

9 - CORROSION ASPECTS OF STEEL RADIOACTIVE WASTE CONTAINERS IN CEMENTITIOUS MATERIALS

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Introduction

In order to safely manage and dispose of radioactive waste it is necessary to package it in suitable containers, whether it be low level waste (LLW), intermediate level waste (ILW, large volumes, intermediate levels of radioactivity) or high level waste (HLW, small volumes of very high levels of radioactivity). The waste container forms an integral part of the waste disposal system, which normally consists of a series of engineered barriers to isolate the waste from the biosphere. Disposal concepts differ between nations, but two of the generic categories of materials that are often considered for waste containers are carbon steel and stainless steel. Corrosion is the main form of degradation that needs to be considered in assessing the safety of the waste container and the overall disposal system. Steels are often used in conjunction with cementitious materials, either in the form of grouts, which are used to encapsulate the waste materials inside the containers, or as a cementitious buffer or backfill material to surround the waste container in a geological disposal facility (GDF). For example, in the case of the GDF concept in the U.K., ILW is typically encapsulated in stainless steel containers before entering a period of storage, either above-ground in a surface store, or underground in a GDF, before finally being surrounded by a cement-based backfill material. In the case of the Belgian Supercontainer concept, HLW will be first sealed into a stainless steel container, then placed in a carbon steel overpack and surrounded by a cement-based buffer inside an outer stainless steel envelope. This complete assembly would then be emplaced in a GDF. These examples illustrate the need to understand the corrosion behaviour of both stainless steel and carbon steel in contact with cementitious materials, under conditions that are representative of the waste disposal process. The aim of this talk is to give an overview of the important corrosion processes affecting carbon steel and stainless steel in the types of cementitious material that will be encountered during waste disposal. The review makes use of experience gained by the author while working on research programmes in support of the U.K. programme on ILW disposal and the Belgian Supercontainer concept.

Nature of the cementitious environment

From a corrosion perspective the most important component of a cementitious material is the porewater that is trapped in the porespace, since any corrosion reactions will require a source of water. Cements are fine mineral powders that form a paste when they are mixed with water and harden as the hydration process occurs. The main components of ordinary Portland cement (OPC) are tri-calcium and di-calcium silicates, calcium aluminate and ferroaluminate; they are present in various ratios depending on the source of the cement. After hydration, which is an exothermic process, the main components of the solid structure are hydrated calcium sulphoaluminates and calcium silicate hydrates, which form a rigid gel (C-S-H gel). Solid Ca(OH)_2 , Portlandite, is also produced in the hydration reaction at a concentration of about 25 wt%. Although it does not contribute to the strength of the cement, the Ca(OH)_2 , together with the NaOH and KOH that are present in small amounts, have an important effect on the corrosion behaviour of metals embedded in the cement, because they control the composition of water

present in the capillary pores of the cement structure. In particular they can increase the pH of the water to values as high as 13.6. The pores have dimensions of about 10 to 50 nm if the cement paste is well hydrated, but can reach 3-5 μm if there is a high water: cement ratio or if the cement is not well hydrated. The pore sizes and the degree of interconnectivity affect the transport processes into the concrete and hence control the transport of aggressive species from the external environment to the surface of the embedded metal. Various pozzolanic materials (i.e. similar to the naturally occurring mineral 'Pozzolana'), such as pulverised fly ash (PFA), can be added to cement to produce a material with the required mechanical and physical properties. Blast furnace slag (BFS) also reacts with $\text{Ca}(\text{OH})_2$ and is used for producing cements with a fine porosity. In the U.K. a range of grout compositions have been investigated as possible encapsulants for waste in stainless steel waste containers.

In terms of corrosion, the transport properties of the cement are important. Concrete can be penetrated through its pores by gases, such as oxygen and carbon dioxide, and water containing dissolved ions, such as chloride. Transport can occur through a number of processes, such as capillary suction, permeation (due to pressure gradients), diffusion (due to concentration gradients) and electro-migration. Hence the kinetics of transport processes in concrete are determined by the environmental conditions external to the cement. The amount of water present in the cement will depend on the supply of water external to the cement (e.g. whether the concrete is fully immersed in water) or the relative humidity of the atmosphere, for example during storage of radioactive waste.

The composition of the porewater is an important factor determining the corrosion behaviour of metals exposed to cement. Porewater expression experiments show that the water is predominantly a mixture of NaOH and KOH, with a highly alkaline pH (typically in the range 12.5 to 13.5). If carbonation occurs (i.e. reaction with CO_2 in the atmosphere) this pH can fall to values as low as 9, which increases the corrosion susceptibility of steels. The corrosion resistance of both carbon steel and stainless steel is strongly affected by the pH. In addition to K^+ , Na^+ and OH^- ions, there will also be trace amounts of a range of other ions, including Al^{3+} , NH_4^+ , and sulphur species such as SO_4^{2-} , SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$, particularly in BFS-based cements. Chloride ions may penetrate from the external surfaces of the cement, or from the waste material itself, and this is an important factor determining the corrosion resistance of both carbon steel and stainless steel containers during waste disposal.

Overview of corrosion of steel in cementitious materials

In the highly alkaline conditions that exist in cement, both carbon steel and stainless steel are protected against corrosion by the presence of a thin 'passive' layer. In the case of carbon steel the film is composed of a mixture of Fe(II) and Fe(III) oxy-hydroxides, whereas stainless steel is protected by a more corrosion-resistant film which is rich in chromium oxy-hydroxides. However, both types of passive film can be penetrated by reaction with aggressive species, such as chloride or thiosulphate ions. Possible sources of chloride ions during waste disposal include chloride in the waste itself, or chloride in the groundwater surrounding a GDF. In essence, the corrosion process involves two balancing electrochemical reactions. The first reaction is the electrochemical oxidation of the metal to release electrons (viz. $\text{M} \rightarrow \text{M}^{n+} + n\text{e}^-$), which is balanced on the surface of the corroding metal by the reduction of either oxygen, with the consumption of electrons ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$) in oxygenated conditions, or water in anoxic conditions ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$). Carbon steel is much more susceptible to chloride-induced corrosion than stainless steel because the passive film is more easily broken down than the film on stainless steel. For this reason, carbon steel tends to suffer from a more general or 'uniform' type of corrosion attack and stainless steel is more susceptible to highly localised corrosion effects. The latter are frequently categorised as pitting corrosion, crevice corrosion and stress corrosion cracking. In addition there are a number of other types of corrosion that need to be considered in assessing the applicability of carbon steel and stainless steel for use as waste container materials. These include galvanic corrosion, microbial corrosion and radiation-induced corrosion. Each type of corrosion has a potential effect on the safety aspects systems;

for example wall thinning or pitting could lead to a loss of structural strength or ultimately to loss of containment for radionuclides; similarly stress corrosion cracking could lead to a failure of lifting features and prevent safe handling practices, so it is important to assess the potential for each type of corrosion during the waste disposal process, on a case by case basis. In the talk the research that has been conducted in relation to these various types of corrosion in the context of radioactive waste disposal will be briefly reviewed, for both carbon steel and stainless steel. The environmental parameters that affect the corrosion behaviour are mainly temperature, pH of the porewater (which may vary with time due to carbonation or long-term changes in the cement chemistry), oxygen concentration, water availability and the concentration of ionic species, particularly aggressive ones such as chloride and thiosulphate. In addition corrosion susceptibility is affected by the metallurgical state and the surface condition of the metal. Much of the work that will be described in the oral presentation was carried out as part of the U.K. and Belgian research programmes.

Specific corrosion processes affecting waste containers in cementitious environments

In the absence of aggressive species such as chloride the general corrosion rate of carbon steel in cementitious environments is very low, under both oxygenated and anoxic conditions. This accounts for the durability of reinforcement bars in concrete structures. Thus the internal corrosion rates for carbon steel containers of cement-encapsulated waste during storage are expected to be very low ($<1 \mu\text{m yr}^{-1}$). In anoxic conditions, such as will be experienced post-closure in a GDF, iron corrodes anaerobically with the concomitant release of hydrogen. There has been considerable research effort expended to measure the rate of hydrogen generation by anaerobic corrosion in alkaline conditions, because the production of hydrogen may have a deleterious effect on the performance of a GDF. The carbon steel corrosion rates are low enough not to pose a long-term threat to the integrity of the containers, but the hydrogen produced could be of greater importance. Similarly, the general corrosion rate of stainless steel in cement is extremely low and in long-term tests it has not been possible to detect the generation of any hydrogen through the anaerobic corrosion of stainless steel (Smart 2004a, 2009a). The U.K. research programme took account of such factors as the surface condition, temperature, pH and chloride concentration and a similar programme of work is currently underway in support of the Belgian Supercontainer concept to measure the anaerobic corrosion rate of the carbon steel overpack surrounding the central stainless steel container (Smart, 2009b). This programme is also taking account of the possible effects of γ -radiation on the anaerobic corrosion rate of carbon steel in cementitious environments. It has been found that with clean carbon steel surfaces the corrosion rate is typically initially high (over $10 \mu\text{m yr}^{-1}$) but that it falls over a period of several thousand hours to $0.1 \mu\text{m yr}^{-1}$ or less. The corrosion product formed on carbon steel in alkaline conditions during anaerobic corrosion is normally magnetite, Fe_3O_4 .

In oxygenated conditions and in the presence of chloride ions, there is a risk of pitting corrosion of both carbon steel and stainless steel. In deoxygenated conditions the electrochemical potential of both materials (i.e. the corrosion potential) falls below the critical pitting potential and pitting does not occur. However, in the presence of oxygen both materials can suffer from pitting, the risk of which is governed mainly by the oxygen concentration, the temperature and the ratio between the concentrations of the chloride and the hydroxide ions in solution, since hydroxide acts as a pitting inhibitor. Research work carried out within the U.K. programme (Smart, 2006) has investigated the critical ranges of the $[\text{Cl}^-] : [\text{OH}^-]$ ratio for both stainless steel and carbon steel; in addition there is a considerable body of research in the literature on the factors controlling carbon steel corrosion in concrete because of its importance to the civil engineering industry. In recent years stainless steel has become an option for use as a concrete reinforcement material, where it has been found that stainless steel is resistant to corrosion in the presence of high concentrations of chloride. This has been confirmed by a long-term research programme in the U.K. on prototype stainless steel waste containers filled with waste simulant. In contrast carbon steel suffers from broad-fronted corrosion in the presence of relatively low porewater chloride concentrations (Smart, 2009a).

Crevice corrosion occurs at the junction between two mating metal surfaces, where it is possible to develop occluded cells in which localised acidic conditions can develop due to the hydrolysis of dissolved metal ions. The alkaline environment provided by a cementitious porewater has been found to inhibit the onset of crevice corrosion around the stainless steel lid flanges typical of 500 litre drums used in the U.K. (Smart, 2006).

There are a number of substances that can cause stress corrosion cracking (SCC) of both carbon steel (Smart, 2009a) and stainless steel (Smart, 2006). This process can lead to the formation of cracks at stresses considerably below the normal tensile strength of the material and this could raise concerns with regard to the handling capability of waste containers. Most attention has been focussed on the possibility of trace sulphur compounds (particularly thiosulphate in BFS-based cements) causing stress corrosion of stainless steels. For carbon steels the concentrations of aggressive species are likely to be too low in cementitious environments to cause SCC.

In some circumstances microbial activity can enhance the corrosion rate by several orders of magnitude (Smart, 2006). However, the high pH provided by cementitious environments will inhibit microbial activity and so this form of corrosion is not regarded as significant for waste containers in contact with cement, unless niches of microbial activity are allowed to develop (e.g. in voids caused by trapped gas bubbles).

Galvanic corrosion arises when dissimilar metals come into direct electrical contact within an electrolyte, such as that provided by the porewater of a cement. Research was carried out within the U.K. research programme to investigate the effect of electrically coupling a range of dissimilar metals in a cementitious medium (Smart, 2006) and a galvanic series was developed for metals in cement. This showed that the only common waste material more noble than stainless steel was graphite.

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