Mat. Res. Soc. Symp. Proc. Vol. 807 © 2004 Materials Research Society

Investigations of Resistance Variations in Electrically Heated Canisters for Deep Repository

Baohua Zhu[1], Hans-Peter Hermansson[1], Rolf Sjöblom[2] and Gunnar Ramqvist[3]
[1]Studsvik Nuclear AB, SE-611 82 Nyköping, Sweden
[2]Tekedo AB, Spinnarvägen 10, SE- 611 37 Nyköping, Sweden
[3]Swedish Nuclear Fuel and Waste Management Co, Äspö Hard Rock Laboratory, SE-572 95 Figeholm, Sweden

ABSTRACT

At the end of 2001, measurements indicated that the resistance between the conductors had fallen in SKB's (Svensk Kärnbränslehantering AB) electrically heated test canisters. Electrochemical impedance spectroscopy (EIS) was employed together with chemical analysis of gas compositions and corrosion products to investigate the causes of the resistance decrease inside the canister. The measured system is complicated and the evaluation not straightforward. However, it seems that the plug connecting the external electrical power supply to the heaters in the canister is a critical component and that a moisture film around the electrical contacts of the plug may explain the resistance decrease. It is suggested to continue to monitor the EIS spectra with time to gain more information about the cause of the resistance drop.

INTRODUCTION

According to the Swedish programme, spent nuclear fuel will be disposed of in a repository in crystalline rock. The technical barriers will comprise a bentonite buffer together with a composite canister having an outer vessel of copper for protection against corrosion and an inner one of steel for mechanical integrity.

In the Äspö Hard Rock Laboratory (HRL), full-scale tests on canisters are going on as part of a programme to demonstrate and understand the function of different components of the repository system. Another aim is to show that a high quality can be achieved in design, construction and operation of the repository. The experience gained from over almost twenty years of operation in a prototype repository at HRL will be used in planning the next stage of expansion of the repository.

The prototype repository will provide a demonstration of the integrated function of the repository and provide a full-scale reference for test of predictive models concerning individual components as well as of the complete repository system. The prototype repository project is co-funded by the European Commission and comprises six full sized canisters with internal electrical heaters to simulate the waste. A section with four canisters and bentonite was fully installed during 2001. This section has been back-filled and plugged and is presently in operation and the test is planned to continue during at least 10 and possibly up to 20 years. Two additional canisters will be installed in another section. In another so-called canister retrieval test, one full-scale deposition hole has been installed for the purpose of testing technology for retrieval of canisters after the bentonite buffer has become saturated. This Retrieval Canister, which includes electrical heaters, and its surrounding bentonite buffer were installed in 2000.

A problem with reduced resistance in the electrical system of the heaters in the canisters occurred at the end of 2001. This in itself posed no threat to the experiment. However, continued resistance reduction might occur, and also it is unsatisfactory not to have an explanation to the phenomenon. A full-scale test has therefore been run in KI Maskinverkstad AB in Malmö since April 2002 aiming at clarifying the reasons for the problem of resistance reduction. The essential objective is to give recommendations for a safe operation of the test/prototype canister and what actions should be taken for the remaining canisters to be installed. It must be clearly realised that the resistance reduction problem relates only to the particulars of the experimental arrangements in the prototype repository and that there is no link whatsoever to the issue of long-term safety of the repository itself.

The specific goals of the present study included (a) pinpointing the location(s) of the resistance reductions as well as explaining them; (b) developing recommendations on how to install new canisters; (c) developing recommendations for emplaced canisters; and (d) defining appropriate schemes for the continued operation and monitoring of the canisters. A comprehensive SKB technical report about the above mentioned purpose will be published later.

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out in order to localize the area of the resistance drops and to understand why they occur. Such measurements were performed on the test canister in Malmö as well as on the four prototype canisters in operation and the Retrieval Canister at the HRL. At Studsvik in Nyköping, EIS measurements were also run on canister components, including an electrical heater and one electrical connector from the GISMA Company. The water contents in the MgO of the heater and the acetic acid concentration in polymeric insulating materials (such as the electrical isolation of cables and the silicone of Gisma plugs) have also been analyzed at Studsvik. Gas composition, moisture surface deposits, and corrosion products were also analyzed in the Malmö canister. In this way a better picture of the environmental situation inside the canister was established. By evaluating the EIS and other analytical results, the main source of the resistance variation could be deduced.

EXPERIMENTAL RESULTS

Figure 1 is a schematic description of the measured canister system. For the EIS measurements on the canisters a sine wave potential was superimposed between the wire connected to the kanthal wire in the middle of the heater (inside the MgO-filling) and electrical ground. Also, measurements were performed between the wire which is terminated at the Gismaplug (no heater connected) and ground. The stainless steel of each heater shell is always connected to ground. The EIS-measurements were performed with a Solartron 1287 Electrochemical Interface (Potentiostat) and a Solartron 1255 Frequency Response Analyser, using the software package Zplot. EIS was run in the frequency range 100 kHz to 0.1 Hz. The amplitude was 1 V, which is high normally. However in the high resistance system that we measured this is a reasonable value.

Figure 2 is an example of the EIS results obtained on the test-canister in Malmö. The behavior of these EIS curves was unusual. Comparing the different curves, we found that all curves coincide at low frequencies. At high frequencies, there is a significant difference between the results measured on the wires connected to the heater and that measured on the wire that was not connected to the heater. The difference between different heaters at high frequencies is also significant. Figure 3 is obtained from a laboratory test on a single heater of the type used in the canister. The semi-circle complex plane impedance in the figure represents a parallel RC circuit. The impedance (which is very high) increased when the heater was heated.

In conjunction with the opening of the full-scale test-canister in Malmö, sampling and subsequent analyses were also made of inside gases, surface deposits and corrosion products. These results are presently being evaluated but indicate an inner environment containing oxygen, nitrogen, water and hydrogen. There are also corrosion products on copper, beside copper oxides, that comprise copper acetate and formiate. Corrosion products on iron surfaces essentially comprise magnetite and iron(III)-oxidehydroxides. A sticky surface deposit remains a long time after opening the canister and seems to comprise siloxanes.

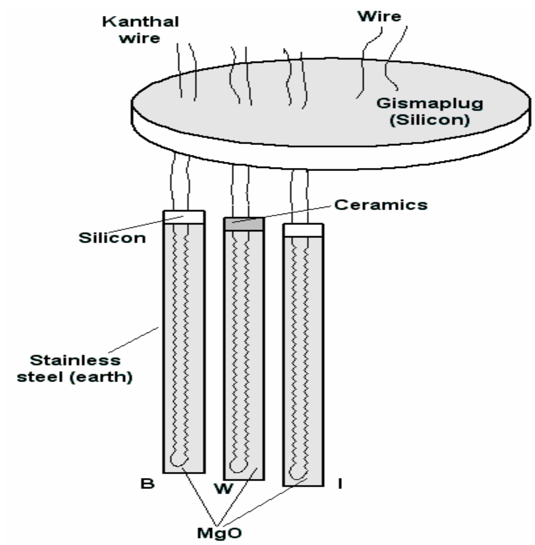

Figure 1. Schematic description of the measured system.

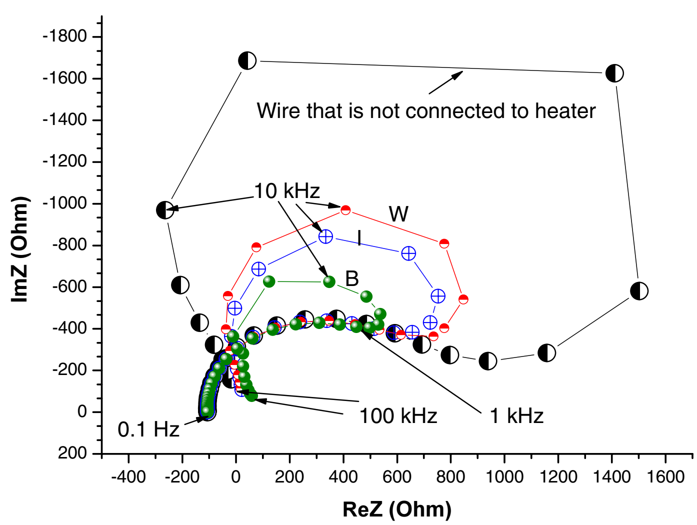

Figure 2. An example of the impedance complex plane plots carried out for the test-canister in Malmö. B stands for the Backer heater, W for Watlow and I for Irca.

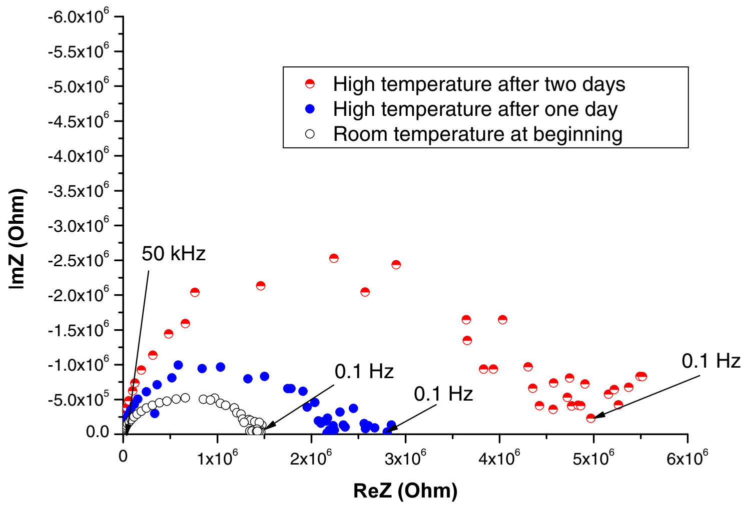

Figure 3. Impedance complex plane plots for the heater filled with MgO as electrical insulation and thermal conduction materials. The measurements were carried out between the kanthal wire in the middle and the stainless steel outside and around the MgO.

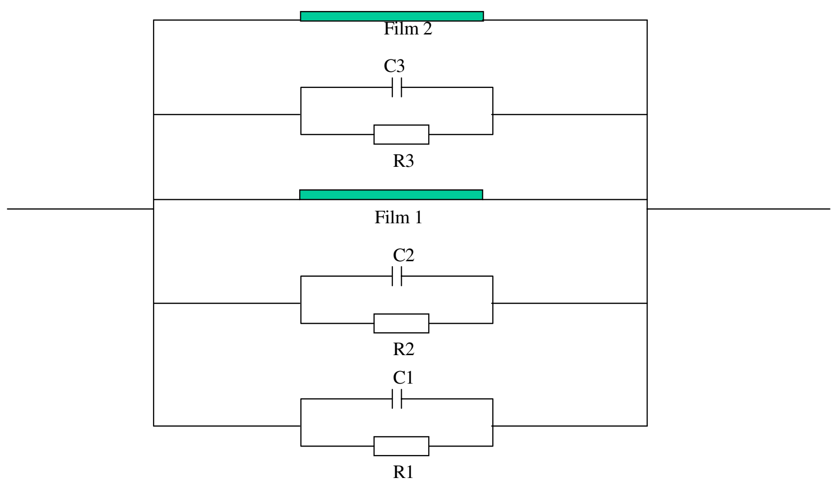

Figure 4. Equivalent circuit for the measured canister system.

DISCUSSION

Since the measured system is complicated, the EIS results could be caused by a lot of reasons. All materials (MgO, silicon, ceramics) that could form a current path are seen in figure 1. They could act as an electrolyte or semiconductor either directly or through a moisture film when exposed in a humid environment with oxygen, HAc, and hydrogen at a high temperature.

The equivalent circuit to describe the measured system in a canister is shown in figure 4. R1 (resistance) and C1 (capacitance) represent the MgO electrolyte in the heater. R2 and C2 describe the polymer material of the contact to the heater. R3 and C3 represent the gismaplug. The impedance for these components are very high at both room temperature and at 100°C, as in the example shown in figure 3. The resistance of the polymer or ceramic material is even higher. The question became therefore the following: what made a current path in the system? One most probable reason is that there were some film formed on the gismaplug or on the contact surface in a humid environment at high temperature. The resistance of these surface deposits may be very low because of the moisture containing oxygen, hydrogen and HAc etc. As indicated in figure 3, the impedance caused by the films are in parallel circuit with the impedance caused by Gismaplug, MgO and the contact material. The total resistance is determined by:

$$\frac{1}{R_{tot}} = \frac{1}{R1} + \frac{1}{R2} + \frac{1}{R3} + \frac{1}{R_{film1}} + \frac{1}{R_{film2}} \quad (1)$$

Equation (1) shows that the lowest resistance of the films determines the total resistance since the resistances of other components are very high. The total capacitance of the system is increased according to equation:

$$C_{tot} = C1 + C2 + C3 + C_{film1} + C_{film2} \quad (2)$$

As indicated in figure 2, semi-circles are obtained at high frequencies, which can be explained well by the equivalent circuit in figure 4. However, the impedance behavior has been changed at lower frequencies, and a negative real part of the impedance was obtained. Similar results are reported in literature, explaining negative impedance as a result of passivation of the electrode. A decreased current is then obtained and negative impedance is observed [(1)]. Our system is complicated and the interaction between the Gismaplug and the surface deposit is not clear. However, it seems that the main source to the resistance variation was the Gisma plug on which a surface film might be formed. Another source to the resistance drop seems to come from the contacts on the top of the heater, where a film could also be formed in the moist environment with oxygen, acetic acid, hydrogen etc at a high temperature.

Water was present in the magnesium oxide of the heaters when they were installed. The total amount of this type of water was probably a few to several tens of grams in each canister. In addition, water might have been present in crevices between the rectangular steel “pipes” and the cast steel and between copper and cast steel. The water in the canister can react with iron in which case iron oxide-hydroxides are formed. The amount of hydrogen detected in the atmosphere corresponds to a consumption of about 40 grams of water. The oxygen content of the atmosphere (initially air, about one cubic meter) was essentially halved and it was estimated that around 200 grams of oxygen reacted with iron to form oxide-hydroxides.

The largest amount of organic material – around 1,8 kg - was introduced in the form of cable insulation between the Gisma plugs and the heaters. They consisted mainly of polydimethylesiloxane (silicone) rubber and glass fibre textile. Organic acids of low molecular weight were generated by decomposition of organic matter and to some extent also by a curing reaction in the plugs of the heaters. The total amount was estimated to be at least one or a few grams. Part of these acids formed salts with the metals present.

The silicone rubber contains low molecular components from its manufacturing. At elevated temperatures and over time these will diffuse through the rubber, evaporate and condense at cold spots. Moreover, any water present will hydrolyse the polymer to low molecular species which diffuse, evaporate and condense in the same way.

Since the Gisma plugs were located at the cold spot, condensation will take place there. Silicone oil is well-known for its low surface tension and its excellent creep properties. This means that the oil together with the associated water and organic acids will creep on the surfaces and into the area where the contacts are and cause the development of observed stray resistances.

Pure silicon oil as well as pure water are poor electrical conductors. When acids and salts are dissolved they dissociate and conductivity increases. Moreover, the magnesium oxide transferring the heat from the resistance wire in the heaters to the surrounding pipe also has significant semiconductor properties. These are closely associated with the presence and content of water. In this regard it is important to consider that water moves in two ways, radially and axially. All of the above discussed effects could contribute to moisture film formation and affect the measured impedance spectroscopy. The main reason for the observed resistance decrease is therefore believed to be the moisture film formation on the cold spot Gisma plugs.

CONCLUSIONS

Electrochemical impedance spectroscopy is a useful in situ method to measure and study the problem of the resistance variations inside a closed canister system. Since the amplitude used in EIS measurements is quite small the disturbance to the canister system should be insignificant. Furthermore, other analytical methods have also been used to a large extent to support EIS in order to enable interpretation of the rather complex spectra.

EIS measurements showed that the measured system is complicated from electrochemical point of view and the evaluation is not straightforward. However, it seems that a moisture film around the electrical contacts of the Gisma plug may explain the observed resistance decrease. It is suggested to follow the change of the EIS with time to gain more information to finally determine the main source of the resistance drop. Such measurements would also be a potential diagnostic tool on canisters in operation, as well as a tool to monitor the effects of mitigative measures as a function of time.

The over-all results of the measurements agree with the hypothesis that a humid environment containing oxygen, hydrogen and perhaps organic acids was formed inside the canister and formed a conducting film on critical surfaces, which contributed to the resistance drop. However, there are also variations in the EIS data between heaters from different suppliers, which may imply that several mechanisms are important.

ACKNOWLEDGMENTS

The Swedish Nuclear Fuel and Waste Management Company is gratefully acknowledged for financial support and valuable discussions.

The authors thank Per Borgström, KI Maskinverkstad AB, Ulf Flinth, Nöjdhs Marin Installation AB and Thomas Karlsson for their help with the field experiments.

Thanks are also due to Birgitta Strömberg, TPS Termiska Processer AB; Bo Arnberg and Lars Ljungqvist, OKG AB, Kristofer Warman, Alcontrol AB, and Jöns Hilborn, Institute of Materials Chemistry, University of Uppsala, for their collaboration.

Anders Molander, Studsvik Nuclear AB, is acknowledged for his valuable discussions in evaluating the experimental results.

REFERENCES

1. I, Epelboin, C. Gabrielli, M. Keddam and H. Takenouti, *The Study of the Passivation Process by the Electrode Impedance Analysis (Chapter 3)*, Comprehensive Treatise of Electrochemistry, Vol. 4, Plenum Press, New York, 1981