CORROSION PROPERTIES OF HLW AND SPENT FUEL OVERPACKS IN HIGHLY ALKALINE ENVIRONMENTS

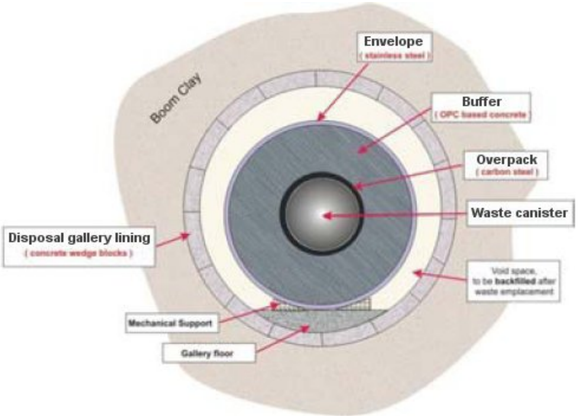
Background

Throughout the world, deep geological disposal in stable rocks with low groundwater flow is considered for the long-term management of long-lived radioactive waste (vitrified high-level waste – VHLW – and spent fuel – SF).

Since a few years, the Supercontainer design (SC) is the Belgian reference design for the final disposal of VHLW and SF. This concept is schematically illustrated in the picture on the right.

The SC consists of a 30 mm thick carbon steel overpack, containing two VHLW canisters or four SF assemblies, which is surrounded by a concrete buffer, which in turn is entirely encased in a 6 mm thick stainless steel envelope.

The rationale behind the SC concept is the Contained Environment Concept (CEC). The CEC aims at establishing and preserving a favourable chemical environment around the carbon steel overpack, so that it will be exposed to essentially unchanged, benign conditions for at least the duration of the thermal phase.



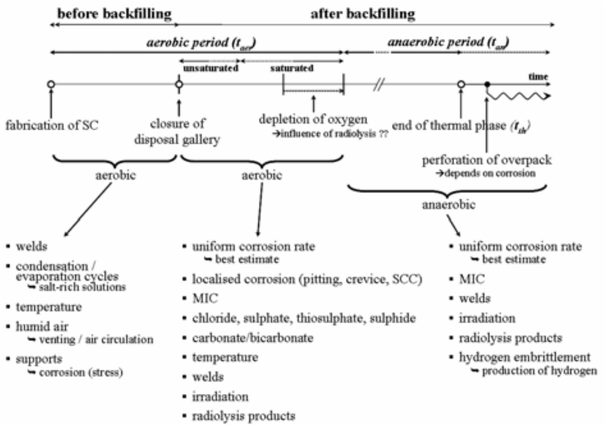
The main advantage of the SC design, with respect to corrosion, is that under the predicted conditions (*i.e.* highly alkaline concrete buffer), the carbon steel overpack is expected to undergo uniform corrosion (passive dissolution).

Objectives

The key objective of this study is to demonstrate that the carbon steel overpack will be able to ensure complete containment of the radioactivity at least during the thermal phase, *i.e.* the period during which the temperature of the host rock is expected to lie above the range of temperatures within which nominal radionuclide migration properties can be relied upon.

Principal results

Our current experimental programme is mainly aimed at investigating the interactions between carbon steel and concrete. An integrated R&D methodology has been developed to demonstrate and to defend that the integrity of the carbon steel overpack can be ensured during at least the thermal phase. This integrated approach consists of three steps: lifetime prediction, validation, and confidence building.



The lifetime of the overpack is predicted on the basis of the corrosion evolutionary path (CEP), illustrated in the picture on the left. The CEP describes the evolution of the environmental conditions the overpack is exposed to during the different phases of, and also prior to, the disposal period.

The environmental conditions surrounding the SC are likely to change with time:

- oxidising conditions will gradually change to reducing conditions following repository closure;
- temperature will decrease as heat production of the radioactive waste decreases, and also
- the geochemistry of the concrete buffer surrounding the carbon steel overpack will gradually be modified as Boom Clay pore water penetrates the SC.

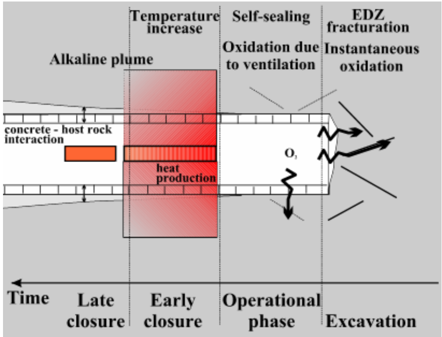
The approach to predict the lifetime consists in dividing the evolutionary path in different phases (aerobic, anaerobic) and determining the 'best estimate' uniform corrosion rate for each of these phases. Lifetime predictions are then estimated by integrating these corrosion rates over the duration of the different phases. The prediction of the overpack lifetime as described above is based on the assumption that corrosion is uniform over the entire overpack surface. In the high pH environment of the SC, the carbon steel overpack is covered with a protective passive film. However, if the protective passive film is destroyed locally, localised corrosion (pitting, crevice corrosion) and stress corrosion cracking (SCC) may occur. Furthermore, our integrated approach aims at finding a sound argumentation that each corrosion mechanism, other than uniform corrosion, cannot take place under the circumstances described in the corrosion evolutionary path. This is called the 'exclusion principle'.

In a second step, the data of the corrosion evolutionary path, the suitability of the 'exclusion principle', and the newly developed interface models should be validated through a limited set of well-defined tests (*e.g.* an *in situ* experiment).

An active publication policy (*a.o.* publications in peer reviewed journals), together with a periodical review of the programme by a panel of experts in the field, forms part of a third step. This should help to enhance the confidence in the predicted lifetime of the SC.

Currently, only modelling studies have been performed, such as geochemical modelling of the evolution of the near-field environment surrounding a disposal gallery and of the concrete buffer surrounding the carbon steel overpack.

The evolution of the near-field environment surrounding a disposal gallery is schematically illustrated, from right to left, in the graph on the right.



Excavation of the gallery creates fractures up to about 1 m in the surrounding host rock. Oxygen will come in contact with the initially anoxic Boom Clay and will interact mainly with pyrite and organic matter, two important compounds of Boom Clay. Along the fractures, oxygen can easily intrude up to a depth of about 1 m. During the operational phase, a stiff concrete liner needs to be used to keep the plastic clay in place and to minimise traction. Because of the high plasticity of the clay, the fractures will seal fast. Water is continuously drained towards the gallery, limiting the oxygen intrusion into the host formation. Experimental observations and modelling results, neglecting the reactivity of the oxygen with remaining pyrite and organic matter, reveal that the in-diffusion of oxygen will not exceed about 2 m, even after 20 years of ventilation. Consequently, the extent of the oxidised zone remains limited to the first meters, while the degree of oxidation in this layer will increase with time. During the early closure phase, the heat-emitting waste will cause a temperature increase, lasting for several hundreds (VHLW) to thousands (SF) of years. Meanwhile, reactions between the high pH concrete and the slightly alkaline surrounding host rock will start to occur, resulting in mineralogical and geochemical changes (alkaline plume). As this is a very slow process, these reactions will mainly continue throughout the late closure phase. The extent of this alkaline plume within the Boom Clay is limited to about 2.5 m after 100,000 years.

Calculations on the evolution of pH and the concentration of aggressive anionic species from the Boom Clay at the carbon steel overpack have also been carried out. The initial pH of the concrete pore fluid is about 13.5, controlled by the dissolved alkalis (K^+ and Na^+), and decreases to 12.5, regulated by portlandite solubility, in about 1,000 years. The pH 12.5 is predicted to maintain for at least 80,000 years, after which it will slowly start to drop. The increase of the temperature (~80°C) during the thermal phase will decrease the pH to about 12, owing to the effect of temperature on hydrolysis properties of the system.

Future work

An experimental programme to study the effect of gamma radiation on the anaerobic corrosion rate of carbon steel in cementitious media, by means of measuring the hydrogen gas generation rate, was developed in 2007. This programme will be carried out in 2008 in co-operation with Serco Assurance (UK).

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Main reference

Bruno Kursten and Frank Druyts, "Methodology to make a robust estimation of the carbon steel overpack lifetime with respect to the Supercontainer design", THIRD INTERNATIONAL WORKSHOP ON LONG-TERM PREDICTION OF CORROSION DAMAGE IN NUCLEAR WASTE SYSTEMS, May 14-18, 2007, Pennsylvania State University State College, Pennsylvania, USA.

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