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Electrochemical study of the corrosion of different alloys exposed to deaerated 80 °C geothermal brines containing CO₂

N. Mundhenk^{a,*}, P. Huttenloch^b, R. Bäßler^c, T. Kohl^a, H. Steger^a, R. Zorn^b

^a Institute of Applied Geosciences/KIT, Germany

^b European Institute for Energy Research (EIFER), Karlsruhe, Germany

^c BAM Federal Institute for Materials Research and Testing, Berlin, Germany

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1. Introduction

Geothermal energy can contribute a significant portion of electricity to the future energy mix [1]. However, technical challenges towards a viable use of these virtually infinite resources have remained unsolved so far. In Germany and France, the Upper Rhine Graben (URG) offers favourable conditions for geothermal utilization and several projects producing electricity in binary-type power plants (e.g. Soultz, Bruchsal and Landau) have emerged in the last decades. One major obstacle is corrosion of materials and components in contact with corrosive high-temperature geothermal fluids [2,3]. Especially, production pumps are prone to suffer irreparable damage which leads to extensive downtime periods. The prediction of material behaviour in such environments is challenging due to the complex chemistry, the presence of dissolved gases, varying temperatures, and flow conditions [4]. With increasing size of future geothermal power plants, corrosion engineering will receive increased attention.

This research relies on two geothermal sites in the URG: Soultzsous-Forêts (France) and Bruchsal (Germany). With the kind permission of the operators, GEIE (Soultz) and EnBW AG (Bruchsal), we were authorized to sample brine from the process stream for the laboratory experiments. The brines are extracted from deep

ABSTRACT

Corrosion of metallic engineering materials accounts for problems during geothermal operation in the Upper Rhine Graben (URG). Herein, we study the electrochemical behaviour of various metal alloys in an 80 °C simulated geothermal environment by using potentiodynamic polarisation and open-circuit potential measurements. Two different natural geothermal waters from URG geothermal sites were used for the experiments. The measurements reveal spontaneous passivation to be a key process for all alloys. This ennoblement protects more noble alloys from significant corrosion (e.g. titanium gr. 2, alloy 625) and brings less noble alloys to failure, mostly due to pitting corrosion (e.g. 316L).

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water saturated rock formations. In the case of Soultz, the brine is produced from a 5 km deep borehole penetrating the granitic basement. Bruchsal produces brine from a 2.5 km deep borehole in the Buntsandstein formation [5]. The brines can be classified as Na-Ca-Cl brines with a total dissolved solid content of approx 97 g l^{-1} (Soultz) and 123 g l^{-1} (Bruchsal), respectively. The presence of CO_2 in these brines leads to a pH < 5, while O_2 is virtually absent. The redox potential $E_{\rm h}$ of the brines is below -200 mV vs. SHE [5-7]. Even though both brines are considered to be genetically related, they have unique characteristics in terms of composition [5,6]. In the URG, the brines are usually produced with 120-160 °C, cooled to about 70-80 °C and reinjected into the same rock formation. To sum up, these factors set up a corrosive environment which challenges passive alloys, including stainless steels. To give an example, Pfennig and Bäßler showed that substantial corrosion occurred on 13% Cr alloys in 60 °C CO2-saturated brine [8].

In a previous study, various test metals (stainless steels, Ni alloys, and titanium gr. 2) have been exposed to an 80 °C in situ environment in Soultz in order to evaluate and quantify the corrosion behaviour [7]. Most metals remain unaltered and the coupons show only negligible weight loss, or even weight gain. Others alloys, however, show features of corrosion. For example, 316L stainless steel was obviously challenged and some coupons showed pitting corrosion after few days of exposure. Given these results, the following question came up: how do these metals react





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^{*} Corresponding author. Tel.: +49 721/608 47764; fax: +49 721/608 43374. E-mail address: niklas.mundhenk@kit.edu (N. Mundhenk).

in such a corrosive environment and in which way do we measure ongoing corrosion processes?

The material performance of an alloy strongly depends on the ability to passivate in a given environment. Passivity can be described as the phenomenon that "a metal substantially resists corrosion in a given environment despite a marked thermodynamic tendency to react", e.g. that there is a high corrosion resistivity at relatively high electrochemical potentials [9]. This behaviour is related to the formation of a nanometer-scale oxide film which greatly reduces the rate of corrosion. Iron usually does not form a passivating oxide under acidic conditions in the presence of chloride [10]. Thus, the integrity and characteristics of the passivating oxide film, and the corrosion resistance of an alloy, depend strongly on the content of alloying elements such as chromium, nickel, and molybdenum. While nickel is less readily oxidized and usually absent in the oxide film, chromium and molybdenum are incorporated in the passive film [11.12]. In particular, molybdenum shows a complex oxide chemistry with different states of oxidation [13]. According to Olsson and Landolt, a static passive film does not exist. Depending on environmental parameters such as potential, the presence of halides in the electrolyte, pH, and temperature, film growth and dissolution, adsorption, and ion incorporation take place [13].

An adverse property of the passive film is the susceptibility to localized attack, particularly in the presence of aggressive anionic species such as chloride ions [14–16]. Previous electrochemical studies of pitting corrosion suggest that characteristic electrochemical potentials exist, which can be used to assess the susceptibility to pitting corrosion [15,16]. These are the critical pitting potential $E_{\rm P}$, the repassivation potential $E_{\rm R}$, the transpassive potential E_{TR} , and the open-circuit potential OCP. Once these potentials are experimentally determined by potentiodynamic polarisation and OCP measurements, they can be used to compare different materials and to rank them according to their pitting susceptibility. The following relations are generally accepted in corrosion research: If OCP $\ll E_{\rm P}$, no pitting corrosion will occur, whereas pitting corrosion takes place when OCP $\ge E_P$. If OCP $\approx E_P$, pitting corrosion may occur, since even slight changes in the oxidizing capacity of the brine may raise the OCP to $E_{\rm P}$ [17]. Therefore, the difference between the $E_{\rm P}$ and OCP, or domain of passivity, is a margin of safety and can be used as an indicator of the susceptibility to pitting corrosion [18,19]. Other authors [20,21] suggest OCP $< E_R$ as the principal constraint for pitting stability, considering the capability of repassivation. The range of stable passivation between $E_{\rm R}$ and OCP is a more conservative measure of the pitting susceptibility [15]. The difference between $E_{\rm P}$ and $E_{\rm R}$, the domain of metastable pitting or metastable passivation, is related to the extent of hysteresis in a cyclic polarisation curve. Generally, alloys that are susceptible to pitting corrosion exhibit a large hysteresis. For a material that is very susceptible to pitting, the OCP will be higher than $E_{\rm P}$ and the material will spontaneously pit [15].

Table 1	
Representative compositions of Soultz and Bruchsal brine [5,6]].

The electrochemical results in this study are combined with the pitting resistance equivalent number (PREN) concept, which is an established way of ranking the pitting susceptibility of stainless steels [15,22,23]. It is based on observations that some elements, including Cr, Mo, N, Si, and W, are beneficial alloying elements against pitting corrosion. The PREN can be obtained from the weight fractions *w* of Cr, Mo, and N (in wt.%) as follows:

$$PREN = w_{Cr} + 3.3w_{Mo} + 16w_N \tag{1}$$

The concept can be regarded as a helpful decision support tool in a material selection process. However, the PREN concept only has been acceptably tested for stainless steels and not for nickel or titanium alloys. According to different authors, a PREN of 32 is considered as the minimum for seawater pitting resistance (at 20 °C) of stainless steel [DIN81249-1]. When we apply this concept to geothermal situations with even higher salinities and temperatures and usually lower pH, it is evident that a higher PREN is recommended to provide sufficient resistance.

2. Experimental

The present experiments were aimed to provide insights into the reactions of six alloys and non-ferrous metals with deaerated and CO_2 -saturated natural geothermal brines of pH 4.8. In order to simulate the environment of the cooled brine after heat extraction, the experiments were carried out at 80 °C.

2.1. Geothermal test brines

The test brines were sampled in the surface installations of the two geothermal sites (Bruchsal and Soultz) by flashing and cooling to ambient temperature. Representative brine compositions are given in Table 1. For the purpose of control, experiments with pure sodium chloride solutions were conducted. The chloride content in these synthetic solutions was similar to that of Bruchsal brine (75.2 g l⁻¹). Deaeration was achieved by degassing with a vacuum pump for at least 1 h. Afterwards, the brine was pressurized with CO₂ up to 6 bar (4.8 technical grade) for at least 30 min in order to achieve CO₂-saturation. Before the pH was finally adjusted to 4.8 by addition of HCl, the brine was filled into the glass cell and heated up to 80 °C.

2.2. Test materials

On the basis of previous research, six metals have been tested due to their specifications and commercial availability. They are promising candidates for demanding geothermal applications: 316L (austenitic CrNiMo stainless steel), 318LN (duplex alloy), 904L (special austenite), alloy 31 (super austenite), alloy 625 (Ni-base alloy), and titanium grade 2. Table 2 gives the chemical

	рН	Na ⁺ g l ⁻¹	$\stackrel{\rm K^+}{{\rm g}}l^{-1}$	${ m Ca}^{2+}$ g l $^{-1}$	Mg^{2^+} mg l^{-1}	Cl^- g l^{-1}	SO_4^{2-} mg l $^{-1}$	SiO ₂ mg l ⁻¹	${ m NO_3^-}\ { m mg}\ { m l}^{-1}$	$rac{NO_2^-}{mg l^{-1}}$	NH ₄ mg l ⁻¹	PO_4^{3-} mg l ⁻¹
Soultz Bruchsal	4.5–5 4.5–5	27.5 38.1	3.25 2.2	6.9 7.74	125 434	59 75.2	59 387	427 41.8	<0.5 n/a	<0.01 n/a	23.5 n/a	<0.1 n/a
Soultz Bruchsal	Br mg l ¹ 220 230	B ³⁺ mg l ⁻¹ 35 4	F ⁻ mg l ⁻¹ 4.5 0.85	Sr ²⁺ mg l ⁻¹ 450 324	Li ⁺ mg l ⁻¹ 140 166	Mn ²⁺ mg l ⁻¹ 15 n/a	Ba ²⁺ mg l ⁻¹ 10 4	Fe _(tot) mg l ⁻¹ 100 78	Al ³⁺ mg l ⁻¹ 0.05 n/a	As ³⁺ mg l ⁻¹ 6 n/a	Rb⁺ mg l ⁻¹ 22 1.9	Cs ⁺ mg l ⁻¹ 14 2.2
Soultz Bruchsal	Ni ²⁺ µg l ⁻¹ 100 n/a	Cu ²⁺ µg l ⁻¹ 45 n/a	Co ²⁺ μg l ⁻¹ 50 n/a	Cr ³⁺ μg l ⁻¹ 40 n/a	Cd ²⁺ µg l ⁻¹ 10 n/a	Zn ²⁺ μg l ⁻¹ 3000 n/a	Ag ⁺ μg l ⁻¹ <5 n/a	Ti ⁴⁺ μg l ⁻¹ 200 n/a	Pb ²⁺ μg l ⁻¹ 300 n/a	Ge ⁴⁺ µg l ⁻¹ 53 n/a	Be ²⁺ μg l ⁻¹ 30 n/a	TDS g l ⁻¹ 97 123

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