO_4 decreasing and whether the decrease of dissolution at low temperature region or prevention to precipitate in production well, the flow and anhydrite dissolution test was done using inhibitor in laboratory condition.

5.4 Laboratory flow test

Anhydrite dissolution flow test was carried out as follows;

1) Test was carried out at room temperature.

2) Anhydrite crystal was crushed until from 30 to 60 mesh size.

3) This crushed anhydrite was filled in 1cm diameter and 10 cm length flow cell. This system was done to similar reservoir condition.

4) Fluids flowed into the cell as 1ml/min rate and extracted water was sampled every 15 minutes. Ca and SO_4 concentrations were measured.

Firstly, distilled water flowed into anhydrite cell. Ca concentration was reached 600ppm during the first 15min and constant during the 2 hours flow. Such as Ca, SO_4 concentration was constant at 1400ppm.

Secondly, after distilled water flow in 1 hour, 20ppm inhibitor solution flow into anhydrite cell. As soon as inhibitor reached the cell, Ca and SO_4 concentration rapidly decreased and finally Ca and SO_4 concentration reached 300ppm and 700ppm (Figure 11). This concentration change shows that inhibitor prevent to dissolve anhydrite at room temperature.

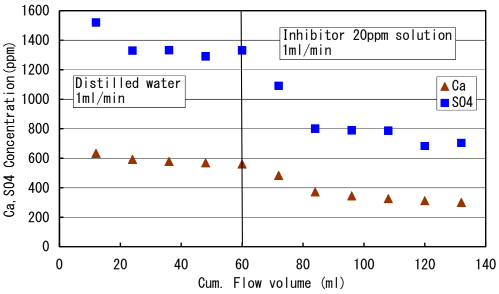

Figure 11: Ca and SO_4 concentration at anhydrite flow cell. After distilled water flowed 1 hour, 20ppm inhibitor including water flowed.

Figure 12 shows the effect of inhibitor on calcite precipitation and anhydrite dissolution. Therefore, in EGS system, sodium polyacrylate inhibitor prevents to dissolve anhydrite in reservoir near injection well. Ca and SO_4 concentration of reservoir fluid decrease than no inhibitor condition. This leads to lesser anhydrite scaling in production well and calcite scaling in surface pipeline by Ca ion effect of inhibitor.

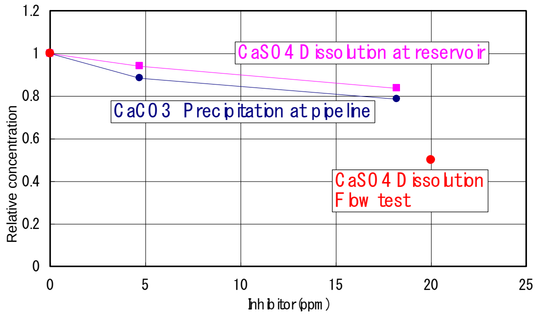

Figure 12: Effect of inhibitor on calcite precipitation and anhydrite dissolution

6. CONCLUSION

Several kinds of scale were found in Hijiori EGS system and scale inhibitor test was carried out. Results are as follows;

1) The ratio of silica and calcium carbonate depends on fluid temperature and chemical composition. In the case of HDR-2a nearer to the injection well, wellhead temperature is about 120℃ after thermal breakthrough and the major scale is calcium carbonate, calcite and aragonite. In the case of HDR-3 further from the injection well, wellhead temperature is kept about 160℃ during the circulation test and amorphous silica scale precipitated slightly.

2) Anhydrite dissolution and precipitation influenced scaling in the pipeline. In the pipeline of HDR-2a, high content Ca reacted with CO_2. High Ca content came from dissolved anhydrite in the reservoir and kept during the lower temperature of production well.

3) At inhibitor test, Ca concentration increased with inhibitor; this suggests the inhibitor prevents the precipitation of calcite such as in many geothermal fields using this inhibitor.

4) SO_4 concentration decreased with inhibitor, this means that the effect of inhibitor to anhydrite is different for calcite. After we checked the solubility of anhydrite with inhibitor, it becomes clear that this inhibitor prevent to dissolve anhydrite at lower temperature.

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