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Post examination of copper ER sensors exposed to bentonite

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HIGHLIGHTS

- Copper sensors were used for monitoring corrosion in bentonite during 4.2-y exposure.
- Corrosion rates were estimated by applying three different methods.
- Average corrosion rates for copper in bentonite are several μm/year.

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ABSTRACT

Copper corrosion in saline solutions under oxic conditions is one of concerns for the early periods of disposal of spent nuclear fuel in deep geological repositories. The main aim of the study was to investigate the corrosion behaviour of copper during this oxic period. The corrosion rate of pure copper was measured by means of thin electrical resistance (ER) sensors that were placed in a test package containing an oxic bentonite/saline groundwater environment at room temperature for a period of four years. Additionally, the corrosion rate was monitored by electrochemical impedance spectroscopy (EIS) measurements that were performed on the same ER sensors. By the end of the exposure period the corrosion rate, as estimated by both methods, had dropped to approximately 1.0 μm/year. The corrosion rate was also estimated by the examination of metallographic cross sections. The post examination tests which were used to determine the type and extent of corrosion products included different spectroscopic techniques (XRD and Raman analysis). It was confirmed that the corrosion rate obtained by means of physical (ER) and electrochemical techniques (EIS) was consistent with that estimated from the metallographic cross section analysis. The corrosion products consisted of cuprous oxide and paratacamite, which was very abundant. From the types of attack it can be concluded that the investigated samples of copper in bentonite underwent uneven general corrosion.

1. Introduction

The strategy of countries that are close to licensing the final disposal of high-level radioactive waste (Sweden, Finland, Canada) foresees the enclosure of spent nuclear fuel inside tightly sealed copper canisters embedded in bentonite in bedrock at a depth of 500 m [1–3]. It is planned that such a repository should be constructed with materials that occur naturally in the earth's crust [4]. Besides rock movement, copper corrosion is the biggest threat to these canisters. Initially, a limited amount of air will be left in the repository after emplacement. During the water saturation phase, oxygen will be trapped by the rim of the groundwater-saturated bentonite, which has a low permeability [1,5,6]. After water saturation the chemical environment in the vicinity of the copper surface consists of the bentonite pore water and the saline groundwater from the surrounding rock. The entrapped oxygen is consumed through reactions with minerals in the rock and the bentonite, as well as through copper corrosion and microbial activity. After the oxygen has been consumed, the corrosion is controlled by the supply of dissolved sulphide to the surface of the copper [7,8].

In the case of copper corrosion in bentonite, the corrosion stages can be split into an oxic period, and an anoxic period when the consumption of sulphides and microbial activity may have significant effects. The most important task is therefore to monitor the corrosion rates and to understand the mechanisms which are expected to take place at all stages of the service life of the 5 cm thick copper canister wall.

The evolution of environmental conditions which develop over time in deep geological repositories, and the effect of these conditions on the corrosion behaviour of copper, have been extensively

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examined [1–3,8–16,20,22–30]. Many studies have been oriented towards the corrosion of copper in the oxic period [12–16], whereas others have paid attention to copper corrosion under anoxic conditions [8,22–25], where the effect of sulphides and microbial activity become predominant [5–7,26–32].

The beginnings of the electrochemical study of the behaviour of copper under oxic conditions, when inside of bentonite that is saturated with saline groundwater were presented in papers that were published by Rosborg et al. [12,13]. In these papers a description is given of the electrochemical impedance and potentiodynamic techniques which were used at early exposure times of up to 5 months. Later on, the copper corrosion study was expanded to include trial long-term monitoring of copper in a bentonite/groundwater environment. For this purpose a test package which contained some of the copper from test parcel A2 from the Aspö Hard Rock Laboratory was designed and equipped with copper electrical resistance (ER) sensors for long-term monitoring over a span of a few years [14–16]. The construction of the test parcel and the corrosion rate monitoring equipment have been described in a corresponding SKB report [16]. Further analysis of monitoring techniques by means of ER sensors have been described in [14], whereas estimation of corrosion rates from of electrochemical impedance spectroscopy (EIS) measurements on ER sensors are given in the study by Rosborg [15].

In general, the resistometric technique on electrical resistant probes is used relatively frequently for corrosion monitoring in various fields, particularly in the oil and gas industries [21]. The ER sensors which are used in the field of copper corrosion monitoring are, in fact, a modification of sensors that are used for the monitoring of steel corrosion in concrete [17,19]. So far, however, experience in the field of the monitoring of copper corrosion in bentonite is fairly limited [13–16]. A similar resistometric method was recently developed for measuring the corrosion rate of carbon steel in an anoxic bentonite environment [18].

In previously published papers which were concerned with a study of copper corrosion in an oxic bentonite/saline groundwater environment inside a bentonite test package which was monitored over a 4 year exposure period both electrochemical impedance spectroscopy (EIS) measurements and measurements by means of thin electrical resistance sensors, i.e., ER measurements, were performed, and separately analysed [14,15]. The corrosion rate of pure copper as obtained by means of the ER probes (measurements of thickness reduction), was found to decrease from more than 15 μm/year down to 1 μm/year after more than 4 years of exposure [14]. The EIS results showed good agreement with those obtained by the ER sensors [15]. The corrosion rate of copper in the studied environment was less than 1 μm/year [14,15].

In the present paper the results obtained by ER and EIS measuring techniques were further analysed, together with a post-exposure investigation on the copper ER sensors after 50 months of exposure. The main question was, whether the corrosion damage would be localised, and if so, to what degree. The results of the performed spectroscopic examination of the excavated sensors, and of the metallographic evaluation of the remaining material, are presented and discussed, including the corrosion rate estimated by means of the different methods. An attempt to correlate the corrosion damage and the type of corrosion products occurring was also made.

2. Materials and methods

The corrosion rate of pure copper (99.99% Cu) was measured by means of thin ER sensors, which were placed for 4.2 years (i.e., 1539 days, or approx. 50 months) in a bentonite test package with an oxic bentonite/saline groundwater environment. This period is referred to in the present work referred as a “four year exposure” [14]. A series of ER and EIS measurements were performed at regular intervals during the exposure period. As mentioned above, the early results of the study have already been published [14,15].

The electrical resistance (ER) sensors were made of electronic grade oxygen-free copper (quality No. C10100; 99.99% Cu). The copper sensors were made of 35 μm thick copper foil. Further details about the fabrication and installation of the ER sensors, and of the measurements performed using them, are given in [14]. The width of the electrical leads in the sensor elements was about 0.7 mm. The nominal surface area of each sensor element was 3.5 cm^2, so that the nominal surface area undergoing corrosion amounted to 7.0 cm^2.

2.1. Analysis of the corrosion damage

After more than 4 years of exposure, a detailed examination of the copper ER sensors was performed. The specimens were dismantled as is shown in Fig. 1. After the ER probes had been removed from the bentonite, they were inspected by means of an optical and confocal Carl Zeiss, Axio Vision microscope.

In order to exactly evaluate the corrosion damage on individual sensors, metallographic sections were prepared and analysed. The metallographic samples were grinded and polished with a 1 μm polycrystalline diamond suspension. The cross sections were examined by means of a Carl Zeiss AXIO Imager M2z metallographic microscope, equipped with AXIO VISION 9/2009 software. The areas of the cross sections were measured by image analysis, using MultiPhase software. The general corrosion rate was estimated from the average area of the cross section of the protected elements of the sensor and of the corroded elements. Particular sections of the sensors were also examined by means of the confocal microscope and the results were compared to those obtained by the image analysis performed on the cross sections.

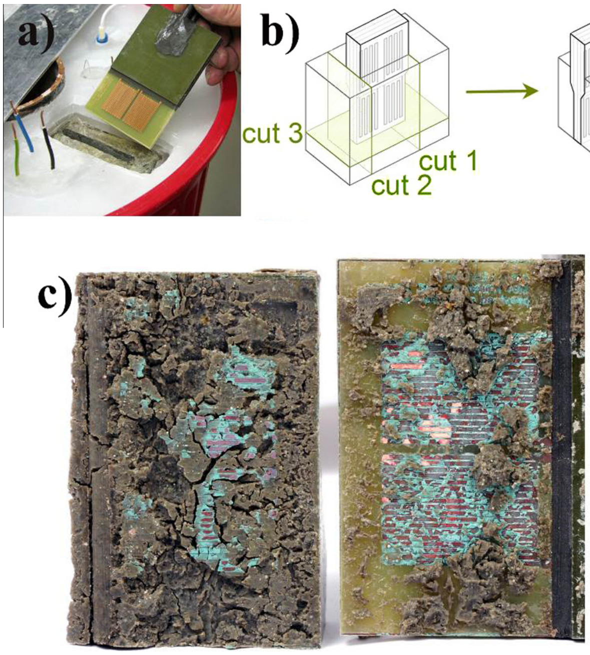

Fig. 1. (a) Sensor placement, (b) de-attachment of the bentonite after the exposure, and (c) images of the corrosion products on sensor ER 3.