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ELECTROCHEMICAL CORROSION STUDIES ON A SELECTED CARBON STEEL FOR APPLICATION IN NUCLEAR WASTE DISPOSAL CONTAINERS: INFLUENCE OF RADIOLYTIC PRODUCTS ON CORROSION IN BRINES

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Summary

In previous corrosion studies, carbon steels were identified as promising materials for the manufacturing of long-lived high-level waste containers that could act as a radionuclide barrier in a rock-salt repository. In the present work, the influence of some important oxidizing radiolytic products generated in gamma irradiated brines on the electrochemical corrosion behaviour of the preselected fine-grained steel TStE 355 was studied. The steel was examined by potentiodynamic and potentiostatic polarization methods at 90°C in a disposal relevant NaCl-rich brine containing radiolytic products such as H_2O_2, ClO^-, ClO_3^- and ClO_4^- at concentrations between 10^{-4} and 10^{-2} M/l.

The polarization curves indicate that in all brines with and without radiolytic products, the steel exhibits active corrosion. A non-uniform general corrosion was observed without any signs of pitting corrosion. ClO_3^- and ClO_4^- additions of 10^{-4}-10^{-3} M/l to the brine do not increase significantly the initial corrosion rate of the steel compared to the value in the pure brine. However, additions of ClO^- and H_2O_2 to the brine change the cathodic process from activation polarization to diffusion polarization and strongly enhance the corrosion rate of the steel beyond the value of the pure brine. At concentrations of 10^{-3}-10^{-2} M/l ClO^- and H_2O_2 in the brine, the initial corrosion rates are higher by a factor of about 11-100 than in the pure brine. Nevertheless, at the lower concentration of 10^{-4} M/l, the increase in rate is higher by a factor of 2-10 only compared to the value in the pure brine.

In general, it can be stated that the significance of the radiolytic products to steel corrosion depends on their concentration at the metal-brine interface, which, in turn, depends on many factors such as the dose rate, the amount of water present in the disposal area, the escape of gases (e.g. H_2) etc. Immersion tests of up to 1-2 years are in progress to examine whether high concentrations of radiolytic products such as H_2O_2 and ClO^- can also influence the long-term corrosion rate of the steel which is of decisive importance for long-term predictions of the container lifetime.

Elektrochemische Korrosionsuntersuchungen an einem ausgewählten Stahl als Werkstoff für Endlagerbehälter: Einfluß von Radiolyseprodukten auf die Korrosion in Salzlösungen

Zusammenfassung

Bisherige Korrosionsuntersuchungen ergaben, daß Kohlenstoffstähle aussichtsreiche Materialien für langzeitbeständige Behälter zur Endlagerung von hochradioaktiven Abfällen in Steinsalzformationen sind. In dieser Arbeit wurde der Einfluß wichtiger Radiolyseprodukte, die bei der Gamma-Bestrahlung von Salzlösungen entstehen, auf das Korrosionverhalten des ausgewählten Feinkornbaustahls TStE 355 untersucht. Die Untersuchung des Stahls erfolgte mittels potentiostatischer und potentiodynamischer Messungen bei 90°C in einer endlagerrelevanten NaCl-reichen Lösung, die oxidierende Radiolyseprodukte wie H_2O_2, ClO^-, ClO_3^- und ClO_4^- in Konzentrationen zwischen 10^{-4} und 10^{-2} M/l enthielt.

Die Untersuchungsergebnisse zeigen, daß der Stahl in allen Salzlösungen aktiv korrodiert. Es wurde eine ungleichmäßige Flächenkorrosion ohne Anzeichen für Lochkorrosion festgestellt. ClO_3^- und ClO_4^--Konzentrationen von 10^{-4} und 10^{-3} M/l in der Lösung haben keinen signifikanten Einfluß auf die Anfangskorrosionsrate des Stahls. Zusätze von ClO^- und H_2O_2 in die Lösung ändern den kathodischen Prozeß von Aktivierungspolarisation zur Diffusionspolarisation und bewirken dadurch eine starke Erhöhung der Anfangskorrosionsrate. Bei ClO^-- und H_2O_2-Konzentrationen von 10^{-3}-10^{-2} M/l in der Lösung sind die Korrosionsraten um den Faktor 11-100 höher als in der Lösung ohne Radiolyseprodukte. Allerdings beträgt bei der niedrigeren Konzentration dieser Produkte von 10^{-4} M/l die Erhöhung der Korrosionsraten nur das 2-10-fache des Wertes in der reinen Lösung.

Im allgemeinen kann festgestellt werden, daß die Signifikanz der Radiolyseprodukte für die Stahlkorrosion stark von ihrer Konzentration an der Grenzfläche Metall/Lösung abhängt. Diese wiederum hängt von vielen Faktoren, wie Dosisleistung, Menge des vorhandenen Wassers im Endlagerbereich, Flüchtigkeit der Gase (z.B. H_2) etc. ab. Inwieweit hohe Konzentrationen von Radiolyseprodukten einen Einfluß auch auf die Langzeit-Korrosionsrate des Stahls haben, die für Auslegung der Behälterwandstärke entscheidend ist, soll durch Langzeit-Immersionsexperimente geklärt werden.

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1. Introduction

Previous corrosion studies [1-4] have shown that the unalloyed fine-grained steel TStE 355 is a promising material for the manufacturing of long-lived high-level waste (HLW) containers that could act as a radionuclide barrier in a rock-salt repository. Its promising nature is based primarily on the fact that so far only general corrosion has been observed in disposal relevant salt brines such that the long-term corrosion behaviour of the steel can be predicted in a reasonable manner. Furthermore, the corrosion rates of the steel determined imply acceptable corrosion allowances for thick-walled containers.

To characterize the corrosion behaviour of the fine-grained steel TStE 355 in more detail, further electrochemical and long-term corrosion studies are being performed in brine environments. An essential aspect of the corrosion studies on the steel is the investigation of the influence exerted by the radiation of the waste on its corrosion behaviour in disposal relevant salt brines. Of the various types of radiation, only gamma radiation is present at the surface of the container. The dose rate depends on the design of the container and the nature of the waste inside.

Corrosion studies under gamma irradiation are important for two reasons. Firstly, the interaction of gamma radiation with the salt brines produces reduced/ oxidizing reactive particles and stable products such as e^-_{aq}, H_2, H_2O_2, etc.[5] which may change the rate and mechanism of corrosion. Secondly, the absorption of gamma radiation in the semi-conducting protective oxide layers of metals will induce photoradiation effects [6,7] which can change the corrosion rate by facilitating cathodic/anodic reactions at the oxide layer/electrolyte interface. Glass [7] concludes that the radiolytic products will exert the greatest effect on the corrosion process of metals.

Previous immersion corrosion experiments on carbon steels in an $MgCl_2$-rich brine [2] have shown that a high gamma dose rate of 10^5 rad/h strongly enhances the corrosion rate. In contrast to this, lower dose rates of up to 10^4 rad/h did not influence the rate. It was concluded that the effect of radiation on corrosion is strongly dependent on the concentration of radiolytic products in the brines. Strong oxidizing agents such as H_2O_2, ClO_3^- etc. were considered as being mainly responsible for the increase in corrosion since they are known as cathodic depolarizers. To determine the individual contribution of the most important oxidizing radiolytic products on steel corrosion and to obtain information on the corrosion mechanism, electrochemical studies were performed in a brine containing radiolytic products at various concentrations.

2. Amounts of radiolytic species in salt brines

The gamma radiation effects on salt brines have been investigated almost exclusively by Jenks [5]. On the basis of these results, Glass [7] concludes that the following radiolytic products should be expected to be present in salt repositories: H, $OH^{\cdot}$, e^{-}_{aq}, H_3O^+, OH^-, H_2, H_2O_2, $HO_2 \leftrightarrows O_2^-$ with H_2 and H_2O_2 being stable molecular products as well as various oxychlorides and oxybromides such as ClO^-, ClO_2^-, ClO_3^-, ClO_4^-, BrO_3^-. Cl_2^- may also be an important transient species. Gases such as Cl_2, and O_2 may be produced in measurable amounts. Furthermore, it has to be noted that the generated radiolytic species may further react with each other or with other solutes present in the brines.

In order to determine the amounts of radiolytic species expected in the salt brines, computer codes such as RADIOL [8] and SWAATS-LOOPCHEM [9] have been developed. Having a 5-M NaCl brine expected to occur in a salt repository, an amount of $2x10^{-4}$ M/l H_2O_2 was calculated after irradiation at a gamma dose rate of $3.5x10^6$ rad/h and an initial oxygen concentration of 1.5 ppm. Additional laboratory investigations by McDougall [10] show in agreement with [9] that the maximum amounts of H_2O_2, ClO_3^- and ClO_4^- in saturated brines are of the order of 10^{-4}-10^{-3} M/l.

According to the literature data mentioned above, the corrosion experiments on the steel were conducted in a disposal relevant brine containing H_2O_2, ClO^-, ClO_3^- and ClO_4^- at concentrations of 10^{-4}-10^{-3} M/l. In the case of the strong oxidant H_2O_2, a concentration of 10^{-2} M/l was examined in addition. The concentrations of radiolytic products used in the experiments correspond to gamma dose rates of 10^6-10^8 rad/h. As the gamma dose rate expected on the surface of the thick-walled steel container discussed here is about 10^3 rad/h only, the tests can be considered as overtests.

3. Experimental

The fine-grained steel TStE 355 used in the corrosion experiments had the following composition in wt.% :

0.17 C; 0.44 Si; 1.49 Mn; 0.06 P+S; bal. Fe.

The corrosion of the steel was investigated at 90°C in a disposal relevant NaCl-rich brine (pH=7) containing radiolytic products such as H_2O, ClO^-, ClO_3^- and ClO_4^- at concentrations of 10^{-2}-10^{-4} M/l. The brine had the following composition in wt.%:

25.9 NaCl; 0.24 K_2SO_4; 0.20 $CaSO_4$; 0.16 $MgSO_4$; 73.5 H_2O.

The radiolytic products were added to the brine by using a commercial 30 % H_2O_2-solution, 15 % NaClO-solution, crystallized $NaClO_3$ and $NaClO_4xH_2O$, respectively. The radiolytic species and their concentrations used in the experiments are listed in Tab. 1.

The experimental setup consisted of an electrochemical three-compartment cell containing the steel as part of the working electrode, a saturated Hg/ Hg_2SO_4/SO_4^{2-} reference electrode (R.E.), a platinum counter electrode, and a P.A.R. model 273 potentiostatic coupled to a computer data acquisition system. Cathodic and anodic potentiodynamic polarization experiments were conducted at a low scanning rate (0.2 mV) in the potential range from −250 mV to +1400 mV. vs the free corrosion potential in order to determine the influence of radiolytic species on steel corrosion. The following polarization parameters were obtained from the curves:

- Free corrosion potential (E_{corr}) and Tafel slopes (ba, b_c), which are representative for the cathodic and anodic processes.
- Corrosion current densities (i_{corr}), which permit to calculate the initial corrosion rate (v_{corr}) of the steel in the brines.

In order to obtain information on the reaction kinetics in H_2O_2- and ClO^--containing brines, potentiostatic polarization tests were conducted at −1220 mV, -900 mV and +500 mV vs. R.E. in addition to the potentiodynamic polarization measurements. Each experiment was repeated at least twice.

4. Corrosion of steel in NaCl-rich brine

Fig. 1 shows the current density-potential curve of the steel in the pure NaCl-rich brine (reference curve). This curve is typical for the active corrosion of a metal. No passivity and no susceptibility to localized corrosion is observed in the region between the corrosion potential and values up to +900 mV vs. R.E.. The anodic and cathodic branches show charge-transfer polarization (the rate is determined by the uptake or release of electrons).

As cathodic reaction, the reduction of water forming molecular hydrogen, and as anodic reaction the oxidation of iron to Fe^{2+} are considered. The anodic and cathodic Tafel slopes determined are 43 mV/dec. and 103 mV/dec., respectively. The initial corrosion rate of the steel calculated by the Tafel method is 0.096 mm/a (Tab. 1).

5. Influence of H_2O_2 on steel corrosion

5.1 Potentiodynamic polarization studies

Polarization curves of steel specimens in NaCl-rich brine with and without the addition of H_2O_2 (10^{-3}-10^{-2} M/l) are plotted in Fig. 2. It is shown that:

- The steel exhibits active corrosion in the H_2O_2-containing brines, like in the pure brine.
- In the presence of H_2O_2, the polarization parameters E_{corr}, i_{corr}, and bc are significantly higher than in the pure brine. They increase with growing H_2O_2 concentration (Tab. 1). At the highest H_2O_2 concentration of 10^{-2} M/l in the brine, the corrosion potential reaches a value of −1018 mV vs. R.E. which is higher by about 137 mV than in the pure brine. The initial corrosion rate of the steel strongly increases with the H_2O_2 concentration. At H_2O_2 concentrations of 10^{-4}-10^{-2} M/l in the brine, corrosion rates of 1.1-10 mm/a were calculated which are higher by a factor of about 11-100 than that in the pure brine (Tab. 1).
- The cathodic polarization curves show diffusion polarization, indicating that the prevailing reduction reaction is controlled by mass transport.

As H_2O_2 is a thermodynamically unstable species, it cannot be excluded that it could decompose during the potentiodynamic polarization experiment lasting about 1.5 hour, which would cause a change of the H_2O_2 concentration in the brine. In order to test whether the initial concentration in the brine remained unchanged during the potentiodynamic polarization duration, additional potentiostatic polarization measurements as well as studies at the free corrosion potential were conducted on the steel in the brine containing 10^{-2} M/l H_2O_2. These measurements, in which the corrosion current and the free corrosion potential are measured as function of time, permit to study the kinetics of the reactions.

5.2 Potentiostatic polarization studies

Figs. 3-5 show potentiostatic polarization curves of the steel determined in pure brine and in H_2O_2-containing brine (10^{-2} M/l) at potentials of −1220 mV, −900 mV and +500 mV vs. R.E., respectively. In addition, the potentiostatic polarization curves in ClO^--containing brine (10^{-3} M/l) are plotted. They have already been discussed in section 4. The plots show that:

- At −1220 mV vs. R.E. (cathodic polarization), the current densities of the steel measured in the H_2O_2-containing brine show fluctuations of ±120 µA during the test time (Fig. 3). This indicates a modification of the steel surface state. The initial value of the current density amounts to 2100 µA/cm^2 which is very close to that obtained by the potentiodynamic polarization method. This confirms the validity of the potentiodynamic measurements (Fig. 2). With increasing measuring time, the value of the current density decreases and reaches a constant value of 550 ±120 µA/cm^2 after 500 s.

- At −900 mV vs. R.E. (anodic polarization) in the H_2O_2-containing brine (Fig. 4), the current density amounts to 20 mA/cm^2 which is lower by about a factor of 4 than the value in the pure brine. This value remains constant during the test period of 400 s and corresponds well to that determined by the potentiodynamic polarization method (30 mA/cm^2) (Fig. 2).

- By an anodic polarization of +500 mV vs. R.E. (Fig. 5), the initial value of the current density in the H_2O_2-containing NaCl-rich brine of 1.1 A/cm^2 is somewhat lower than that in the pure brine. With increasing measuring time, the value increases and reaches the value of the pure brine of 1.3

A/cm^2 after 80 s. This value is very close to that obtained by the potentiodynamic polarization method (Fig. 2) at the same potential.

5.3 Studies at free corrosion potential

The behaviour of the free corrosion potential of the steel with time was measured before and after the addition of 10^{-2} M/l H_2O_2 to the NaCl-rich brine. Furthermore, the redox potential of the brine was measured. The results presented in Fig. 6 show that by an addition of H_2O_2 to the brine both the free corrosion potential and the redox potential of the steel increase considerably. Then, these potentials slightly decrease with time. After 75 min., values of −1050 mV and −160 mV vs. R.E., respectively, were recorded for the free corrosion potential and the redox potential in the H_2O_2-containing brine.

5.4 Discussion

The electrochemical corrosion results obtained in H_2O_2-containing brines show the high aggressivity of H_2O_2 for steel corrosion. H_2O_2 as a thermodynamically unstable species can decompose to O_2. However, no indication of this was noticed, as both the free corrosion potential and the redox potential in the H_2O_2-containing brine remained fairly constant during the experimental duration of 1.5 hour.

Furthermore, the results obtained from potentiostatic polarization experiments show good agreement with those of the potentiondynamic polarization studies, which confirms the validity of the results obtained. The strong influence of H_2O_2 on the corrosion of the fine-grained steel in the brine is attributed to the reaction of H_2O_2 with Fe und Fe^{2+} leading to the formation of Fe^{3+}, as already reported in literature [11].

6. Influence of ClO^- on steel corrosion

6.1 Potentiodynamic polarization studies

The current density-potential curves of the fine-grained steel determined in NaCl-rich brine with and without additions of ClO^- (10^{-4}-10^{-3} M/l) are presented in Fig.7.

In all brines with and without additions of ClO^- and potentials ranging from the free corrosion potential to +300 mV vs. R.E., the steel corrodes in an active manner. After exposure to the brines, a non-uniform corrosion accompanied by shallow pits was observed on the specimen surface. The free corrosion potentials and the cathodic Tafel slopes determined for specimens immersed into ClO^--containing brines are slightly higher than those determined in the pure brine. Furthermore, the initial corrosion rate determined in the ClO^--containing brines at concentrations of 10^{-4} and 10^{-3} M/l are higher by about a factor of 2 and 11, respectively, than the value in the pure brine (Tab. 1).

6.2 Potentiostatic polarization studies

Because of the thermodynamic instability of ClO^-, potentiostatic polarization studies of the steel were performed in ClO^--brines, as in the case of H_2O_2, in order to obtain more information on the kinetics of the reactions. The experimental procedure used is the same as that already described for the H_2O_2-containing brine.

Figs. 3-5 show potentiostatic polarization curves of the steel obtained in pure brine and ClO^--containing brine (10^{-3} M/l) at potentials of −1220 mV, −900 mV, and +500 mV vs. R.E. For comparison, the results in H_2O_2-containing brine (10^{-2} M/l) are given as well.

The potentiostatic polarization curves show:

- At −1220 mV vs. R.E. (Fig. 3), fluctuations of ±120 mV occur, as in the case of H_2O_2 additions to the brine, indicating again modifications of the steel surface state. The initial value of the current density of +900 µA/cm^2 in the ClO^--containing brine is significantly lower than that obtained in the H_2O_2-containing brine (2020 µA/cm^2). However, after an experimental duration of 500 s, a constant value of 500 µA/cm^2 was established both in the ClO^--

and H_2O_2-containing brines. The initial value of 900 µA/cm^2 obtained from the potentiostatic studies is three times higher than that obtained by the potentiodynamic polarization method.

- At –900 mV vs. R.E. (Fig. 4) (anodic polarization), the current density in the ClO^--containing brine is 65 ±5 mA/cm^2 which agrees very well with the value of 67 mA determined by the potentiodynamic polarization method (Fig. 7).
- At +500 mV vs. R.E. (Fig. 5) (anodic polarization), a constant current density of 1.25 A/cm^2 was measured in both brines with and without ClO^- additions (Fig. 5). This result is very close to that obtained by the potentiodynamic polarization method indicating a value of 1.5 A/cm^2.

6.3 Discussion

The corrosion results obtained for the steel from the potentiodynamic and potentiostatic polarization methods show some differences. A possible explanation for the lower value of the initial current density of the potentiodynamic polarization experiments compared to the potentiostatic polarization studies is that partial decomposition of ClO^- took place during the experiments. According to literature data [12] for chlorinated solutions at pH=7, the oxidizing species are present in two principal forms, namely, HClO and ClO^-. The slight increase in the free corrosion potential and the increase in the initial corrosion rate are attributed to the occurrence of the following reactions:

$$HClO + H^+ + 2e^- \rightarrow H_2O + Cl^-$$

$$ClO^- + 2H^+ + 2e^- \rightarrow H_2O + Cl^-$$

These reactions are controlled by mass transport which explains the increase in the cathodic Tafel slope.

7. Influence of ClO_3^- and ClO_4^- on steel corrosion

The experiments were conducted at 90°C in the NaCl-rich brine containing ClO_3^- and ClO_4^- at concentrations of 10^{-4}-10^{-3} M/l and pH=7. Under these conditions, the steel exhibited a non-uniform general corrosion accompanied by shallow pits. The current density-potential curves plotted in Figs. 8 and 9 show that:

- ClO_3^- at concentrations of 10^{-4}-10^{-3} M/l leads to an increase in the free corrosion potential of the steel from −1155 mV in the pure brine to −1118 mV and −1062 mV, respectively. However, no increase in the initial corrosion rate of the steel was observed in comparison to the rate in the pure brine (Tab. 1).

- In ClO_4^--containing brines (10^{-4}-10^{-3} M/l), no increase of the free corrosion potential was observed in comparison to the value of the pure brine. Nevertheless, an increase in the initial corrosion rate of the steel by a factor of 2 was noticed in comparison to the value in the pure brine (Tab. 1).

- Both, additions of ClO_3^- and ClO_4^- to the brine slightly increase the cathodic Tafel slopes which indicates changes in the cathodic reaction processes.

8. Conclusions

From the electrochemical corrosion studies on the preselected container material fine-grained steel TStE 355 at 90°C in a disposal relevant brine, the following conclusions can be drawn:

- In NaCl-rich brine with and without radiolytic products such as H_2O_2, ClO^-, ClO_3^- and ClO_4^- the steel is subjected to non-uniform general corrosion. Pitting corrosion in the sense of an active-passive corrosion element was not observed.

- ClO_3^- and ClO_4^- at concentrations of 10^{-4}-10^{-3} M/l in the brine do not enhance significantly the initial corrosion rate of the steel beyond the value measured in the pure brine.

- On the contrary, ClO^- and H_2O_2 concentrations of 10^{-3}-10^{-2} M/l in the brine strongly increase the initial corrosion rate of the steel by a factor of about 11-100 compared to the value in the brine without radiolytic products.

However, at the lower ClO^- and H_2O_2-concentrations of 10^{-4} M/l, the corrosion rates are higher by the factor of 2-10 only than the value in the pure brine. Even the experiments at 10^{-4} M/l are considered to be overtests, as this concentration corresponds to a gamma dose rate of 10^6 rad/h which is higher by about a factor of 1000 than that expected on the surface of the thick-walled steel container discussed.

- The electrochemical studies are in agreement with previous irradiation-corrosion experiments [2] and show that the significance of the radiolytic products to steel container corrosion depends on their concentration at the metal-brine interface. This, in turn, will depend on numerous factors such as the dose rate, temperature, amount of water present, escape of gases (e.g. H_2) etc. In case of an intrusion of limited amounts of water into the disposal area, the radiolytic products generated will be consumed by corrosion reactions with Fe. Therefore, the long-term corrosion rate will be much lower than the initial corrosion rate determined in this study. Immersion tests of up to 1-2 years are in progress with a view to determine the long-term corrosion rate of the steel in brines containing radiolytic products.

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Table 1: Results of the electrochemical corrosion studies on the fine-grained steel TStE 355 at 90°C in NaCl-rich brine with and without additions of radiolytic species

Radiolytic species added	Concentration (Mol/l)	E_{corr} (mV vs.R.E.)	b_a (mV/dec)	b_c (mV/dec)	I ($\mu A/cm^2$)	V_{corr} (mm/a)
no	-	-1155	43	103	8.3	0.096
H_2O_2	10^{-4}	-1120	44	570	95	1.1
H_2O_2	10^{-3}	-1022	44	390	140	1.6
H_2O_2	10^{-2}	-1018	63	420	865	10.0
ClO^-	10^{-4}	-1150	45	110	20	0.23
ClO^-	10^{-3}	-1133	47	170	95	1.1
ClO^-_3	10^{-4}	-1118	39	125	9	0.1
ClO^-_3	10^{-3}	-1062	40	178	10	0.11
ClO^-_4	10^{-4}	-1151	43	137	20.5	0.24
ClO^-_4	10^{-3}	-1155	44	130	15.5	0.18

E_{corr} = free corrosion potential

b_a, b_c = anodic and cathodic Tafel slopes

I_{corr} = corrosion current density

V_{corr} = initial corrosion rate

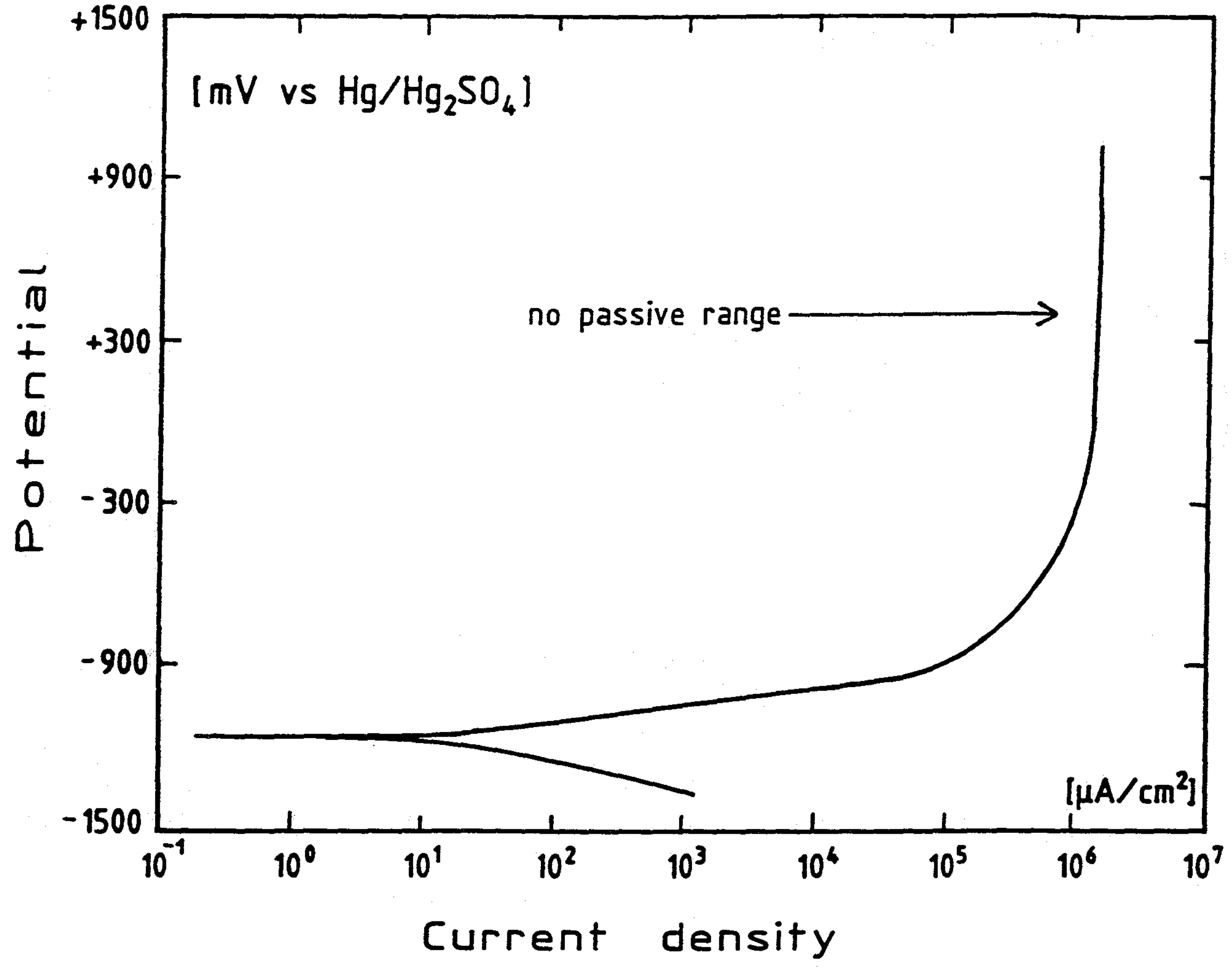

Fig. 1: Potentiodynamic polarization curve of the fine-grained steel TSt E 355 in deaerated NaCl-rich brine at 90°C (pH = 7).

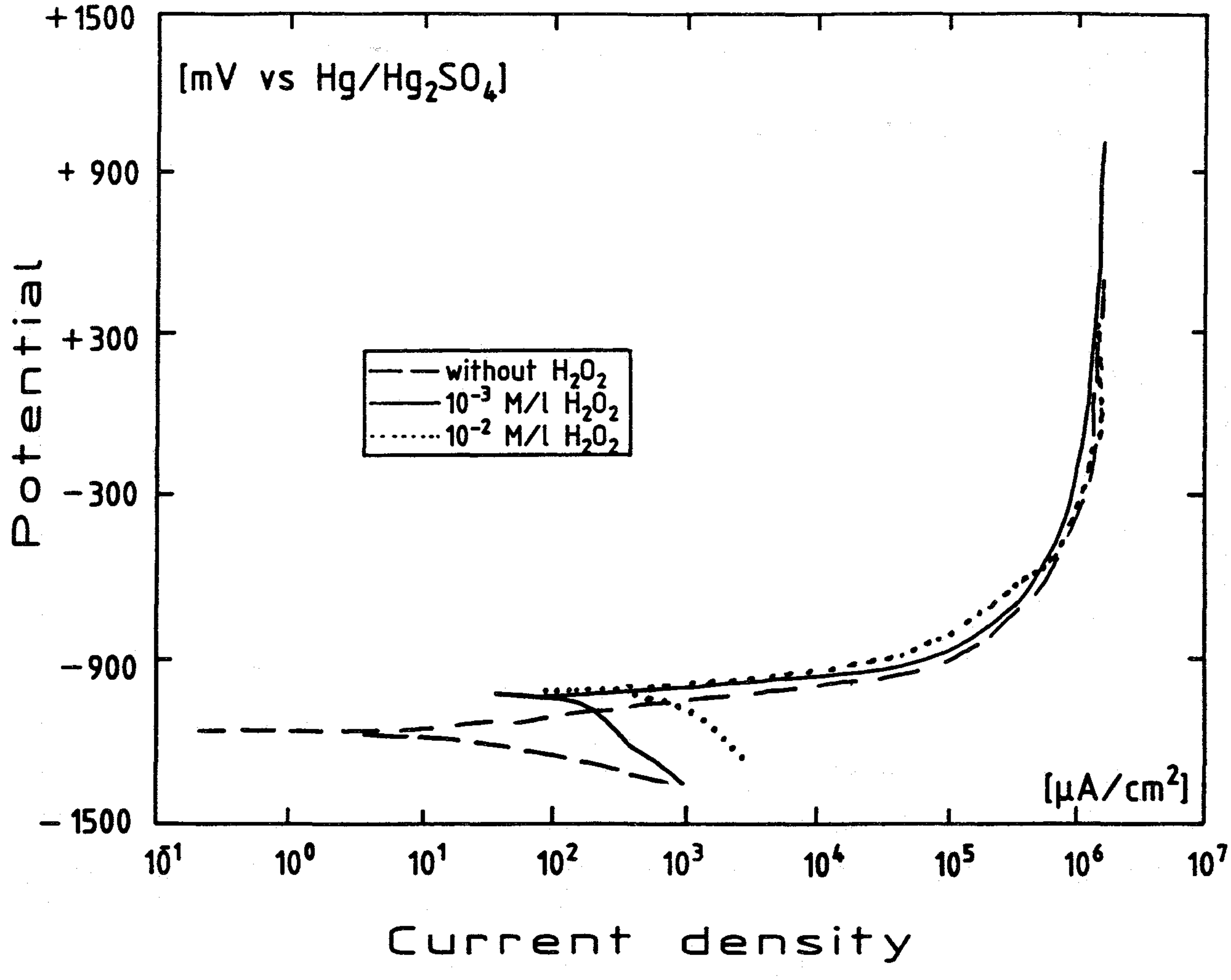

Fig. 2: Potentiodynamic polarization curves of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of H_2O_2 (pH=7).

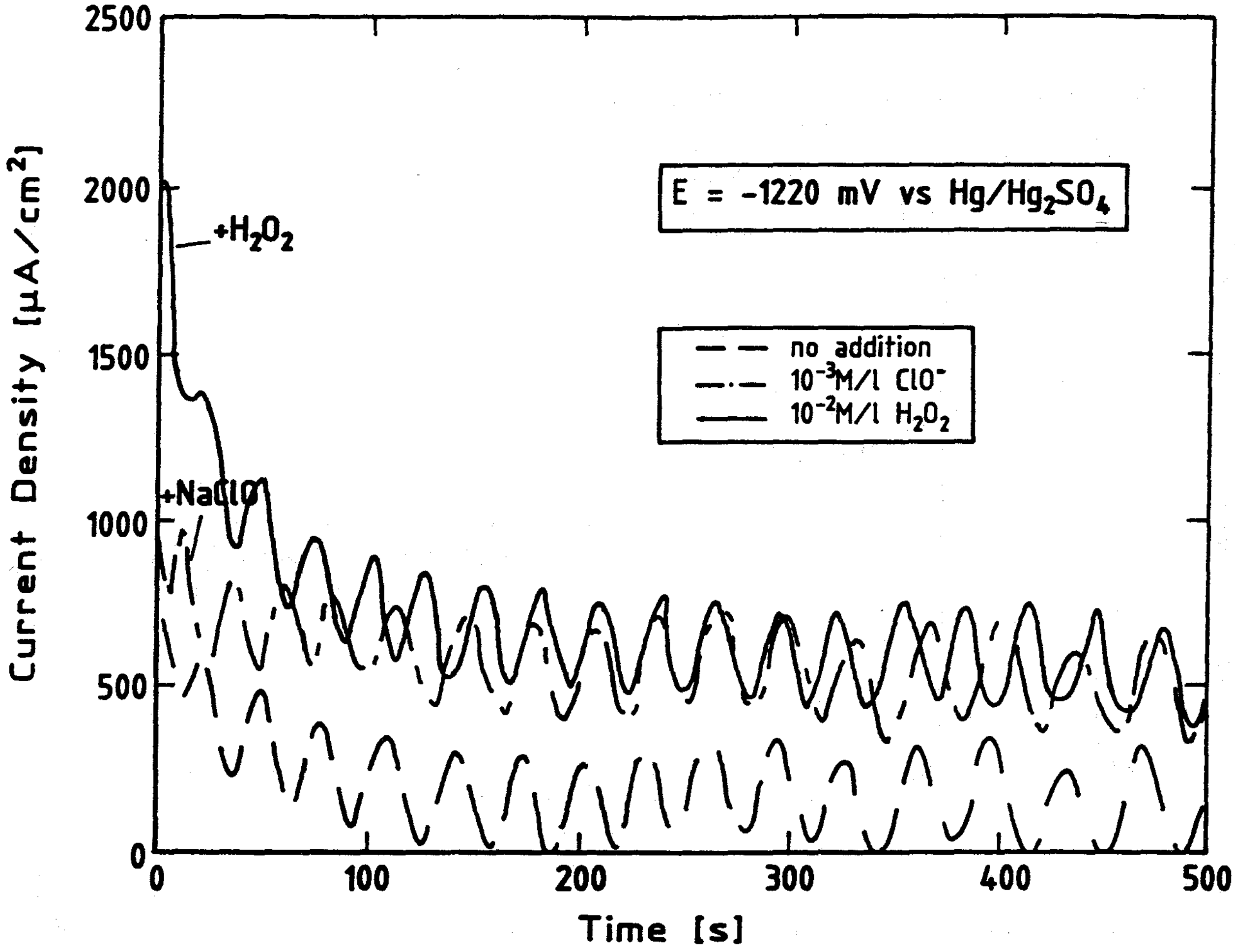

Fig. 3: Potentiostatic polarization curves of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of H_2O_2 and ClO^- (E= -1220 mV vs. R.E.).

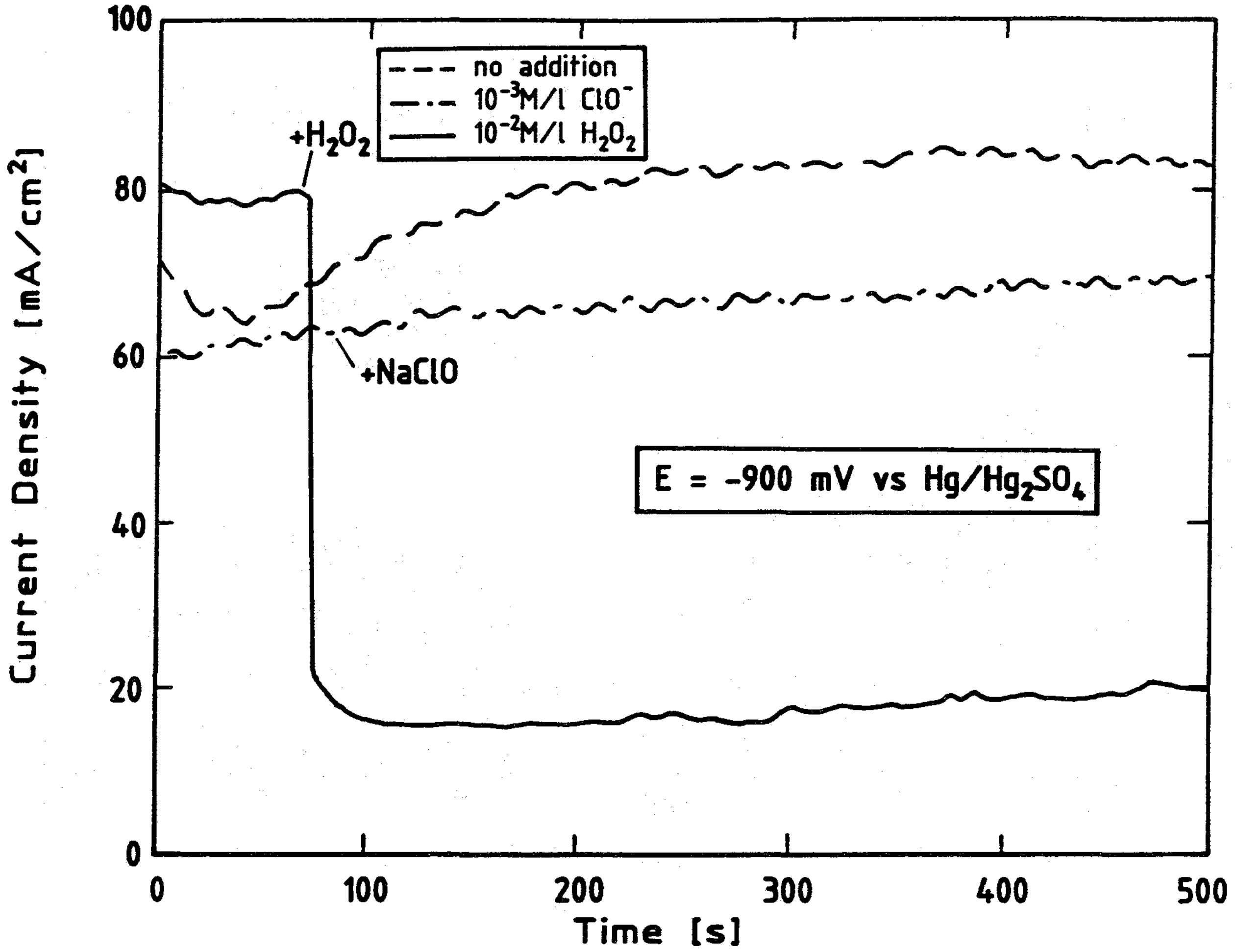

Fig. 4: Potentiostatic polarization curves of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of H_2O_2 and ClO^- (E = -900 mV vs. R.E.).

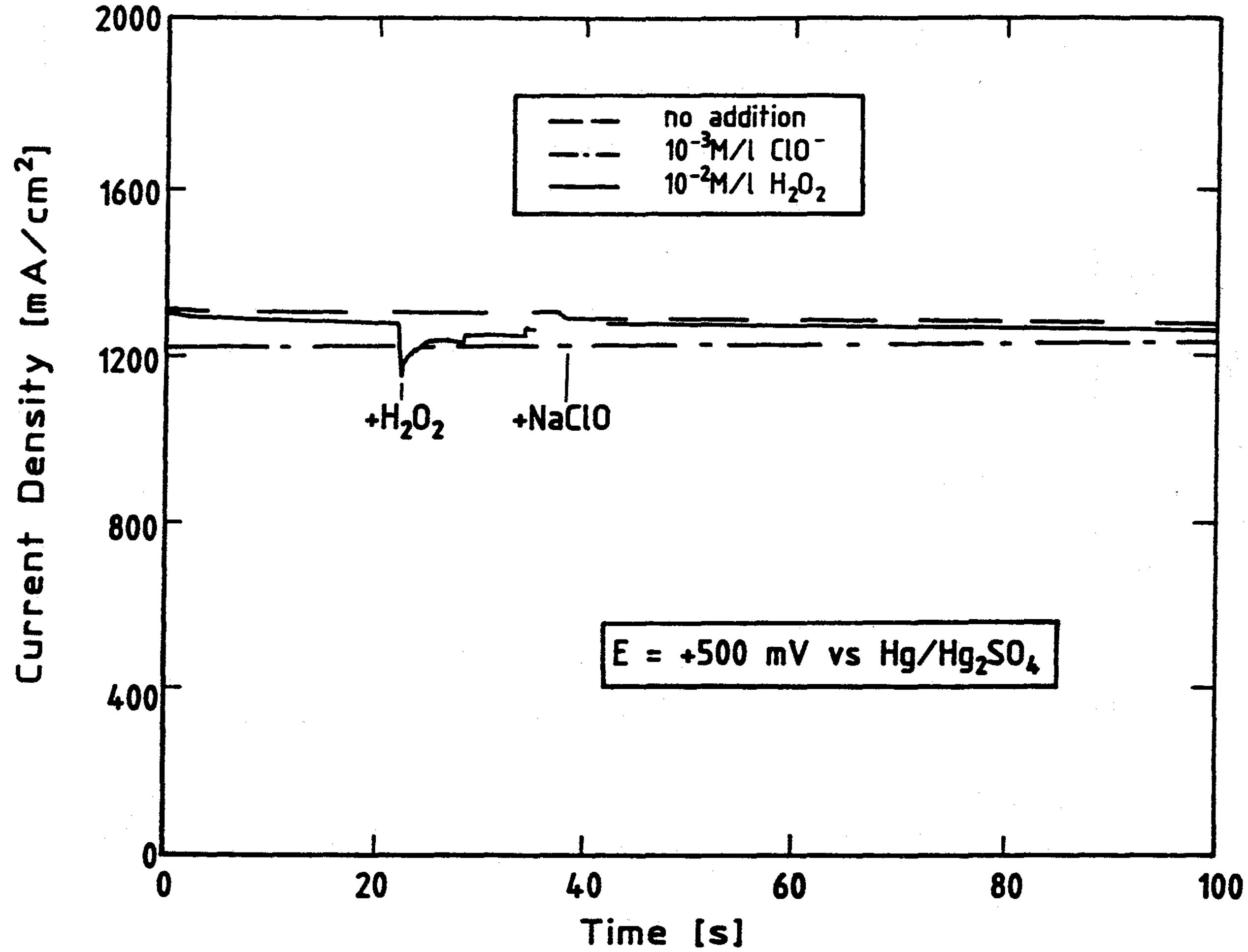

Fig. 5: Potentiostatic polarization curves of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of H_2O_2 and ClO^- (E = +500 mV vs. R.E.).

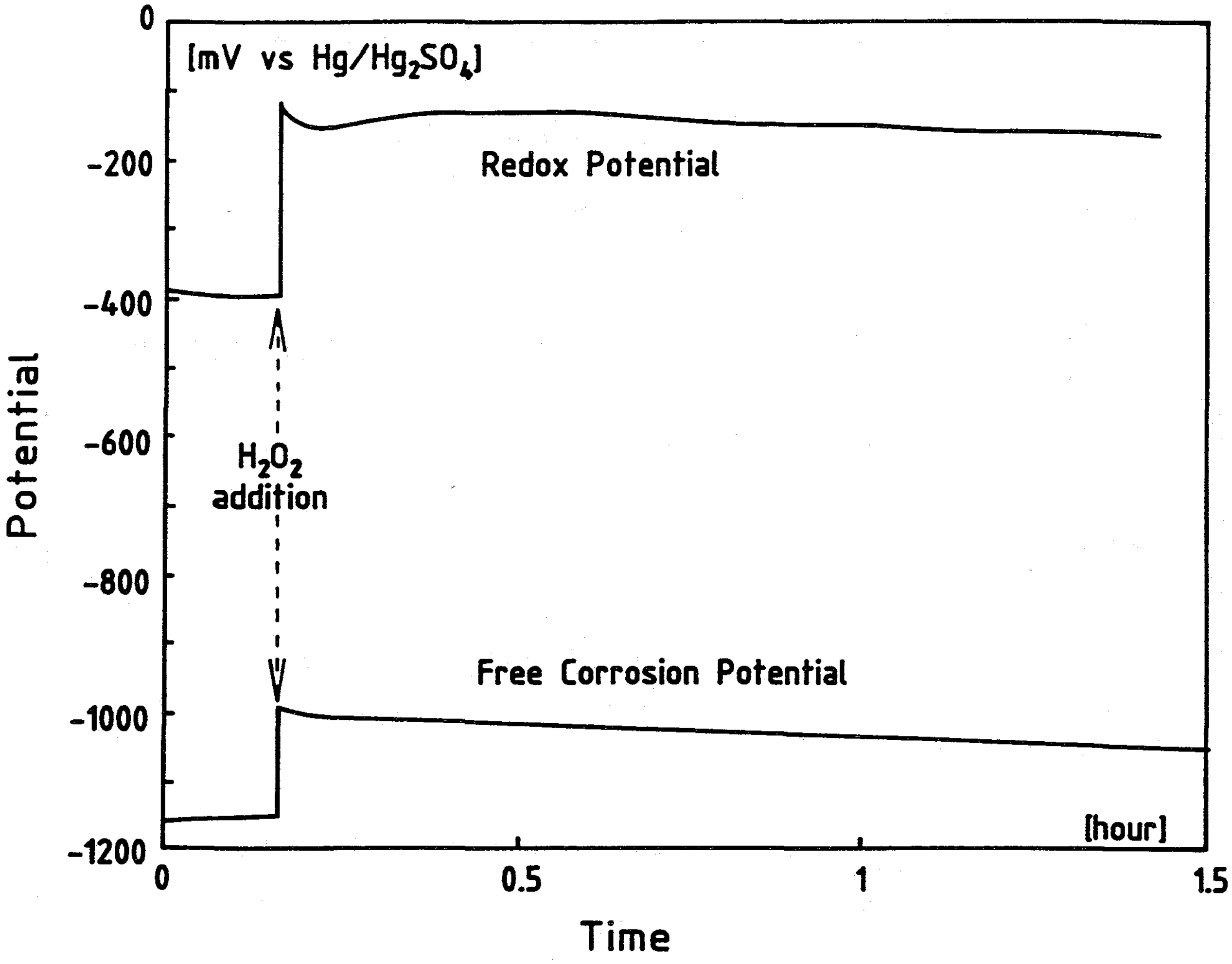

Fig. 6: Redox potential and free corrosion potential of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of H_2O_2 (10^{-2} M/l H_2O_2, pH=7)

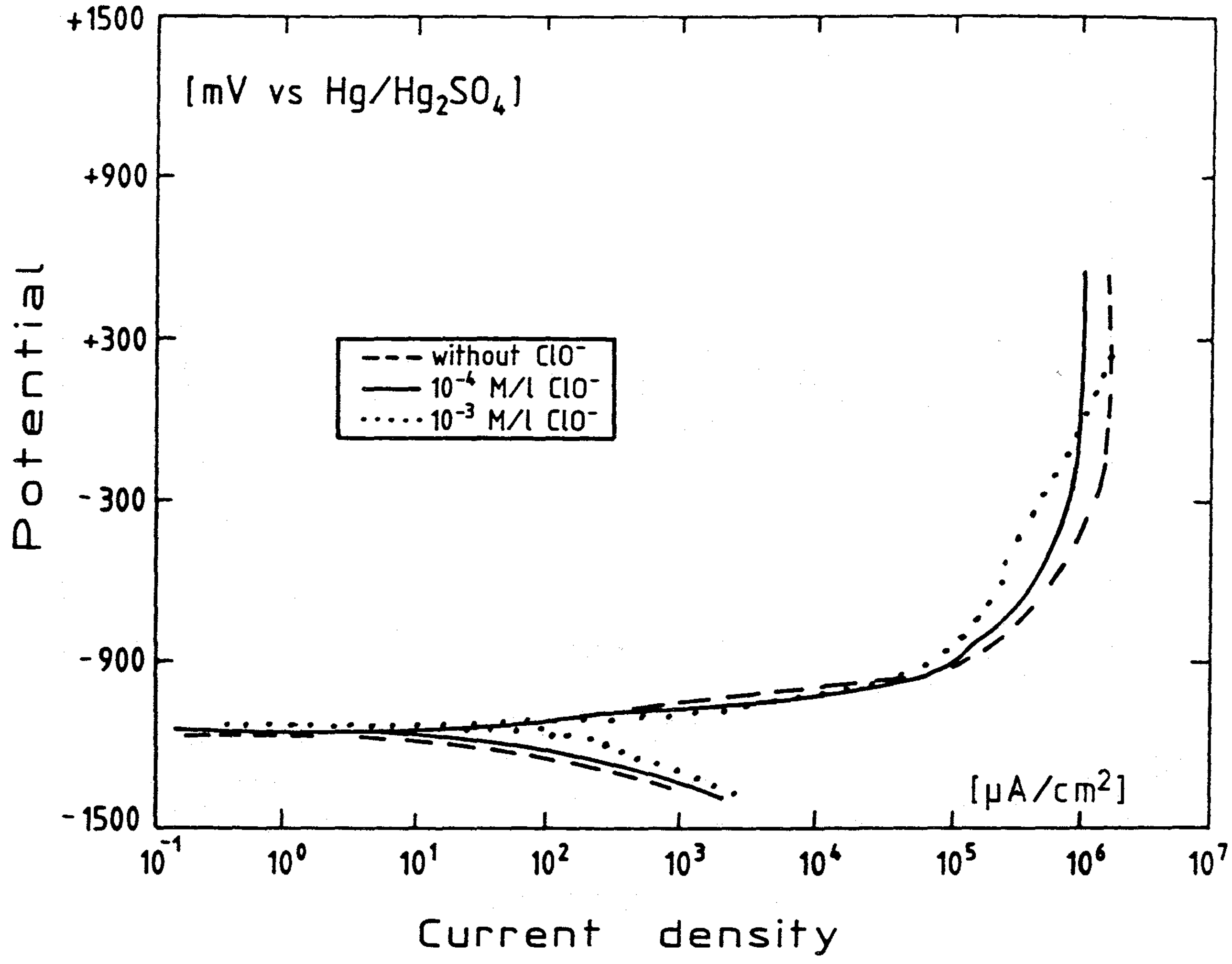

Fig. 7: Potentiodynamic polarization curves of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of ClO^-

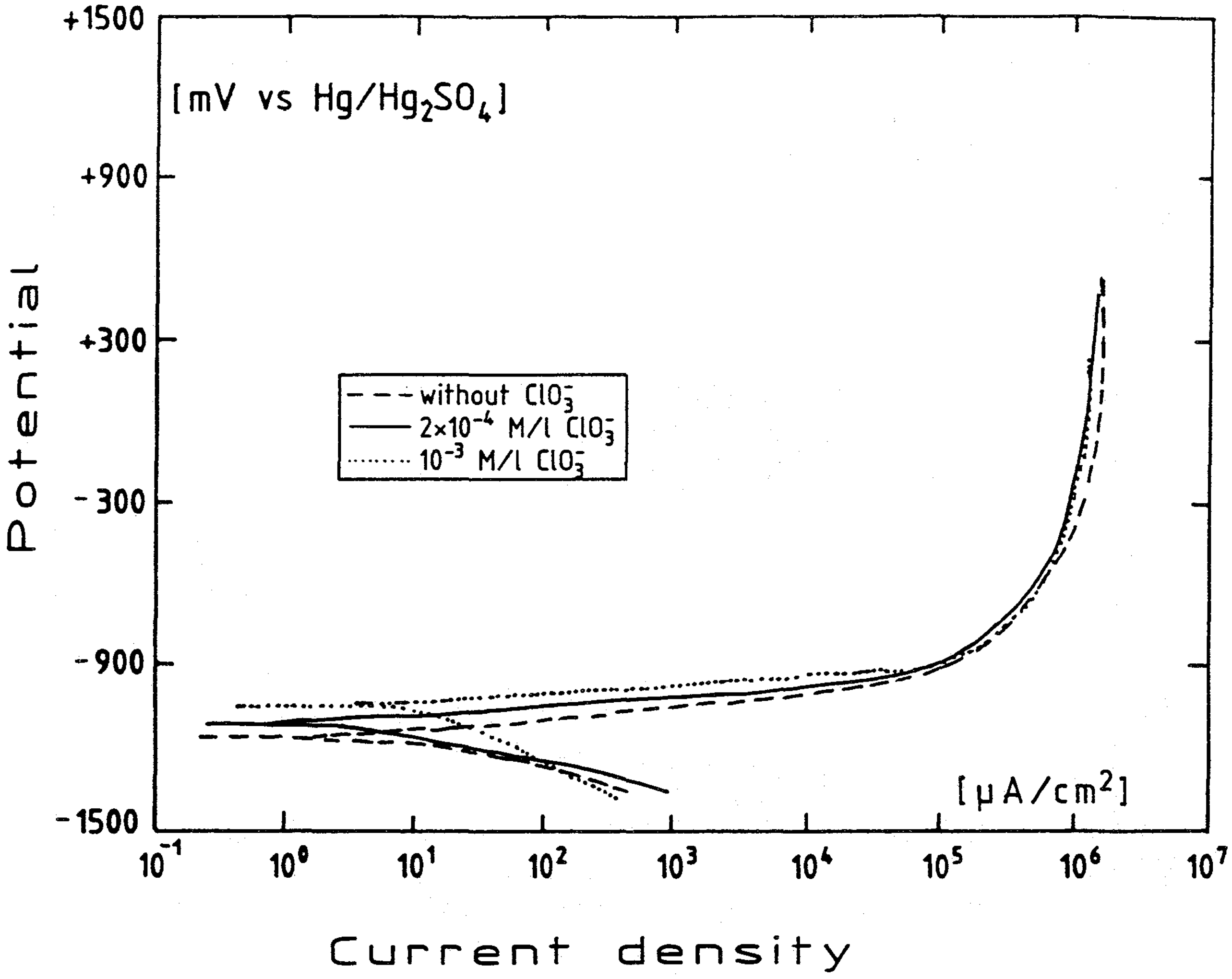

Fig. 8: Potentiodynamic polarization curves of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of ClO_3^-

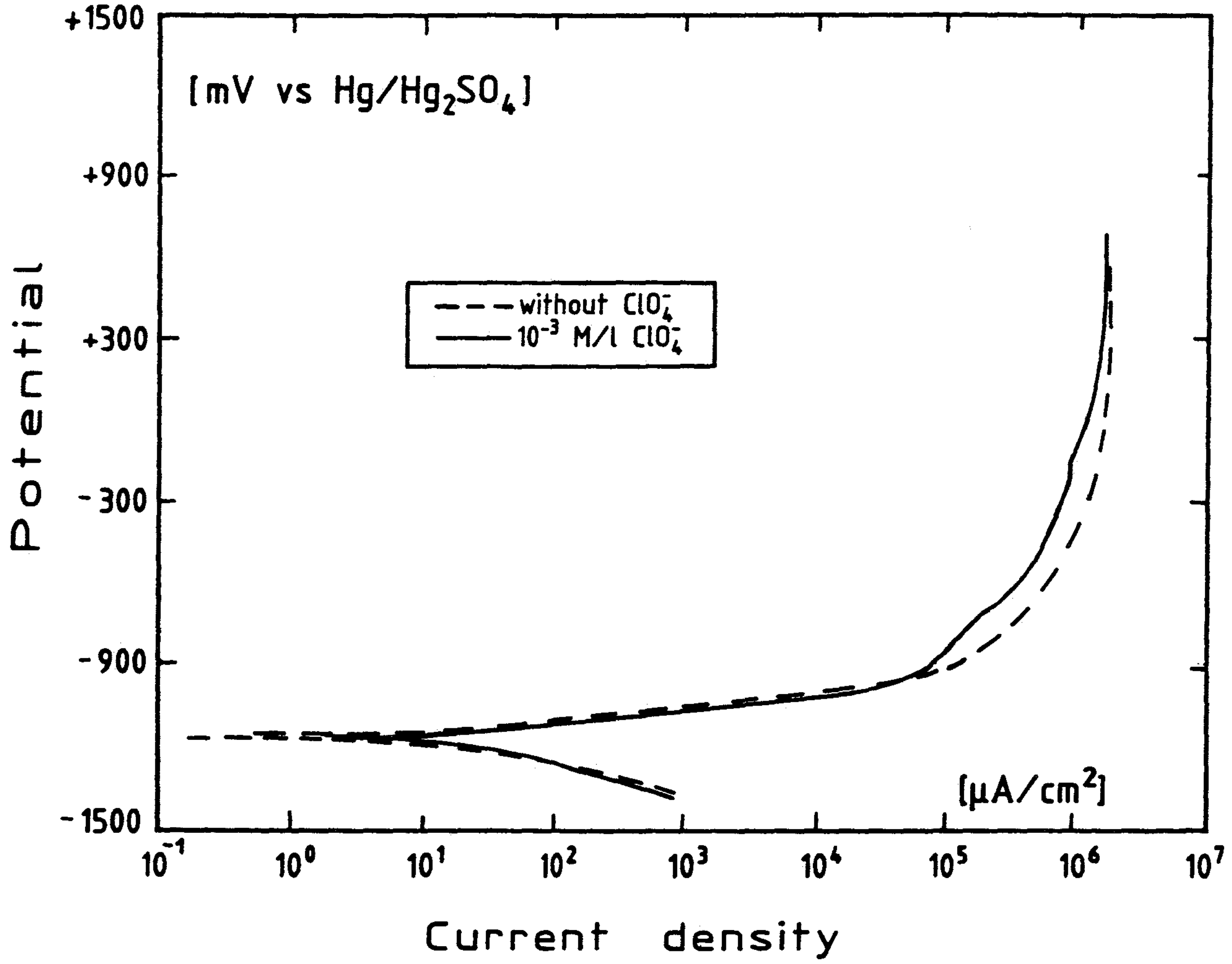

Fig. 9: Potentiodynamic polarization curves of the fine-grained steel TSt E 355 at 90°C in NaCl-rich brine with and without additions of ClO_4^-