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Materials Evaluation for Geothermal Applications in Different Geothermal Waters

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ABSTRACT

The corrosion behavior of carbon steel and different high-alloyed metals 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.

The suitability of low alloyed steel UNS G41300, stainless steels UNS S31603 UNS S31803, UNS S32760 and super austenitic steel UNS N08031 in these geothermal waters, investigated by electrochemical measurements and exposure tests, is limited. The nickel based alloy UNS N06059 shows excellent corrosion resistance against pitting corrosion. Excluding its high cost, it is a very good alternative 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.

Besides the higher alloyed materials, also the low-alloyed steel UNS G41300 could be employed as a constructional material for the geothermal power plant in non-saline environments with moderate pH, as long as the wall thickness of the material vs. corrosion rate is taken into account.

1. INTRODUCTION

Since geothermal reservoirs 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 and 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 (Bäßler et al., 2009). Consequently, GFZ has built a research facility concerning geosciences and corrosion at Groß Schönebeck, a former deep well located in the geothermal area of the North German Basin (NGB) (Regenspurg et al., 2013). 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 (Herzberger et al., 2010; Mundhenk et al., 2014).

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 stainless steels and Ni-based alloys in different geothermal waters commonly found in Germany, including the NGB (Sarmiento Klapper et al., 2011), URG and MB. A second project is dedicated to the situation in volcanic brines of Indonesia (Keserović et al., 2013).

This paper gives an update on recent experiences from laboratory tests performed at service conditions on different materials in artificial geothermal waters 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. EXPERIMENTAL SETUP

2.1 Materials and Conditions

The corrosion resistance of the stainless steel UNS S31603, duplex stainless steel UNS S31803, super duplex stainless steel UNS S32760, austenitic stainless steel UNS N08031 and nickel-based alloy UNS N06059 were evaluated by exposure and electrochemical tests in artificial geothermal waters of MB, 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.

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

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 waters based on the chemical analysis of aquifer fluids in Groß Schönebeck (NGB), Bruchsal (URG), Unterhaching (MB) and Lahendong/Indonesia (LHD) carried out by GFZ were used for the investigations. The chemical compositions of the artificial waters are presented in table 2.

Table 2: Composition of investigated waters.

	Content [g/L]												pH
	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	Fe^{2+}	Pb^{2+}	Sr^{2+}	SiO_2	
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
LHD	1.5	1.6	-	-	-	0.2	1.0	-	-	-	-	-	2

For the measurements at 150 °C, the oxygen concentration in the waters 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 (DIN, 1987) 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, right). In order to prevent interaction between the different materials and their corrosion products the materials were placed in glass vessels and tested separately. The specimens were completely immersed in the water. 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.

Figure 1: Specimen design for electrochemical, crevice corrosion, SCC and exposure tests.

Beside the determination of weight loss, susceptibility to stress corrosion cracking (SCC) tested using U-Bend specimens (see figure 1, 3rd from left) and localized corrosion phenomena were investigated as well on the gravimetric specimens. 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 waters 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. 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, left). 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. Crevice conditions were simulated using a rubber band shown in Figure 1 (2nd from left). All electrochemical measurements were carried out using a Gamry REF600 potentiostat.

3. RESULTS

3.1. Exposure Tests

Except in low pH solutions, all materials evaluated showed after 24 weeks of exposure, corrosion rates lower than the threshold value specified previously at 0.3 mm/year. All materials exhibit a sufficient, respectively remarkable corrosion resistance within the selected media. No evidences of SCC-susceptibility have been found. At pH of 2, carbon steel exhibited corrosion rates > 1 mm/year

Figure 2: Carbon steel after 6 months exposure in artificial waters; left: MB, 150 °C; Center: LHD, 175 °C; right: NGB, 150 °C.

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

Specimens of the materials UNS S31803 and UNS S32760 showed some signs of crevice corrosion in the area of fixation by PTFE-cord in both high saline solutions, and UNS N08031 just in NGB (Sarmiento Klapper et al., 2011) 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 3: Materials after 6 months exposure in artificial URG-water at different temperatures; from left to right: UNS S31803, UNS S32760, UNS N08031 and UNS N06059.

3.2. Electrochemical Tests

All measured values are summarized in tables 3 and 4. Some of the NGB-results have been described previously (Sarmiento Klapper et al., 2011). In the following text selected test results in URG-water are described in more detail.

The open circuit potential of super duplex steel UNS S32760 in the artificial water 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).

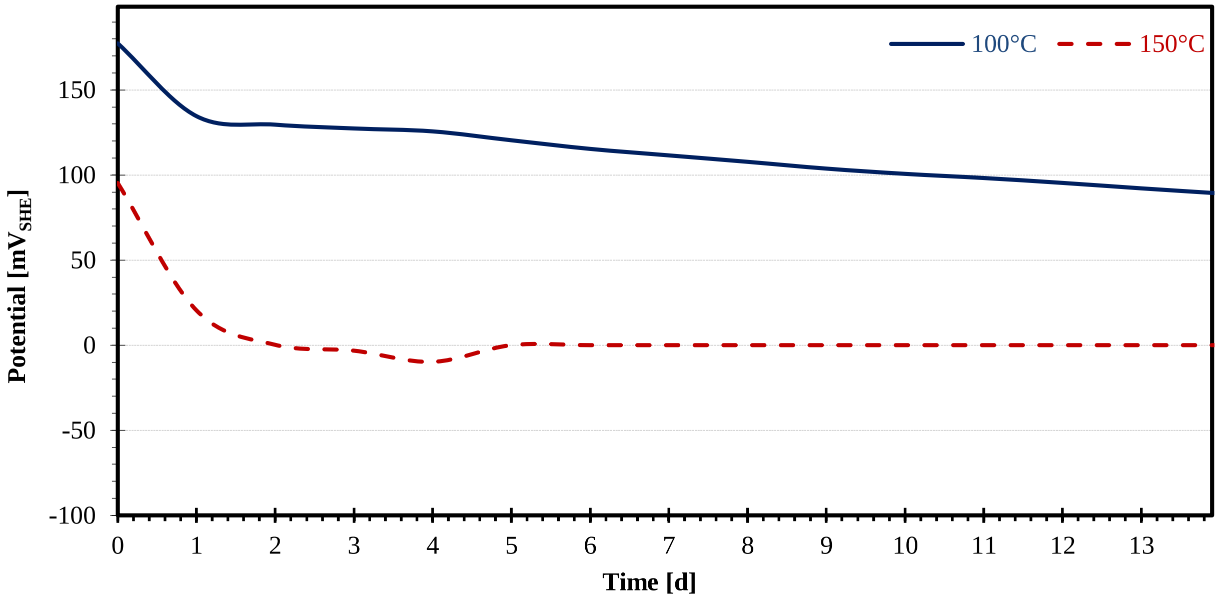

Figure 4: Open circuit potential of UNS S32760 in artificial URG-water at different temperatures.

The critical pitting potential (CPP) 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 water of URG are presented as examples. Despite of slight fluctuations within the current, the CPP of UNS S32760 at 100 °C varies between 350 and 450 mVSHE. 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 the cathodic direction. The CPP was then between 300 and 350 mVSHE, and the repassivation potential could not be determined due to its shift to values far more cathodic than the OCP. Once pitting was initiated the active sites were difficult to repassivate under OCP conditions. Consequently the super duplex stainless steel UNS S32760 was considered as not suitable in URG-water at 150 °C as well.

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

The higher alloyed materials exhibit a different behavior.

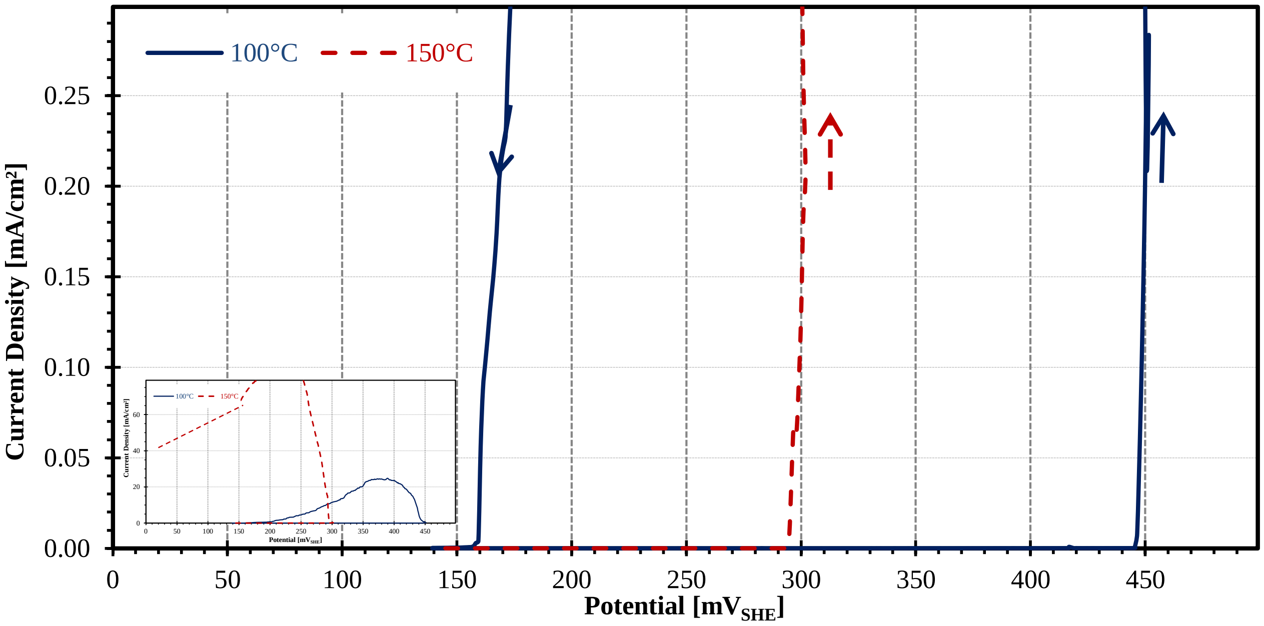

Figure 5: Cyclic polarization curves of UNS S32760 in artificial URG-water at different temperatures.

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

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

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

Cyclic polarization measurements at the Ni-based alloy at 100 °C in NGB-water show high critical pitting and crevice potentials. Therefore, this alloy exhibited a very good corrosion resistance because the critical and the repassivation potentials were already within the transpassive area and much more anodic than the free corrosion potentials. 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 was always observed before pitting (Sarmiento Klapper et al., 2011). The critical crevice corrosion potentials (CCP) were certainly more cathodic than critical pitting corrosion potentials (CPP) but still much more positive than the free corrosion potentials (OCP). This means that crevice corrosion is not to be expected under OCP-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 (Bäßler et al., 2009) 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 stainless steel UNS S32760, the critical crevice potential (CCP), located at 150 mVSHE, was very close to its OCP (125 mVSHE). In some experiments performed on UNS S32760 at 175 mVSHE, pitting and crevice corrosion took place simultaneously.

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

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

Table 4: Electrochemical parameters of the high-alloyed materials in URG-water.

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 stainless steel UNS S31803 showed limited corrosion and repassivation properties at both temperatures. The CPP at 100 °C was certainly more anodic than the OCP, but decreased with increase in temperature to 150 °C and came 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 were 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 also be excluded at 150 °C under OCP conditions. However, there is no difference between beginning of crevice corrosion and pitting. Both critical potentials were close to the OCP.

For super duplex UNS S32760 a slightly better performance was observed. It was able to repassivate at 100 °C, because the REP has slightly more positive values than the OCP. Also the CCP was a bit more anodic than OCP. At 150 °C it behaved similar to the duplex stainless steel as mentioned previously.

A much better resistance was exhibited the superaustenitic stainless stel UNS N08031. CPP and REP were 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 shifted to more cathodic values at 150 °C, but were still more anodic than OCP. Therefore a good corrosion resistance can be concluded.

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

Within the URG-water 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 waters MB and LHD.

Material	OCP [mV_{SHE}]		CPP [mV_{SHE}]		REP [mV_{SHE}]	
	MB 150 °C	LHD 175 °C	MB 150 °C	LHD 175 °C	MB 150 °C	LHD 175 °C
UNS G41300	-350 - -200	-450	200 - 300	(active)	no repass.	(active)
UNS S31603	254 - 348	-65 - -55	586 - 784	302 - 394	91 - 261	-44 - -10
UNS S31803	177 - 207		867 - 901		245 - 295	
UNS N08031		-50 - 250		725 - 775		325 - 375

For MB-conditions the critical potentials of low alloyed steel were sufficiently far away from the open circuit potentials, so no critical corrosion rates would be expected during operational variations of the medium. Alloy UNS S31603 exhibited large differences between OCP and CPP, meaning it was quite stable and suitable. Within the LHD-water, electrochemical methods revealed that the open circuit potential of material UNS G41300 was in the range of critical values, pointing to active conditions (Keserović et al., 2014).

Mild steels showed a fair resistance to pitting due to the large difference between CPP and OCP. However, the repassivation possibility was limited. So, special care needs to be taken to prevent the beginning of localized corrosion of these alloys. In acidic waters poor repassivation behavior needs to be considered.

4. CONCLUSION

By exposure and electrochemical tests in the laboratory the corrosion behavior of different metallic materials can be assessed. According to the experimental results obtained in different artificial geothermal waters in the laboratory, the following conclusions can be drawn:

- Crevice corrosion susceptibility has been determined to be the most important aspect.
- For low saline, MB-solution low alloyed steel UNS G41300 showed 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. There is no need to switch to higher alloyed (more expensive) materials. Lower pH (as in LHD) results in corrosion rates above the acceptable limits, and consequently the low alloyed material is not suitable for low pH fluids.
- Higher saline fluids require higher alloyed materials, because the corrosion rate of low alloyed steel is too high.

- The duplex stainless steel UNS S31803 and the super duplex stainless steel UNS S32760 were not considered as being suitable for geothermal applications in waters having compositions comparable to NGB and URG, due to their critical susceptibility to localized corrosion in form of pitting and crevice corrosion at service conditions.

- Superaustenitic steel UNS N08031 is suitable in URG and low saline waters. In NGB water was considered as suitable at 100 °C, but its susceptibility to crevice corrosion limits its applicability. Beside its good resistance tyo corrosion its repassivation behavior is responsible for its limited applicability in low pH waters.

- The nickel-based alloy UNS N06059 was considered suitable and represents a safe option to be used in geothermal facilities even when working with highly saline waters.

5. 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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