

Critical Pitting Temperature Measurements for Evaluating Superaustenitic Stainless Steels Resistance to Solutions Modeling Wastewater Treatment of Flue Gas Desulfurization Plants

B. Eremiáš, V. Čihal, E. Kalabisová, and L. Turek

SVÚOM Ltd., CZ-16400 Prague 6, V Šareckém údolí 2329, Czech Republic
e-mail: info@svuom.cz

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Critical pitting temperature (CPT) determination by potentiostatic procedure is often used as a method of screening stainless steels in solutions with activity range 0.067 – 4.3. Values of activity of chloride ions as well as pH values for those solutions are quite different from the values of the same parameters in solutions modeling wastewater treatment of flue gas desulfurization plants. In those waters the soluble components, mainly calcium chloride (which must be treated by evaporation and crystallization) can give solutions with pH values below 4 and activities of chloride ions much more higher. Thus, even small changes of CaCl_2 concentration can give an increase in chloride ions activity. In the work reported here the effect of two different activities of chloride ions was investigated using potentiostatic CPT measurements on superaustenitic stainless steels in $c = 5.685$ and 5.88 mol L^{-1} CaCl_2 solutions with pH values below 4. The results demonstrated that an increase in the activity of chloride ions causes a decrease in the potential at which, for given a temperature, the growth of stable pits is possible.

Key words:

Electrochemical tests, stainless steels, flue gas desulfurization plants

Introduction

Measurements of critical pitting temperature (CPT) by potentiostatic techniques is a method commonly used to establish the resistance of stainless steels to solutions with activity range 0.067 – 4.3. Most frequently, this method was applied to the development of high-alloy stainless steels resistant to seawater.¹ For this environment, the value of the potential at which such tests were to be conducted was determined by a given material-medium combination. That is why the value of the potential should be at least at the level of the maximum corrosion potential occurring for this combination. At temperatures higher than 30 °C the highest value of the maximum corrosion potential of stainless steels in seawater is $E_{\text{H}} = 390 \text{ mV}$ (on the standard hydrogen electrode scale).² Owing to this fact, different types of stainless steels were tested for their resistance to pitting corrosion in seawater by potentiostatic polarization at this potential. Occasionally, somewhat higher potentials were used, reflecting the shift of the corrosion potential of stainless steels encountered in cases where biofilms were formed in the given environment. The results obtained under such conditions were found to be useful in practical applications (for example, when determining the critical chloride concentration for a given type of material and a given temperature of exposure). In line with the progress of the developments in stain-

less steel types (resistant not only to seawater but also to chloride solutions of pH 1.5 containing Fe^{3+} ions) this value of potential ($E_{\text{H}} = 390 \text{ mV}$) had to be changed. The conditions of the potentiostatic CPT measurements were thus adapted to make use of potentials corresponding to the maximum corrosion potential of these stainless steels under such highly oxidizing conditions. Consequently, the CPT measurements tended to conditions where the stainless steel specimen was polarized potentiostatically at the potential of $E_{\text{H}} = 940 \text{ mV}$. The CPT data for certain stainless steels, established under these conditions, may also be of interest for the chloride solutions of pH ~ 6, inasmuch as the high values of anodic potential promote pit growth and stability.³ Unfortunately, they contribute little in the case of brines where the solubility of oxygen is reduced and at higher temperatures in particular, becomes so low that it displaces the corrosion potential of the stainless steel or alloy toward relatively low values even in solutions having pH < 4. Similar types of environments include e.g. highly concentrated CaCl_2 solutions used to simulate the media produced at the wastewater treatment plants of desulfurization installations. This is a medium where CaCl_2 constitutes the major soluble component, which has to be removed by evaporation and subsequent crystallization, owing to the limitations on the brine loading of water streams imposed by environmental legisla-

tion. An evaluation of the resistance to pitting corrosion in high-alloy stainless steels or similar alloys intended for this application is contingent to performing tests in CaCl_2 solutions having concentrations higher than 40 %, at temperatures exceeding 100 °C. Owing to the various impurities contained in CaCl_2 , this environment may exhibit $\text{pH} < 4$ and may markedly differ, in terms of its activity of chloride ions as well as its pH, from the NaCl solutions of $\text{pH} \sim 6$ ($0.5 - 1 \text{ mol L}^{-1}$ NaCl) used most frequently in the potentiostatic CPT measurements on stainless steels. However, a certain similarity with this environment can be exhibited by the saturated (56.8 %) NaCl solution of pH 3 at 80 °C, used to simulate the environments encountered at radioactive waste repository sites.⁴ Recently, the NiCrMo-based C22 alloy has been tested for its pitting corrosion resistance under such conditions.⁴ It has been found that under these conditions (pH 3, 80 °C) the maximum corrosion potential of this alloy is very low indeed: it can attain values of $E_{\text{H}} = 150$ and 250 mV for deaerated and aerated solutions, respectively. It is probable that these values of corrosion potential may serve as guidance for the choice of potentials at which the potentiostatic CPT measurements can be performed on high-alloy stainless steels or similar alloys in brine environments. Therefore, it is desirable, from the standpoint of evaluating the pitting corrosion resistance of superaustenitic stainless steels in CaCl_2 solutions near their saturation point, to establish the CPT data for various materials within the potential range which also covers these values of potential. It should be taken into account when working with these solutions that in the area of high concentrations, even a minute CaCl_2 concentration difference will bring about a significant change to the activity of chloride ions. In view of the fact that, in addition to material quality, temperature, and potential, this is a parameter of considerable importance to the assessment of the pitting corrosion resistance, we were interested in finding out to what extent its relatively small changes can influence the CPT of the materials examined.

Experimental

Three special superaustenitic stainless steels, designated 254SMO (S31254), 1925hMo (NO8926) and 654SMO (S32654), were chosen for the tests. The chemical composition of these materials is given in Table 1. Sheet specimens having a pickled-and-passivated surface finish inspected by the sheet manufacturer were used. The measurements were carried out in two CaCl_2 solutions with pH values smaller than 4. No impurities have been added to the test solutions but commercial purity

Tab. 1 – Chemical composition of tested superaustenitic steels

Material	w/%					
	C	Cr	Ni	Mo	N	Others
254SMO	0.017	19.7	17.9	6	0.195	Cu: 0.7
1925hMo	0.002	20.65	24.9	6.43	0.188	Cu: 0.84
654SMO	0.02	23.9	22.2	7	0.452	Cu: 0.4

chemicals (from different Czech producers) used for preparation of CaCl_2 solutions produced spontaneously acidic solutions. For these highly concentrated solutions it was necessary to use Pitzer parameters⁵ to be able to calculate activity coefficients and following a_{Cl^-} values corresponding CaCl_2 at high ionic concentrations.

(1) 5.88 mol L^{-1} (43.51%) CaCl_2 solution of an a_{Cl^-} equal to 102.835 and pH 3.655

(2) 5.685 mol L^{-1} (42.75%) CaCl_2 solution of an a_{Cl^-} equal to 86.795 and pH 3.868

CPT measurements were carried out in a special polarization cell. This cell consisted of two cylindrical parts made of glass loaded PTFE. These parts were machined from one side to get through the intersection space between them and then glued together. This arrangement enabled installation of a stirrer and heater element at the left-hand side of polarization cell in order to attain the preset temperature within the right-hand side of this cell where the auxiliary electrodes and the thermometer were located. The samples were pressed against a rubber O-ring onto the opening made at the bottom of the right-hand side of the polarization cell. In this specimen mounting arrangement, the working electrode exposed surface area was $A = 0.283 \text{ cm}^2$ and the auxiliary electrodes – a platinum (polarization) electrode and a silver/silver chloride (reference) electrode – were situated close to the working electrode. The volume of solution used in each experiment was $V = 100 \text{ ml}$.

Owing to the difference in composition of the test materials, as a rule it was necessary to apply a different value of polarization potential (E_{app}) for each of them, in order to guarantee that stable pitting corrosion would develop for the material/medium combination in question under the conditions of the test which was performed at a controlled heating rate of the test medium. In all cases, therefore, the working electrode (specimen) was polarized potentiostatically to a potential that, under conditions of the heating as subsequently applied, could overstep the critical potential of pitting corrosion characteristic of the given material in the given medium. The polarization potentials for the two so-

lutions were chosen based on indicative measurements and were within the range of E_H 105 to 305 mV. In all its other aspects the potentiostatic CPT measuring technique as applied in all the experimental runs was in compliance with the ISO draft standard⁶ *i.e.* after a one-minute holding of the working electrode at the selected potential the test medium was heated at the rate of $r = 1.7 \cdot 10^{-2} \text{ }^\circ\text{C s}^{-1}$ until a stable pitting corrosion developed, as indicated by the time recording of the current passed between the polarization electrode and the working electrode. The stable pitting corrosion corresponding to CPT was characterized by a sudden change of current density on the working electrode, whereupon this quantity continued to assume values higher than $j = 200 \text{ } \mu\text{A cm}^{-2}$. In case of the high-alloy steels exposed to chloride solutions, the overstepping of this value is interpreted as being connected with a permanent loss of protective properties of the passive film.⁷

Results and discussion

The results obtained for the different materials are summarized in the E_{app} – CPT diagrams shown in Figs. 1–3. The data presented here are located exactly on the line without scattering due to high reproducibility of CPT values ($\pm 0.1 \text{ }^\circ\text{C}$). This fact is not surprising because the operating conditions of all tests were fixed very thoroughly. This means that the same piece of test specimen with only different parts of tested surface was used for different potentials applied at potentiostatic polarization. At the same time, the same heating rate, the same initial temperature, and the same stirring velocity were used for rather short time experiments. Figs. 1–3 show that a pair of measurements was carried out in two different solutions (having different a_{Cl^-} values) at the same polarization potential selected for each material. As indicated by Figs. 1–3, all the three materials tested under these conditions yielded CPT values which, for any given material, were always lower for the solution with higher a_{Cl^-} value (no. 1 solution). It can be seen at the same time that for grade 654SMO material this difference in the CPT values is less than those for the grades 254SMO and 1925hMo. From Figs. 1–3 it is also obvious that the CPT value decreases as the potential grows; this applies to all the materials tested in either of the solutions (both no. 1 and no. 2). The CPT values obtained, as plotted in the E_{app} –CPT diagrams, lend themselves easily to extrapolation to the temperature of $122 \text{ }^\circ\text{C}$ (near boiling point of the test solutions), yielding safe corrosion potential values for the different material grades when exposed to either of the two test solutions. Fig. 4 indicates that under

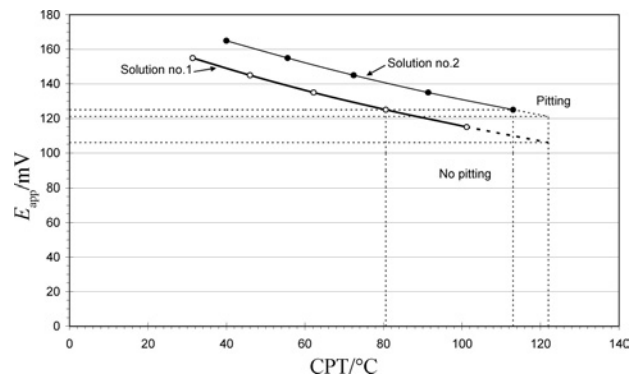


Fig. 1 – E_{app} –CPT diagrams for material 254SMO (S31254)

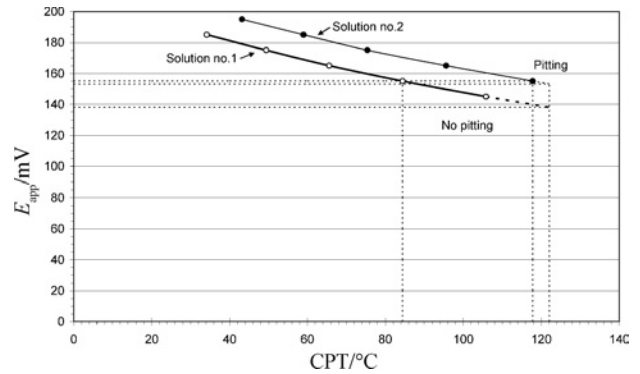


Fig. 2 – E_{app} –CPT diagrams for material 1925hMo (NO8926)

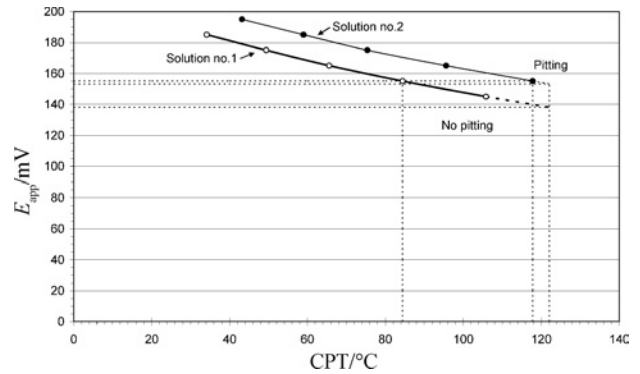


Fig. 3 – E_{app} –CPT diagrams for material 654SMO (S32654)

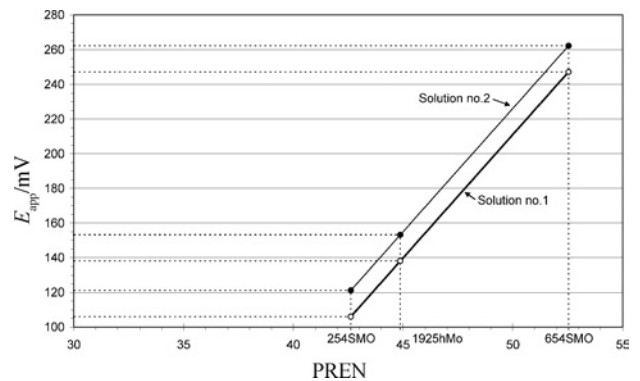


Fig. 4 – Safe corrosion potential values - PREN diagrams for the different material grades in solutions no. 1 and 2 at $122 \text{ }^\circ\text{C}$

conditions where the concentrated CaCl_2 solutions are subject to evaporation and subsequent crystallization, the values of these potentials are influenced by the values of the PREN parameter (the pitting resistance equivalent number reflecting the effects of alloying which impacts the pitting corrosion resistance). For this parameter it holds that⁷

$$\text{PREN} = \% \text{Cr} + 3.3 \% \text{Mo} + 16 \% \text{N} \quad (1)$$

It can be seen from Fig. 4 that for the material grades 254SMO and 1925hMo the values of the safe corrosion potentials are way below $E_{\text{H}} = 250$ mV. However, this value of the maximum corrosion potential for similar types of environments and material in cases of prolonged exposure⁴ must be taken into consideration to arrive at a realistic estimate of the conditions that make a given corrosion system susceptible to stable pitting corrosion. From this standpoint, therefore, the material grades 254SMO and 1925hMo cannot, on the basis of the results obtained, be expected to be resistant to pitting corrosion in the given environment. In contrast, as indicated by Fig. 4, the safe potential value for grade 654SMO material under the experimental conditions applied herein is in the vicinity of $E_{\text{H}} = 250$ mV, indicating that its application for the given material/environment combination is marginally feasible. Therefore, should 654SMO grade material be applied for this purpose, it is desirable to check and verify the pH values and the activity of chloride ions of the CaCl_2 solutions initially used, which have to be subjected to evaporation and subsequent crystallization. The results of the potentiostatic CPT measurements confirm that these are the decisive parameters determining the suitability of this material for the given environment.

Conclusions

The results of CPT measurements, carried out in model solutions simulating desulfurization plant wastewater treatment (5.685 mol L⁻¹ and 5.88 mol L⁻¹ CaCl_2) using a potentiostatic technique, have confirmed that, at pH values lower than 4, the differences encountered in the activity of chloride ions of the two test solutions are of great importance to the CPT values of the materials examined. To facilitate a practical utilization of the results, a procedure has been proposed whereby the condition of safe use can be established for the test materials

with a view to their exposure as part of a given material/medium combination. Having applied this procedure to the experimental CPT results for three grades of superaustenitic stainless steels immersed in the above solutions, it has been found that the grades 254SMO and 1925hMo will meet this condition only at relatively low corrosion potentials. However, in order to arrive at a realistic estimate of the conditions making the material susceptible to stable pitting corrosion in the given medium, a higher value of corrosion potential has to be reckoned with and should never be overstepped. Considering the material grades examined, it is solely the 654SMO superaustenitic steel which has approached these limiting conditions of applicability.

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List of symbols

A	– surface area, cm ²
a	– activity, mol L ⁻¹
c	– concentration, mol L ⁻¹
E	– potential, mV
E_{H}	– potential vs. SHE, mV
j	– current density, $\mu\text{A cm}^2$
T	– temperature, °C
T	– rate of temperature change, °C s ⁻¹
V	– volume, ml
w	– mass fraction, %
γ	– mass concentration

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