Estimation of corrosion product formation in MYRRHA

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Corrosion-related issues

- **Materials**
  - Thinning of the material cross-section
  - Altered near-surface material properties
  - Impaired properties of functional surfaces
  - Overall change of geometric dimensions, e.g., material plus solid corrosion scale

- **Corrosive medium**
  - Depletion in corrosive agents
  - Contamination with corrosion products
  - Contaminant diffusion and convective transport
  - Subsequent chemical reactions
  - Re-precipitation of absorbed elements
  - Deposition of solid matter

- **Plant operation**
  - Reduced efficiency of plant components
  - Risk of premature material failure
  - Short- and long-range secondary effects, e.g., plugging of narrow sections
  - Contribution to the emission of pollutants
MYRRHA reactor: Process medium and materials

- **Process medium**
  - Lead-bismuth eutectic (LBE)
  - Addition of oxygen so as to favour oxidation over solution of material elements
  - Oxygen activity or concentration required is material- and temperature-dependent

- **Materials**
  - Austenitic steels:
    - 316L for the main structural components,
    - 15-15Ti in the core
  - 9Cr ferritic/martensitic steels:
    - T91 for parts of the core support and spallation target assembly

Under MYRRHA-relevant conditions, the same steel may show different corrosion modes in oxygen-containing LBE!
Objectives and approaches

- **Estimation of corrosion product formation in respect of**
  - Solution of steel elements by the LBE
  - Oxygen consumption, i.e., depletion if oxygen is not replaced
  - Uptake/precipitation of solid oxides

- **Work performed**
  - Analysis of availability of required corrosion data: mechanisms, rate laws, activation energies, incubation times, surface area affected by local processes
  - Simplified spread sheet calculations for design operating conditions of MYRRHA, separately for the corrosion modes to be considered
  - Specific calculations for reactor start-up and first power cycles

Available data is incomplete, requiring a number of assumptions and simplifications!
### MYRRHA design data used

#### Design operating parameters

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Surface area (m²)</th>
<th>Oxygen conc. (mass%)</th>
<th>Average flow velocity (m/s)</th>
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#### Duration (days) | Temperature (°C)

**Start-up** | 180 | 270°C

**1st Power cycle** | 90 | Components at design operating temperature; temperature transients

**Downtime** | 90 | 270°C

**2nd Power cycle** | 90 | As above

**Early operating stages**

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Oxidation of 9Cr ferritic/martensitic and austenitic steels in oxygen-containing LBE

- **Protective scaling**
  - Thin Cr- (Si-) rich oxide scale (thickness ~1 µm or less)
  - Precursors of this scale are likely to be present already on the original material
  - Local degradation gives way to faster corrosion processes
  - Dominant oxidation process for Type 316 steels and 15-15Ti, especially at $T \leq 450^\circ\text{C}$ and $c_O \leq 10^{-6}$ mass%
  - Release of steel elements is likely to be negligible
  - Oxygen consumption mainly confined to the initial formation of this scale
Oxidation of 9Cr ferritic/martensitic and austenitic steels in oxygen-containing LBE

- **Accelerated oxidation**
  - Typical for and, finally, the general corrosion process of 9Cr steels, after failure of the thin Cr-rich scale
  - Less frequent occurrence on austenitic steels, especially at T ≤ 450°C and c_O ≤ 10^{-6} mass%
  - Comparatively thick scales generally consisting of Fe_3O_4, Fe(Fe_xCr_{1-x})_2O_4 and an internal oxidation zone
  - Release of Fe to the LBE at the oxide scale surface
  - Oxygen consumption due to continuous growth of oxides
Solution-based corrosion in oxygen-containing LBE

- **Type 316 steels, 15-15Ti**
  - Selective leaching of Ni and Cr
  - Formation of a ferritic depletion zone that is penetrated by the liquid metal
  - Occasionally oxide (precipitated) on the surface, but transfer of removed elements to the LBE dominates
  - Starts locally from failure of the thin Cr-scale

- **9Cr ferritic/martensitic steel**
  - Probably starts from penetration of LBE into the oxide scale formed during accelerated oxidation
  - Steel elements may be selectively (Cr) or generally removed, depending on local conditions
  - Predominance of steel element release over accumulation in oxides not always clear
Quantitative results from experiments in the CORRIDA loop: T91 in LBE at 450–550°C, 2 m/s and 10⁻⁶% dissolved oxygen

- **Accelerated oxidation**
  - Thickness of magnetite approximates the overall increase in specimen radius
  - Dissolved Fe from balancing the mass consumed and present in oxides
  - Extrapolation of data naturally depends strongly on the type of rate law assumed

- **Solution-based corrosion**
  - Significantly increased material loss
  - Comparatively small database for kinetic analysis
  - Underlying corrosion mechanisms may differ for the particular data points
Quantitative results from experiments in the CORRIDA loop: Type 316 in LBE at 450–550°C, 2 m/s and 10⁻⁶% dissolved oxygen

- **Accelerated oxidation**
  - Observed locally at 550°C
  - In parts continuous scale after long exposure time
  - Not observed at 450°C

- **Solution-based corrosion**
  - Only few sites on investigated specimens may be affected
  - Mostly selective leaching of Ni and Cr
  - But also general dissolution of all steel elements at 450°C
  - Incubation time decreases from around 5000 h at 450°C to 1000 h at 550°C
Estimation of steel element transfer

- **Procedure:**
  - Calculate material- and area-specific transfer of metals at relevant temperatures after given time
  - Multiply by associated surface area in the reactor

- **Protective scaling**
  - Neglected

- **Accelerated oxidation**
  - Neglected for 316L and 15-15Ti
  - T91:
    - Only release of Fe into the LBE considered
    - Mass of Fe in consumed steel (ST) balanced with mass of Fe accumulated in Fe(Fe\text{a},Cr_{1-x})_2O_4 (SP) and Fe_3O_4 (M)
    - Parabolic rate laws of steel recession and scale thicknesses as observed in flowing LBE at 450°C, 10^{-6} mass% O and 2 m/s:
      - \( k_{2,ST} = 0.023 \) \( k_{2,SP} = 0.013 \) \( k_{2,M} = 0.025 \) \( \mu m^2/h \)
    - Activation energy 160 kJ/mol considered for start-up, downtime or transient temperature during power cycle

- **Solution-based corrosion**
  - Not considered for T91 due to the lack of appropriate mechanism and kinetic data (not justified at low oxygen concentration?)
  - Selective leaching of 316L, 15-15Ti:
    - Linear kinetics in terms of maximum depth of attack as observed for 316L at 500°C, <10^{-8} mass% O, static LBE; \( k_1 = 0.017 \mu m/h \) (Yamaki et al., 2011)
    - Activation energy 75 kJ/mol (Yamaki et al., 2011)
    - Complete solution of Ni, 50 and 10% of available Cr and Fe, resp.
Results on transferred mass of steel elements

- **Regular operation starting at t=0**
  - Remarkable influence of Fe release due to accelerated oxidation of T91 components confined to the first 10 h
  - Average transfer rates in the order of 1–2 g/h for each Fe, Cr and Ni

- **Start-up operation and first two power cycles**
  - Transfer of 0.2–0.4 g/h of each Fe, Cr, and Ni during start-up at 270°C
  - Fe release due to accelerated oxidation of T91 components negligible for power cycles and intermittent downtime at 270°C
  - Power cycle: 1–2 g/h of each Fe, Cr and Ni released into the LBE from austenitic steels
Estimation of oxygen consumption

- **Procedure:**
  - Calculate material- and area-specific oxygen consumption at relevant temperatures after given time
  - Multiply by associated surface area in the reactor

- **Protective scaling**
  - All steels/component surfaces initially form a thin chromia (Cr$_2$O$_3$) scale
  - An equivalent mass of 0.5 µm scale thickness has to form, irrespective of the actual operating temperature
  - Instantaneously – in 1 h – 10 h – 100 h …

- **Accelerated oxidation of T91**
  - Formation of adherent Fe($x$Cr$_{1-x}$)$_2$O$_4$ and Fe$_3$O$_4$ (M) under design operating conditions
  - Same assumptions in regard of the oxidation process as for steel element transfer

- **From solved steel elements**
  - Steel elements released into the LBE may oxidise somewhere in the reactor

Initial demand for oxygen replacement

After typical corrosion processes have established
Results on oxygen consumption for design operating conditions

- **Protective scaling**
  - 3.2 kg of oxygen being consumed when formation of 0.5 µm thick scale is assumed.
  - Corresponds to 43.5 kg or 2.2 Ncm³ of PbO and gaseous O₂, respectively.
  - 3.2–32 g/h average rate of oxygen consumption if the scales form in 10–100 h.
  - Initial oxygen concentration in LBE may be higher than required, i.e., only partial replacement of consumed oxygen needed.

- **Subsequent corrosion processes**
  - Solid oxides on T91 surfaces initially contribute by 50% to the overall oxygen consumption.
  - Oxidation of previously solved steel elements dominates oxygen consumption in the long run.
  - Oxygen consumption rate averages 2–3 g/h.
Amount of formed oxides

- **Design operating conditions**
  - Estimation without protective scaling
  - Qualitative same results as for oxygen consumption in regard of accelerated oxidation (T91) and transformation of solved elements
  - Average formation rate in the order of 1–2 cm³/h
  - Oxides formed on steel surfaces are immobile as long as they do not detach

- **Start-up operation and first power cycles**
  - Average 1.25 cm³/h oxide formation estimated for the first power cycle
  - Associated oxygen consumption of 1.8 g/h
Summary and conclusions

- **In regard of the method of estimating corrosion products**
  - Simplified procedure
  - Gives estimates of the order of magnitude
  - Overall conservative, because most detrimental corrosion was assumed especially for austenitic steels (selective leaching)
  - More sophisticated estimating procedures useful only after existing gaps in the available quantitative corrosion data were closed

- **Implications for “chemistry control”**
  - 2–3 g/h oxygen needs to be replaced using an oxygen-transfer device, possibly except for the very initial stage (for protective scaling of steels)
  - Initially higher than required oxygen concentration in the LBE may partially compensate for increased consumption (up to 30 g/h?)
  - 1–2 cm³/h of produced solid oxides are to be removed by filters or other
  - Oxide particle size and distribution not yet investigated in detail
Thank you for your attention!