

MEKANISKA EGENSKAPER HOS GJUTJÄRN OCH KOPPAR

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Design of the KBS-3 canister with BWR internal structure



Design requirements of nuclear waste canisters

- The canister contains the spent fuel and prevents the release of radioactive substances into the surroundings. The canister shields also radiation and prevents criticality. The disposal canister will be subjected to varying loads in the repository conditions caused by **hydrostatic pressure, bentonite swelling, and shift of the bedrock.**
- The main aspects of the canister are the **copper shell thickness, corrosion resistance and creep strength/ductility**, as well as, the **strength and pressure-bearing capacity of the canister insert.**
- The **bentonite buffer** provides a self-healing medium when wet. This inhibits transportation of oxygen and sulphide ions to the canister surface, and the transport of released radionuclides from the canister if failed. The bentonite buffer accelerates the establishment of **anoxic conditions on the copper surface.** The bentonite buffer will **prevent the microbial activity** on the copper surface due to the high swelling pressure.
- Since all the **mechanical loads** on the canister are transferred through the **bentonite buffer**, the material properties of the bentonite clay define important conditions for the design analysis of the canister.
- The **initial state** of the canister is defined as the state when the canister is deposited in the repository. The **reference design** specifies, for example, that the maximum allowed surface temperature of the canister is 100°C and maximum allowed surface dose rate is 1 Gy/h. The long-term performance of the copper canister is based on the **ideal conditions** prevailing for centuries.

Embrittlement mechanisms of cast iron – definitions

- **Hydrogen embrittlement** of cast iron occurs because even small amounts of hydrogen can severely embrittle the ferrite matrix. Embrittlement occurs between -100 and +100°C and is enhanced by slow strain rate. Fracture mode is brittle cleavage fracture of ferrite.
- **Irradiation** of cast iron results in hardening due to vacancies and precipitates and embrittles the metal. Radiation-induced segregation of different chemical species towards defect sinks (grain boundaries, dislocations, etc.) occurs also.
- **Strain aging** (dynamic and static) (blue brittleness) of cast iron is similar to that of carbon steels. Small preliminary plastic strain of iron and low temperature aging causes hardening due to free C and N atoms, i.e. very marked yield point, and brittleness of the material even at room temperature. Due to the pronounced high yield point the material rapidly reaches a high stress and failure occurs at a low elongation. Fracture mode is ductile dimpled fracture.
- **Creep** of cast iron is caused by plastic flow under constant stress under a long period of time. Some form of transient creep will occur at all temperatures, but creep rate is very temperature dependent.

Hydrogen absorption to copper and cast iron

- In sulphide-containing environments copper corrosion ($2\text{Cu} + \text{HS}^- \Rightarrow \text{Cu}_2\text{S} + \text{H}^+ + \text{e}^-$) is supported by the evolution of hydrogen. Some water remains trapped inside the fuel elements after the canister is closed and hydrogen is also formed inside the canister in corrosion reactions of cast iron.
- Hydrogen can be absorbed in copper canister both on outside and inside surfaces.
- A majority of the hydrogen atoms formed in corrosion combines to form hydrogen gas, but a fraction enters the copper and cast iron.
- Corrosion on copper surface is also controlled by the transport rate of gaseous H_2 away from the canister surface. Diffusion in compacted, water-saturated bentonite is, however, low.
- Ionizing radiation may enhance hydrogen absorption in copper and cast iron in a number of ways.

Motivation to study hydrogen effects on cast iron

- There are both internal and external sources of hydrogen in the copper canister that can cause **hydrogen embrittlement**. In accordance with the design conditions for the canister, the amount of water left in each canister must be less than 600 g. It is plausible that oxygen-free iron corrosion can occur, causing hydrogen uptake and producing hydrogen gas.
- There are relatively few research reports on hydrogen embrittlement of ductile cast iron with a ferritic matrix.
- The hydrogen content of the cast iron (about 2 wt.-ppm) is much higher than that in carbon steel, for example, even with a high pearlite content.
- A systematic study was made on hydrogen effects on ductile cast iron used for the copper canister insert structure to understand the mechanisms of hydrogen embrittlement of cast iron better.
- At present there are no data on the effects of blue brittleness, radiation-induced embrittlement, hydrogen embrittlement and creep together. The future aim is to study these embrittlement mechanisms and their joint interaction with hydrogen embrittlement.

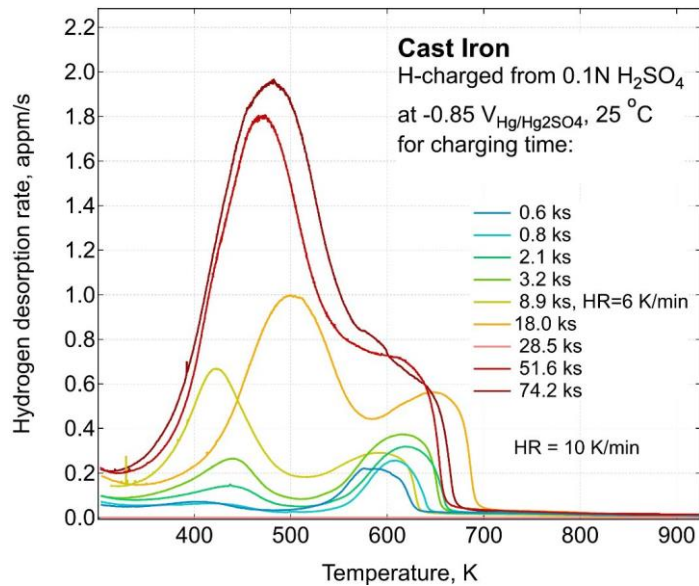
Experimental. Studied material and methods



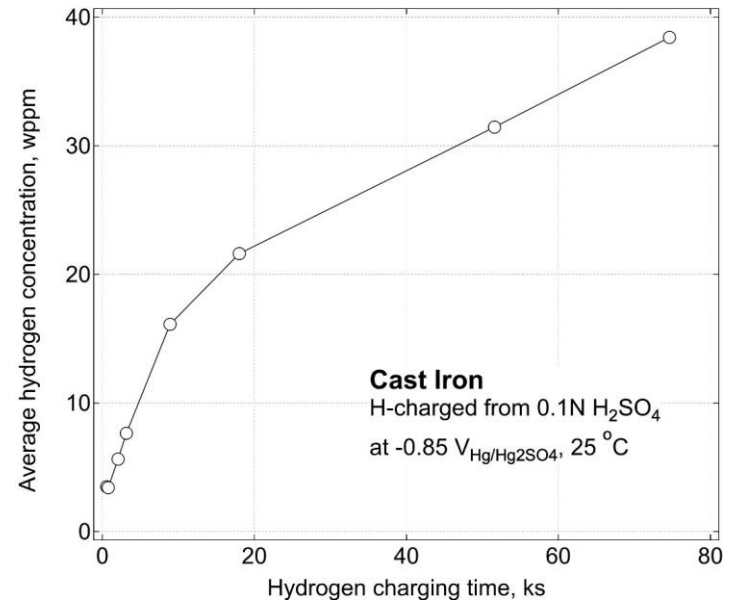
- *TDS apparatus designed and assembled at Aalto University School of Engineering;*
- *Vacuum in the UHV chamber better than 5×10^{-9} mbar;*
- *The apparatus allows to measure a small quantity of hydrogen in metals up to 0.1 at. ppm;*
- *The temperature of the TDS measurements ranges from RT to 1200 °C;*
- *The heating rates of the specimen are in the range of 1 to 10 K/min.*

Hydrogen uptake in cast iron under electrochemical hydrogen charging

TDS curves vs. temperature after electrochemical H-charging for different times

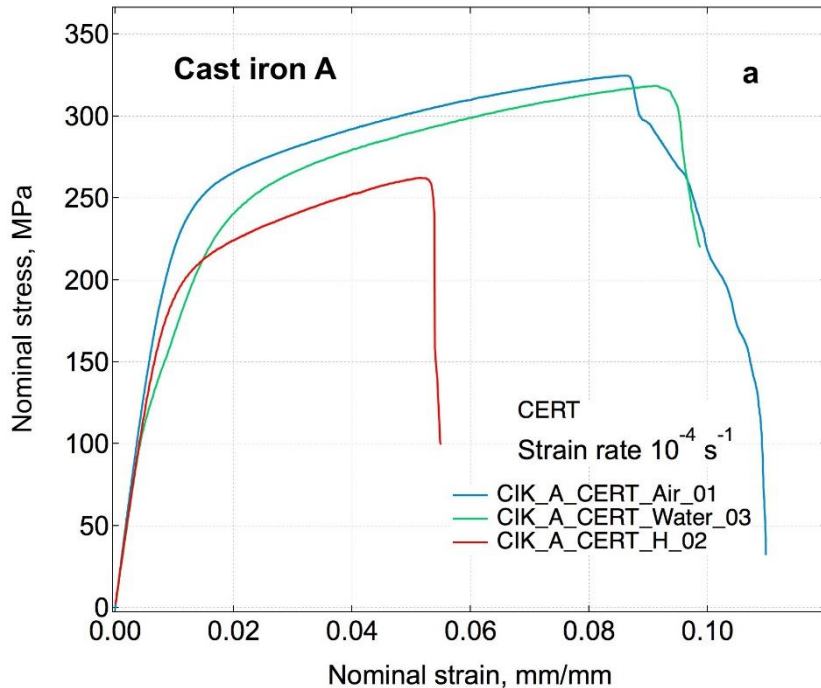


Hydrogen content vs. H-charging time

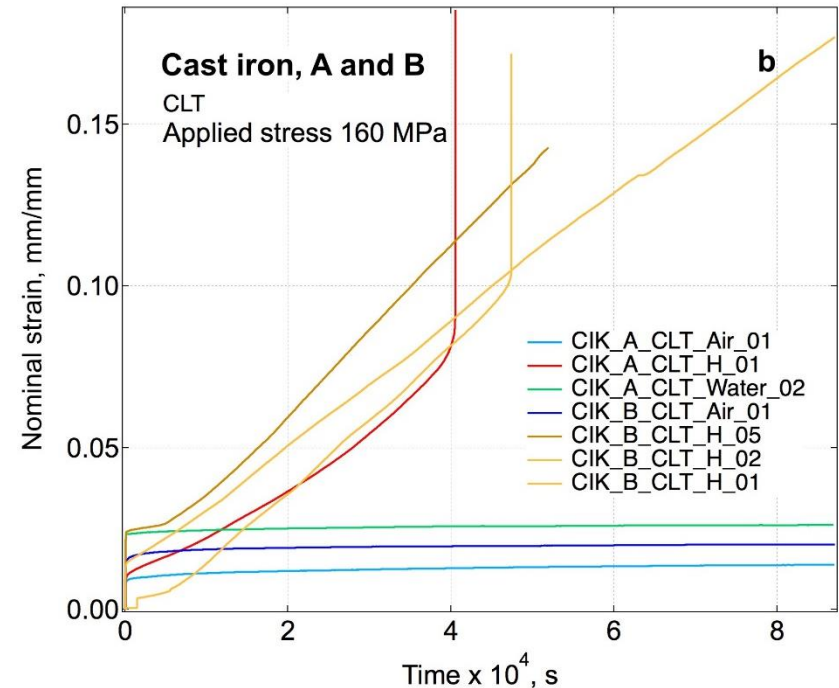


Hydrogen effects in tensile testing of cast iron

CERT



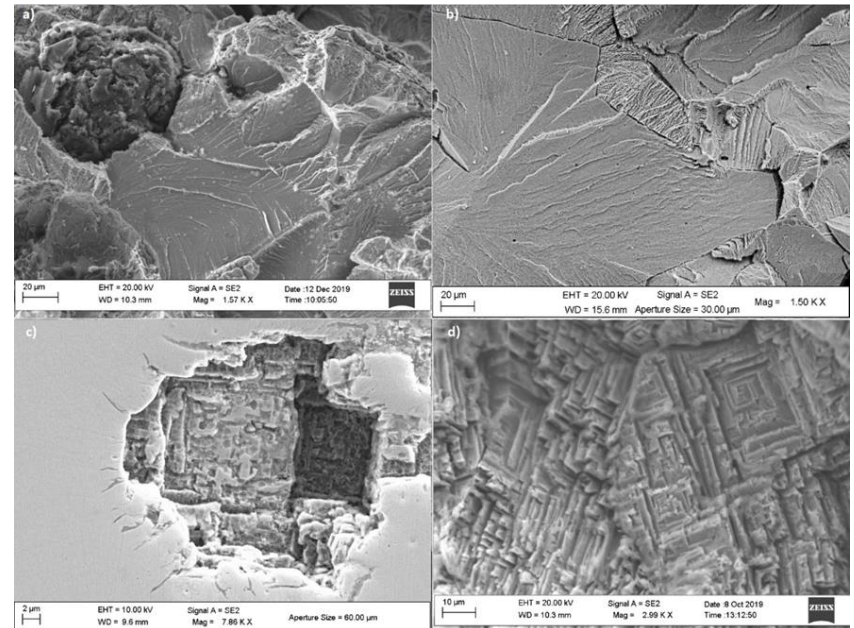
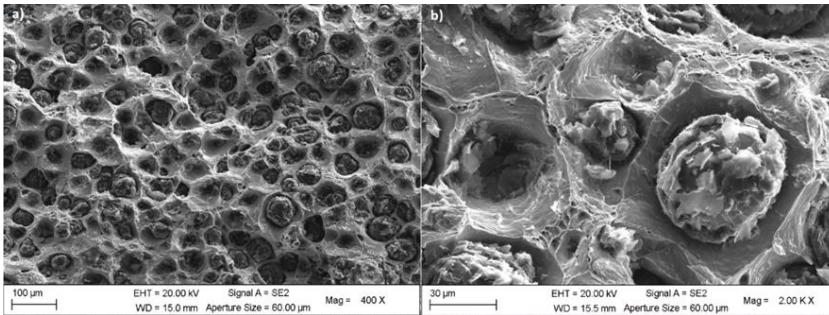
CLT



a). CERT of A-type specimens in air, distilled water, and under continuous hydrogen charging.

b). CLT at applied stress of 160 MPa in air and distilled water, as well as under continuous hydrogen charging. A remarkable increase of strain and strain rate in CLT under continuous hydrogen charging is observed.

Fracture surface examination



- Above: the fracture surface of uncharged CERT sample
- Right: hydrogen charged CLT specimen

Summary of hydrogen effects on cast iron insert

- The damage tolerance analyses of the cast iron insert are based on the allowed defect sizes and actual mechanical properties without properly taking into account, e.g., hydrogen embrittlement, blue brittleness, irradiation embrittlement and creep.
- The mechanical degradation mechanisms for cast iron inserts in deposition conditions include only ductile collapse (buckling). Brittle cleavage fracture is excluded and cast iron is considered to be ductile material in all expected conditions in the repository. However, ductile cast iron has a ductile-to-brittle transition temperature in low temperatures and at increased strain rates.
- The ductility of ductile cast iron is affected drastically by hydrogen and brittle cleavage fracture occurs around the graphite nodules. The separation of graphite from the matrix takes place before the initiation of cracks, and the susceptibility to brittle cracking increases if the strain rate decreases.
- There is no data summarizing effects of hydrogen embrittlement, blue brittleness, irradiation embrittlement, hydrogen embrittlement and creep together on performance of ductile cast iron which is prone to all these embrittlement mechanisms.

Motivation to study effects of static strain aging on nodular cast iron

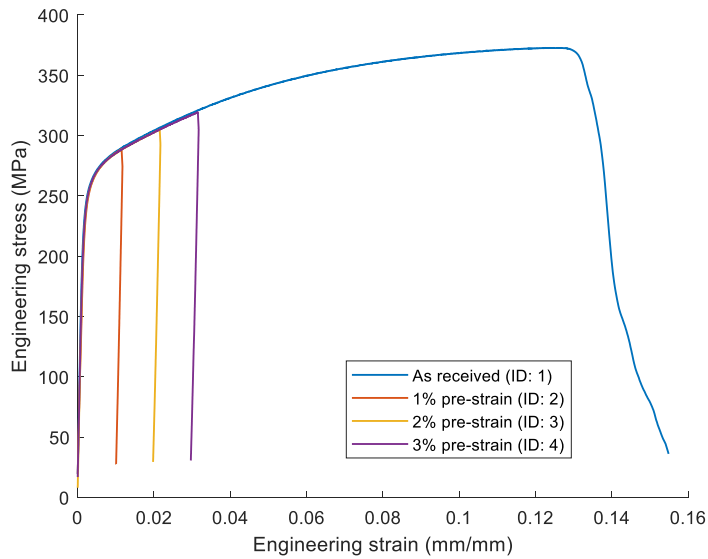
- The nuclear decay of the spent fuel causes the temperature inside the canister insert to increase up to 125 °C.
- The canister may be subject to bending and yielding due to a rock shear movement crossing the deposition hole.
- The cast iron insert may be subject to static strain aging (SSA):
 - SSA is a known phenomenon of ferritic steels even at low temperatures
 - SSA of ductile cast iron has not been studied, yet
- It has to be studied if SSA can occur in the cast iron insert in the repository conditions and how SSA affects the mechanical properties of the cast iron.

Experimental methods

- Specimens were pre-strained to 1%, 2% or 3% plastic strain with constant cross-head speed of 0.016 mm/s.
- Specimens were aged at RT, 100°C, 200°C, 300°C and 400°C for varying times.
 - Additionally non-strained specimens were aged at 100°C and 200°C in order to rule out thermal aging (no effect was found).
- Tensile tests were performed for aged specimens with the same constant cross-head speed.
- 4 specimens were patterned with spray paint and pre-straining and tensile tests were performed using digital image correlation (DIC).

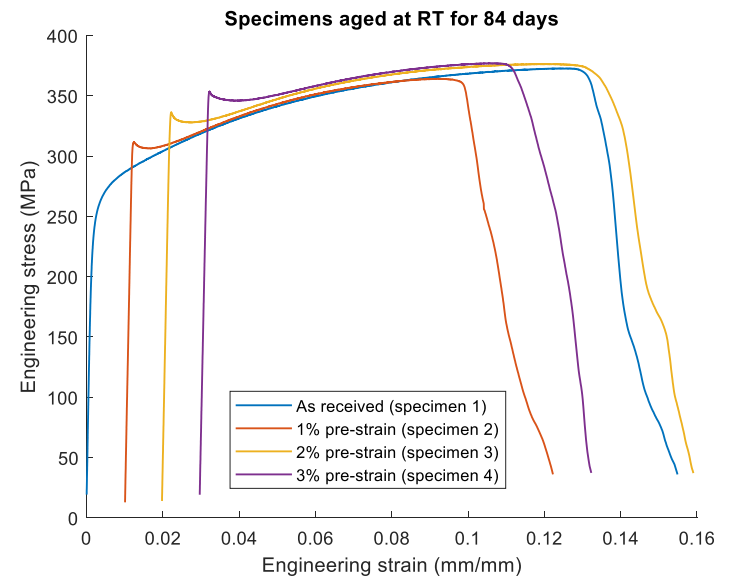


Results



Pre-straining

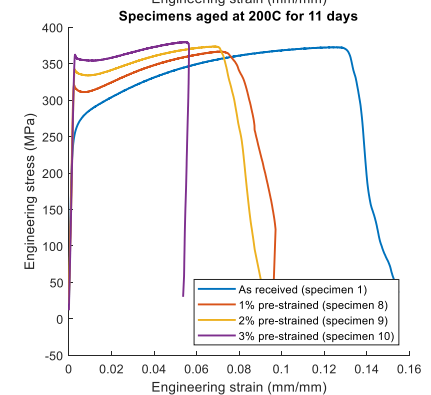
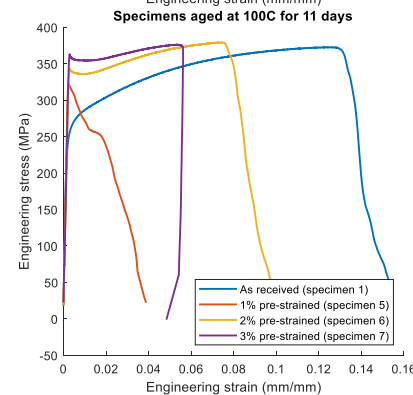
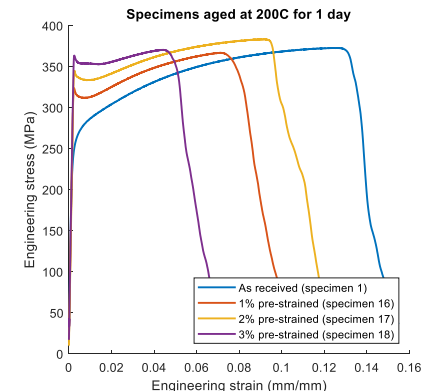
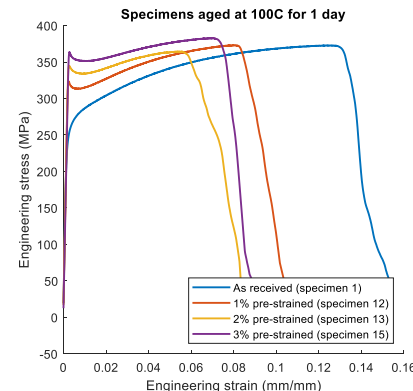
Aging



Tensile test

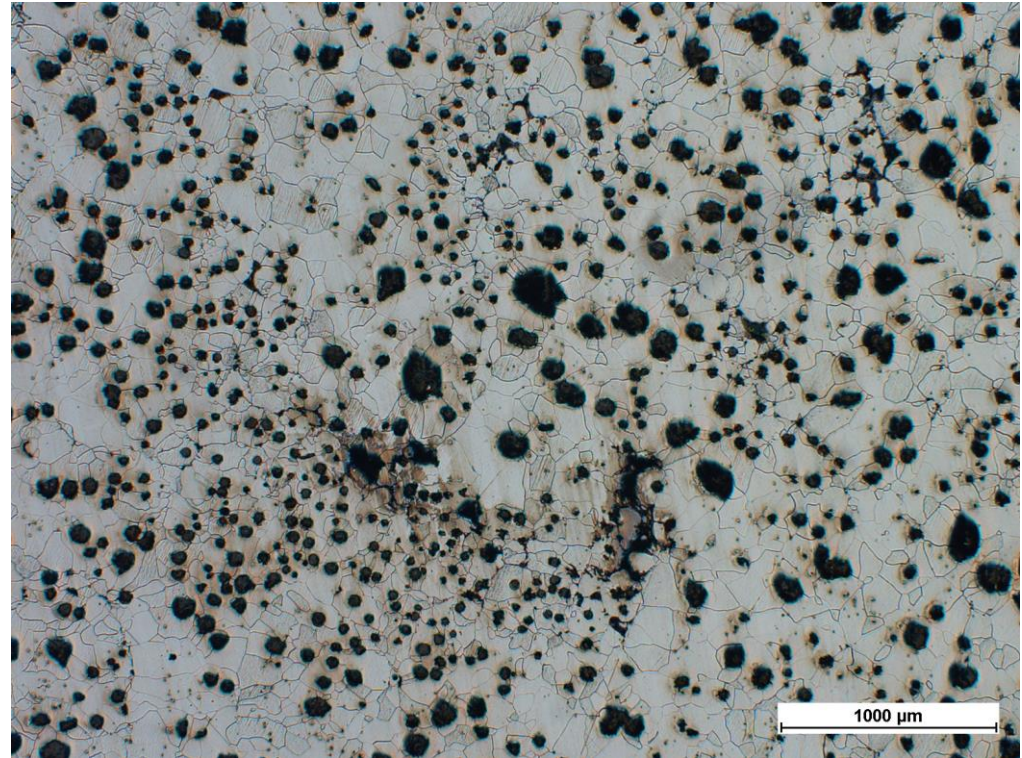
Results

- Aging saturates already after 1 day aging at 100°C:
 - No further yield stress increase at higher temperatures.
 - No marked difference in yield stress between 1 day and 11 days aging at 100°C and 200°C.
 - The scatter in the elongation to fracture is caused by casting defects and natural scatter in the microstructure.



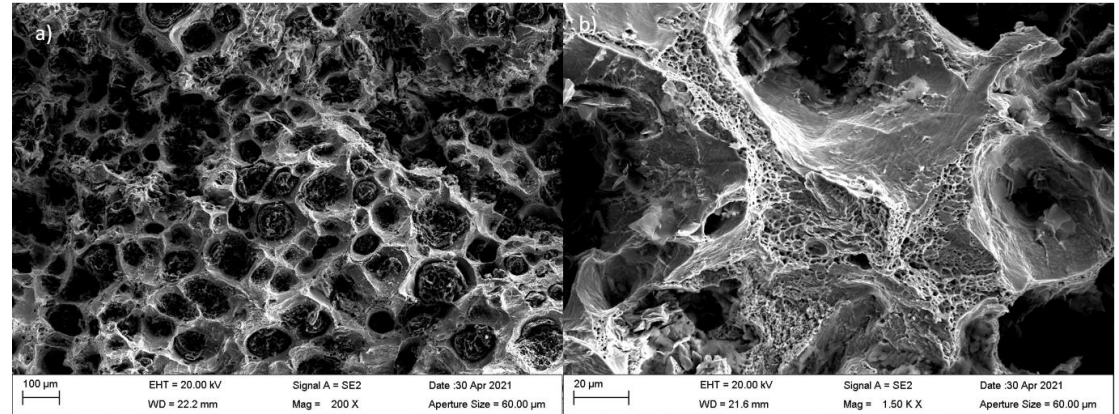
Scatter in the microstructure

- Size of the graphite nodules varies markedly even locally.
- Some casting defects can be seen in the micrograph.

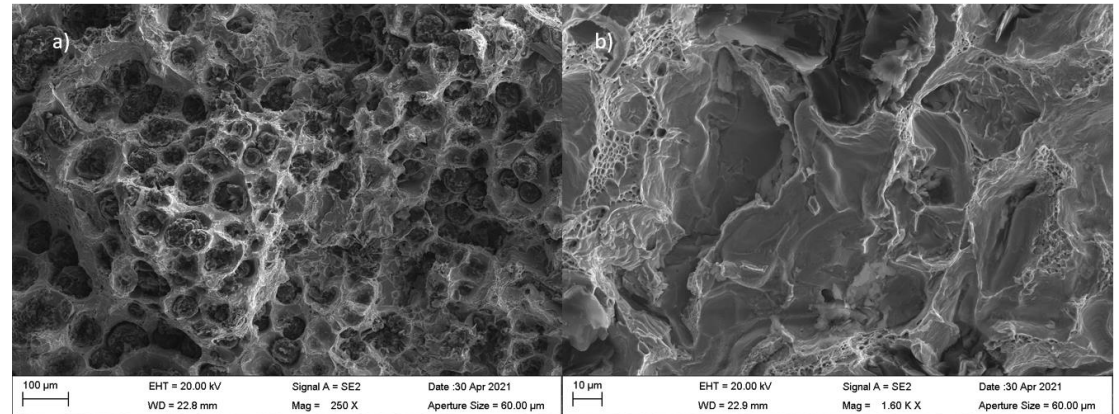


Fractography

- Reference material



- Pre-strained to 1% and aged at 100 °C for 11 days



Embrittlement mechanisms of cast iron – general conclusions

- Hydrogen embrittlement, irradiation embrittlement, strain aging (dynamic and static) (blue brittleness) and creep of cast iron insert are the important embrittlement mechanisms which occur in all repository conditions during the whole deposition period.
- The embrittlement processes have been examined only a little as separate phenomena, even though they occur simultaneously. Therefore, their additive and synergistic effects have to be examined and the safety analysis must be based on the real material properties of the cast iron instead of those of the initial state.
- Possibility of canister failure due to hydrostatic pressure or rock shear is considered low. The probability of a large earthquake in the vicinity of the repository site is low, but may become significant due to the long time scale involved. Only a small fraction of deposition holes, that will be intersected by fractures capable for significant rock shear movements, are affected.
- Excessive shear loading of the canister can be avoided by locating deposition holes outside the major fracture zones and avoiding high rock stresses. Probability that the shear movement will occur more than once on the same canister is considered low.

Geological spent nuclear fuel disposal in Sweden

The Swedish Land and Environment Court gave the conditional decision of the KBS-3 application on 23th January 2018. The operation is approved if:

1. SKB shows data which confirms the long-term safety of the site due to the uncertainties of copper canister corrosion performance affected by:

- Corrosion in oxygen-free groundwater;
- Pitting corrosion in sulfide solutions, including so-called Sauna-effect;
- Stress corrosion cracking in sulfide solutions, including Sauna-effect;
- Hydrogen embrittlement;
- Effects of irradiation on pitting and stress corrosion as well as hydrogen embrittlement.

2. SKB has to clarify who has according to the Swedish law the long-term responsibility on the geological spent nuclear fuel disposal site.

Geological spent nuclear fuel disposal in Sweden

A safety analysis of Szakalos and Leygraf (2019) estimates that:

“40% of the canisters collapse already within 100 years after repository closure due to SCC, HE, HS (in the welds) and the remaining 60% within 1000 years after closure due to SCC, HE and internal corrosion. More specifically, failures due to HE and HS will dominate in a Forsmark repository since these degradation processes operate without any applied load, in contrast to SCC.”

In Chapter 6 of KLR 2022 Kärnavfallsrådet has examined the background of the above estimates and statements, i.e. hydrogen uptake and penetration in copper, hydrogen sickness, hydroxide penetration in copper and sulfide stress corrosion cracking of copper (see also KLR 2020).

Hydrogen and hydroxide uptake of canister copper exposed 7 years in SKB prototype repository in the Äspö Hard rock laboratory (Szakalos and Leygraf, 2019)

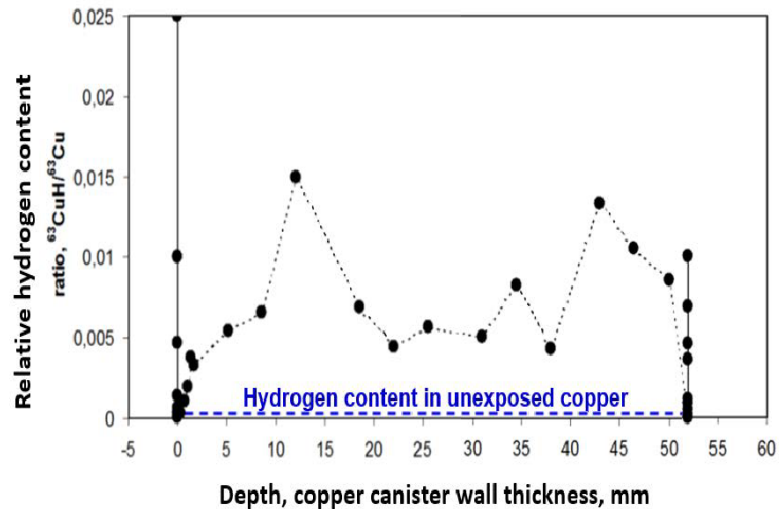


Figure 3.12. Full thickness canister copper exposed to the Swedish groundwater for seven years in the heated prototype repository, 80-90°C, at Äspö hard rock laboratory. The remarkable result shows that the copper canister is hydrogen charged throughout the whole thickness. The outermost surfaces have a very high H-content due to formation of corrosion products containing hydrogen and hydroxide. The hydrogen content in the first 10 mm of the inner/outer thickness has been subjected to spontaneous de-gassing when exposed to air since the hydrogen activity in the copper metal in contact with air is close to zero. The accepted hydrogen content in canister copper is 0.6 weight-ppm which coincide with the blue dotted line (unexposed copper). The hydrogen is detected by SIMS measurements and based on the H/Cu-ratio it can be estimated that the average hydrogen content in the copper is significantly higher than 1 wt-ppm.

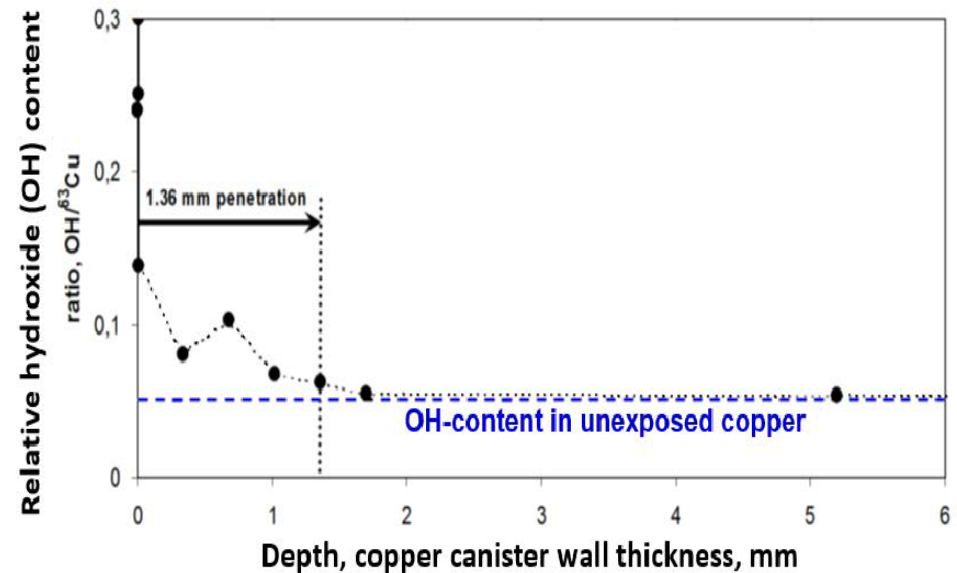


Figure 3.13. The hydroxide content of the first few mm of the full thickness canister copper exposed to the Swedish groundwater for seven years in the prototype repository at Äspö hard rock laboratory. The graph shows that hydroxide penetrates the copper metal, most probably in defects including grain boundaries. Once OH has entered the metal it is accumulated there, i.e. it is thermodynamically stable, i.e. evidence for internal anoxic corrosion. The hydroxide is detected by SIMS measurements.

Embrittlement mechanisms of copper – general conclusions

- Hydrogen concentration dissolved in copper in equilibrium can be evaluated using Sievert's law: $c_{\text{H}_2} = k \cdot p_{\text{H}_2}^{1/2}$, where c_{H_2} is dissolved hydrogen in metal, p_{H_2} hydrogen pressure (in atm) in gas phase, and k the temperature dependent solubility constant. In general, hydrogen content in copper canister is in balance by diffusion and desorption according to Sievert's law as a function of temperature, hydrogen content in copper and hydrogen pressure both around the canister and in hydrogen-induced pores in the metal.
- Hydrogen sickness is not expected to occur in the repository conditions, since the reaction with absorbed hydrogen and oxide inclusions takes place at elevated temperatures, $>300^\circ\text{C}$. FSW will be carried out in an inert atmosphere of Ar shielding gas after careful cleaning of the copper surfaces before welding to avoid oxide inclusions.

Embrittlement mechanisms of copper - general conclusions

- Internal anoxic corrosion of copper by penetration of hydroxide or sulfur atoms in the copper metal is opposite to the general knowledge that sulfur and oxygen atoms as well as hydroxide ions are not able to diffuse into copper metal.
- SIMS is a sensitive surface analysis method in nm-scale and therefore the choice of the method for hydrogen and hydroxide analyses in $\mu\text{m}/\text{mm}$ scale has likely affected the results. For the critical analysis of OH^- penetration and internal corrosion in copper the relevant information about the measurements has to be published to allow the proper scientific evaluation.
- In sulfide corrosion of copper small intergranular cracks form which may be caused by hydrogen-induced stress corrosion cracking. Since hydrogen sulfide and sulfide ions have only a limited access through the bentonite to the copper surface only small amounts of hydrogen is formed.