

## **Material qualification in saline, copper containing geothermal water**

Anastasia Stoljarova  
Freie Universität Berlin  
Institute for Chemistry and Biochemistry  
Takustraße 3  
14195 Berlin  
Germany

Ralph Bäßler  
BAM  
Federal Institute for Materials Research and Testing  
Unter den Eichen 87  
12205 Berlin  
Germany

Simona Regenspurg  
GFZ  
German Research Centre for Geosciences  
Telegrafenberg  
14473 Potsdam  
Germany

### **ABSTRACT**

Geothermal wells are a feasible energy source to replace fossil fuel supply. Hence, 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. However, some additional aspects might rise.

During circulation tests at the geothermal research facility in Groß Schönebeck (Germany), massive copper precipitation has been observed downhole clogging the production well. Occurring mechanisms and measures to prevent copper precipitation or scaling needed to be investigated.

This contribution deals with the evaluation of the corrosion behavior of different metals ranging from carbon steel via stainless and duplex steels to titanium in a copper containing artificial geothermal water, simulating the conditions in the Northern German Basin, using electrochemical measurements and exposure tests. While carbon steel exhibits copper deposition (scaling) and copper precipitation, higher alloyed materials show different response to Cu-species in saline geothermal water. Here, no relevant formation of insoluble Cu-species could be detected.

Based on these results, the suitability of the investigated high alloyed materials and Ti-alloy can be concluded for use in such conditions, as long as no crevice conditions in combination with non-metallic parts occur. Carbon steel is not recommended to be used.

**Keywords:** copper, corrosion, steel, geothermal energy

## 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, due to the chemical composition of hydrothermal fluids and temperatures, service conditions in geothermal facilities are demanding in many cases in terms of corrosion. Therefore, materials selection based on preliminary material qualification is essential to guarantee a secure and reliable operation of the facilities.

Since operational conditions in geothermal power plants are crucial in terms of corrosion special attention is paid to materials selection<sup>1-3</sup>.

During fluid circulation test at the geothermal research facility Groß Schönebeck (Germany), massive copper precipitation has been observed downhole in 4200 m depth, clogging the production well and reducing the productivity. Presumably Cu forms directly in the borehole by reduction of dissolved  $\text{Cu}^{2+}$  by oxidation of iron from the steel casing<sup>4,5-6</sup>, leading to clogging of reservoir pores in the well bore-near area and galvanic copper deposition on equipment and piping<sup>7</sup>.

In order to evaluate the corrosion behavior of different metals ranging from carbon steel via stainless and duplex steels to titanium, exposure and electrochemical tests were performed in a copper containing artificial geothermal water, simulating the conditions of formation water in the Rotliegend formation in the Northern German Basin (highly saline, about 150 °C).

By these experiments suitability of these materials was evaluated, especially regarding the prevention of copper precipitation and deposition.

## EXPERIMENTAL SETUP

### Materials and Conditions

The corrosion resistance of various metallic materials (see Table 1) and their influence on the copper reduction was investigated by exposure and electrochemical tests in artificial geothermal water at 150 °C, simulating downhole conditions.

For the measurements, the oxygen concentration in the water was adjusted to very low values by purging the solution with argon for 10 min prior to start of measurements. The test pressure of 1500 kPa was achieved using argon pre-pressurization. The medium was not stirred or purged during exposure.

Test solution was artificial geothermal water (called NGB), having a composition according to a reference analysis of an aggressive geothermal fluid found in Groß Schönebeck.<sup>2</sup> The chemical composition of this test solution with a pH of 5 is shown in table 2. For investigations presented here, 1 m mol  $\text{CuSO}_4$  was added.

**Table 1:**  
**Chemical Composition according manufacturer's datasheets<sup>8</sup>**

	Content [mass%]							
	Cr	Ni	Mo	Fe	Mn	C	N	Cu
<b>ST 37</b> (S 235 JR, 1.0038)	-	-	-	R	≤ 1.4	≤ 0.17	-	-
<b>S31700</b> (317L, X2CrNiMo18-15-7, 1.4438)	17.5-19.5	13-16	3-4	R	≤ 2	≤ 0.03	≤ 0.11	-
<b>S31726</b> (317LN, X2CrNiMoN17-13-5, 1.4439)	16.5-18.5	12.5-14.5	4-5	R	≤ 2	≤ 0.02	0.1-0.2	-
<b>N08904</b> (904L, X1NiCrMoCu25-20-5, 1.4539)	19-21	24-26	4-5	R	≤ 2	≤ 0.03	≤ 0.11	1.2-2
<b>S31603</b> (316L, X2CrNiMo17-12-2, 1.4404)	16.5-18.5	10-13	2-2.5	R	≤ 2	≤ 0.03	≤ 0.11	-
<b>S31653</b> (316LN, X2CrNiMoN17-13-3, 1.4429)	16.5-18.5	11-14	2.5-3	R	≤ 2	≤ 0.03	0.12-0.22	-
<b>S31803</b> (318LN, X2CrNiMoN22-5-3, 1.4462)	21-23	4.5-6.5	2.5-4.5	R	≤ 2	≤ 0.03	0.1-0.22	-
<b>R50400</b> (Ti grade 2B348, 3.7035)	-	-	-	≤ 0.2		≤ 0.08	≤ 0.03	-

**Table 2:**  
**Composition of investigated artificial geothermal water**

Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Content [g/L]			pH
				Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	
166	0.05	-	56.5	0.5	3.1	38.7	5

### Exposure Tests

Exposure tests were carried out according to DIN 50905/4<sup>9</sup> with gravimetric determination of time dependent corrosion within a heating cabinet to provide uniform temperature distribution. Tests were carried out in 1-Liter-autoclaves (figure 1) having a glass-inlay. Three specimens were completely immersed into the solution. Exposure time was up to one month at 150 °C.

Copper deposition was determined after 1 day and one week.



**Figure 1: Vessels for exposure tests**

Test specimens were machined from a plate by water jetting. Before testing, surfaces were ground by 120 SiC-paper, degreased by acetone and dried. The size for test specimens (l x w x t) was 20 x 7 x 6 mm. A set of 3 specimens was used. Each exposure test specimen had a 5 mm hole for fixation using a polytetrafluoroethylene (PTFE)-cord (figure 2, left).

To prevent interaction between the different materials and their corrosion products, the specimens were placed in glass beakers inside the autoclave and tested separately for each material. The specimens were completely immersed in the water. The threshold for suitability was set to be a corrosion rate of 0.1 mm/year. This corresponds to a wall thickness reduction of 2 mm by uniform corrosion during 20 years of service.



**Figure 2: Specimen design for exposure (left) and electrochemical (right) tests**

Beside the determination of weight loss, localized corrosion phenomena were investigated on the gravimetric specimens as well.

A distinction was drawn between pitting and shallow pit corrosion to use the right criteria for the suitability assessment. This means when pitting occurs, the material is not suitable. In case of shallow pitting the depth of the shallow pit was extrapolated to one year resulting in the corrosion rate. Specimens were evaluated after the tests using optical microscopy.

## Electrochemical Tests

For electrochemical characterization open circuit potentials ( $E_{\text{cor}}$ ) were recorded for 1 to 10 days. Afterwards current density potential curves (CPC) were recorded starting at -200 mV relative to  $E_{\text{cor}}$  and proceeded in the anodic direction with 0.2 mV/s linear sweep rate. As soon as the potential was 1.2 V higher than  $E_{\text{cor}}$  or  $i_{\text{cor}}$  exceeded 25 mA/cm<sup>2</sup> (the max. allowed current density), the scan was reversed in the cathodic direction, back to -200 mV vs.  $E_{\text{cor}}$ . The critical potential,  $E_{\text{crit}}$  and the repassivation potential  $E_{\text{rep}}$ , were determined at  $i_{\text{cor}} = 0.1$  mA/cm<sup>2</sup>. Before immersion of test specimens, the solution was purged by argon to keep the oxygen-content very low.

Investigations were carried out using a typical 3-electrode configuration within a 1-L-autoclave equipped with a PTFE-encapsulated saturated Ag/AgCl reference electrode (-220 mV<sub>SHE</sub>) 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 to avoid electrical interferences between heater and measurement device (figure 3). The specimen size for electrochemical tests resulted in 8 cm<sup>2</sup> surface (figure 2, right). All specimens were ground to grit 320 to have comparable surface conditions.

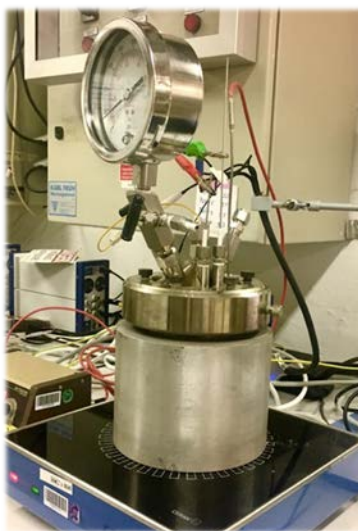


Figure 3: Test setup for electrochemical tests

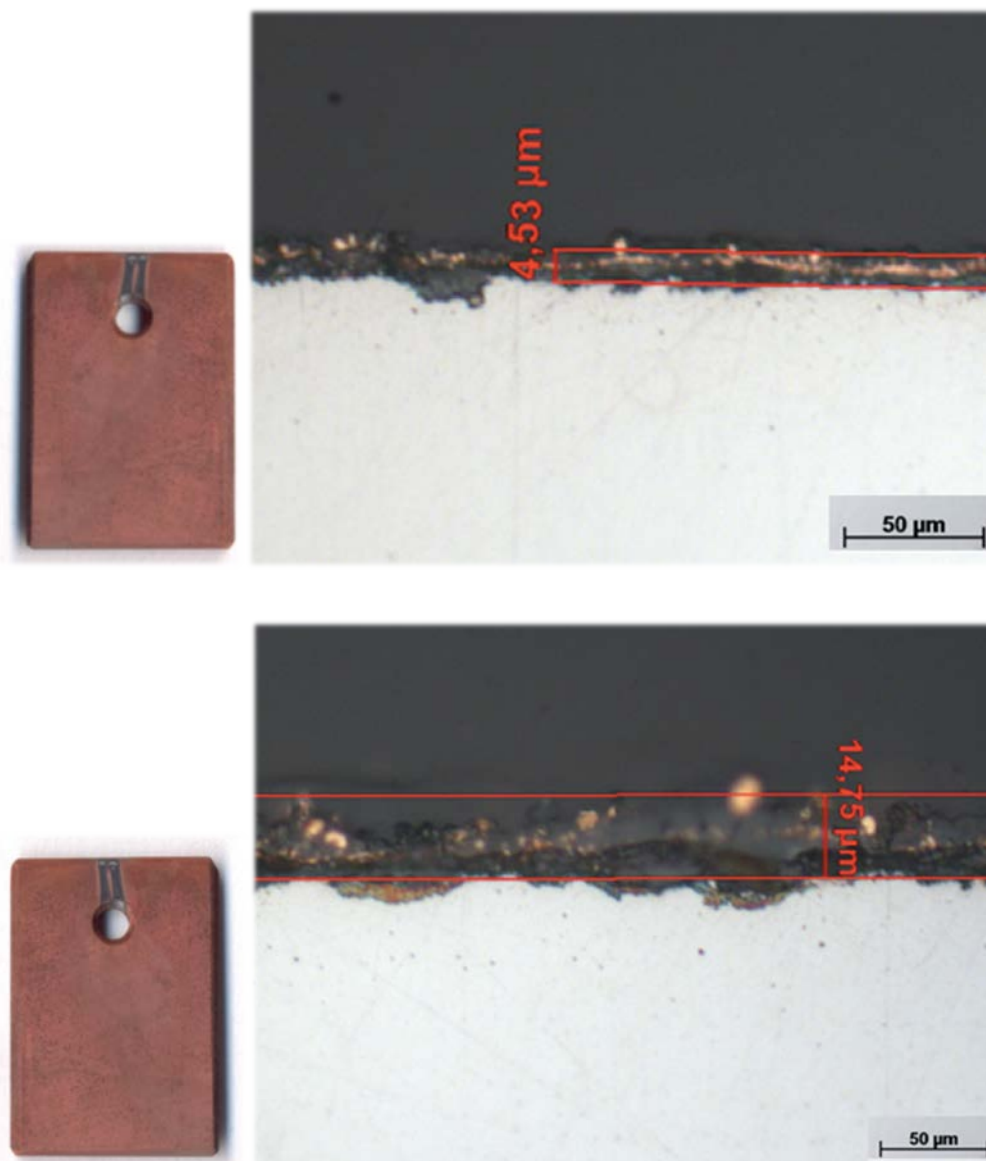
## RESULTS

### Exposure Tests

#### Cu-deposition

Already after 24 hours a uniformly distributed copper layer was found on carbon steel. Appearance of specimen surface and thickness of deposited Cu-layer are shown in figure 4. After one day a thickness of 4.53  $\mu\text{m}$  was determined growing to 14.75  $\mu\text{m}$  after one week.

Additionally, the copper concentration of the medium was measured. At the beginning it was 63 mg/L, after 24 hours 9.5 mg/L and after one week 5.4 mg/L. So continuous deposition could be observed. Also, a reddish precipitation (presumably Cu and iron hydroxide) was detected.



**Figure 4: Copper deposition on carbon steel after 1 day (top) and 1 week (bottom)**

Exposure tests with highly alloyed steels did not show detectable copper depositions. Much less precipitation could be detected. The copper content of the solution decreased from 63 mg/L to 54.3 mg/L after one week and 48 mg/L after one month.

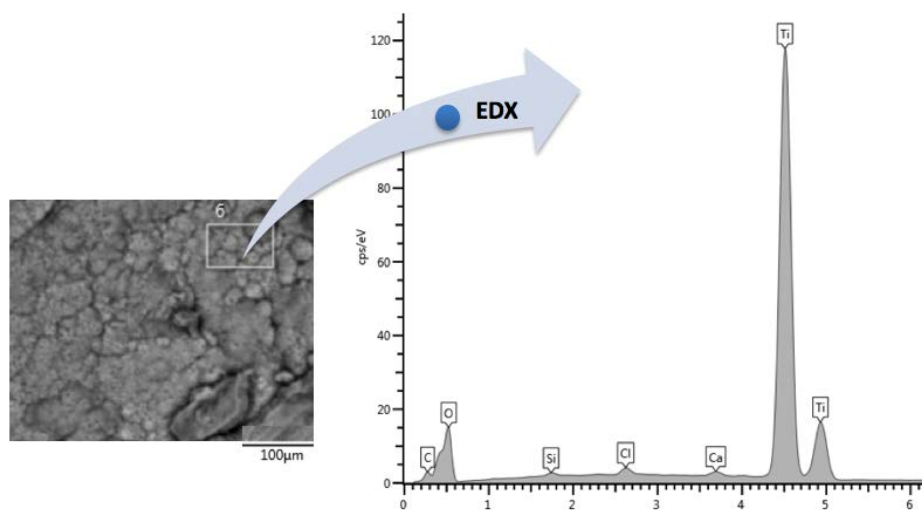
Appearance of the high alloyed and Ti-alloy test specimens after certain times of exposure in Cu-containing artificial geothermal water is shown in figure 5.

In addition to no Cu-deposition, no signs of general or pitting corrosion could be detected. Within the area of fixation some markups pointed to a potential susceptibility to crevice corrosion, as discussed already in previous publications <sup>1-3</sup>.





**Figure 5: Surface appearance after one week and one month exposure in Cu-containing geothermal water**



**Figure 6: EDX spectrum on R50400-specimen after one month exposure**

EDX-analysis of Ti-alloy surface after 1 month exposure showed, that depositions found on the surface consist of salt-components of the geothermal water (figure 6). No Cu-species could be detected.

## Electrochemical Tests

### Open Circuit Potential (OCP)

All specimens exhibited quite stable open circuit potentials within one week of exposure. Selected recorded potentials are shown in figure 7. A survey of measured values is given in table 3. As expected,

OCP of C-steel was the lowest, followed by the high-alloyed materials. Ti-alloy showed the most positive OCP.

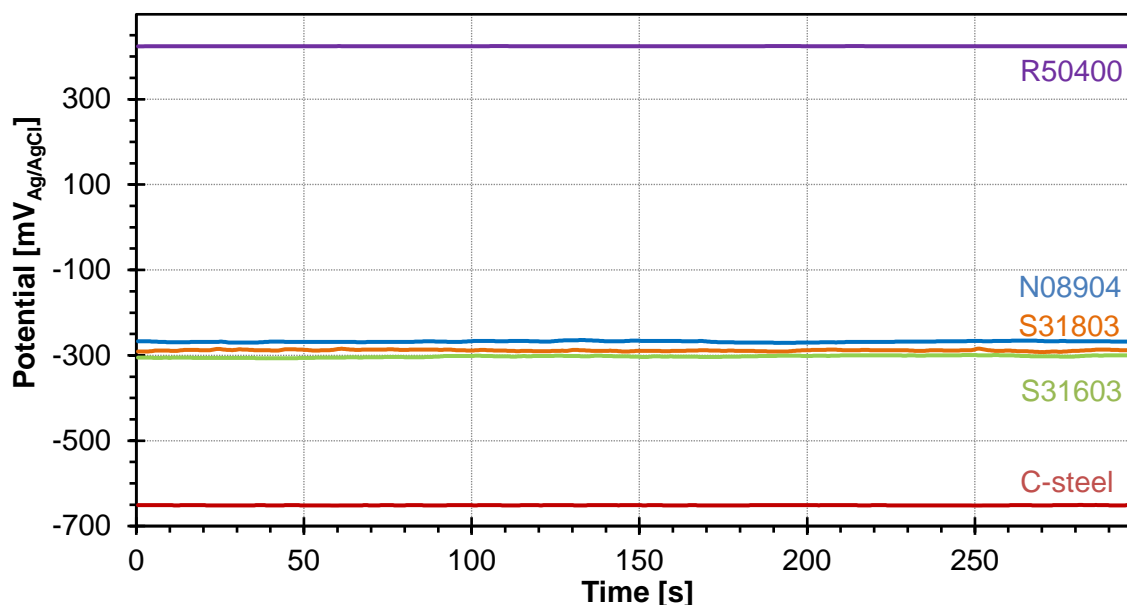


Figure 7: Open circuit potentials in artificial Cu-containing geothermal water

### Current Density Potential Curves

Current density potential curves measured at different materials are shown in figure 8. A significant difference was found, following the OCP ranking.

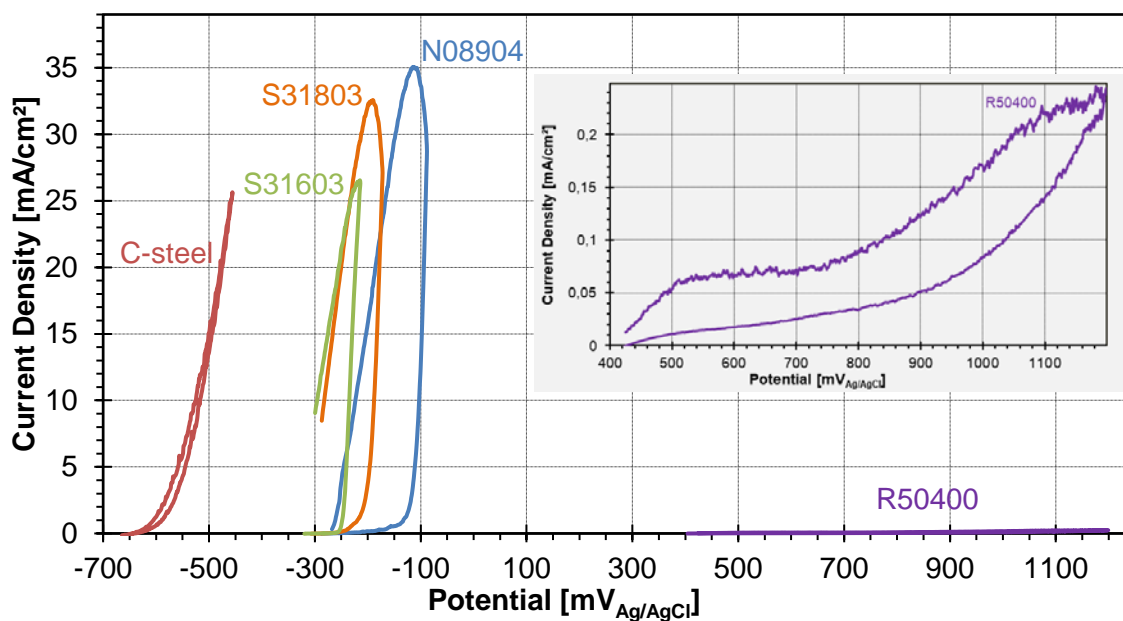
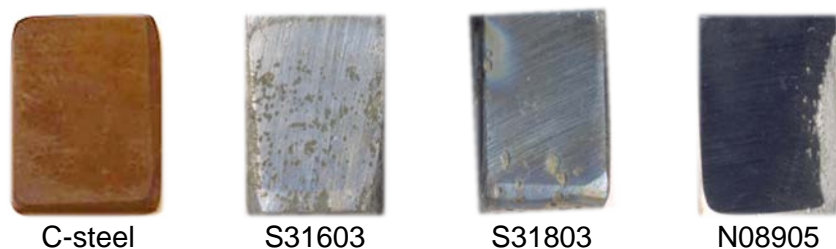


Figure 8: Current density potential curves in Cu-containing artificial geothermal water



Polarizing the specimens caused Cu deposition on C-steel. Hysteresis (pointing to localized corrosion and bad repassivation behavior) could be found for S31603, S31803 and N08904. No pitting was found on R50400. Surface appearance is shown in figure 9.



**Figure 9: Surface appearance after potentiodynamic polarization**

The crevice effect, seen in the fixation areas during exposure tests was not investigated furthermore, since this effect has been described in previous publications <sup>1-3, 10</sup>.

### Evaluation

In table 3 results of electrochemical tests are summarized. The last column contains the evaluation resulting from comparison of open circuit and critical potentials. As already described above, critical potentials were determined being close to the OCP, indicating corrosion susceptibility for S31603 and S31803. For C-steel Cu-deposition process is dominant. At N08904 the critical corrosion potential is far away from open circuit potential. So, no corrosion susceptibility would be expected. However, for all the tested high alloyed materials the repassivation potentials are below (S31603, S31803), or at least close (N08904) to the OCP, indicating a bad repassivation behavior. Hence, once corrosion has started due to changes in the system, these materials might not become passive again. The susceptibility to this behavior is less for N08904 than for S31603 and S31803. For Ti-alloy, no critical values could be found.

**Table 3: Critical potentials from electrochemical measurements**

	$E_{cor}$ [mV <sub>Ag/AgCl</sub> ]	$E_{crit}$ [mV <sub>Ag/AgCl</sub> ]	$E_{rep}$ [mV <sub>Ag/AgCl</sub> ]	status at $E_{cor}$
<b>C-steel</b>	$-651 \pm 6$	$-604 \pm 42$	$-589 \pm 61$	active
<b>S31603</b>	$-300 \pm 18$	$-257 \pm 26$	$-336 \pm 19$	still passive
<b>S31803</b>	$-287 \pm 17$	$-254 \pm 78$	$-313 \pm 19$	still passive
<b>N08904</b>	$-269 \pm 2$	$-132 \pm 52$	$-261 \pm 11$	passive
<b>R50400</b>	$424 \pm 10$	$1034 \pm 10$	$839 \pm 10$	passive

## CONCLUSIONS

By exposure and electrochemical tests in the laboratory the Cu-effect on corrosion behavior of carbon steel, high-alloyed steels and Ti-alloy can be assessed.

Critical materials specific properties were determined by static exposure and electrochemical tests in an artificial geothermal water with high salinity and low pH, containing Cu. Conclusions were drawn using characteristic potential values.

It could be shown that significant Cu-deposition and -precipitation only occurred in combination with carbon steel. High-alloyed materials (S31603, S31653, S31700, S31703, S31803 and N08904) prevent the disturbing Cu-agglomeration. Therefore, they are suitable to be chosen for future design of the piping system, either in massive or in clad form, if formation of crevices with non-metallic materials can be excluded.

From the interactions and pitting corrosion point of view, R50400 seems to be most favorable.

## OUTLOOK

Publication of results achieved so far will contribute to a materials selection for a new well to be drilled for re-activating Groß Schönebeck research facility.

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<sup>†</sup> Trade name

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