Research

Galvanic and Stress Corrosion of Copper Canisters in Repository Environment

A Short Review

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SKI perspective

Background

In the planned repository for spent nuclear fuel in Sweden according to the KBS-3 concept, a canister consisting of an outer copper shell and an cast iron insert plays an important role to isolate the waste. The function of the copper shell is to give corrosion resistance. SKI has earlier studied different forms of general and localised corrosion on copper, using the results as one basis (among others) in its reviews of SKB's RD&D Programmes and reviews of performance assessments.

Purpose of the project

To complete the picture of copper corrosion also galvanic and stress corrosion needs to be covered. The purpose of this project is to study and review material about galvanic corrosion, especially work performed on behalf of SKB, and to point out weaknesses in assumptions and statements. Regarding stress corrosion cracking a literature search is performed on threshold values for stress corrosion on copper.

Results

The report discusses galvanic corrosion in a broad sense and points out areas that need further focus. This includes the corrosion of copper of a unbreached canister due to inhomogeneities in either the copper material or the environment, as well as corrosion of the iron insert in a breached canister, influenced by the metallic contact of the copper and iron. In the latter case the state of the copper and its surface films as well as the types of corrosion products formed on the iron needs to be further investigated.

The literature search for threshold values for stress corrosion did not reveal any studies that had determined such results. The report indicates methods for experimentally determining the threshold value.

Continued work

The report points out areas where further studies are needed to get a better understanding of the corrosion processes and their importance for the long-term performance of the canister in the repository.

Effects on SKI work

SKI will use the results both in developing its own knowledge of corrosion processes and as a basis in its forthcoming reviews of SKB's programme.

Project information

Responsible for the project at SKI has been Christina Lilja.
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SKI Project Number 00078

Abstract

The Swedish Nuclear Power Inspectorate, SKI, has studied different aspects of canister and copper corrosion as part of the general improvement of the knowledge base within the area. General and local corrosion has earlier been treated by experiments as well as by thermodynamic calculations. For completeness also galvanic and stress corrosion should be treated. The present work is a short review, intended to indicate areas needing further focus.

The work consists of two parts, the first of which contains a judgement of statements concerning risk of galvanic corrosion of copper in the repository. The second part concerns threshold values for the stress intensity factor of stress corrosion in copper. A suggestion is given on how such values possibly could be measured for copper at repository conditions.

In early investigations by SKB, galvanic corrosion is not mentioned or at least not treated. In later works it is treated but often in a theoretical way without indications of any further treatment or investigation.

Several pieces of work indicate that further investigations are required to ensure that different types of corrosion, like galvanic, cannot occur in the repository environment. There are for example effects of grain size, grain boundary conditions, impurities and other factors that could influence the appearance of galvanic corrosion that are not treated. Those factors have to be considered to be completely sure that galvanic corrosion and related effects does not occur for the actual canister in the specific environment of the repository. The circumstances are so specific, that a rather general discussion indicating that galvanic corrosion is not probable just is not enough. Experiments should also be performed for verification.

It is concluded that the following specific areas, amongst others, could benefit from further consideration. Galvanic corrosion of unbreached copper by inhomogeneities in the environment and in the copper metal should be addressed. The surface area of electrode areas formed on the metal are important as are also their surface conditions like oxide or sulfide coverage and the physical and chemical status of the covering film.

Consequences of the formation of other passivating films than magnetite like pyrite or mixed sulfides on anode areas formed on the cast iron in a breached canister should also be studied. Thermal effects, inhomogeneous distribution of water flow, radiolytic supply of oxidants and the influence of microbes are also of importance.

Regarding SCC, an overview of possibilities to perform multi-axial determinations of threshold values for the stress intensity factor in copper is presented. It is concluded that threshold values can probably be measured for repository environment but will require development of specimens and/or techniques.

Sammanfattning

Statens kärnkraftinspektion, SKI har studerat olika aspekter av kapsel och kopparkorrosion som del av en allmän kvalitetshöjning av befintlig kunskapsbas inom området. Allmän och lokal korrosion har studerats genom såväl experiment som termodynamiska beräkningar. För att förbättra kunskapsbasen bör också galvanisk korrosion och spänningskorrosion behandlas. Föreliggande arbete utgör en begränsad överblick över nämnda områden och avsikten är att klargöra behov av ytterligare insatser.

Arbetet har delats upp i två delar. Den första omfattar en sammanställning och bedömning av utsagor om risk för galvanisk korrosion av kapseln i slutförvaret. Den andra delen behandlar tröskelvärden för spänningskorrosion hos koppar och dessutom ges ett förslag på hur spricktillväxt möjligen kan mätas i koppar i förvarsmiljö i ett fleraxligt spänningsfält.

I tidiga utredningar av SKB nämns inte galvanisk korrosion eller utvärderas åtminstone inte. I senare arbeten behandlas galvanisk korrosion teoretiskt men utan indikationer om fortsatta mer praktiska undersökningar.

Flera arbeten indikerar behov av att göra ytterligare undersökningar för att säkra att fenomen som galvanisk korrosion inte kan inträffa i förvarsmiljön. Det föreligger exempelvis med stor sannolikhet inflytande av bl a materialets kornstorlek, korngränsförhållanden, föroreningar och andra faktorer som skulle kunna inverka på galvanisk korrosion och som inte behandlas. Dessa faktorer måste utvärderas för att full säkerhet ska uppnås om att galvanisk korrosion och liknande effekter inte uppträder i förvarsmiljön för den aktuella kapselkonfigurationen. Omständigheterna är så specifika att en generell, teoretisk diskussion, som indikerar att galvanisk korrosion inte är sannolik, troligen är otillräcklig. Verifierande experiment bör också utföras.

Slutsatsen av denna genomgång är att följande speciella områden bör utredas närmare. Bl.a. bör inverkan av en icke homogen miljö, samt av ett icke homogent material utvärderas för den obrutna kapseln. Metallernas ytförhållande är viktigt vid galvanisk kontakt mellan koppar och kolstål, vilket också deras yttillstånd är. Med det senare avses bl.a. om ytorna är täckta med oxid eller sulfid, samt hur de fysikaliska och kemiska egenskaperna hos en sådan film inverkar.

Konsekvenserna av bildandet av andra passivfilmer än magnetit på gjutjärn vid galvanisk kontakt bör utredas. Magnetit anses minska den galvaniska korrosionen genom sin passiverande verkan på gjutjärnet. Eventuella effekter av att en pyrit eller blandsulfidfilm bildas istället bör utredas. Dessutom bör effekterna av temperaturgradienter, inhomogent vattenflöde, radiolytisk försörjning av oxidanter samt inverkan av mikrober utredas.

En översikt ges av möjligheterna att utföra fleraxliga bestämningar av tröskelvärden för spänningskorrosion i koppar. Slutsatsen är att sådana tröskelvärden möjligen kan bestämmas i slutförvarsmiljö, men att utveckling är nödvändig av provstavsgeometri och/eller utrustning.

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1 Introduction

The Swedish Nuclear Power Inspectorate, SKI, has studied different aspects of canister and copper corrosion as part of the general improvement of the knowledge base within the area. In a recently reported work [1] general and local corrosion were treated by experiments as well as by thermodynamic calculations. In order to complete the knowledge base also galvanic and stress corrosion should be treated. The present project is a short review, intended to indicate areas needing further focus.

The work consists of two parts. One is a judgement of statements found in literature concerning the risk of galvanic corrosion of copper in the repository. The work was performed mainly as an evaluation of material about galvanic corrosion produced by SKB. More specifically, focus was on evaluating strengths and weaknesses in statements and assumptions made by SKB in their analyses.

Completing work is suggested in order to secure the quality in present statements on galvanic corrosion in the canister system.

The second part consists of a search for stress threshold values in literature of stress corrosion in copper. Furthermore a proposal is given in this section on how crack growth in copper at one-, two- and three- axial loads in the repository environment might be measured.

As there are few experiences on multi-axial loads, development of specimens and/or methods will probably be necessary as an introduction to experimental work.

2 Galvanic corrosion in copper

2.1 Background

The Advanced Cold Process Canister (ACPC) is currently being considered by SKB for the disposal of nuclear waste. Although the final design has not yet been chosen, all the present options under consideration involve an outer copper casing and an inner cast iron container. It is highly likely that these two parts of the canister will come into metallic contact. Therefore a penetration of the outer copper canister caused by the surrounding groundwater electrochemical reactions at the copper canister's surface or by other mechanisms would influence the corrosion behavior of cast iron. This process is known as galvanic corrosion and it could have a major impact on the time to failure of the inner cast iron container.

The first part of this work has been focused on literature produced by SKB on galvanic corrosion of copper. The first step is a literature search, the result of which is accounted in the next section.

2.2 Literature

A search was performed in the INIS data-base for literature between 1970 - 1999 strictly on galvanic corrosion related to the repository environment. Beside this information, open SKB reports as well as reports from the series SKB-PR (internal) were also searched. An account of found information is given in the following. All relevant documents found are presented below in a concentrated way.

In [2, 3] trends in modeling waste package performance are reviewed mainly from the perspective of the Swedish SKB studies. Examples are given, which illustrate the approaches for modeling different waste forms, i.e. high level waste, HLW, glass and spent nuclear fuel, and candidate canister materials, such as copper and steel. The relative importance of thermodynamics, reaction kinetics and near-field transport are discussed. However, nothing is at this time said about galvanic corrosion.

In [4, 5, 6] a near-field performance evaluation of the ACPC for spent fuel disposal was performed and reported. The canister consists of a steel load-bearing casing, with an outer corrosion shield of copper. In the analysis, as well internal (i.e. corrosion processes from the inside of the canister) as external processes (mechanical and chemical) were considered both prior to and after canister breach. Throughout the analysis, present day underground conditions were assumed to persist during the service life of the canister.

It was concluded that internal processes cannot cause the canister to breach under foreseen conditions, i.e. localized corrosion for the steel or copper canisters is dismissed as a failure mechanism.

The evaluation of the effects of processes outside of the canister indicates that there is no rapid mechanism to endanger its integrity. Consequently the service life of the canister is said to be several million years. This factor is said to ensure the safety of the concept.

For completeness an evaluation of post-failure behavior was also carried out. Analyses were focussed on low probability phenomena from faults in canisters.

Some items were identified where further research was considered as justified in order to increase knowledge of the phenomena and thus strengthen the confidence of safety margins. However, it was concluded that the risks of these scenarios could be judged to be acceptable. This is due to the fact that firstly, the probability of occurrence of most of these scenarios is said to be controlled to a large extent through technical measures. Secondly, the consequences are judged not be severe.

It is summarized that the ACPC seems to meet at least the same safety targets as the KBS-3 canister.

In 1994 [7], a limited performance assessment was done for the copper/steel canister that was chosen as the reference canister in the RD&D-programme 92 [8]. The areas given specific attention were scenario development methodology, the effect of corrosion products, hydrogen gas transport and the retardation effect of the canister internals.

The main philosophy was that a final repository for spent nuclear fuel should be based on multiple barriers. The safety of the repository shall not depend on one safety barrier only. Traditionally, the barriers have been defined as the rock, the buffer material, the canister and the waste form. The canister is very important since it alone is able to completely protect the waste from the groundwater for a very long time. The canister also differs from the other barriers in the sense that its main safety function is the confinement of radionuclides instead of dilution.

Originally, in the KBS-3 [9], there were two different canister designs, a hot isostatically pressed pure copper canister and a lead filled copper canister. In the PASS study [10], different canister designs were compared and ranked. The outcome of this project was that a steel canister with a copper overpack was the most favorable alternative. In the RD&D-programme 92 [8] the copper/steel canister was chosen as the reference canister alternative for the future.

In [11] work conducted in recent years to identify processes and interactions of importance to the evaluation of long-term safety of a KBS-3 type deep repository for spent nuclear fuel is documented.

Some programs have studied galvanic corrosion of other cladding materials than copper [12], [13]. In [14] galvanic corrosion of copper alloys was studied for the US program but is related to a tuff repository.

In [15] the development of the copper/iron canister proposed by SKB was studied. The study focused on choice of materials, manufacturing technology and quality assurance, all of which could be essential for subsequent corrosion phenomena.

It was concluded that the microstructure achieved in the extruded copper tubular for the first canister was unacceptable. Similar problems existed with plates used for the fabricated tubular but some more favorable structures were achieved by this route. It was proposed that a grain size of 250 μm would be acceptable. Later on a grain size range of 180-360 μm has been suggested [16]. In [17] an evaluation is made of the canister development into the present situation of the oxygen free copper, OFC, alternative with a 50 ppm addition of phosphor and a cast iron bearing liner. It is stated in [17] that the cast iron will not give the type of corrosion characteristics as the magnetite coating on carbon steel is supposed to give. This fact could imply consequences for galvanic corrosion. Welding of lids and bottoms to the copper canister is also said to be problematical from the corrosion point of view, as a coarse grain size will arise in the material processed by the proposed manufacture routes. Further construction requirements and results from test manufacturing were recently accounted and discussed in [16], [18] and [19]. Especially in [16] corrosion effects are discussed and evaluated but galvanic corrosion is not treated explicitly and therefore remains to be addressed.

All of this indicates that further studies are required on crevice and galvanic corrosion as well as stress corrosion cracking in the OFC copper 50-ppm phosphorus alloy intended for the latest canister concept.

In [20] recent data from site investigations suggests that the ionic content of the granitic groundwater in SKB´s repository will be significantly higher than originally envisaged. It has been found that the rate at which hydrogen is evolved by the anaerobic corrosion of carbon steel is considerably faster in the new high ionic strength groundwaters than in the original dilute ones. However, if the pH of the high ionic strength groundwater is increased from pH 8.0 to pH 10.5 the hydrogen evolution rate reverts back to the low rate observed in dilute solutions. This effect is supposed to be linked to increased stability of the protective magnetite film at the higher pH. In the SKB waste repository, the presence of the bentonite clay backfill is said to provide the required increase in pH.

The magnetite films that form on carbon steel have been shown to anodically limit the corrosion reaction. Therefore galvanic coupling of the outer copper canister and the inner carbon steel container is said not to alter the rate at which hydrogen is evolved.

In [21] the effect of galvanic coupling between the copper outer canister and the carbon steel inner container on the corrosion resistance of the ACPC was reviewed for a standard case. It was concluded that galvanic coupling can occur only when both metals are in direct contact with the repository's groundwater. This requires a breach in the outer copper canister. If such a situation occurs during the aerobic stage the galvanic couple will increase the rate of corrosion of the carbon steel. However, if oxygen from the outside is the only possible oxidant, the slow diffusion rate of oxygen through the surrounding bentonite clay is expected to reduce the galvanic effect. If the copper canister is breached during an anaerobic stage, galvanic coupling between the copper and the carbon steel is said not to accelerate the corrosion rate of the carbon steel significantly. In summary, it is said in this work that galvanic coupling is unlikely to notably change the life expectancy of the ACPC from that estimated by the conservative models of the uncoupled canister.

A range of methods, both electrochemical and direct gas measurement, have been used to assess the rate of corrosion and the associated hydrogen gas production [22]. The results indicate that under the "conditions of interest" an oxide film protects carbon steel. Good agreement was found between the various methods of corrosion rate measurement. Long term corrosion rates will be in the range 0.1 to 1.0 μm/year over the temperature range 25°C to 90°C. The application of hydrogen overpressure over the range of 1 to 100 atmospheres was found not to significantly affect the corrosion rates observed. Following the long term tests the corrosion products identified, by X-ray diffraction, were mixed phases of magnetite and deposited magnesium carbonate. Scratching electrode tests under anaerobic conditions resulted in the re-growth of a thin oxide film and a return to the pre-scratch corrosion potential.

In [23] a literature survey on galvanic corrosion behavior of different candidate corrosion allowance and corrosion-resistant metallic container materials in various environments is presented. Alloys covered include carbon and low alloy steels, Cu-Ni and Ni-Cu alloys, stainless steels, Ni-rich and Ni-base alloys, and Ti and its alloys. A discussion on galvanic corrosion susceptibility of welded joints containing dissimilar metals is also included. Results of several studies on the effect of coupling carbon steel to many different metals and alloys in a range of environments are presented in the survey. The environments include industrial, urban/rural, marine, natural water, and seawater. The precise environment surrounding of the waste packages in the potential repository is yet to be determined. However, the various tested environments cited in this report should cover possible environmental conditions that might be encountered by the candidate container materials. Apart from environmental parameters, factors unique to galvanic corrosion include anode to cathode area ratio, electrolyte resistivity, and geometric shapes. An unfavorable area ratio exists when the surface area of the more noble metal is larger compared to that of the less noble metal. Changing the distance between the two electrodes may vary the electrolyte resistance. In order to prevent or minimize galvanic corrosion, several measures can be taken. Combinations of metals or alloys widely separated in the relevant galvanic series should of course be avoided. Unfavorable area ratios should also be avoided. The area of the more anodic metal or alloy surface should be larger. Other factors, such as the presence of crevices, will strengthen the effect of the galvanic couple.

In [24] galvanic interaction of stainless steel 304L, Ni 270, Cu, Ti-6Al-4V, Sn, 4130 steel, Cd, and Zn has been studied in 3.5% NaCl using galvanic current and weight loss measurements in 24-hour tests. Galvanic couples of 4130 steel and one of the Al alloys 1100, 2024, 2219, 6061, and 7075 were also evaluated in tap water and distilled water. Galvanic current data can be used to assess both the effect of different dissimilar cathode materials as well as the relative susceptibility to galvanic corrosion of anode materials. For 3.5% NaCl, it was found that the effect of the cathode material decreased in the order Cu > Ni > stainless steel > Ti-6AI-4V, while the relative susceptibility of anode materials decreases in the order Sn > Zn > 14130 steel > Cd.

One aim of this systematic study was to rank materials in galvanic series based on kinetic measurements for coupled materials rather than on corrosion potentials of uncoupled materials. It was also demonstrated that the effect of area ratio is an important parameter determining the rate of galvanic corrosion, and can be predicted.

2.3 Discussion of galvanic corrosion

2.3.1 General

In order to complete the knowledge base of canister and copper corrosion, SKI suggested that also galvanic and stress corrosion should be treated. The present work comprises a short review, intended to point out areas of galvanic corrosion needing further focus beyond those indicated by SKB. The treatment here is slightly broader than indicated by the formal definition of galvanic corrosion. The strict general definition of galvanic corrosion is dissolution of the anodic metal in a bi-metal electro-chemical cell. However, there are several possible modifications of this definition. The cathode could for example comprise a nobler part of the same metal due to variations in metal composition or other property variations. The cathode could also comprise another conducting material than a metal like graphite or an oxide or a sulphide. The environment could also vary over a larger area of the same metal constituting anodic and cathodic areas.

The discussion is founded on literature findings accounted for in section 2.2. Specific effort is focused on but not limited to listing of SKB statements about galvanic corrosion. The objective is to evaluate the strength/weakness of the statements and on valuating the quality of the integral work on galvanic corrosion performed by SKB. The need for completing work is also discussed in order to secure the quality in present statements on galvanic corrosion in the canister system.

The main philosophy of SKB is that a final repository for spent nuclear fuel should be based on multiple barriers. The safety of the repository should not depend on one safety barrier only. Traditionally, the barriers have been defined as the rock, the buffer material, the canister and the waste form. The canister is very important since it alone is able to completely separate waste and groundwater for a very long time. The canister also differs from the other barriers in the sense that its main safety function is the confinement of radionuclides. Therefore, extremely high demands are focused on the integrity of the canister and every known or suspected weakness has to be properly investigated.

Galvanic corrosion in the broad sense of the canister can occur in two main categories. One of those is galvanic corrosion of the unbreached copper caused by environmental and materials inhomogeneities. This corrosion could result in a breach in the long run. The other is galvanic coupling between copper and the inner carbon steel as a result of a breached copper layer. This type of corrosion can worsen the effects the lost integrity of an already breached wall.

The two main cases of galvanic corrosion have either not been treated at all or at least very scarce in earlier works by SKB. In later works galvanic corrosion is treated, but only in brief theoretical discussions without an objective to formulate any practical investigations. In a recent main document from SKB [16] corrosion is treated as one of several design prerequisites for the canister, but canister susceptibility for galvanic corrosion is not mentioned. However, many if not all special forms of corrosion cannot easily be treated only theoretically as there are too many parameters to consider. The importance of some of those can be foreseen theoretically but the evaluation of others requires that experiments be performed in a relevant environment. Several works found in literature also indicate that further investigations are required to ensure that different types of corrosion like galvanic, cannot occur in the repository environment. There are for example supposed influences by factors as grain size, grain boundary conditions, impurities and others that have not been treated at all for the first type. Those and other factors have to be considered, probably by performing experiments in order to conclude with certainty that galvanic corrosion of the canister does not occur in the specific environment of the repository.

In the case of the SKB canister the second type of galvanic coupling between the main metals of the canister can occur when the outer copper and the steel insert both are in direct contact with the repository's groundwater as a result of a breach in the copper. The latter supplies the electrolyte necessary for the galvanic process. The water also supplies chemical species participating in the electrode reactions as well as the transportation route for such species. If such a situation occurs during an aerobic stage a galvanic couple will be formed and could increase the rate of corrosion of the carbon steel of the insert. If the copper canister is breached during an anaerobic stage, galvanic coupling between the copper and the carbon steel is said not to accelerate the corrosion rate of the carbon steel significantly. This is true if other driving forces than those involving oxygen are not considered.

Apart from environmental parameters, general factors unique to galvanic corrosion include anode-to-cathode area ratio, electrolyte resistivity, and geometric shapes. An example of a problem in this context with the canister is the high risk of unfavorable ratios of electrode areas. In the canister case this ratio could be very unfavorable with a very large cathode area of copper and a very small anode area of carbon steel in the shaft of a breach or a pit. This situation is going to further promote the dissolution of the carbon steel as soon as a breach or pit is opened through the copper shell.

Beside those apparent examples of important factors, other important features to consider in relation to galvanic corrosion are treated in the following. It is also discussed whether SKB has properly considered them or not. The factors are sorted as related to canister conditions and electrolyte and environment conditions, respectively. In several cases, however, the difference is not very distinct.

The continuation of this discussion treats both main types of galvanic corrosion as defined above subdivided into canister conditions and environmental conditions.

2.3.2 Canister conditions

Factors important for galvanic corrosion mainly related to canister conditions are the following. They are not primarily sorted in any order of importance, as this could be difficult to judge. Some factors turn out to be a strict requirement for galvanic corrosion to occur and others are complementary. The latter seem to be less important at a first glance and they are therefore the easiest to neglect.

- Canister breach. This is a strict requirement for galvanic corrosion of the second kind mentioned above to appear, as there has to be electrolytic contact between the metals. The breach could happen in a variety of ways, either mechanically or as a result of corrosion. Different types of micro-galvanic corrosion of the first kind are examples of attacks that in the long run could cause a breach. This has not been fully treated so far by SKB. Examples of factors of importance for initiation and development of micro galvanic corrosion forms of the first kind are grain size, alloying elements, impurity concentration and distribution and the appearance of small pits, cracks, crevices and welding faults. All aspects of the breaching problem are critical and not fully treated by SKB.

  Further examples of micro galvanic corrosion that could end up in a breach are uneven metal surface conditions, inhomogeneous ground water composition and any uneven temperature distribution. Such phenomena are in some cases mentioned by SKB but not thoroughly evaluated.

- Metallic contact between dissimilar metals. This is a requirement for galvanic corrosion of the second kind to appear. If any process forms a semi conducting or isolating layer between metals, this will in varying degree hinder further galvanic attack. However, in the canister the contact surface between copper and carbon steel/cast iron is so large that the probability of isolation is negligible. A good metallic contact can be foreseen in virtually all situations as the copper will creep onto the insert due to the swelling of the bentonite.

- Status of metal surfaces. This includes the mechanical status as coarseness, stresses, effective surface area, etc of the metal surfaces as well as their coverage or not by a passivating film and the type and character of such a film.

  For the present case, the large copper cathode area in relation to a small anode area (via a crack or a pit) of the carbon steel/cast iron is very unfortunate. This unfortunate electrode relation can also be developed in the case of the appearance of different electrode areas on the copper surface in the unbreached canister case.

  It should also be noted that copper sulfides instead of copper oxides might cover the copper surface. This would give very different conditions than can be foreseen for the oxide case. As copper sulfides are very good electrical conductors their function is far from an insulator. A sulfide surface could also give a much larger effective surface area of the cathode compared with oxide coverage as sulfide whiskers could grow. The ability to catalyze or inhibit possible electrode reactions in different ways should also be different from that of the oxides. Sulfide appearance on the cathode surface and its influence on galvanic corrosion processes could be complex and should merit evaluation. This has not been done by SKB.

It should also be considered that iron sulfides and mixed iron-copper sulfides could be formed in the system. It should be evaluated whether the appearance of such phases would inhibit the formation of a good passivating magnetite layer on the steel/cast iron surfaces. Furthermore the formation of magnetite could be hindered by a decreased pH due to hydrolysis on the anodic surfaces. Bentonite water could be geometrically hindered to compensate for this pH drop and thus magnetite might not be formed. Much of the discussion in [21] is founded on the formation of a magnetite layer but is not fully considering the requirements for the formation of such a layer.

- Temperature differences of the canister. There are at least three main types of temperature gradients that could occur. One is the general gradient axially along the copper outer surface. The other is a gradient that could occur because of inhomogeneous heat conductivity away from the canister surface. The third is radially from the inside and out to the copper surface.

  As already mentioned all of these temperature differences or gradients can cause galvanic effects. As copper have a much better thermal conductivity than the carbon steel/cast iron, the radial gradient could be a concern if heat conductivity away from the copper surface is good in combination with isolating iron based corrosion products in between copper and the steel/cast iron. Thus the anode could be significantly warmer by the residual heating from the fuel than the cathode, promoting the electrode reaction of iron dissolution. The cathode surface is large and the cathode reaction would probably not hinder such a thermal increase of the anode reaction. Such a phenomenon has not been discussed by SKB.

2.3.3 Electrolyte and environment conditions

Factors important for galvanic corrosion mainly related to electrolyte and environment conditions could be the following. The factors are not primarily sorted in any order of importance, as this could be difficult to judge. Some factors are of course a strict requirement for galvanic corrosion to appear.

- Transportation rates of reactants in electrolyte. Transportation phenomena comprise diffusion and convection. Such phenomena could be very inhomogeneous and cause a similarly inhomogeneous distribution in size and position of electrode surfaces over the canister thus influencing the first type of galvanic corrosion. Most inhomogenities tend to contribute to the enhancement of galvanic corrosion.

- Presence of chloride, sulfide, oxygen, hydrogen and other oxidants or reductants. The presence of different chemical species of course will have different influences on galvanic corrosion. Specifically it is necessary to have a good supply of oxidants on the cathode surface. It should be pointed out, however, that oxygen is not the sole candidate as an oxidant in this context. Others like hydrogen peroxide from the process of radiolysis as well as polysulfides and Fe(III) could not be ruled out in an environment where copper and sulfur is present at the same time. It should also be pointed out that it is possible to have a redox cycling in the repository. The cycling could be due to ingress of oxygenated surface waters at future events like ice ages. At canister breach and fuel damage it is also possible that radioactive matter could distribute onto the copper cathode surfaces and cause a local electrode surface supply of oxidants through radiolysis. This would enhance the galvanic processes and thus accelerate the canister degradation. In such a case one severely damaged canister could also by some transportation process supply its neighbor canisters with a deposit of radionucleii causing the same kind of effect on them.

- Radiation induced supply of oxidants. If a breach of the canister is postulated through the copper and steel layers it is possible that oxidants for the cathode reaction can be produced by the radiolysis process of water entering into close contact with the fuel. The transportation of formed oxidants like oxygen or hydrogen peroxide from a place of formation close to the fuel could be performed by convection caused by the heat gradient in the system. Radiolytic gases formed in water close to the fuel could also supply a means of transportation of oxidants and thus contribute to the continuation of a galvanic attack.

- Microbes could when active probably catalyze galvanic corrosion. One interesting way could be by making sulfate available for the cathodic reaction. Another would be by sulfide production. Such a process would in general terms increase the probability of corrosion attack on copper and probably also for galvanic.

2.4 Conclusions

- There are at least two main types of galvanic corrosion and sub variants possible in the canister.
- One main type is galvanic corrosion of the copper in an unbreached container. This is caused by inhomogeneities in the environment and in the copper metal and its properties.
- The other main type is galvanic contact between copper and cast iron via a breach or through-pit in the copper layer.
- Good metallic contact between metals in a breached canister as well as between different electrode areas on copper can be foreseen.
- The status of electrode surfaces could vary strongly depending on materials parameters as well as on the nature of a surface film.
- The character of different surface films and their influence on galvanic corrosion have not been thoroughly discussed by SKB.
- Compared with an oxide covered copper surface, a sulfide film on copper would probably further increase the effective surface area due to a tendency to whisker growth.
- The formation of a magnetite film on the cast iron anode in the breached canister is considered by SKB to decrease any galvanic attack. In the presence of sulfide it is doubtful if such a magnetite film is formed. Sulfide based films as pyrite or mixed

metal sulfides could possibly be formed. The formation of magnetite could also be hindered by an uncompensated drop of pH on anode surfaces.

- Thermal effects of several different kinds are possible and they are not fully discussed by SKB.
- The influence of an inhomogeneous flow distribution on galvanic corrosion has not been considered.
- Chloride, sulfide and oxidizing/reducing agents will have a major influence. In this case radiolytic supply of oxidants on neighbor canisters have not been considered.
- The influence of microbes on galvanic corrosion has not been evaluated by SKB.

2.5 Areas needing further focus

The discussion of galvanic corrosion in a broad sense has revealed several areas needing further focus, namely:

- There are two main types of galvanic corrosion identified in this overview. Both types should be paid attention.
- Galvanic corrosion of unbreached copper by inhomogeneities in environment and in the copper metal and its properties.
- Different types of galvanic attacks of a breached canister. This includes influences of the surface area of metals. Furthermore metal surface conditions like oxide or sulfide coverage and the status of the covering film, i.a. surface enlargement by whiskers and destabilization by pH drop.
- Consequences of the formation of other passivating films than magnetite like pyrite or mixed sulfides on the carbon steel anode.
- Thermal effects of different kinds.
- Inhomogeneous flow distribution.
- Radiolytic supply of oxidants on neighbor canisters.
- The influence of microbes.

3 Stress corrosion in copper

3.1 Background

The appearance of stress corrosion in any material requires a simultaneous combination of materials parameters as stresses in and chemical properties of the material and environmental parameters. The objective of this work has been to find and evaluate literature data on threshold values for stress corrosion in copper and to sketch experiments to measure growth rates in copper at 1, 2 and 3 axial loads in repository environment. As experience of multi-axial loads is scarce, development of experimental methods will certainly be necessary.

3.2 Literature on SCC threshold values for copper

A limited literature survey was performed in the INIS database (1970 - June 2000) using the Boolean search logic: "((stress corrosion) **or** (stress threshold)) **and** copper". A total of 35 documents [25-59] were selected from abstract reading and ordered from the library. There are certainly many pieces of relevant information related to stress corrosion in copper to be found in those documents. However, no values of stress thresholds for SCC in copper in the repository environment could be found. An in-house discussion [60] also confirmed that such values should be rare if any in literature for copper in the specific repository environment.

3.3 Suggested methods to estimate the threshold value, K_{th} of SCC in copper

3.3.1 Crack growth rate measurements in copper

Crack growth rate measurements with potential-drop technique has been done so far on austenitic materials like SS 2333 and Alloy 600 and 690 and weld materials like Alloy 182. Obviously there is nothing contradicting that this technique shouldn't work for copper too. However, the electrical conductivity of copper is larger by a factor 10. The potential drop signal will therefore be smaller. This could be a challenge concerning the technique of measurement. Alternatively the crack length could be measured by compliance technique although it has worse resolution by a factor of 10. This could be compensated by longer testing times.

It should be recognized, however, that the maximum load on a CT-specimen depends on the yield strength of the material. For instance the load for 25 mm CT-specimen of SS2333 with a pre-fatigued crack of 25 mm is around K=30 MPa√m assuming a yield strength of 250 MPa. For materials with lower yield strength either the load has to be reduced or the dimension of the specimen has to be increased. For very pure copper the yield strength is about 50 MPa [16]. A value for copper intended for the canister has not been found, but a significantly larger size than 25 mm of the CT-specimen would probably be necessary for copper.

It is suggested to start by manufacturing one or two CT (compact tension) specimens. Thereafter a fatigue pre-test is made where both compliance and potential-drop techniques are used. The advantage of CT-specimens is that they are already standardized by ASTM and there are solutions for the stress intensity factor K.

3.3.2 Threshold values

A recently used technique for measuring the threshold in stress intensity factors is the rising deplacement technique. A 25 mm pre-fatigued CT-specimen is normally used. The specimen is extended by a constant extension rate. With the help of a LVDT (low voltage displacement transducer), which measure the opening of the crack, the point when the crack starts to grow is registered. As the length of the pre-fatigued crack and the load at which the crack starts to grow are known, the stress intensity factor K can be calculated. Thereafter the same test is repeated but with a lower extension rate and again a value for the stress intensity factor K is received. If there is a difference of more than 5% between the first and the second estimated K-value, another test is done with an even lower extension rate. The procedure is repeated unless the difference between two consecutive values for K is less than 5%.

3.3.3 Present possibilities

When equipment is available we can perform fatigue tests of 12.5, 25 and 50 mm CT-specimens of copper in air and room temperature. Larger sizes have to be evaluated. The crack mode will be mode I, one axial loaded specimen.

If tests are preferred in a specific, controlled environment we have to build suitable equipment. It is preferred that an equipment be employed which could be used for both PWR/BWR tests and in the environment necessary for copper tests. There is presently one such piece of equipment available for normal sized specimens but it contains only one traction motor and can't be used for fatigue tests.

3.3.4 Multiaxial loads

With suitable specimen geometry it might be possible to receive a three-axial stress configuration although a one-axial loading is used.

Some information on multi-axial loading of a CT-specimen of type 304 stainless steel with mixed mode I/III can be found in [61].

There is no equipment for multi-axial loading available at present. However, such equipment can be installed. The cost for such a device is not known and has to be evaluated. As a comparison, a machine from INSTRON model 8800 for single-axial loading costs approximately between 500 and 600 kSEK.

3.3.5 Summary

There are few experiences available on multi-axial loads and development of methods will probably be necessary as an introduction to experimental work. The size of a copper specimen also has to be evaluated.

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