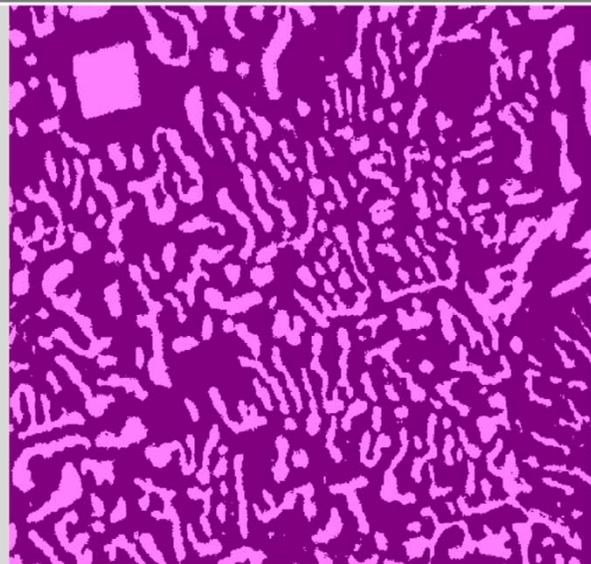


THE ROLE OF DISSOLVED OXYGEN IN CORROSION CAUSED BY LIQUID METALS

Carsten Schroer

INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM-AWP)

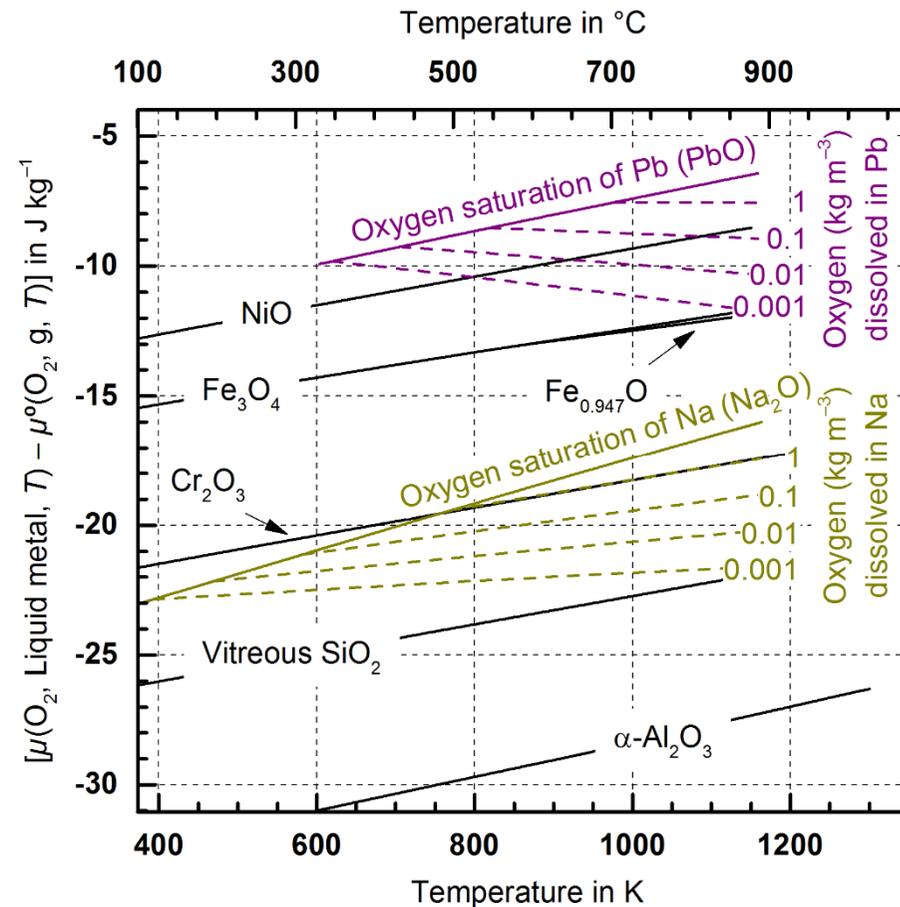


- ❑ **Protective surface scale/ passivation**
 - ❑ Most favorable effect of oxygen on the corrosion resistance of metallic materials, notably steels and Ni-based alloys
 - ❑ A minimum of oxygen must be available so that solid oxides of material elements are stable
 - ❑ These oxides must form a continuous scale on the material surface (type of oxide, concentration of the oxide-forming element)
 - ❑ The scale itself must remain free from defects in the particular environment
 - ❑ Exceptionally protective oxides are Cr_2O_3 , SiO_2 and Al_2O_3 , however also Fe or Ni oxide usually plays a vital role in the formation mechanism of the scale

Possible to take advantage of protective surface oxides in the case of the liquid-metal coolants proposed for advanced nuclear reactors?

- ❑ **Liquid metals with low affinity to oxygen**
 such as lead (Pb) or lead-bismuth eutectic (LBE)
 - ❑ Chemically more noble than the elements in typical steels or Ni-based alloys
 - ❑ Oxygen chemical potential reached before the liquid metal is saturated with oxygen may be sufficient for the formation of solid binary oxides of Ni, Fe, Cr, Si, Al ...

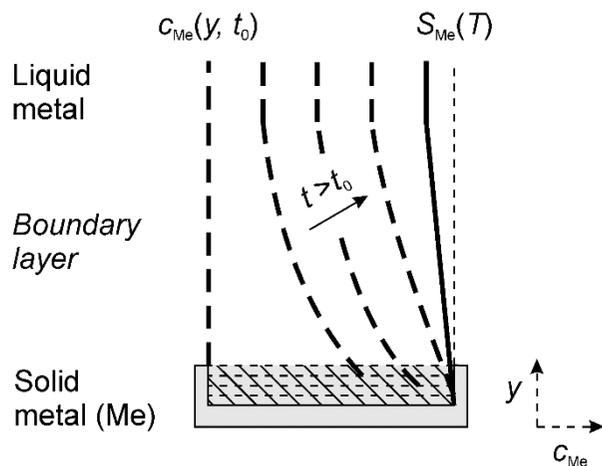
- ❑ **Liquid metals with high affinity to oxygen**
 such as sodium (Na)
 - ❑ Fairly high amount of oxygen (kg/m^{-3}) may generally be available, but with only low chemical potential
 - ❑ Thresholds for the formation of solid binary oxides of the base elements in steels and Ni alloys cannot be passed
 - ❑ Acceleration of corrosion due to ternary oxides formed from constituents of the metallic material and liquid metal, notably in the case of liquid Na



Sources of thermochemical data:
 Pankratz, *Thermodynamic properties of elements and oxides*, 1982; Noden, *J. Brit. Nucl. Ener. Soc.*, 1973 (oxygen solubility in Na); Ganesan et al., *J. Nucl. Mater.*, 2006 (oxygen solubility in Pb).

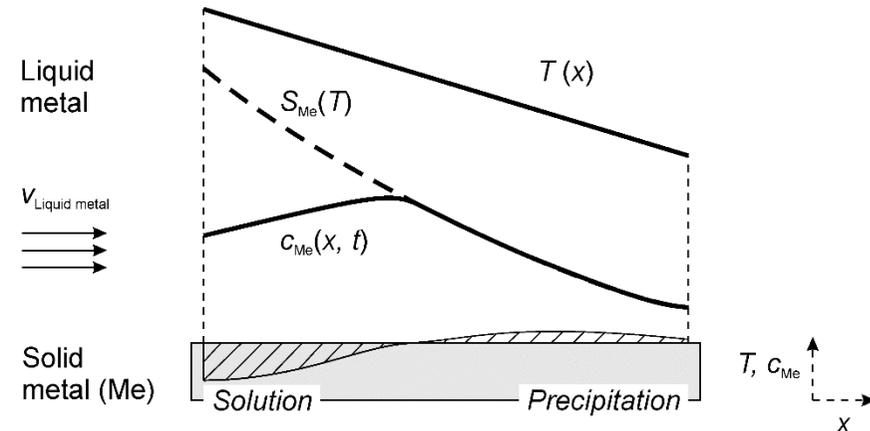
Typical corrosion modes

- ❑ Solution of material elements in the liquid metal
- ❑ Formation of intermetallic phases
- ❑ Degradation of mechanical properties of metallic materials, e.g. liquid metal embrittlement



Isothermal (temperature $T = \text{const.}$)

- ❑ Solution is limited by the solubility $S_{\text{Me}}(T)$
- ❑ Solution rate decreases as saturation with the dissolved material elements is approached



Non-isothermal system

- ❑ Solution changes into re-deposition of material elements where the local solubility $S_{\text{Me}}(T)$ would be passed otherwise
- ❑ Particularly noticeable in combination with convection of the liquid metal in the direction of decreasing temperature
- ❑ Counteracts saturation of the liquid metal in a loop-type system
- ❑ Especially pronounced for liquid metals with high capacity of solving other metals, e.g. LBE
- ❑ Risk of plugging of narrow paths of the liquid metal in the cold leg of the system

- **Minor/ no influence of oxygen on solution if solid oxides of material elements are not stable**

- Enrichment of the metal Me in the liquid metal is still limited only by the **solubility** $S_{\text{Me}}(T)$

- **If solid oxides of material elements are stable, e.g. binary $\text{Me}_{\nu_{\text{Me}}}\text{O}_{\nu_{\text{O}}}$:**

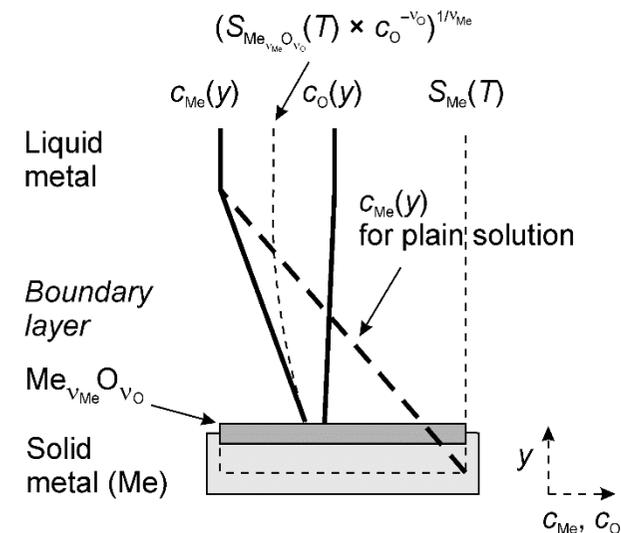
- Enrichment of Me in the liquid metal is governed by the temperature-dependent **solubility product**
 $S_{\text{Me}_{\nu_{\text{Me}}}\text{O}_{\nu_{\text{O}}}}(T) = c_{\text{Me}}^{\nu_{\text{Me}}} \times c_{\text{O}}^{\nu_{\text{O}}}$
- c_{Me} in equilibrium with solid $\text{Me}_{\nu_{\text{Me}}}\text{O}_{\nu_{\text{O}}}$ is a function of the (local) c_{O} and decreases with increasing c_{O}
- Re-deposition of dissolved Me at decreasing temperature generally occurs in the form of oxide
- Applies analogously to ternary oxides, including those formed with constituents of the liquid metal

Generally similar for corrosion caused by liquid metals, aqueous media, certain salt melts or other liquids that may contain oxygen!

Beneficial effect of solid oxide formation

Continuous oxide scale

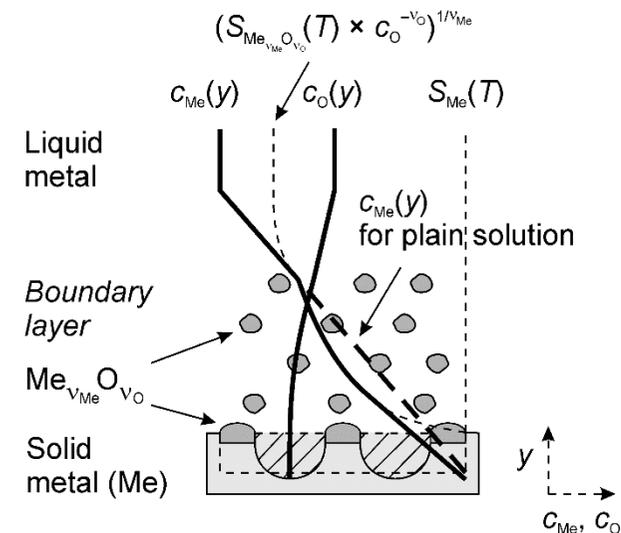
- Acts as a diffusion barrier for further solution of the metal Me
- High oxygen concentration at the scale surface if the oxide grows only slowly
- Enrichment of Me in the liquid metal at the interface with the scale is comparatively slight, the gradient of c_{Me} between oxide surface and liquid metal volume respectively shallow
- Most favorable situation as to minimum material consumption and minimum accumulation of Me in the liquid metal
- But: Solution is unlikely to be zero as long as a gradient of c_{Me} exists!



Adverse effect of solid oxide formation

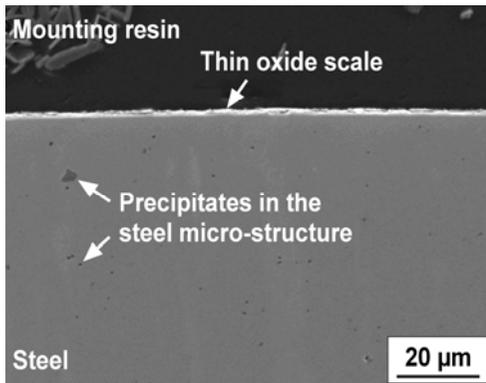
❑ Discontinuous surface oxide

- ❑ Material locally remains prone to solution
- ❑ Oxide precipitation where dissolved Me meets sufficiently high c_O
- ❑ Resulting oxygen depletion increases the possible enrichment of Me in the liquid metal, promoting solution and subsequent oxide precipitation
- ❑ Gradient of c_{Me} at the material surface may be steeper than for plain solution, i.e. solution may locally be faster than in the absence of oxygen
- ❑ Formed oxides are generally prone to solution at the material surface and transition to the bulk of the liquid metal
- ❑ Also applies to local failure of a once continuous oxide scale

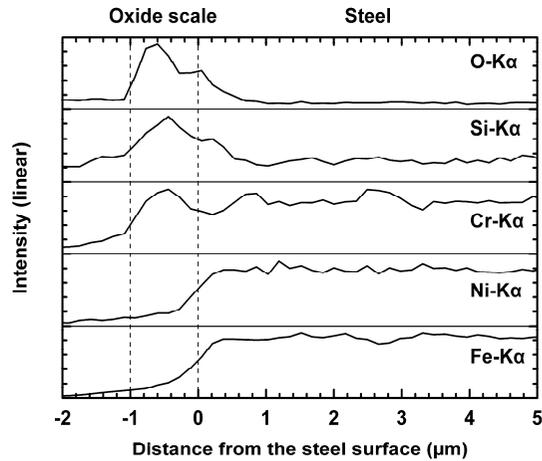


Examples from exposure to oxygen-containing LBE

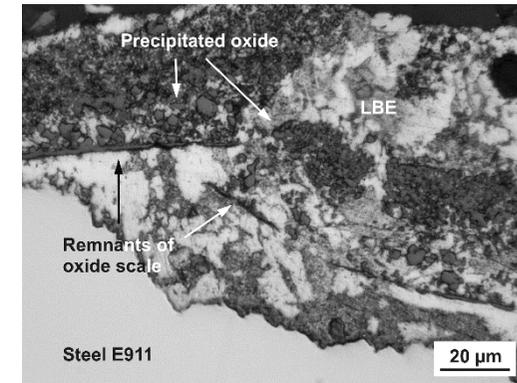
Scaling



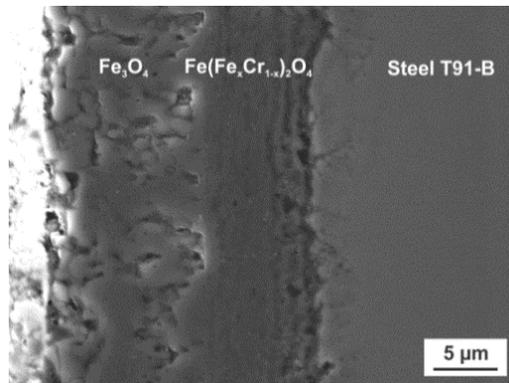
Austenitic steel 1.4571
450°C / 10⁻⁶ % O / 2 m/s



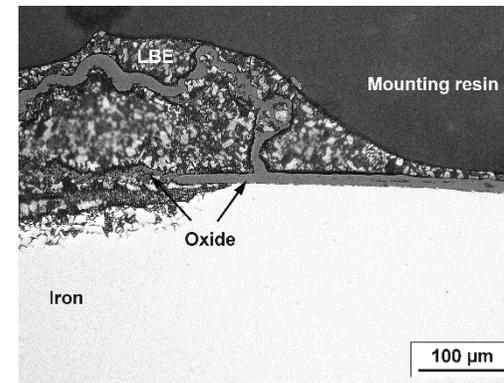
Solution/ precipitation of solid oxide



450°C / 10⁻⁶ % O / 2 m/s

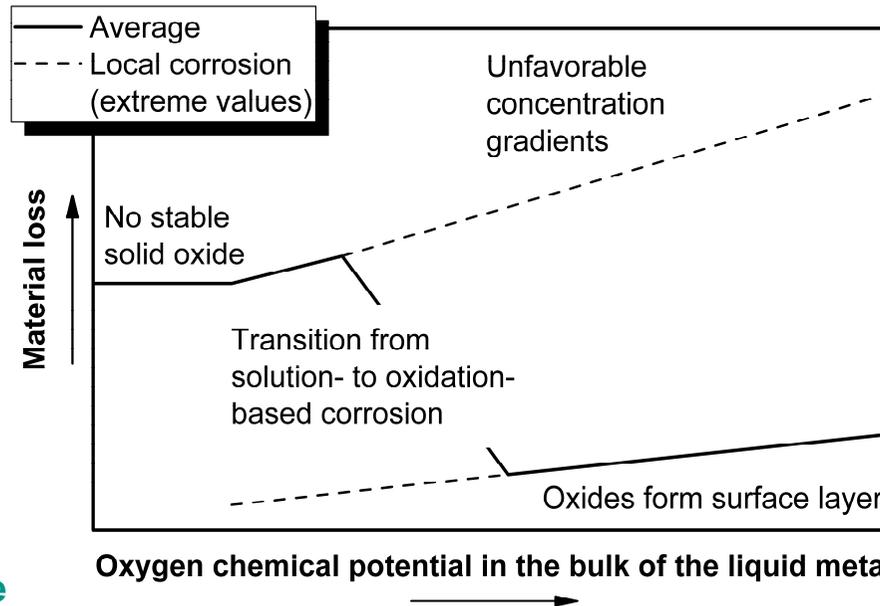


450°C / 10⁻⁶ % O / 2 m/s



450°C / 10⁻⁶ % O / 2 m/s

Impact of oxygen on the loss of material



Oxygen saturation of the liquid metal will occur ...

❑ **Before the change in general corrosion mode**

- ❑ More favorable performance (maximum of corrosion) anticipated for low oxygen concentration in the bulk of the liquid metal
- ❑ Avoid oxygen as much as possible

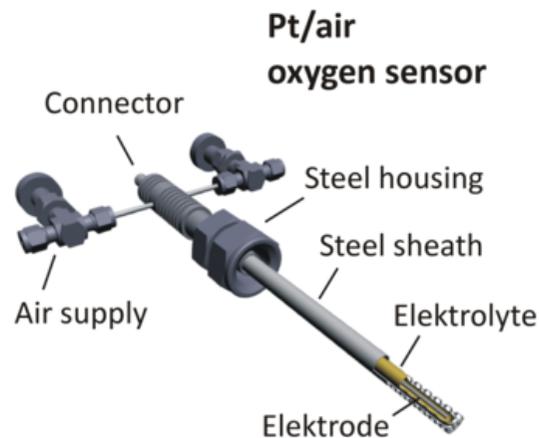
❑ **After this change**

- ❑ Minimum of corrosion anticipated for oxygen concentrations clearly in the domain of scaling (but lower than saturation)
- ❑ Risk of enhanced solution after local failure of the scale

Measurement of oxygen in liquid metals

❑ Chemical analysis

- ❑ Proper sampling required
- ❑ Sampling may be automated
- ❑ Actual analysis for oxygen hardly feasible outside a dedicated laboratory



❑ Plugging meter

- ❑ A certain volume of liquid metal is guided through the instrument
- ❑ Temperature at which plugging occurs is registered
- ❑ The saturation concentration at this temperature is the sought oxygen concentration
- ❑ Automated periodical or continuous (“partially blocked orifice”) measurement

❑ Electrochemical oxygen sensors

- ❑ Transforms oxygen chemical potential into electric voltage
- ❑ Concentration calculates from this voltage and the saturation concentration at the measuring temperature
- ❑ Continuous on-line measurement
- ❑ Proper selection of the solid electrolyte depends on the liquid metal, zirconia-(Pb, LBE) or thoria-based (Na)
- ❑ Thermo-mechanical performance of the electrolyte and joining with the sensor housing are prominent issues

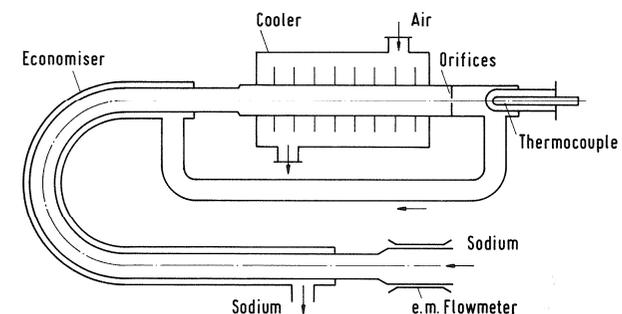
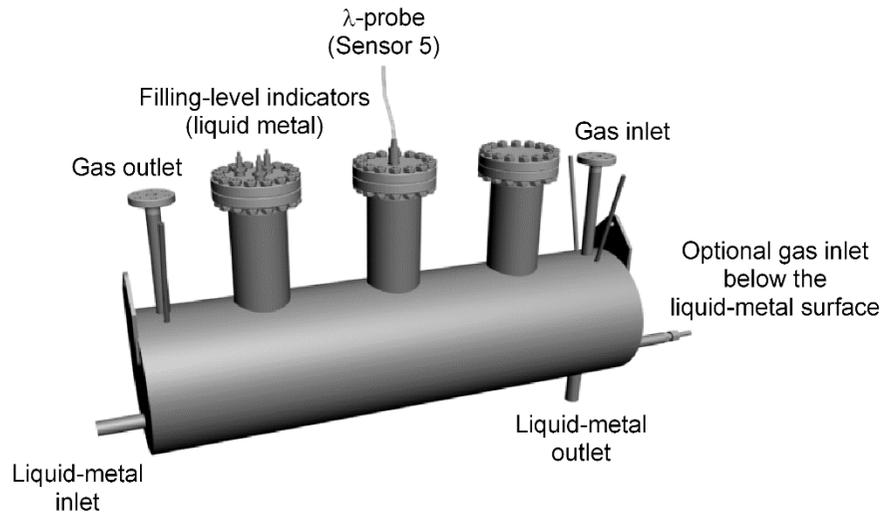
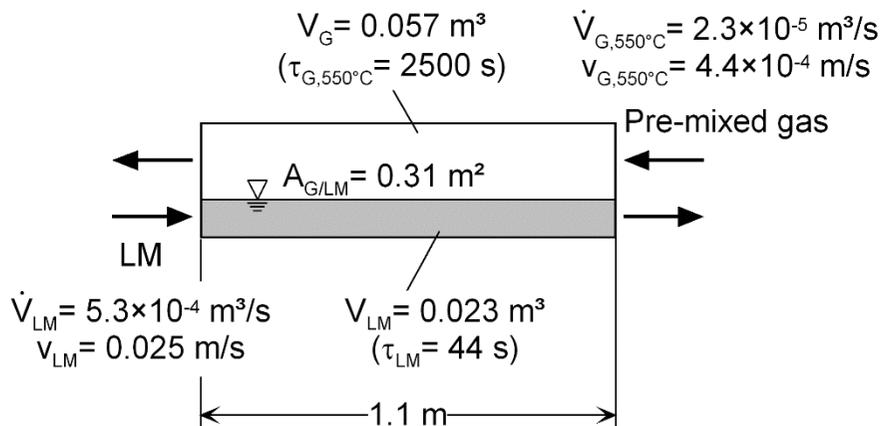


Figure taken from Borgstedt and Mathews, *Applied chemistry of the alkali metals*, 1987.

Oxygen mass transfer to/ from liquid metals



Oxygen mass transfer device of the CORRIDA loop and some basic operating parameters for flowing LBE at 550 °C



Gas/ liquid oxygen transfer

- ❑ Air (O₂) or water (H₂O) serve as a source of oxygen in the gas phase
- ❑ H₂ acts as a gaseous sink for oxygen removal from the liquid metal
- ❑ Variation of O₂ (H₂O) and H₂ content of the gas introduced into the device in accordance to the actual demand for adding or removing oxygen from the liquid metal
- ❑ Continuous and automated process
- ❑ So far, oxidation of the liquid-metal surface has not turned out to be a prominent issue in practical applications (Pb, LBE)
- ❑ Routinely applied to laboratory experiments with liquid Pb or LBE
- ❑ Risk of transfer of activated elements into the gas when applied to the nuclear reactor (safety issue)

Alternative methods of oxygen addition or removal

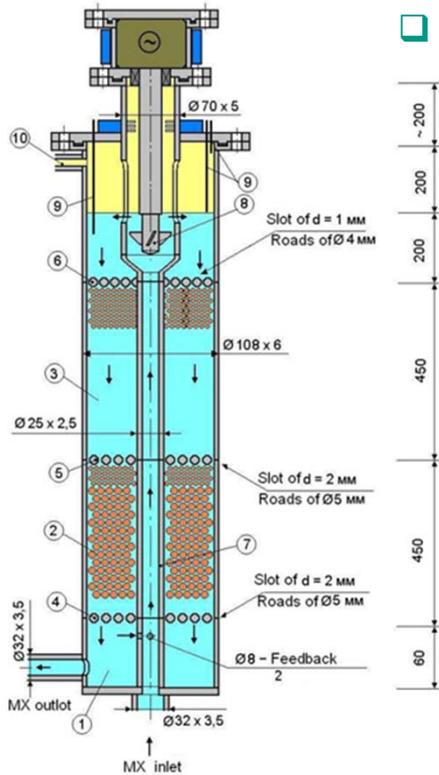


Figure taken from Askhadullin, *Development of oxygen sensors, systems of control of oxygen content in lead coolants for test loops and facilities*, 2007.

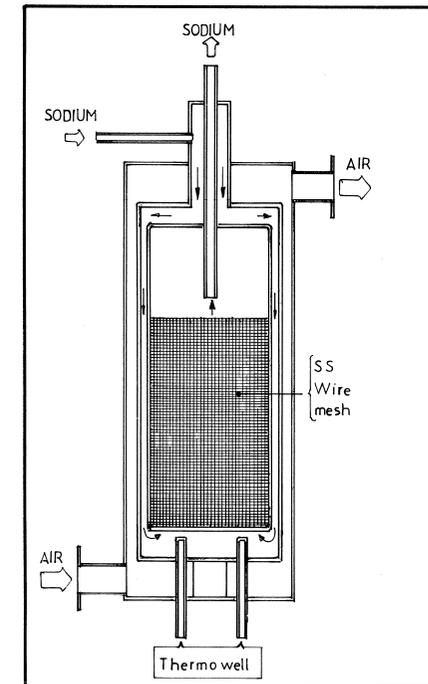
❑ Solid/ liquid oxygen transfer

- ❑ Typically designed for oxygen addition only
- ❑ Solid PbO serves as an oxygen source for Pb or LBE
- ❑ Poisoning of the provided oxide particles must be avoided

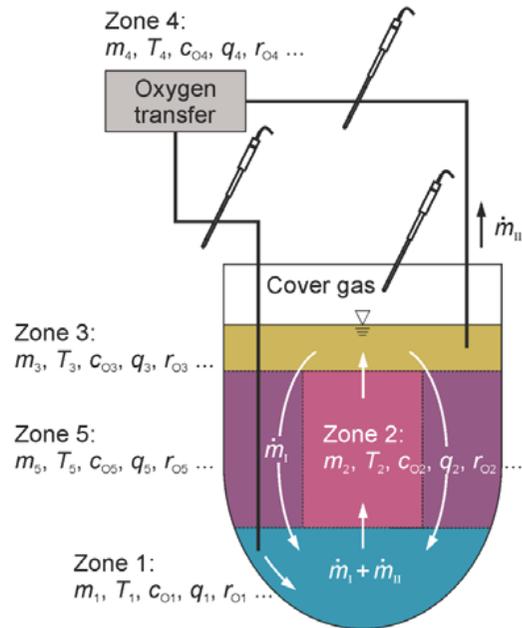
❑ Cold trap

- ❑ Oxygen removal (from liquid Na)
- ❑ Solid oxide (Na_2O) precipitates as the temperature of the flowing liquid metal decreases

Figure taken from Borgstedt and Mathews, *Applied chemistry of the alkali metals*, 1987.



- ❑ Batch-type devices that generally need regeneration after some time of operation
- ❑ Combination of oxygen addition from a solid source and removal by decreasing the temperature is theoretically possible in a single device



❑ Sodium-cooled

- ❑ In order to maintain a constantly low oxygen chemical potential, the lower the better in respect of corrosion
- ❑ Oxygen leaking into the reactor very likely predominates over oxygen consumption
- ❑ Continuous oxygen removal via the oxygen transfer device (cold trap)

❑ Lead-cooled (Pb, LBE)

- ❑ Same as for sodium-cooled, in combination with materials* of low solubility in the liquid metal (especially Pb)

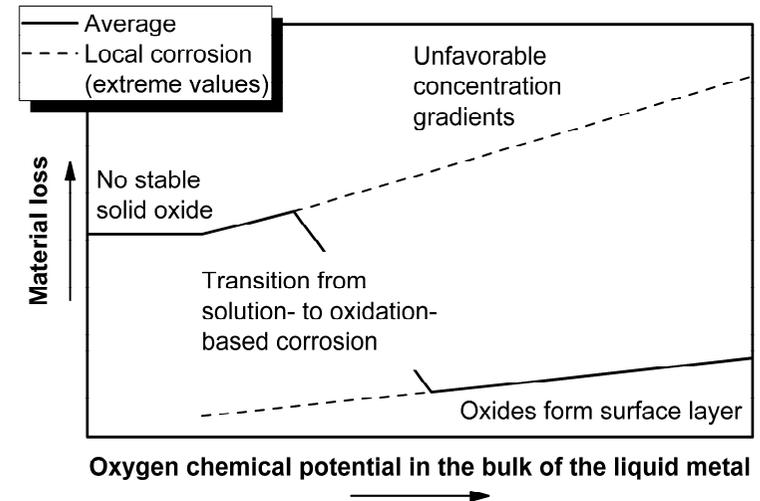
- ❑ Oxygen chemical potential sufficient to avoid solution-based corrosion along with materials* with favorable oxidation performance
- ❑ Time-dependent oxygen consumption may be clearly larger than or in the same order of magnitude of oxygen leakage into the reactor
- ❑ Provisions for both oxygen addition and removal have to be made

* Or respective coatings

Conclusions

❑ Feasibility of forming oxide layers that minimise solution of material elements

- ❑ Naturally depends on the specific pair of (metallic) material and liquid metal
- ❑ High amount of dissolved oxygen in the liquid metal (solubility) at low oxygen chemical potential is detrimental
- ❑ In general, risk of enhanced solution where oxide scale locally fails



❑ Goal of oxygen control

- ❑ Depends on the affinity to oxygen of the liquid metal in question, with saturation of the liquid metal being the natural limit of oxygen addition
- ❑ As low as possible oxygen content if protective scaling cannot be achieved
- ❑ Otherwise, optimised oxygen content at which a protective oxide layer forms and the probability of local failure of this scale is adequately low

Acknowledgements

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Thank you for your attention!