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Corrosion and Scaling Detection in the Soultz EGS Power Plant, Upper Rhine Graben, France

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ABSTRACT

The paper presents corrosion and scaling studies in an EGS power plant located in the Upper Rhine graben: the ORC power plant located at Soultz-sous-Forêts, in France. The Soultz project is an experimental long term research dealing with Enhanced Geothermal System (EGS). Three deep wells have been drilled to 5 km into a granite reservoir, cased between the surface and 4,5 km depth and hydraulically stimulated. An ORC (Organic Rankine Cycle) power plant has been built with a net power capacity of 1,5 MWel.

At Soultz, corrosion and deposits creation were investigated based on on-site test setting by using P110, N80 and P265GH steels, in order to determinate the reaction of those materials to the geothermal brine (having a salinity of 100 g/l and a pH of ~4,8). An innovative corrosion pilot was set up on the geothermal loop at the surface and tested for the first time between September 2008 and February 2009. Steels samples were introduced in the corrosion chambers, where the geothermal fluid circulates, and remained there for different time intervals. A series of physico-chemical parameters, such as pH, Eh, conductivity and temperature, was measured in the meantime. After their extraction, samples were analyzed by various chemical techniques. The main results consist in a significant action of geothermal brine on all studied steels. Newly created deposits, mainly sulfates (barite, celestite) formed on the surface of samples and were characterized by SEM analysis giving access to their structure. Corrosion occurred beneath the deposits and corresponds to pits. Beneath the deposits layer, an interface region was identified, in which various chemical elements (As, Ca, Pb, Si, etc.) were identified.. Corrosion products such as iron oxides (rust were found inside the deposits layer, too.

There are no standard procedures available for on-site corrosion tests at geothermal power plants. Thus, the giveninvestigation methods, results and conclusions could be very helpful for defining comparable and standardized corrosion tests for future geothermal plants within the upper Rhine Graben.

1. INTRODUCTION

In geothermal power plants the material aspect is actually a very important factor. Many aspects as power plant's and maintenance's costs, as well as components mean life, actually depend on it. Two different material bound problems do mainly occur in geothermal systems: corrosion and scaling. Corrosion is the breaking down of essential properties in a material due to chemical reactions with its surroundings; so power plants' components may be damaged by it. This damage decreases mean life of the components 'attacked' by corrosion, so components have tobe changed more often and this increases also the maintenance costs. Also for scaling same considerations may be done, though this phenomenon not only leads to the eventual damaging of components, but it also reduces the pipes sections, so the flow-rate can decrease and the power plant's production, too.

So, corrosion and scaling result to be particularly damaging, not only by considering the components aspect, but also considering a cost increase as well as an effective production decrease.

Both phenomena mainly depend on the geothermal fluid's characteristics, which are different from site to site. So, in order to detect and study both, the geothermal fluid has to be characterized, first. Before the description of the fluid's characteristics, a short description about corrosion and scaling will be given. Finally, the detected corrosion and scaling results at Soultz-sous-Forêts will be exposed. Thus, this paper will bring new results about corrosion and scaling done on steel samples immersed in the geothermal Soultz brine in re-injection conditions.

2. THE SOULTZ-SOUS-FORETS GEOTHERMAL FLUID

2.1 Geothermal Brine Composition

In the Soultz-sous-Forêts power plant, the geothermal fluid is very salty and rich in minerals, as can be seen from the chemical analysis done by BRGM presented in Table 1. This high saline condition makes the risk of deposit and corrosion very high. The chemical and isotopic composition of geothermal brine was evaluated in 1993, 1997 and 1999 after several hydraulic stimulation tests and injections [Sanjuan et al., 2006]. Even if the fluid compositions are very similar from the 5 different deep wells, some discrepancies were observed between fluids produced at different depths. So, for example, the fluid collected at 3500 m depth in well GPK1 and at a temperature close to 165°C indicates concentration of dissolved Cl and Ca slightly higher than those analyzed in the fluid produced at 1800 – 1900 m.

Contrary to well GPK1, it has not been possible to collect and analyze a representative sample of the deep geothermal brine discharged from the wells GPK2, GPK3 and GPK4 because during or after the drilling of these wells, the fluid samples were contaminated by the drilling fluids.

Based on previous studies [Sanjuan et al., 2006; Aquilina et al., 1997], we can state that the main characteristics of the Soultz geothermal fluid are on Table 2.

sample	**Na** (g/l)	**K** (g/l)	**F** (mg/l)	**Ca** (g/l)	**Mg** (mg/l)	**Cl** (g/l)	**SO_4** (mg/l)	**Alk.** (méq/l)	**Alk.** (méq/l)	**SiO_2** (mg/l)	**SiO_2** (mg/l)	**Fe** (mg/l)
GPK2-S2	26,8	2,88	4,6	6,65	75	57,8	171	6,6		409	373	97
GPK2-S3	26,2	2,91	4,5	6,65	77	57,6	172	6,3		392	342	108
GPK2-S4	26,4	2,87	3,9	6,78	98	58,5	170	7,7		364	353	145
GPK2-D1	27,4	3,65	4,7	6,5	98	59	159		6,3		175	96
GPK2-D2						58,5	158		6,3		130	
GPK2-D3	27,5	3,78		6,5	99				6,3		225	

	NO_2 (mg/l)	**N_2** (mg/l)	**Cu** (µg/l)	**NH_4** (mg/l)	**Cr** (µg/l)	**PO_4** (mg/l)	**Pb** (µg/l)	**S^+** (méq/l)	**S^-** (méq/l)	**TDS** (mg/l)	**BI** (%)
GPK2-S2	<0,01	75	76	21,1	<10		320	1634	1640	94880	-0,42
GPK2-S3	<0,01	80	68	21,4	<10		320	1610	1635	94103	-1,52
GPK2-S4	<0,01	100	60	20	<10		270	1625	1664	95415	-2,21
GPK2-D1	0,02	205	260	21,9	18	<0,1	307	1706	1667	97207	2,28
GPK2-D2											
GPK2-D3											

sample	**date**	**depth** (m)	**Analyses done in lab**	**GLR** (%)	**CO_2** (%)	**O_2** (%)	**N_2** (%)	**Ar** (%)
GPK2-S1	4/11/1999	well head	BRGM	13,2	14,3	0,48	29,9	0,23
GPK2-D1	2/12/1999	650	IFP	2,6	15,8	0	43,6	0
GPK2-D3	2/12/1999	700	IFP	17,8	37,2	0	37,2	0
GPK2-S4	continuos monitoring	surface	GFZ	17-29	59-64	0	24-30	0,1-0,2

	He (%)	**H_2** (%)	**Be+H2** (%)	**CH_4** (%)	**C_2H_5** (%)	**H_2S** (%)	**N_2/Ar** (vel.)	**He/Ar** (vol.)
GPK2-S1	1	45,3		6,8	0,12	<0,005	130	391
GPK2-D1	2,2	26,5	28,7	7	0			
GPK2-D3			19,2	6,5	0			
GPK2-S4	5-7			4-6				

Table 1 (a, b) : Chemical Composition of Geothermal Brine [Pauwels et al., 1993; Aquilina et al., 1997; Sanjuan et al., 2001; Naumann et al., 1999].

Temperature	200°C at 4,5 - 5 km depth
pressure	520 bar at 4,5 - 5 km depth
artesian flow	11,8 l/s at GPK2
pH	4,7 - 4,8
total salinity	100 g/l
%Cl	61 g/l
%S	158 mg/l - 172 mg/l
SiO_2	130 mg/l - 427 mg/l
GLR	2,6 % - 29 %
CO_2	14,2 % - 64 %
SO_4	158 mg/l - 172 mg/l

Table 2: Main characteristics of the Soultz geothermal fluid.

It is difficult to give the exact values of the Gas Liquid Ratio as well as of the SiO_2, CO_2 and SO_4 content, because no geothermal brine extraction from the deep wells, at 5000m, has been done yet. More, the geothermal brine is dilute with injected water and it cools off during its rise through the wells and due to this, for example, silica may precipitate.

2.2 Chemical Composition of the Gases

Only three gas samples were collected at well head from GPK2 and GPK4 during the five months fluid circulation test in 2005 and were analyzed by gas chromatography.

As can be seen from Table 3 [Pauwels et al., 1993; Aquilina et al., 1997], the predominant gas is CO_2. The partial pressure of this gas in the reservoir was estimated to be close to 6 bar. From surface samples a higher concentration of H_2 and He was observed. These gases perhaps have been preferentially collected in the down-hole sampler because of their higher mobility (lighter molecules) and their low solubility in water. Interactions between brine and bore-hole material can be also responsible for the high H_2 values observed in the surface samples.

Well	Date	Depth	%CO_2	% O_2	%N_2	%Ar	% He	%H_2	%CH_4
GPK1	1986-1991	well head	46,3	0	27,3	n.a.	1	20,1	4,8
GPK1	1986-1992	1845 m	67,1	0	27,4	n.a.	n.a.	0,61	4,2
GPK1	1986-1993	1930 m	54,3	0	37	n.a.	n.a.	0,25	6,1
GPK1	1993	3470 m	79	0	11	0,074	0,45	7,2	3,4
GPK2	1999	well head	14,2	0,48	29,9	0,23	1	46,3	6,8
GPK2	1999	650 m	15,8	0	48,6	0	2,2	26,5	7
GPK2	1999	700m	37,2	0	37,2	0	n.a.	n.a.	6,5
		surface(from gas separator and casing)	59- 64	0	24-30	0,1 - 0,2	0,5 - 0,8	5 - 7	4 - 6
GPK2	1999	surface(from gas separator and casing)	62	0	27	0,15	0,65	6	5
GPK2	1999	inlet of gas separator and complete degassing in lab	89,7	0	7,2	0,17	0,13	1,7	1,2
GPK2	2005	well head	56,6	0,05	34,3	0,17	1,98	1,9	6,3
GPK2	2005	well head	56,4	0,04	35,5	0,14	1,93	1,9	6,2
GPK4	2005	well head	61,2	0,05	30,8	0,18	1,66	2,8	5,8

Table 3: Chemical Composition of Gases [Pauwels et al., 1993; Aquilina et al., 1997].

2.3 Reservoir Fluid Temperature and Process of Water-rock Interactions

From the chemical composition reconstructed for the nativereservoir brine temperature values of 220 – 240°C are estimated in the deep reservoir using classical chemical geo-thermometers. As these estimations were similar to those previously performed on all the fluids collected from GPK1 and GPK2, the existence of a chemical equilibrium reactions between the native reservoir brine and the mineralogical assemblage at 220 – 240°C was suggested. Further test confirmed this and that the mineralogical assemblage in equilibrium with the brine is partially constituted of sedimentary minerals [Sanjuan et al., 2009]. The reservoir fluid temperature was estimated to be close to210°C, what seems to confirm that the isotopic values are modified by the dissolution of marine sulfate minerals, during the raise and the cooling of the geothermal fluid from the reservoir.

Generally, a cooling of hot fluid during its raise causes silicate mineral precipitation. The risk of silica precipitation is increased when the fluid raise is slow. This probably explains why the concentrations of dissolved Si02 are lowerin most of the fluids. The occurrence of secondary quartz deposition within fracture zone is an argument showing the same behavior of silica precipitation.

Calcite can also be precipitated at surface during the raise of the geothermal brine and CO2 degassing. However, in the case of the Soultz site, the alkalinity measurements tend to increase in solution with decreasing well depth and temperature. Other deposits as magnetite, siderite, galena, barite (BaSO4) and strontianite (SrSO4) are also possible [Sanjuan et al., 2006; BRGM, 2008].

3. CORROSION HISTORY AT SOULZ-SOUS-FORETS

There is no significant work done about corrosion before 1994 at Soultz.

3.1 Corrosion activity and results before 2007

3.1.1 Corrosion Activity and Results between 1994 and 1995

In 1994-1995 the production well GPK2 was drilled to 3876m and stimulated and the corrosion problem was taken in consideration for the first time. In fact, corrosion of the drill pipe during the air drilling effort as well as general corrosion problems with well heads and valves occurred. The corrosion inhibitor Mexel 432/0 was tested for the first time. The inhibitor is an aqueous dispersion of straight-chain aliphatic hydrocarbons containing amine and alcohol functionality and it is thought for open circuits in which circulates salty or un-salted water. Because of its dispersive properties, this mixture can prevent the formation of deposits having mineral or organic origin and is, in so far, able to decrease corrosion speed and to prevent from the Crevice corrosion.

It was thought that the use of this inhibitor could allow to clean up less often the filters from the heat exchanger and that it would decrease corrosion speed. To test the goodness of the inhibitor a corrosion ring was placed in the drilling GPK2. It was determined that this inhibitor reduced metal loss on a carbon steel test ring to 0.03 grams (starting weight was 79.853 grams) over 262 hours, i.e. negligible corrosion rate. As the results showed minor corrosion with the inhibitor and so the use of Mexel dosed at 3-5ppm became generalized during drilling operations.

3.1.2 Corrosion Activity and Results in 1997

In 1997, a 4 months circulation test took place with a production from GPK2 and a re-injection in GPK1: 2000 m^3/day produced at wellhead temperatures from 60 to 142°C and inhibitor was injected at production pump intake at 8 kg/day rate (4ppm). No corrosion was stated on production pump and pipes after the pump pulling and a corrosion pilot system was installed on the surface. The corrosion pilot consisted in 5 corrosion chambers each containing a sample in different material. Geothermal water circulated through the chambers during all the 4 months and during this time the samples were controlled at distances of 2-3 weeks.

Following materials were tested:
- K55 C-steel;
- K55 C- steel coated with Zn;
- Uranus B6;
- Hastelloy;
- 316L stainless steel.

No corrosion was stated on Hastelloy, Uranus B6 or 316L stainless steel probes, while moderate corrosion was stated on K55 carbon steel probes. The zinc-coated samples showed a more evident corrosion, in fact 80% of the size of the coating was destroyed, while the steel under the coating remained undamaged [Baticci et Faucher, 2008].

3.1.3 Corrosion Results in the wells in 2005

On May 2005, Schlumberger [Cantini, 2005 a, b, c, d] made a systematic measurement with an acoustic tool (USIT) designed for evaluating corrosion and cement quality of the casing at Soultz in the different wells. Same analysis took place in 1991 in well GPK1 between surface and 1420m depth.

USIT provides a baseline pipe inspection, with measurement of internal radius and thickness, and the following features can be identified (if present):
- Internal and external corrosion;
- Scaling on the inner wall of the tubular;
- Deformations of the tubular (ovalisation, buckling);
- Eventual tubular defects/holes; USIT is able to spot defects/holes of diameter bigger than 1.2 inches.

The corrosion evaluation log showed a tubular inner diameter and thickness within nominal values and did not show features that could compromise casing integrity. The features observed on the tubular were pitting, scaling and deposits.

In GPK2, GPK3 and GPK4 casing ovalisation, sometimes severe, was identified in several depth intervals. This was considered a risk to the wells integrity because corrosion may develop on eventual micro cracks in the deformed casing and, in the worst case, destroy the well. That is why from July to December 2005, another circulation test took place and the resistance to corrosion of other materials was tested by immerging samples in produced geothermal brine. The results showed a mass loss about 0,4 mm/year on P110 C-steel (GPK4 115°C and GPK2-4 150°C) and 0,6 mm/year on N80 C-steel, but these measurements could be suspicious because of general grease filming protection due to wellhead pack-off systems [Gerard et al., 2007].

3.1.4 Corrosion Results in laboratory in 2005

Other laboratory measurements were made on TU42BT C-steel under following conditions [Muller et al., 2007a]:
- T= 200°C;
- p CO_2 = 0,5 bar;
- pH = 4,6 – 5.

The used inhibitor did not give any significant measured effect at such temperature and after an analysis of the geothermal water and other measurements and tests it came out that the most corrosive species are CO_2, pH, temperature, salt and dissolved gasses, that mainly contain CO_2 [Sanjuan et al., 2006]. The result of this test was that alkalinity, CO_2 and temperature mainly control corrosion in the production well and that, as this inhibitor has no effect over 130°C and as the power plant will work at a maximum temperature of 180°C, a new generation of corrosion inhibitor is required.

3.1.4 Corrosion Results in laboratory in 2006

In 2006, laboratory experiments to quantify corrosion effects took place with a particular test set-up consisting of an outer structure and two corrosion chambers [Rummel and Weber, 2005 a, b; Rummel and Weber, 2006].

Through the corrosion chambers, containing the samples, circulated the corrosion fluid with a circulation flow rate of 2 l/min at a temperature of 80°C. Then, to study the inhibition effect of two corrosion inhibitors, the Soultz geothermal fluid was mixed with them. The hydraulic circulation system was installed in an insulated laboratory oven with constant temperature of 80°C while the test samples were placed in the corrosion chambers, consisting of glass tubes.

The steel casing samples were in P110 which is a CrMn carbon steel with a yield strength of 750 MPa and their dimensions were 50 x 10 x 6 mm with a surface area of about 2000 mm^2 and a sample weight of about 20g. Somesamples were furnished with drill holes, drill grooves and with pre-stressed sawcuts for pitting or stress corrosion starters [Rummel and Weber, 2006].

The corrosion rate was determined by sample weight measurements using a precision balance of 0,01 g accuracy at intervals of about 20 hours and, depending on corrosion rate, every test lasted up to about 170 hours. The corrosion fluids consisted of the Soultz formation brine sampled during the circulation test in 2005, with a density of 1,06 g/cm^3, a salt content of 100g/l and a pH value of 4,9 ,and a HCl acid with a concentration of 0,2 % to 10 % and pH values ranging from 3,2 to 0,6.

By studying the only effect of the Soultz water, it came out that the corrosion type occurred to the samples depends on the HCl concentration. In fact, for a concentration smaller than 5% of HCl, pitting occurs, while we have no pitting for HCl > 5%. The test showed maximal corrosion with HCl acid concentration between 2% and 5% and the highest weight reduction was about 24 g/m^2h. The two used additives showed no significant influence on the corrosion process.

3.2 Corrosion results in 2007

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Further test confirmed this and that the mineralogical assemblage in equilibrium with the brine is partially constituted of sedimentary minerals [Sanjuan et al., 2009]. The reservoir fluid temperature was estimated to be close to210°C, what seems to confirm that the isotopic values are modified by the dissolution of marine sulfate minerals, during the raise and the cooling of the geothermal fluid from the reservoir.

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3.3 Corrosion results in 2008

3.3.1 Corrosion Results in laboratory in 2008

In 2008, another corrosion study was started to test a new corrosion inhibitor, supplied by industry. The experiment took place in IFE's laboratory under test conditions listed in [Bilkova et al., 2007] and three different steels were exposed to the Soultz brine: P265GH, P110 and N80. During the first 40 h, the corrosion rates decreased from initial values of ca. 10 mm/y to values below 0.1 mm/y. This was followed by an increase in corrosion rates for the next ca. 60 h. The small leak was eliminated around ca. 100h after which the corrosion rates stabilized at values of ca. 0.2-0.3 mm/y. The samples were examined, after exposure, visually and under a low magnification microscope. The corrosion films were generally uniform. After removal of the films numerous small pits were observed on all specimens.

So addition of 30 ppm inhibitor resulted in a marked decrease of the corrosion rate from several mm/y to around 0.1 mm/y after the first day. After one week's exposure the corrosion rates had increased slightly to 0.2 - 0.3 mm/y.

3.3.2 Scaling in 2008

During the test on the geothermal loop in summer 2008, 3 samples were collected in the filtering system in surface. By using X Ray diffraction methods, and SEM (Scanning Electronic Microscope) done by BRGM [BRGM, 2008], the 3 samples were fully characterized. The deposits from the geothermal fluid, but also some silicate minerals coming from the granite reservoir, collected from the filters were finally analyzed to find out their chemical or mineralogical composition.

Sample 1 was collected in the mud channel:
- Fe, Si, Cl, Al, O, Cu, K, Zn, Na, Pb, S, Ba, Sr
- Fe-oxide, quartz, Ca carbonate, Sodium chlorure, Silicate, Barite, Celestite, PbS

Sample 2 was collected in production filter n°1:
- Pb, S Ca,Ba, Al, Cl, Fe, Sr, Cu, F locally
- Fe- oxide, PbS with some Cu, Pb bound with Cl, Ca carbonate, Barite, Celestite, silicate, particles containing much Al, particles containing F and C

Sample 3 was collected in re-injection filter n°4:
- S, Ba, Sr, Cl, O, Al, Ca, Fe, Cu, Na, Pb, Si, As, F
- Barite, Celestite, Pb bound with S or Cl, Al bound with Cl, silicate, Ca carbonate, particles containing C and F.

Another sample was taken on 16th July 2008 in the production filter. Its chemical composition shows as the main elements Pb (10000mg/kg), B (1000mg/kg), Fe (10000 mg/kg), Zn (4000mg/kg), W (4000mg/kg), Ca (6000mg/kg) and Sr (5000 mg/kg).

4. RECENT CORROSION AND SCALING STUDIES AT SOULTZ-SOUS-FORETS (LOW TEMPERATURE CONDITIONS)

Recently, from September 2008 till March 2009, corrosion and scaling studies on-site were carried out at the geothermal power plant of Soulz-sous-Forêts. The aim of the study [Baticci, 2009] was the characterization of the geothermal brine's action on three common steels: P110 (casings), N80 (casings) and P265GH (surface pipes).

These materials were chosen, as their corrosion resistance is lower than other on-site used materials. More, from an economical point of view, the casings as well as surface pipes surely play an important role. So, the priority was given to these steels. From each steel, different samples were prepared, exposed to the geothermal brine and analyzed.

Figure 1: The Soultz Corrosion Pilot installed at Re-injection Conditions.

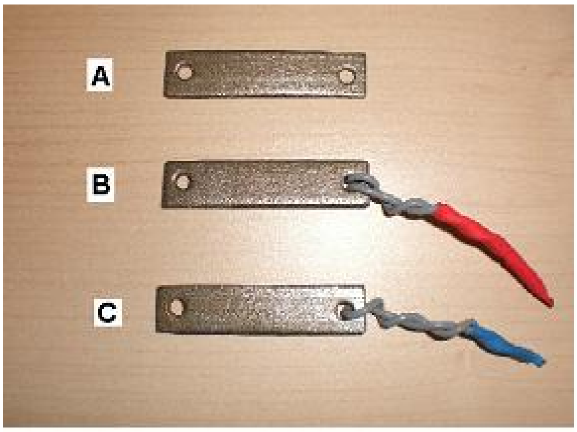

Figure 2: Identification of Samples in P110 and N80.

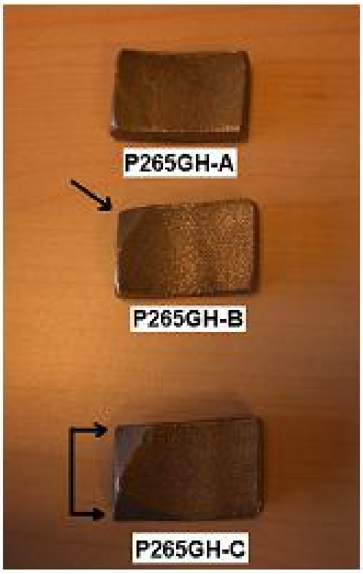

Figure 3: Identification of Samples in P265GH.

4.1 Test Set-Up: The Corrosion Pilot

For the first time in Soultz’s history, an on-site test was carried out with a particular and innovative set-up, the so-called corrosion pilot, shown in Figure 1.

The corrosion pilot is composed of three vertical pipes, each one containing a corrosion chamber, in which samples were introduced, and of an outer structure, containing measurements stations for pH, Eh, conductivity and temperature equipped by BRGM. Before the introducing of the vertical pipe containing these measurements stations, another pipe with a flow-meter was used.

The corrosion ring was placed on the pipe between the reinjection well and the heat exchanger for the ORC cycle. This position was chosen, because of the low temperature conditions of the geothermal fluid there, as most of the measurement probes (for T, pH, Eh, conductivity) are not efficient over 120°C. Temperature and pressure in the corrosion pilot will be approximately the same ones, as those at the re-injection side, about 70-100°C and 15-19 bar. The geothermal fluid coming from the heat exchanger for the ORC cycle flews through the pipe, on which the corrosion ring is placed. Only a part of this fluid will flow up through the U-ring of the corrosion pilot itself. This upcoming fluid will be split in three; each split part will flow through a different corrosion chamber. On the exit of the corrosion chambers the fluid is re-joint and flews, through the corrosion ring connected pipe, to the re-injection well GPK3.

The corrosion chambers were projected and realized by MeSy GmbH and are composed from an inner chamber in PEEK (Polyetheretherekton) and an outer chamber in brass.

4.2 Samples Design, Preparation and Identification

Three samples in each steel were prepared and, before introducing them inside the corrosion chambers, they had to be prepared and identified. Both operations were done, by following as far as possible, ASTM norms. Specimens in P110 and N80 were almost available, while samples in P265GH were cut from a metal ring, as it was the only easily regaining piece in this material. All samples were sandblasted, weighted and identified. For the identification of samples in P110 and N80 a Teflon wire was used (Figure2), while the identification of specimens in P265GH was done by using the edge notching technique (Figure 3).

4.3 Operational Step: Samples’ Immersion

The first step of the corrosion test was the insertion of the samples in the corrosion chambers. In order to be able to recognize each corrosion chamber, they were identified by numbers.

When the power plant was started the 17th November 2008, the corrosion samples could not be introduced in the corrosion chamber starting from that date. In fact, at first the artesian circulation had to take place for warming the production pump equipment. The first hundreds cubic meters were not re-injected in order to avoid to re-introduce fine particles in the reservoir.

During the first week of power plant running, the geothermal water flow circulating through the corrosion pilot was controlled by the flow-meter. The found value, about 4 m^3/h, and the fact that this value remained constant were considered good conditions for the corrosion testing. The samples were put in the corrosion pilot on the 25th November 2008. Table 4 illustrates the main immersion conditions (sample name, identification, date).

In order to avoid galvanic contacts and interactions between different kinds of steels, samples in same steel were put in same corrosion chamber. Later, samples were extracted at different time intervals (313, 501 and 1148 hours). After each time interval one sample from each corrosion chamber was extracted.

In order to do also chemical analysis with an etchant and to have so further information about the eventual corrosion products, it was decided, after the immersion of the samples, to immerse other three samples (type D), one of each steel. These samples were immersed, one in each corrosion chamber, when the second specimens were extracted.

4.4 Test Conditions: Data Acquisition and Analysis

The flow-rate through the corrosion pilot was controlled during the first 15 days of exposure, while after the extraction of the first specimens the flow-meter was replaced by the pipe containing all the measurements probes. So for the first 15 days, no indication about pH, Eh, temperature and conductivity was given. All acquired data were graphically analyzed by the use of the software Visual Manager. As measurement probes were installed for the first time, different technical problems occurred and no reliable measurements about Eh and conductivity could be given.

The measured pH value was under 5, about 4,8 in agreement with water analysis of Aquilina et al., (1997).The flow-rate, was measured to be about 4 m^3/h, while a mean value of temperature was estimated to be around 70°C. The total flow rate was about 100 m^3/h.

4.5 Post Immersion Analysis

After samples extraction, each specimen was analyzed. The aim of all analyses was to chemically characterize corrosion and scaling. The main focus was set on the corrosion products and on the setting of the corrosion speed, type and depth, in order to find out, how severe the eventual corrosion could be, on what it depends and what could be done to avoid it. The analyses used were the SEM and the WDX (Wavelength Dispersive X-ray fluorescence) ones.

Material	Sample's number	Identified by	Corrosion chamber	Hour of immersion
P110	P110-A	nothing	1	15h30
P110	P110-B	2 turns Teflon wire and red plastic tube	1	15h30
P110	P110-C	1 turn Teflon wire and blue plastic tube	1	15h30
N80	N80-A	nothing	2	15h30
N80	N80-B	2 turns Teflon wire and red plastic tube	2	15h30
N80	N80-C	1 turn Teflon wire and white plastic tube	2	15h30
P265GH	P265GH-A	nothing	3	15h30
P265GH	P265GH-B	1 snotched edge	3	15h30
P265GH	P265GH-C	2 snotched edges	3	15h30

Table 4: Immersion Conditions of Samples [Baticci, 2009].

P110		
Time (h)	Sample name	Delta Weight (g)
313	P110-B	0,05
501,5	P110-A	0,17
645,5	P110-D	0,07
1148	P110-C	0,2
N80		
Time (h)	Sample name	Delta Weight (g)
313	N80-B	0,03
501,5	N80-A	0,17
645,5	N80-D	0,06
1148	N80-C	0,2
P265GH		
Time (h)	Sample name	Delta Weight (g)
313	P265GH-B	0,12
501,5	P265GH-A	0,22
645,5	P265GH-D	0,15
1148	P265GH-C	0,28

Table 5: Weight Variation of Samples.

Before the analyses, samples were cut in two parts: on one half WDX analysis (or XRF analysis) took place, while on the other half SEM analysis took place. In fact for the micro X-ray fluorescence (or WDX) analysis samples had to be cut, to study the elements kind and composition and their variation from the inner metal core to the surface. More, for practical reasons bound to dimensional characteristics of the used machines, samples had to be cut anyway. In order to gain time, in contemporary to the fluorescence analysis, the other half of the sample was prepared for further SEM analysis. In order to have further information about the corrosion products, also chemical analyses took place. But, as no chemical and WDX analyses can take place on same samples (because samples were cut in two parts and no sufficient corrosion products or deposits were expected to be on one half sample), other three samples (type 'D') were introduced in the corrosion chambers on the 16th December 2008. This was useful in order to have further information about products detected on the surface of the samples. Last immersed samples were extracted at the same time as those remaining in the corrosion chambers.

4.6 Results

4.6.1 Weight, SEM and XRF Results

Following results concerning weight variation of specimens, XRF, as well as SEM and chemical analysis on samples were reached.

Weight variation of analyzed samples is illustrated in Table 5, while Figure 4 and Figure 5 show, how the weight variation (increase) changed in time, considering and not considering samples type D. From Figure 5 it can be seen, how the weight increase was almost the same for all analyzed steels, as the curves are very similar. The samples's weight increase seems to be almost proportional to the exposure time to the geothermal brine, about 0,1g from 313 to 501,5 hours exposure and about 0,05g from 501,5 to 1148 hours exposure. This could probably mean that deposits 'grew' proportional to the exposure time, what was later confirmed by SEM and XRF analyses.

Results reached from SEM and XRF analyses on all samples showed a similar behavior of all analyzed steels to the geothermal brine, though in different extent. In fact, on all samples three characteristic zones were identified: 'basis' metal, deposit layer and an interface region between both.

The deposit layer, consisting of barite and celestite, grew in time, as it could be seen from its detected thickness, reaching a maximal thickness between 50 µm and 60 µm after 1148 hours of exposure. The layer was anyway not homogeneous for all analyzed samples, though present on almost the whole surface of the specimens and was characterized by a crystal structure. The crystals formed themselves in less than 313 hours of exposure to the brine for steel P110 and P265GH, while they formed later for steel N80.

In the interface region, different elements were detected, as Zr, Si, O, Sb, Ca, Cl, Na, Pb, Cd and As. The content of this last element in the interface seemed to decrease in time and its presence is due to the geothermal fluid, as was confirmed by water analyses. Also Na, Cl, Pb, Si, Sb and Ca derive from the Soultz brine, though probably part of the Si could come from the sandblasting. The presence of Zr is instead only due to the sandblasting.

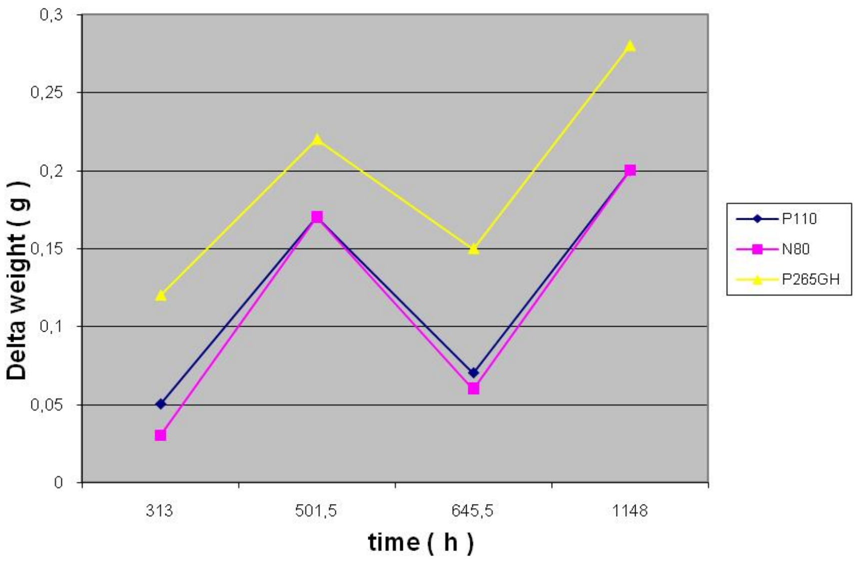

Figure 4: Weight Variation of All Samples: Delta-Weight Time Diagramm.

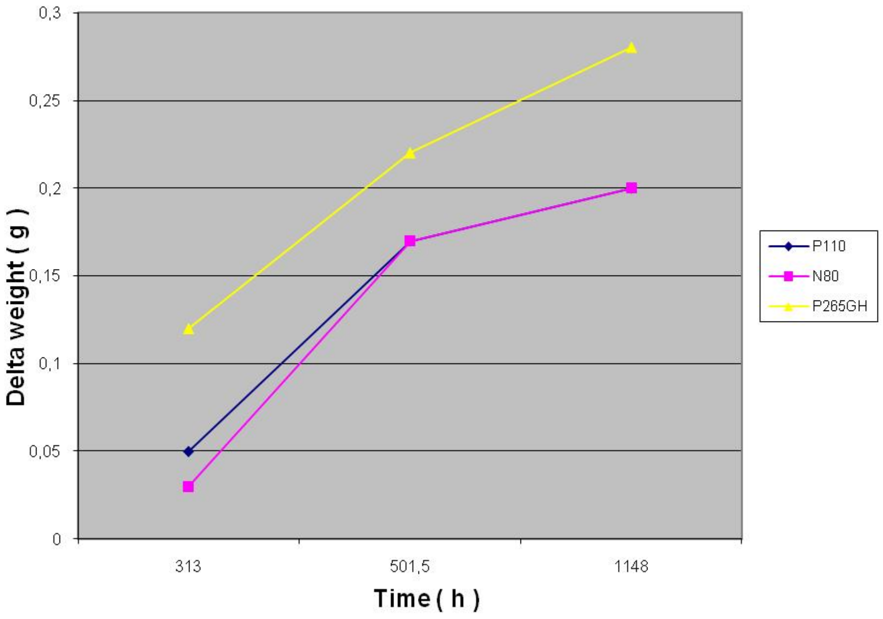

Figure 5: Weight Variation for Studied Samples, without Samples Type 'D'.

Pits were detected on the steels' surface, under the interface region. Their number did not grow in time and inside them rust (Fe_2O_3) and also Ca were detected. Pit's maximal dimension was measured to be about 6μm.

After longer exposure times (1148h), rust was detected between the crystals of barite and celestite on all analyzed steels.

Reached results were confirmed by chemical analyses done on samples type 'D' and are better described in Figure 6, where the three detected regions are clearly shown.

4.6.2 Corrosion rates

Finally, the corrosion rates of all steels were evaluated with following relationship specified in ASTM norm G102-89 'Standard practice for calculation of corrosion rates and related information from electrochemical measurements:

$$CR = (kW) / (ATD) \qquad (1)$$

Where:
CR…corrosion rate in mm/yr;
K……constant (K = 8.76 104 mm/year);
W……mass loss in g;
A…….area of sample in cm2;
T…….time of exposure in h;
D……density of considered alloy in g/cm3.

Evaluated corrosion rates on-site are shown in Table 6 together with corrosion rates evaluated after laboratory autoclave test in 2008.

According to ASTM standards, the use of corrosion rates implies that all mass loss has been due to general corrosion and not to localized corrosion as pitting. So, for analyzed samples, the evaluation of corrosion rate done this way does not have much sense, because no general corrosion was found. Though, corrosion rate was evaluated in order to make a comparison to laboratory results.

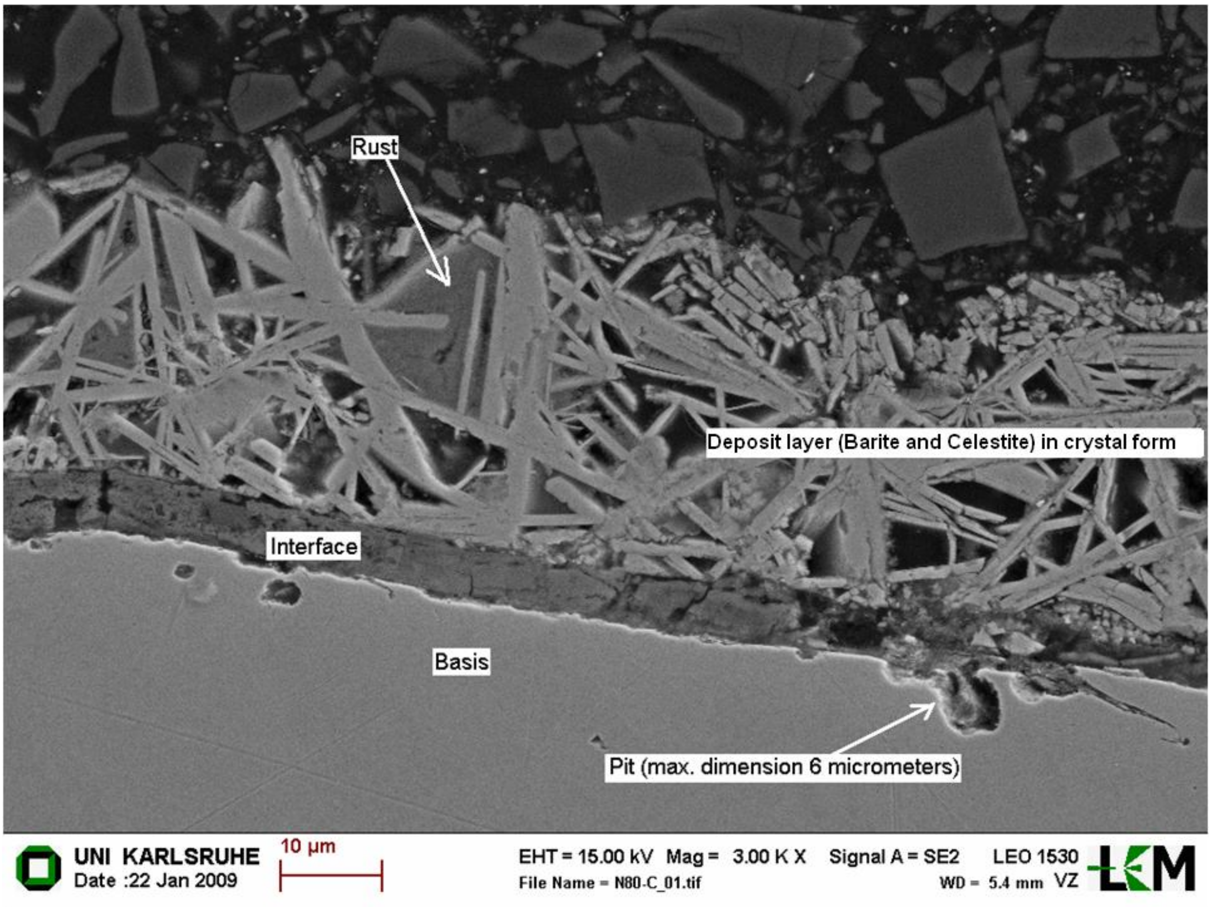

Figure 6: Characteristic zones on analyzed samples by SEM analysis.

Steel	CR on-site (mm/year)	CR lab (mm/year)
P110	0,15	0,2 - 0,3
N80	0,148	0,2 - 0,3
P265GH	0,22	0,2 - 0,3

Table 6: Corrosion Rates On-Site and in LaboratoryExperience.

Values of corrosion rates reached with the on-line pilot seem to be definitely lower in comparison to laboratory results, for steel P110 and N80, while almost the same values are obtained for steel P265GH. Generally, we should expect the opposite thing, as with the use of a corrosion inhibitor (laboratory case) the corrosion rate values should be much lower. But, in lab experience higher temperatures were reached (about 180°C, while temperature in corrosion pilot is about 70°C) and temperature surely plays a very important rule in the corrosion process. More, the difference in the exposure time and the fact that not all corrosion products could be removed from on-site analyzed samples, does not simplify an appropriate comparison.

Finally it has to be considered, that the evaluated corrosion rate, calculated with the formula for generalized corrosion, may overestimate the effective corrosion rate in real case (pitting corrosion). Although it is difficult to make a relevant comparison, the fact that both evaluated corrosion rates have same order of magnitude (0,15 to 0,3) has to be considered as a relevant result.

4.7 Conclusions, recommendations and proposal of standard procedure for further on-line tests

Concluding, the geothermal fluid’s action on analyzed steels was described and was determined to be the same on all analyzed steels. Corrosion and deposits were detected, both. The question was how to correlate both phenomena one to another and to understand the influence of the deposits layer on the corrosion of the steel. In fact corrosion, in form of pits, probably depends on a differential aeration due to the deposits layer. Though that, the number of pits did not increase in time and the corrosion products did not dissolve in the geothermal brine, but seemed to remain blocked in the deposits layer. So it could be concluded that, pits form because of the deposits, but the deposits prevent corrosion products from dissolution in the geothermal brine. Surely, reached results have to be considered only as a first step in the comprehension of the analyzed phenomenon.

Recommendations for further corrosion results were the use of duplicate specimens, as well as the measurement of fluid’s speed or flow rate, in the corrosion pilot, as well as in the power plant’s component realized in the studied material. Finally, statistical analysis should be applied to corrosion results. This could be very helpful in the interpretation of such results, especially in determining when test results differ from one another significantly. This could be a difficult task when, as in the considered case, a variety of materials are under test, but statistical methods provide a rational approach to this problem, resumed in ASTM norm.

As final result of the study, a standard procedure for further on-site tests was worked out. The elaborated procedure is resumed in the following steps:

· *Preparation, Identification and Description of specimens:* Sandblasting, measurement of dimensions and weight, identification, particular attention to the use of duplicate specimens. To have a kind of feed-back of further analysis, it would be good to consider an extra sample only for chemical analysis. It would be recommendable to use samples of same shape and size and to create a sort of standard. The recommended size is those of samples in N80 and P110, as samples in P265GH result to be too big for further analysis, as for example for the SEM analysis, where smaller samples' dimensions are required. For identification, edge notching should be applied.

· *Immersion of specimens:* It could be recommendable to change dimensions of corrosion chambers, in order to be able to insert more samples. During the immersion time different parameters have to be measured for further analysis, as pH, T, Eh and conductivity. More, it would be useful to measure, through for example polarization resistance measurements, as prescribed by ASTM norms, the corrosion current, to better evaluate the electro-chemical processes.

· *Immersion time*: It is difficult to define a recommended immersion time, as no safety about the effectively functioning of the power plant is given. An immersion time should be no less than one week by comparing with laboratory corrosion test. It is recommended to hold samples in corrosion chambers as long as possible, while the geothermal fluid is circulating through the studied application. During the immersion time, values of physico-chemical measurements for pH, Eh, p and T have to be controlled. It would be useful to change the pilot set-up, in order to be able to measure the same parameters as well as the fluid's flow at the same time.

· *Extraction of specimens:* During the extraction of samples from corrosion chambers, particular attention has to be posed on the contamination of samples. Gloves have to be used and the samples have to be introduced, as soon as extracted from the chambers, in sealed containers, in order to avoid any contact with the atmosphere. The extraction should be as fast as possible, in order not to stop for a too long time the flow of the geothermal fluid through the corrosion chambers.

5. FUTURE CORROSION AND SCALING ACTIVITY AT SOULTZ-SOUS-FORETS

After the corrosion test at low temperatures, many ideas for future research in the corrosion and scaling field came out, as for example the testing, in same conditions (low temperature) of other materials used in other plant's components. But, what follows directly from the previous described experience is surely a high-temperature corrosion test. In fact results reached at low temperature conditions, surely showed what happens to materials when exposed to the geothermal brine, but they can not be applied to explain real corrosion and scaling phenomenon, particularly concerning steels P110 and N80. In fact, the components realized in these steels are the casings in the deep wells, reaching depths of 4500m. Here, temperature, pressure and also fluid chemistry are surely different than in the test conditions. So, the need of a high-temperature test becomes important in order to detect real entity of phenomena.

To do a high temperature corrosion test the same corrosion pilot design could be used, but, the test set-up has to be posed on a pipe before the production well, where temperature reaches values up to 160°C. So, materials could be tested in conditions comparable to their real use ones. The only problem concerning this test is the use of measurement probes, as they are not efficient over 120°C. So, probably, no measurements of parameters could be given.

It could also be of relevance to determine fields in which scaling forms itself. This could be done by the use of chemical fluid simulators. By knowing the conditions (pH, T, p) under whose deposits forms, their influence on the corrosion phenomenon should be better analyzed. In fact, it could be determined, if pitting corrosion only occurs together with scaling and what happens to the steels if the deposit is not present. The aim of all would surely be a better comprehension of the interactions between scaling and corrosion.

6. CONCLUSION

Concluding, corrosion as well as scaling are, both, important phenomena in geothermal systems and mainly depend on geothermal brine's conditions. At Soultz-sous-Forêts they have been characterized at re-injection conditions. For a better comprehension of the phenomena and their interaction, ideas for further studies and project are given.

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