Laboratory and *In-Situ* Corrosion Studies in Geothermal Environments

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ABSTRACT

A major factor in the economic exploitation of geothermal resources will be the cost-effective selection of materials that have sufficient resistance to corrosion to maintain component integrity during plant operation. Various metals have been tested in laboratory and in-situ weight-loss exposure tests (Soultz-sous-Forêts) and instrumented exposure (electrochemical polarization) in geothermal brine from Soultz-sous-Forêts, France. Mild steels (N80, P110, P235GH and P265GH) are subject to corrosion. However, the formation of secondary corrosion products (mainly $FeCO_3$) contributes to materials corrosion resistance and reduces the corrosion rate over time. Potentiodynamic polarization has been used to study the passivation tendency of stainless steels and alloys, showing good agreement with exposure tests. 430F showed pitting after 4 weeks of in in-situ and autoclave exposure, while higher-strength materials (316L, 318L, 904L, alloy 31 and Ti grade 2) showed no obvious sign of surface degradation and/or scaling.

Introduction

It is well-known that geothermal environments challenge the resistance of construction materials and once geothermal water is available for heat extraction, two technological challenges become apparent: corrosion and scaling. While geothermal waters worldwide were found to strongly test the corrosion resistance of various materials, scaling has an adverse effect on heat transfer, pump efficiency and may lead to clogging of the pipe system (Miller, 1979, Ellis & Mahon, 1977, DeBerry et al., 1978, Conover et al., 1979). Using appropriate materials can therefore increase the power plant availability and thus decrease the operating costs. Experiences from chemical process industry prove that high-quality materials for extreme environments exist, but economic aspects have to be taken into account leading to a trade-off between performance and costs. The range of candidate materials is wide. For a cost comparison a factor is given in relation to mild steel (Tab. 1). The maximum span is around factor 30. However, it is obvious that there is some world market fluctuation and this factor gives only a cursory guide.

One major aspect in the economic consideration is the possible necessity to replace components that suffer degradation in contact with the processed brine. Basically two fundamental design concepts exist: (1) taking corrosion resistant materials throughout the system or (2) take low-cost materials and accept replacement in case of breakdown. However, for some process equipment high-strength materials are inevitable when common materials have previously failed or are anticipated to exhibit low performance. This would include equipment in which high reliability and near-zero corrosion allowances are required, from a performance, maintenance and/or safety standpoint (Thomas, 2003).

First investigations in Soultz-sous-Forêts have highlighted the applicability of electrochemical and weight-loss methods, which are widely applied in corrosion research (Mundhenk et al., 2012, Baticci et al., 2010, Pound et al., 1985, Carter & Cramer, 1992, MacDonald et al., 1979). Moreover, the contribution of corrosion products to the corrosion resistance has been discussed. This investigation is intended to develop a more integrated understanding of corrosion processes in a geothermal environment with Soultz-sous-Forêts as an example.

By using electrochemical techniques, a statement regarding pitting corrosion resistance can be made. Here, an approach is presented to study the electrochemical characteristics of passivation, relating to localized corrosion, which may help to decide whether or not an alloy or passivating metal is prone to suffer localized attack in a given environment. This approach bases upon measurable potentials which are derived by electrochemical measurement including cyclic polarization and corrosion potential measurements. Tendency to pitting corrosion can be evaluated by comparing the free corrosion potential (or open circuit potential) E_C of an alloy to its pitting (or breakdown) potential E_P. If $E_C << E_P$ no pitting corrosion will occur, whereas pitting corrosion takes place when $E_C \geq E_P$. If $E_C \approx E_P$, pitting corrosion may occur, since even slight changes in the oxidizing capacity of the brine may raise the E_c to

E_P (Pohjanne et al., 2008). However, whether or not pitting occurs, is difficult to predict and occurs apparently random. Other authors suggest $E_C < E_R$ as the principal constraint for pitting stability, considering the capability of repassivation (Bäßler et al., 2009).

Experimental

Weight-loss exposure tests were performed with coupons in the Soultz corrosion bypass and in the laboratory autoclave using geothermal water from Soultz. Maximum in-situ exposure time was 5 month for mild steels. These exposure tests at elevated temperatures and pressures are of great importance to material evaluation, since they represent the original corrosion conditions of the intended use.

Furthermore, electrochemical methods (including potentio-dynamic polarization, corrosion potential measurements) have been performed, using a conventional 3-electrode setup with the test sample as the working electrode. These electrochemical techniques are widely applied in corrosion research, because they provide a sensitive an instantaneous value of the corrosion rate (Pound, 1985). Electrochemical measurements are useful to study the corrosion behaviour of metallic materials by applying external voltage. All metallic materials can be brought to their limits and this method is therefore appropriate to define the limits of use, disregarding whether or not this corrosion is likely to occur in a ‘real’ geothermal environment.

Various metals have been tested in in-situ and simulated geothermal brine environments: Commonly used casing and pipe steels (Fe-based mild steels), standard stainless steels (430F, 316L) and promising candidates (alloy 904L, duplex 318L, super-duplex alloy 31 and Titanium grade 2). The nominal composition, the pitting resistance equivalent (PRE) according to PRE = %Cr + 3.3%Mo + 16%N (Gräfen & Kuron, 1996), some general remarks and a cost comparison are given in Tab 1. The samples were either cut as rectangular samples or slices depending on the received geometry. According to ASTM G5-82 standard the metal samples were polished with SiC abrasive paper (120, 320, and 1000 grit), washed with pure water, degreased in acetone, dried, and weighed.

Experiences from operation show that the Soultz brine strongly tests materials performance (Mundhenk et al., 2012, Baticci et al., 2010), with considerable high concentrations of identified key corrosive species (DeBerry et al., 1978). The brine can be classified as slightly acidic Na-(Ca)-Cl water and has a TDS of approx. 100 g/L. For laboratory experiments the brine was sampled from the surface installations by flashing in a cooling coil. A typical composition is given in Tab. 2. Sanjuan (2010) reports a gas-water-ratio (GWR) of up to 40 vol% with varying amounts of CO_2, N_2, H_2, CH_4 and He. In most samples CO_2 and N_2 contribute more than 80 vol% to the total gas phase. CO_2 acts as mild oxidizing agent on iron, but the primary effects in geothermal waters are on carbonate speciation and pH (DeBerry et al., 1978). CH_4 is also present in significant amounts up to 7 vol%. H_2 can also be found in strongly varying concentration up to 46 vol%. Its presence in combination with a negligible concentration of O_2 represents the most direct indicator of the redox state.

Table 1. Test materials.

Material Group	Tested Metals (Nominal Compositions)	PRE [%]	General Remarks	Costs* (Relative to Mild Steel)
Mild Steels	P110, N80, P235GH, P265GH: > 97.5%Fe		- Low-cost & availability - Ease of fabrication - Appropriate for thick-walled applications	1
Stainless Steels & Alloys	430F: 16-18%Cr 316L:16.5-18.5%Cr, 10-14%Ni, 2-2.5%Mo 318LN (Duplex): 21-23%Cr, 4.5-6.5%Ni, 2.5-3.5%Mo, alloy 904L (special austenite): 19-21%Cr, 24-26%Ni, 4-5%Mo, <2%Cu alloy 31 (Super-Duplex): 26-28%Cr, 30-32%Ni, 6-7%Mo, <1.4%Cu	17 27 34 36 52	- Uniform corrosion rates are generally low - Localized modes of corrosion may occur, e.g. pitting, crevice corrosion	1.7 8.3 7.1 19.4 33
Titanium	Grade 2: 99.2%Ti		- Generally excellent corrosion resistance	16.2

PRE: pitting resistance equivalent (according to median nominal composition)
*Costs according to Alloy calculator© (metalprices.com)

Table 2. Most representative Soultz brine chemistry (Sanjuan, 2010).

T [°C]	Density [g/cm³] @20°C	Cond. [mS/cm] @20°C	pH	O_2 [%]	Eh [mV]	Na [g/l]	K [g/l]	Ca [g/l]	Mg [mg/l]	Cl [g/l]	SO_4 [mg/l]	Alkalinity [meq/l]	SiO_2 [mg/l]	NO_3	NO_2
230?	1.065	120	4-5	0	<-100	27.5	3.25	6.90	125	59	59	5 (85 mg/l HCO_3)	427	<0.5	<0.01
NH_4 [mg/l]	**PO_4 [mg/l]**	**Br [mg/l]**	**B [mg/l]**	**F [mg/l]**	**Sr [mg/l]**	**Li [mg/l]**	**Mn [mg/l]**	**Ba [mg/l]**	**Fe [mg/l]**	**Al [mg/l]**	**As [mg/l]**	**Rb [mg/l]**	**Cs [mg/l]**	**Ge [µg/l]**	**Be [µg/l]**
23.5	<0.1	220	35	4.5	450	140	15	10	100	0.05	6	22	14	53	30
Ni [µg/l]	**Cu [µg/l]**	**Co [µg/l]**	**Cr [µg/l]**	**Cd [µg/l]**	**Zn [µg/l]**	**Ag [µg/l]**	**Ti [µg/l]**	**Pb [µg/l]**	**TDS [g/l]**						
100	45	50	40	10	3000	<5	200	300	97						

Results & Discussion

Electrochemistry

As a first result the applicability of potentiodynamic polarization in geothermal water from Soultz could be demonstrated on mild steels (P235GH, P265GH, N80 and P110) and stainless steel 316L, showing a high reproducibility of potentiodynamic polarization measurements (Fig. 1).

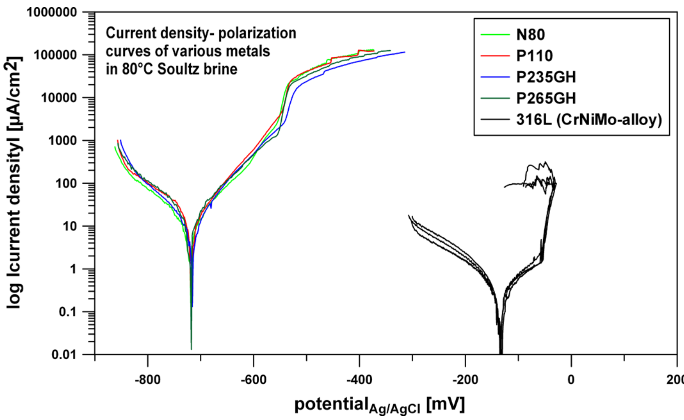

Figure 1. Current density-potential curves for mild steels (N80, P110, P235GH and P265GH) and standard stainless steel 316L in 80°C Soultz brine, showing high reproducibility of measurements.

According to their composition mild steels show virtually identical electrochemical response and show similar corrosion attack including uniform corrosion and shallow cavitation. Corrosion rates determined by linear polarization resistance are between 0.14-0.18 mm/y. However, these corrosion rates are instantaneous result of short-time exposure under scaling-free conditions and do not reflect long-term corrosion behavior.

Stainless steels and alloy show different corrosion behaviour during polarization. Due to their passivation characteristics uniform corrosion rates are very low and the probability of localized corrosion is of higher importance. All stainless steels tested respond to potentiodynamic polarization with pitting corrosion. Except for 430F, all metals show clear active-passive behaviour with stagnating or decreasing current densities in the passive region. Exceeding the critical (pitting/breakdown) potential results either in pitting corrosion (430F, 316L, 316Ti, 318LN and 904L), increased uniform corrosion (Titanium gr. 2) or selective corrosion (alloy 31).

Along with stable values for E_C, a wide range of passivity could be observed for most high-strength materials. Fig. 2 gives the results for alloy 31. After immersion into the hot electrolyte spontaneous passivation begins, shifting the free corrosion potential E_c into the anodic direction. Aeration of the electrolyte leads to a further shift of E_c (Fig. 2 top). The crucial pitting potential E_P can be derived by potentiodynamic polarization (Fig. 2 bottom). However, the E_c does not exceed E_P , making pitting corrosion for alloy 31 in this environment unlikely.

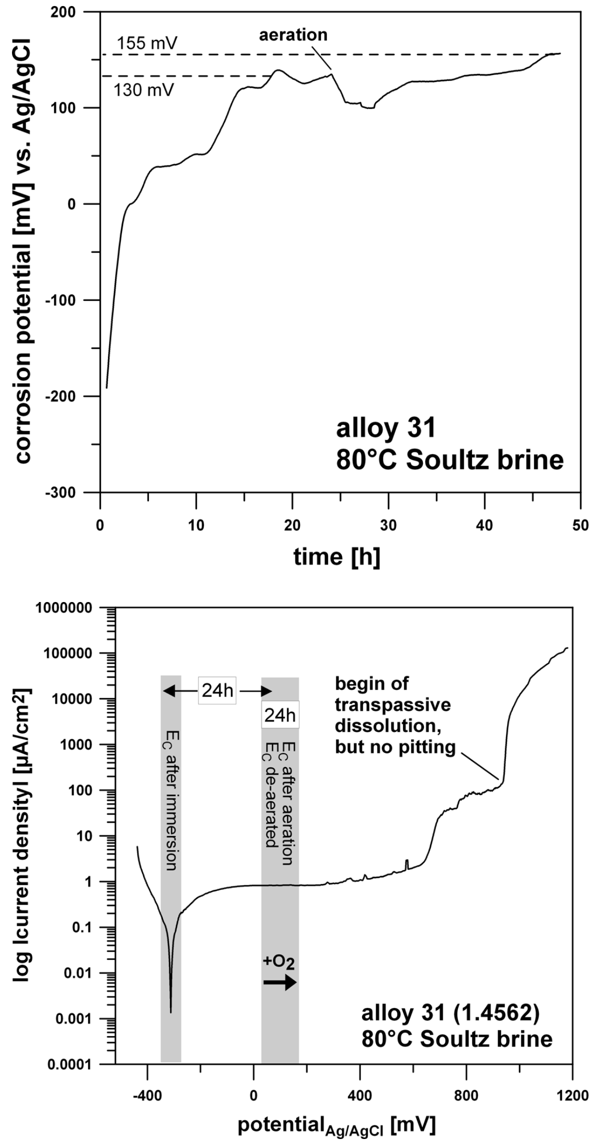

Figure 2. Corrosion potential measurement and current density-potential curve for alloy 31 in 80 °C Soultz brine.

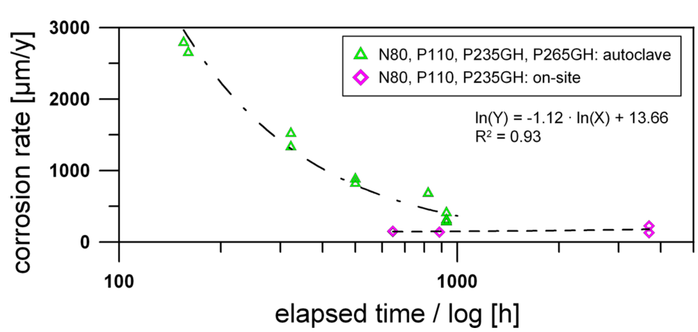

Figure 3. Corrosion rates for mild steels in autoclave and in-situ environment (Soultz).

Weight-Loss Exposure Tests

Weight-loss exposure tests have been performed in the low-temperature bypass in Soultz and in the laboratory autoclave. Results from autoclave exposure tests yield strongly decreasing corrosion rates for mild steels, accompanied by the formation of an adherent corrosion product (Fig. 3). Long-term corrosion rates can be extrapolated to <0.2 mm/y, which is in good agreement

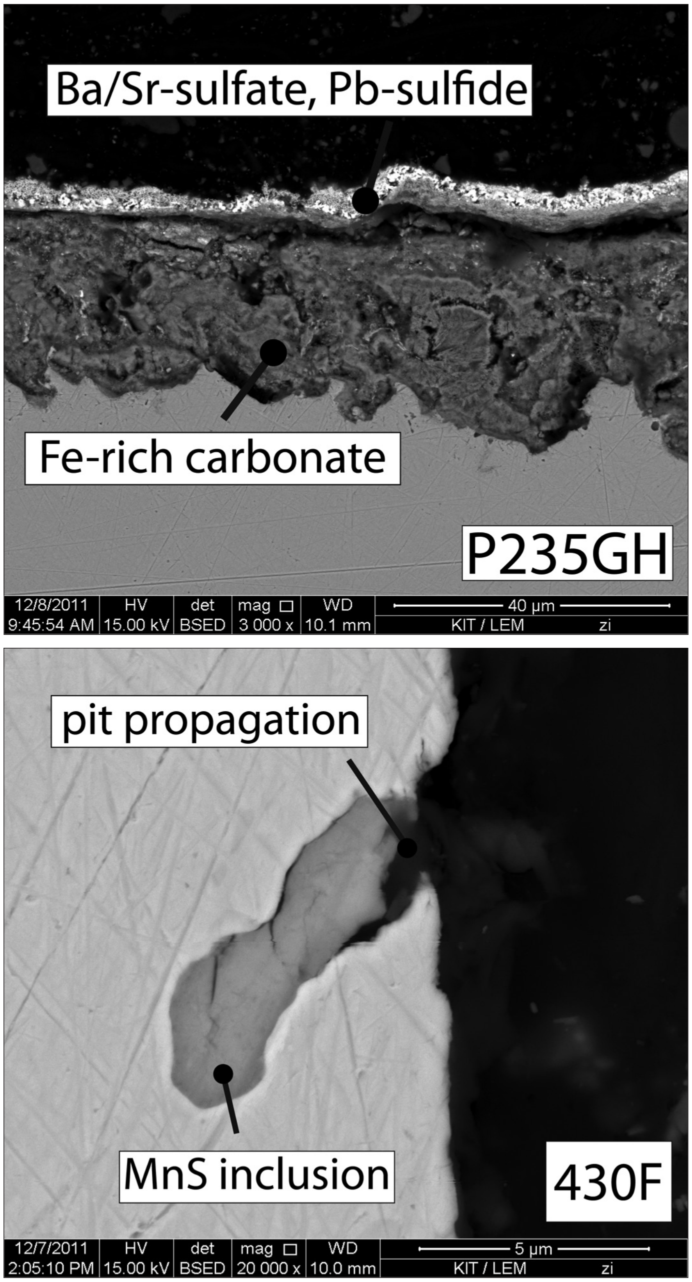

Figure 4. Post-exposure morphology of coupons. (top) P235GH after 4-week in-situ exposure in Soultz; formation of corrosion product. (bottom) 430F after 4-week in-situ exposure; beginning localized (pitting) corrosion along MnS inclusion

with on-site corrosion rates. SEM/EDX analyses on post-exposure samples prove the formation of $FeCO_3$ (siderite) as a corrosion product and the precipitation of low-soluble minerals from the brine, e.g. Pb-sulfide, Ba/Sr-sulfate (Fig. 4 top).

All stainless steel and alloy coupons were blank after extraction from exposure tests and no visible corrosion product could be found (Fig. 4 right). The corrosion rates for stainless steels and alloys are given as a function of the PRE in Fig. 5. Except for 430F, the corrosion rates are negligible low. Moreover, 430F exhibited localized (pitting) corrosion along manganese sulfide (MnS) inclusions after in-situ and autoclave exposure.

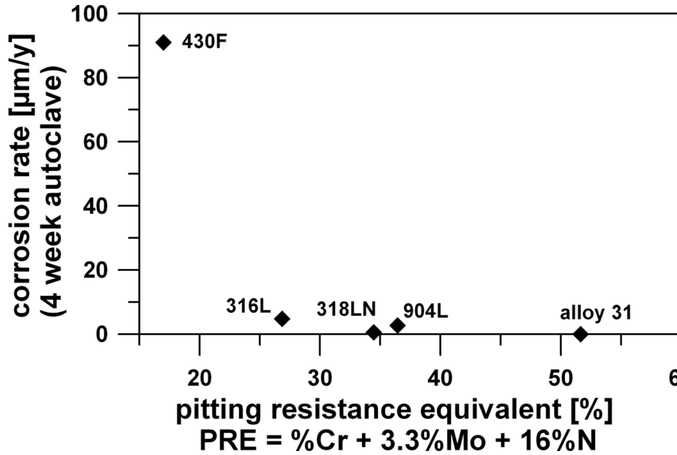

Figure 5. Corrosion rates of stainless steels (based on 4-week autoclave exposure) as a function of the pitting resistance equivalent (PRE).

Conclusions

Two different methods of corrosion research have been applied – potentiodynamic polarization measurements in the laboratory and weight-loss exposure tests in the autoclave and in the LT-corrosion bypass in Soultz-sous-Forêts. Although electrochemical and weight-loss methods are widely applied in corrosion research, material assessment using both methods with a geothermal focus is still uncharted territory. For the Upper Rhine graben with its huge geothermal potential no ambitious efforts have been taken.

Electrochemical polarization experiments are useful for a first characterization and can help in a material pre-selection process. Furthermore, they can provide information about the tendency to passivate (form nm-scale oxide layers) in a given environment. However, in order to get reliable results about the corrosion behavior, long-term exposure tests are inevitable.

Mild steel corrosion rates in exposure tests were found to decrease strongly due to the formation of protective surface layers. In case of mild steels the formation of a protective $FeCO_3$ layer and an additional layer of low-soluble minerals (e.g. Ba/Sr-sulfate, Pb-sulfide) could be observed. Ongoing experiments intend to quantify the influence of temperature on the corrosion rate and on the corrosion product formation.

All stainless steel and alloy coupons were blank after extraction from the test environment and show therefore good anti-scaling characteristics. Cr-alloyed 430F failed in the autoclave and in-situ environment, showing pitting corrosion after 4 weeks of exposure. CrNiMo-alloy 316L did not show significant corrosion after exposure tests. However, results from electrochemical measurements indicate, that these material are strongly tested in the environment. All higher alloyed materials show good to excellent performances.

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References

ASTM G5-82: Standard practice for standard reference method for making potentiostatic and potentiodynamic anodic polarization measurements, in: G.S. Haynes, R. Baboian (Eds.) Laboratory Corrosion Tests and Standards. ASTM Committee G-1 on corrosion of metals, ASTM special technical publication 866, 1985.

R. Bäßler, A. Burkert, A. Saadat, R. Kirchheiner, M. Finke, Evaluation of corrosion resistance of materials for geothermal applications, NACE International Conference Paper, Corrosion, March 22 – 26, Atlanta, 2009.

F. Baticci, A. Genter, P. Huttenloch, R. Zorn, Corrosion and Scaling Detection in the Soultz EGS Power Plant, Upper Rhine Graben (France), Proceedings World Geothermal Congress 2010, Bali, Indonesia, 25-29 April 2010.

J.P. Carter, S.D. Cramer, Materials of Construction for High-Salinity Geothermal Brines, U.S. Department of the Interior, Report of investigations 8792 (1992).

M. Conover, P. Ellis, A. Curzon, Material Selection Guidelines for Geothermal Power Systems - An Overview, in: L.A. Casper, T.R. Pinchback (Eds.), Geothermal Scaling and Corrosion, ASTM Special Technical Publication 717, 1979, pp. 3-10.

D.W. DeBerry, P.F. Ellis, C.C. Thomas, Material selection guidelines for geothermal power systems, first edition, ALO-3904-1, EG-77-C-04-3904, US Department of Energy, (1978).

A.J. Ellis, W.A.J. Mahon, Chemistry and Geothermal Systems, Academic Press, New York, 1977.

H. Gräfen, D. Kuron, Pitting Corrosion of Stainless Steels, Materials and Corrosion 47 (1996) 16-26.

D.D. MacDonald, B.C. Syrett, S.S. Wing, The Use of potential-pH Diagrams for the Interpretation of Corrosion Phenomena in High Salinity Geothermal Brines, NACE Corrosion Vol 35 (1979) No. 1 1-11.

R.L. Miller, Chemistry and Materials in Geothermal Systems, in: L.A. Casper, T.R. Pinchback (Eds.), Geothermal Scaling and Corrosion, ASTM Special Technical Publication 717, 1979, pp. 3-10.

N. Mundhenk, P. Huttenloch, T. Kohl, H. Steger, R. Zorn, Metal Corrosion in Geothermal Brine Environments in the Upper Rhine graben – Laboratory and On-site Studies –, Geothermics (in press).

P. Pohjanne, L. Carpén, T. Hakkarainen, P. Kinnunena, A method to predict pitting corrosion of stainless steels in evaporative conditions, Journal of Constructional Steel Research 64 (2008) 1325-1331.

B.G. Pound, M.H. Abdurrahman, M.P. Glucina, G.A. Wright, R.M. Sharp, The Corrosion of Carbon Steel and Stainless Steel in Simulated Geothermal Media, Aust. J. Chem. 38 (1985) 1130-1140.

B. Sanjuan, R. Millot, C. Dezayes, M. Brach, Main characteristics of the deep geothermal brine (5 km) at Soultz-sous-Forêts (France) determined using geochemical and tracer test data, C. R. Geoscience 342 (2010) 546-559.

R. Thomas, Titanium in the geothermal industry, Geothermics 32 (2003) 679–687.