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MATERIALS EVALUATION FOR GEOTHERMAL APPLICATIONS

Ralph Bäßler*, Amela Keserovi, Joana Sobetzki, Helmuth Sarmiento Klapper

BAM–Federal Institute for Materials Research and Testing, D-12200 Berlin/Germany

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*Corresponding author
ralph.baessler@bam.de

Graphical abstract

Abstract

In order to provide basic information on corrosion resistance to the designers and users of geothermal plants different metallic materials including duplex and austenitic stainless steels as well as a nickel alloy have been evaluated in artificial geothermal fluids simulating the conditions in some locations with geothermal potential in Germany as well as two sites in Indonesia. By electrochemical and long-term exposure tests at 100 °C and 150 °C the suitability of low alloyed steel UNS G41300, stainless steels UNS S31603 UNS S31803, UNS S32760, super austenitic steel UNS N08031 and nickel based alloy UNS N06059 was investigated in these geothermal fluids, using critical potentials and corrosion rates. In high-saline environments the crevice corrosion turned out to be the determining mechanism. The nickel based alloy shows excellent corrosion resistance against pitting corrosion. Excluding its high cost, it is very good to be used in the construction of geothermal facilities having highly saline brines. Stainless and duplex steels exhibit a limited corrosion resistance concerning pitting and crevice corrosion. Therefore they are not suitable for highly saline brines. The super austenite UNS N08031 showed a temperature depending behavior. In non-saline environments the low-alloyed steel UNS G41300 (beside of the higher alloyed materials) could be employed as a constructional material for the geothermal power plant, as long as a sufficient wall thickness of the material is considered.

Keywords: Localized corrosion, stainless steel, Ni-based alloy, geothermal energy

1.0 INTRODUCTION

Since geothermal wells are a feasible energy source to replace fossil fuel supply, many technologies have been developed to take advantage of geothermal energy. Nevertheless, service conditions in geothermal facilities are due to the chemical composition of hydrothermal fluids and temperatures, in many cases, extreme in terms of corrosion. Therefore, materials selection based on preliminary material qualification is essential to guarantee a secure and reliable operation of the facilities.

Preliminary investigations carried out by the German Research Centre for Geosciences (GFZ) have shown that geothermal fluids in Germany having temperatures above 140 °C could be used for production of electric energy [1]. In consequence, GFZ has built a research facility concerning geochemistry, geosciences and corrosion at Groß Schönebeck, a former deep well located in the geothermal area of the North German Basin (NGB) [2]. Also for the Upper Rhine Graben (URG) and the Molasse Basin (MB) there are facilities designed and already in operation for production of electric energy [3, 4].

Nevertheless, until now, corrosion resistance data of possible construction materials in these differently saline fluids at service conditions are not available. Currently, a project in Germany deals with the evaluation of long-term corrosion behavior of different metallic materials including low-alloyed steels, austenitic stainless steels, duplex steels and Ni-based alloys in different geothermal fluids commonly found in Germany including the NGB [5], URG and MB. A second project is dedicated to the situation in volcanic brines of Indonesia [6].

This paper gives an update on recent experiences from laboratory tests performed at service conditions on different materials in artificial geothermal fluids having different chemical compositions.

Within a long-term project financed by the German Ministry of Environment, Nature Protection and Reactor Safety a catalogue of suitable materials for applications in German geothermal power plants shall be created based on results and experiences gathered in the laboratory and on-site. Users shall be enabled to have a basis for designing such facilities.

2.0 EXPERIMENTAL

2.1 Materials and Conditions

The corrosion resistance of the duplex steel UNS S31803, the super duplex steel UNS S32760, the austenitic stainless steel UNS N08031 and the nickel-based alloy UNS N06059 was evaluated by exposure and electrochemical tests in artificial geothermal fluids of NGB and URG at 100 °C and 150 °C (1500 kPa). The low alloyed steel UNS G41300 was exposed to low saline media only. The chemical compositions of the investigated materials are included in Table 1.

Corrosion tests at 100 °C should simulate conditions in the technical facilities e.g. heat exchanger above ground. On the other hand, tests at 150 °C consider downhole conditions. Since the natural geothermal fluids become unstable at normal pressure, they cannot be used for laboratory investigations at atmospheric conditions. Therefore, artificial fluids based on the chemical analysis of aquifer fluids in Groß Schönebeck (NGB), Bruchsal (URG), Unterhaching (MB) and Sibayak (SBY) carried out by GFZ were used for the investigations. The chemical compositions of the artificial fluids are presented in Table 2.

For the measurements at 150 °C, the oxygen concentration in the fluids was adjusted to very low values by purging the solution with argon for 10 min prior to the start of the measurements. The pressure of 1500 kPa was further achieved by using argon.

2.2 Setup

Exposure tests were carried out according to DIN 50905/4 [7] with gravimetric determination of time dependent corrosion at 100 °C. The specimen size for exposure tests was 50 x 15 x 3 mm (length x width x thickness). Three specimens of each material were exposed for 24 weeks. Each specimen had a 5 mm hole for fixation using a polytetrafluoroethylene (PTFE)-cord (see Figure 1, left).

Figure 1 Specimen Design for Exposure, SCC, Crevice Corrosion and Electrochemical Tests

In order to prevent interaction between the different materials and their corrosion products all materials were tested separately using a glass vessel. The specimens were completely immersed in the fluid. The threshold for suitability was set to be a corrosion rate of 0.3 mm/year. This corresponds to a wall thickness reduction of 6 mm by uniform corrosion during 20 years of service.

Beside the determination of weight loss, susceptibility to stress corrosion cracking (SCC) and localized corrosion phenomena were investigated as well. It has been distinguished between pitting and shallow pit corrosion in order to use the right criteria for suitability evaluation. If pitting would occur, the material is not suitable. In case of shallow pitting the depth of the shallow pit during exposure was extrapolated to one year resulting in the corrosion rate. Specimens were evaluated by optical microscopy.

The susceptibility to localized corrosion of the materials in the artificial geothermal fluids was additionally investigated by determination of open circuit potential (OCP), cyclic potentiodynamic polarization and potentiostatic measurements. A typical 3-electrode configuration including a saturated Ag/AgCl reference electrode and a graphite-counter-electrode were used for the electrochemical measurements at 100 °C.

Investigations at 150 °C were carried out within an autoclave using a special saturated Ag/AgCl reference electrode and a Ti-oxide covered titanium mesh as a counter electrode (see Figure 1, right). The temperature in the autoclave was adjusted by an external hotplate and constantly monitored by a thermocouple. The autoclave was additionally located in a sand bath in order to avoid electrical interferences between heater and measurement device. The specimen size for electrochemical tests was 20 x 15 x 3 mm, resulting in 8 cm² surface (Figure 1, right). All specimens were ground to grit 320 in order to have comparable surface conditions.

Cyclic potentiodynamic measurements were carried out after 336 hours of exposure. During this time (14 days) the OCP was monitored. Polarization was started from OCP in anodic direction using 0.2 mV/s. After reaching a current density of 1 mA/cm² or a potential of 1.2 V vs. OCP the polarization was switched in cathodic direction in order to evaluate the repassivation behavior. In addition, the susceptibility to crevice corrosion was electrochemically determined by means of potentiostatic measurements. Critical pitting potentials (CPP), repassivation potentials (REP) and critical crevice corrosion potentials were determined at a current density of 0.1 mA/cm^2. Crevice conditions were simulated using a rubber band shown in Figure 1 (3rd). All electrochemical measurements were carried out using a Gamry REF600 potentiostat.

Table 1 Composition of materials obtained by spark emission spectrometry

	Content [%]										
	C	**Si**	**Mn**	**P**	**S**	**N**	**Cr**	**Mo**	**Ni**	**Cu**	**Fe**
UNS G41300 (25CrMo4, 1.7218, A29)	0.29	0.40	0.90	0.025	0.040	-	1.2	0.3	-	-	R
UNS S31603 (X2CrNiMo17-12-2, 1.4404, 316L)	0.03	0.41	1.80	0.030	0.003	-	16.8	2.53	10.8	-	67.0
UNS S31803 (X2CrNiMo-22-5, 1.4462, F51)	0.03	0.37	1.51	0.022	0.003	0.15	22.64	3.12	5.92	0.18	65.8
UNS S32760 (X2CrNiMoCuWN25-7-4, 1.4501, F55)	0.04	0.26	0.85	0.023	0.002	0.23	25.29	3.73	6.97	0.54	61.1
UNS N08031 (X1CrNiMoCu32-28-7, 1.4562, alloy 31)	0.03	0.06	1.69	0.020	0.006	0.11	27.94	6.28	30.68	1.12	32.8
UNS N06059 (NiCr23Mo16Al, 2.4605, alloy 59)	0.02	0.11	0.07	0.007	0.005	-	21.69	13.95	62.8	0.04	0.98

Table 2 Composition of investigated fluids

	Content [g/L]												
	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	Fe^{2+}	Pb^{2+}	Sr^{2+}	SiO_2	**pH**
NDB	166	0.05	-	56.5	0.5	3.1	38.7	0.2	-	0.2	1.55	-	5.6
URG	102	1.5	-	10.9	1.9	3.7	47.9	-	0.25	-	0.5	0.15	6
MB	0.175	0.025	0.4	-	0.011	0.16	0.15	0.05	-	-	-	-	8.1
SBY	1.5	0.02	0.015	0.2	-	0.25	0.6	-	-	-	-	-	4

3.0 RESULTS AND DISCUSSION

3.1 Exposure Tests

All evaluated materials showed after 24 weeks corrosion rates lower than the threshold value specified previously at 0.3 mm/year. All materials exhibit a sufficient respectively remarkable corrosion resistance to corrosion within the selected media. No evidences of SCC-susceptibility have been found

The investigated carbon steel showed uniform corrosion in all media. The corrosion rate increased with increasing salinity (Figure 2). Signs of crevice corrosion susceptibility were observed in the area of fixation.

Specimens of the materials UNS S31803 and UNS S32760 showed nevertheless some signs of crevice corrosion in the area of fixation by PTFE-cord in both high saline solutions, and UNS N08031 just in NGB [5] but not in URG (Figure 3). Therefore, specific electrochemical tests regarding susceptibility to crevice corrosion were carried out. According to the results of the exposure test the nickel alloy UNS N06059 could be considered as suitable at 100 °C and 150 °C.

Figure 2 Carbon steel after 6 months exposure in artificial fluids; Left: MB, 150 °C; Center: SBY, 175 °C; Right: NGB, 150 °C

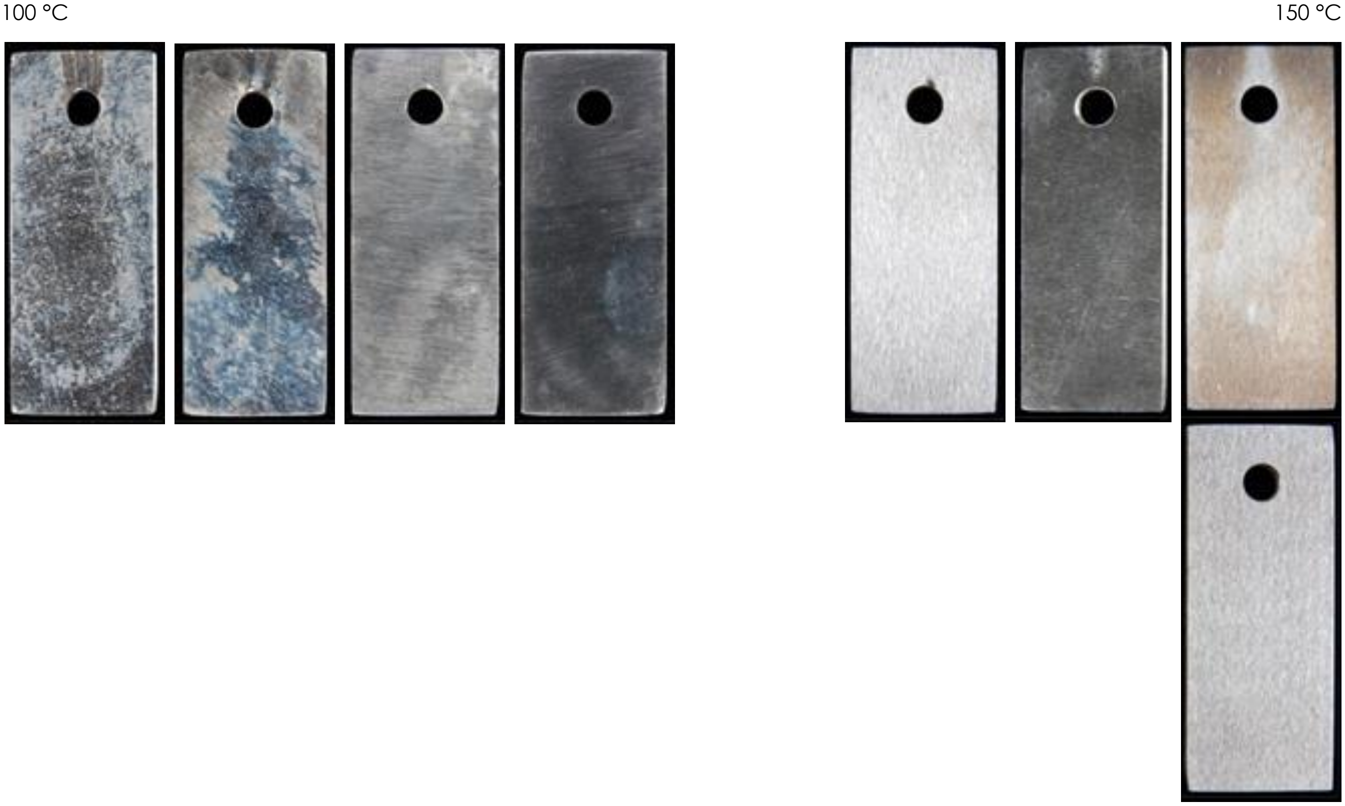

Figure 3 Materials after 6 months exposure in artificial URG-Fluid at different temperatures; from Left to Right: UNS S31803, UNS S32760, UNS N08031 and UNS N06059

Electrochemical Tests

All measured values are summarized in the following tables and figures. Some of the NGB-results have been described previously [5]. In the following text selected test results in URG-fluid are described in more detail.

The open circuit potential of super duplex steel UNS S32760 in the artificial fluid of URG at 100 °C stabilizes after 8 to 10 days resulting in values around 100 mV_{SHE} after 14 days. Increasing the temperature to 150 °C leads to more negative OCP around 0 mV_{SHE} (Figure 4).

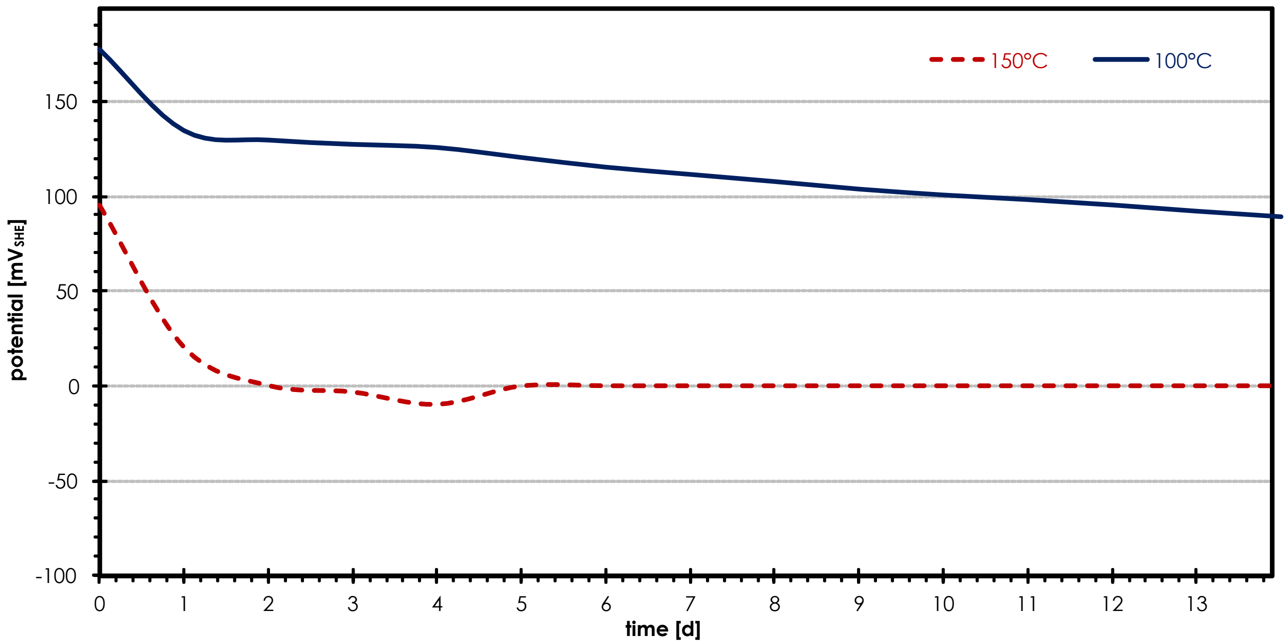

Figure 4 Open circuit potential of UNS S32760 in artificial URG-fluid at different temperatures

The critical pitting potential and the repassivation behavior of the materials were determined by means of cyclic potentiodynamic measurements. In Figure 5 the polarization curves of UNS S32760 in the artificial fluid of URG are presented as an example. Despite of slight fluctuations within the current, the CPP of UNS S32760 at 100 °C varies between 350 and 450 mV$_{SHE}$. In addition, UNS S32760 exhibits a repassivation potential (REP) more positive than its OCP, being between 150 and 250 mV$_{SHE}$.

When increasing the temperature to 150 °C, the CPP of UNS S32760 shifts slightly in cathodic direction. The CPP is now between 300 and 350 mV$_{SHE}$, and the repassivation potential could not be determined due to its shift to values far more cathodic than the OCP. Once pitting has been initiated the active site will not have the chance to repassivate. Consequently the super duplex steel UNS S32760 is considered as not suitable in URG-fluid at 150 °C as well.

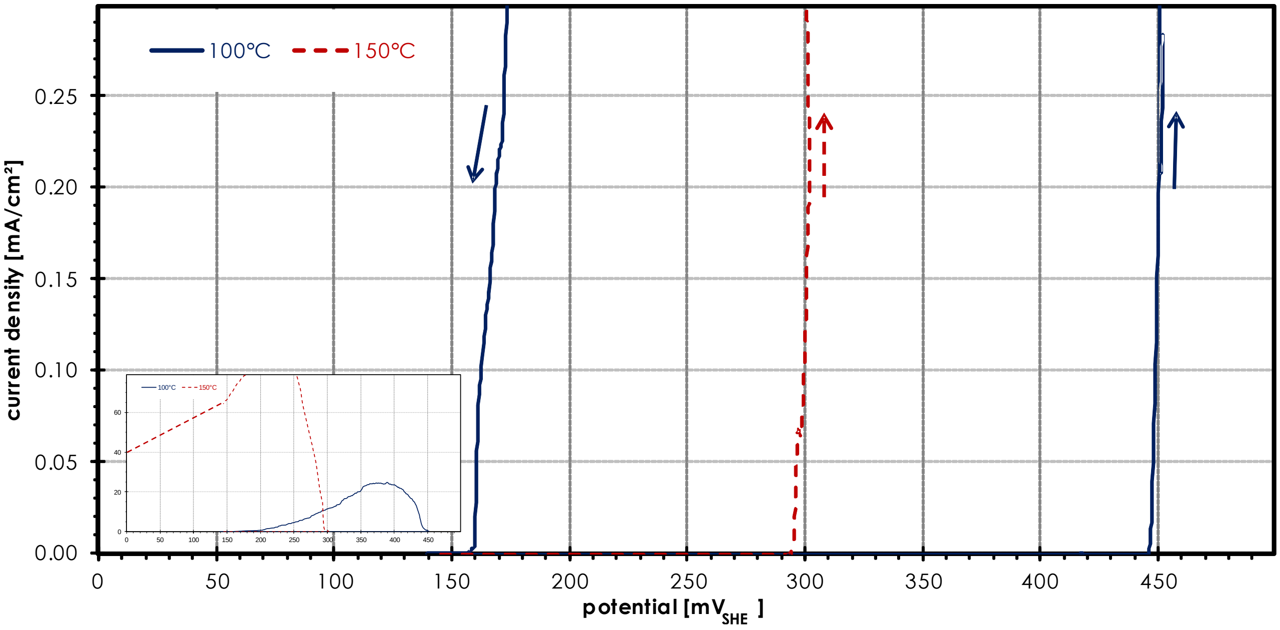

Figure 1 Cyclic polarization curves of UNS S32760 in Artificial URG-fluid at different temperatures

The duplex steel UNS S31803 exhibits, in general, a similar performance as the super duplex steel in the URG-fluid, so it is not acceptable for this medium either. It needs to be concluded that this fits to the results in the NGB-fluid as well, where UNS S31803 has not been tested, but the UNS S32760 has.

The higher alloyed materials exhibit a different behavior.

Tables 3 - 5 summarize the electrochemical parameters obtained from the OCP and the potentiodynamic measurements carried out on the different materials.

Cyclic polarization measurements at the Ni-based alloy at 100 °C in NGB fluid show high critical potentials. Therefore, this alloy exhibits a very good corrosion resistance, because the critical and the repassivation potentials are already within the transpassive area and much more anodic than its free corrosion potential. So, occurrence of corrosion is very unlikely. If the material is exposed to certain high potentials (within potentiostatic polarization tests) it is still much higher than the free corrosion potential. Crevice corrosion has been observed always before pitting [5]. The critical crevice corrosion potentials are certainly more cathodic than critical pitting corrosion potentials but still much more positive than the free corrosion potentials. This means that crevice corrosion is not to be expected in these conditions.

Concerning susceptibility to crevice corrosion, as mentioned above, during exposure tests, crevice corrosion was found in the area in contact with the PTFE-cord of the specimens of the steels UNS S32760 and UNS N08031. A preliminary study [1] has shown that undefined metal/polymer-crevices are in fact more critical than metal/metal-crevices especially for austenitic stainless steels. For this reason, potentiostatic measurements using the special rubber crevice set-up shown in Figure 1 (3rd) were carried out at 100 °C.

In the case of the super duplex steel UNS S32760, the CCP, located at 150 mV$_{SHE}$, was very close to its OCP (125 mV$_{SHE}$). In some experiments performed on UNS S32760 at 175 mV$_{SHE}$, pitting and crevice corrosion took place simultaneously.

Austenitic steel UNS N08031 was susceptible to crevice corrosion as well, but its susceptibility was considerably lower than for UNS S32760. A CCP of 275 mV$_{SHE}$ was determined for UNS N08031 being relatively close to its OCP (180 mV$_{SHE}$).

For nickel-based alloy UNS N06059 its CCP at 325 mV$_{SHE}$ was clearly more anodic than for UNS N08031. Because of the significant difference between OCP and CCP of UNS N06059 in NGB-fluid at 100 °C its susceptibility to crevice corrosion is negligible. So, only the nickel-based alloy UNS N06059 was found to be not susceptible to crevice corrosion in the artificial fluid of NGB at service conditions.

Table 3 Electrochemical parameters of the high-alloyed materials in NGB-Fluid

Material	OCP [mV$_{SHE}$]		CPP [mV$_{SHE}$]		CCP [mV$_{SHE}$]	REP [mV$_{SHE}$]	
	100 °C	150 °C	100 °C	150 °C	100 °C	100 °C	150 °C
UNS S32760	75 - 125	-50	280 - 330	25 - 50	150	≤ OCP	< OCP
UNS N08031	170 - 180	120 - 150	550 - 580	425 - 450	275	330 - 380	< OCP
UNS N06059	90 - 160	125 - 300	> 900	500 - 590	325	≅ CPP	420 - 450

Table 4 Electrochemical parameters of the high-alloyed materials in URG-Fluid

Material	OCP [mV$_{SHE}$]		CPP [mV$_{SHE}$]		CCP [mV$_{SHE}$]	REP [mV$_{SHE}$]	
	100 °C	150 °C	100 °C	150 °C	100 °C	100 °C	150 °C
UNS S31803	-10 - 140	-20 - 100	225 - 230	160	200	170	< OCP
UNS S32760	80 - 160	40 - 100	325 - 350	300	275	230	< OCP
UNS N08031	50 - 180	80 - 100	600 - 630	440	500	600	290
UNS N06059	20 - 260	250 - 360	700 - 900	780	600	≅ CPP	≅ CPP

The duplex steel UNS S31803 shows limited corrosion and repassivation properties at both temperatures in URG-Fluid. The CPP at 100 °C is certainly more anodic than the OCP, but decreases with increasing the temperature to 150 °C and comes close to the OCP. That means there is not much effort necessary (e.g. fluctuation within the service conditions) in order to initiate corrosion of this material. The repassivation potentials are within the range of OCP or more cathodic than OCP. So, once corrosion has started a repassivation is very unlikely at 100 °C and can almost be excluded at 150 °C. However, there is no difference between beginning of crevice corrosion and pitting. Both critical potentials are close to OCP.

For super duplex UNS S32760 it looks slightly better. It has the possibility to repassivate at 100 °C, because the REP has slightly more positive values than the OCP. Also the CCP is a bit more anodic than OCP. At 150 °C it behaves similar to the duplex steel as mentioned previously.

A much better resistance exhibits the superaustenite UNS N08031. CPP and REP are close together and relatively far away from OCP (in anodic direction) at 100 °C. This means, there is a big effort necessary in order to initiate the corrosion. Furthermore a very quick repassivation occurs. Crevice corrosion occurs before pitting. CPP and REP shift to more cathodic values, but are still more anodic than OCP. Therefore a good corrosion resistance can be concluded.

As already in NGB-fluid, the nickel-based alloy UNS N06059 is the most resistant material. Again the CPP and REP are within the transpassive area at 100 °C, far away from OCP. Still there is a quick repassivation possible. Also critical crevice and pitting corrosion potentials achieved by long-term tests are far more anodic than OCP. Due to temperature increase CPP and REP certainly shift in cathodic direction, but only slightly. Here also a quick repassivation is possible.

Within the URG-fluid only the nickel-based alloy and the superaustenite provide a sufficient corrosion resistance, whereas the duplex and the super duplex steel just show a certain resistance up to 100 °C.

Table 5 Electrochemical parameters of selected materials in low saline fluids MB and SBY

Material	OCP [mV_{SHE}]		CPP [mV_{SHE}]		REP [mV_{SHE}]	
	MB 150 °C	SBY 175 °C	MB 150 °C	SBY 175 °C	MB 150 °C	SBY 175 °C
UNS G41300	-350 - -200	-381 - -347	200 - 300	-338 - -226	no repass.	-372 - -298
UNS S31603	254 - 348	110 - 158	586 - 784	698 - 716	91 - 261	-20 - 84
UNS S31803	177 - 207		867 - 901		245 - 295	
UNS N08031		540 - 560		735 - 877		395 - 475

For MB-conditions the critical potentials of low alloyed steel are sufficiently far away from the open circuit potentials, so no critical corrosion rates would be expected during operational variations of the medium.

Within the SBY-fluid electrochemical methods reveal that the open circuit potentials of material UNS G41300 are in the range of critical values, indicating that even a slight intrusion of oxidizing species in the system or change in the service conditions can cause a substantial increase in material's activity. On contrary alloys UNS S31603 and UNS N08031 exhibit large differences between OCP and CPP, meaning they are quite stable and suitable.

4.0 CONCLUSION

By exposure and electrochemical tests in the laboratory the corrosion behavior of certain metallic materials can be assessed. According to the experimental results obtained in different artificial geothermal fluids in the laboratory, crevice corrosion susceptibility has been determined to be the most important aspect. For fluids SBY and MB low alloyed steel UNS G41300 shows uniform corrosion below the accepted threshold of 0.3 mm year. So it can be considered suitable for low saline geothermal conditions, as tested for MB and SBY. There is no need to switch to higher alloyed (more expensive) materials. Higher saline fluids require higher alloyed materials, because the corrosion rate at low alloyed steel is too high. The duplex steel UNS S31803 and the super duplex steel UNS S32760 are not suitable for geothermal applications in fluids having a compositions comparable to NGB and URG, due to their critical susceptibility to localized corrosion in form of pitting and crevice corrosion at service conditions. Austenitic steel UNS N08031 is suitable in URG- and low saline fluids. In NGB fluid it seems to be suitable at 100 °C, but its susceptibility to crevice corrosion limits its applicability. The nickel-based alloy UNS N06059 is suitable and represents a safe option to be used in geothermal facilities even when working with highly saline fluids.

5.0 OUTLOOK

Publication of results achieved so far will provide a basis for a catalogue of materials suitable for diverse applications in geothermal power plants. The collection and compilation is the main task of a still running project supported by the German Ministry of Environment, Nature Protection and Reactor Safety.

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