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Consequences of humid Refractory in Vacuum Metallurgy



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1. Introduction

- Humidity in the vessel of a vacuum induction furnace is dangerous, affects the cleanliness of the alloy and corrodes the lining. Therefore the drying of the lining has to be conducted very carefully. This paper adds the basic principles for a better understanding of the Consequences of humid Refractory in Vacuum Metallurgy.

2. Level of Cleanliness

Water steam downgrades the cleanliness of the melt because the assimilated oxygen forms oxides:

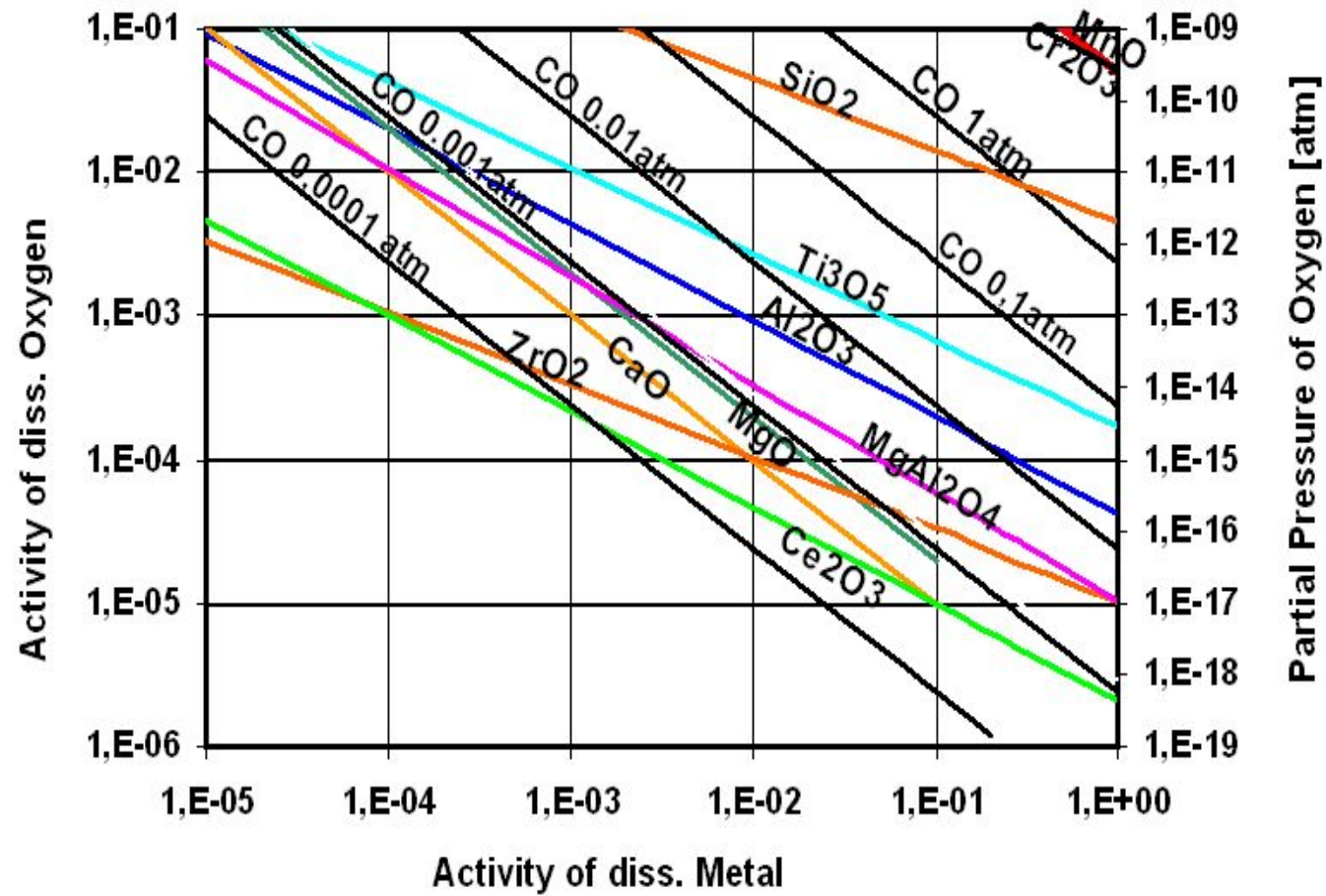
$$\frac{1}{2}O_2 = [O], \Delta G^0 = -137118 + 7,79 \cdot T [J / FU]$$

$$\ln K = -\Delta G^0 / R \cdot T \quad \text{at } 1600^\circ\text{C} :$$

$$K_{[O]} = 2,62 \cdot 10^{+3} \quad P_{O_2} = 1,54 \cdot 10^{-7} \cdot [O]^2 [atm].$$

The deoxidation products show lower values

Equilibrium of Deoxidation of Iron at 1600°C



3. Humidity in the Lining

3.1 Steam Explosion

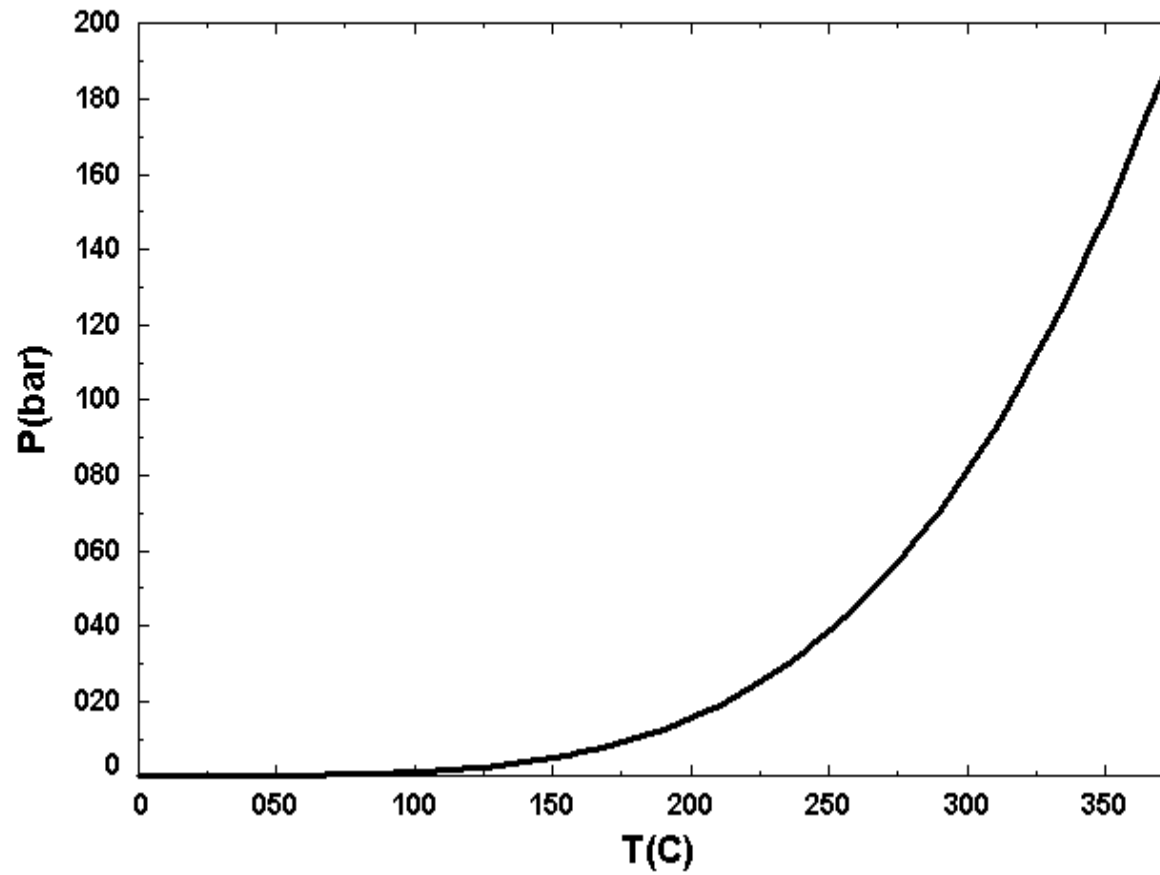


Damage of a Brick by steam explosion / pers. memo. D. Lenzner (2012)

Drying of Refractory

Real Vapour Pressure of Liquid Water

0 - 375°C



3. Humidity in the Lining

3.1 Steam Explosion

18g water at room temperature is evaporated and heated up to 1500°C

$$V = \frac{m_{H_2O}(g)}{M_{H_2O} \cdot T} \cdot 22.400 \cdot T(K) = \frac{18 \cdot 22.400 \cdot 1800}{18 \cdot 300} = 134 \text{ l.}$$

Example: A brick explodes and flies 2,5m until it drops down.

$$P \cdot V = \frac{m}{2} \cdot u^2, \quad u_h = \sqrt{2g \cdot h} \quad \xrightarrow{t = t_h} P \cdot V = \frac{m \cdot g \cdot x^2}{h} [Pa \cdot m^3]$$

$$m = 100\text{kg}, x = 2,5\text{m}, h = 2\text{m}$$

The pressure of the steam depends on the temperature:

$$P[Pa \equiv Kg / ms^2] = 5 \cdot 10^{10} \cdot \exp\left(-\frac{2250}{0.460 \cdot (T_{\circ C} + 273)}\right)$$

The volume of steam which is necessary to bring up the required energy is

$$V = \frac{100kg \cdot 9,81m / s^2 \cdot (2,5m)^2}{3,228 \cdot 10^6 kg / ms^2 \cdot 2m} = 1,9 \cdot 10^{-3} m^3 = 1,9L$$

The amount of liquid water in the refractory at room temperature (300K) is

$$m_{H_2O} = \frac{V \cdot M_{H_2O} \cdot T_{KR}}{22,4 \cdot T_K} = \frac{1,9L \cdot 18g / mol \cdot 300K}{22,4L / mol \cdot 473K} = 1g$$

This is a humidity of 0,001%. → Reason: pushing of liquid by steam

3.2 Hydrogen in Aluminium

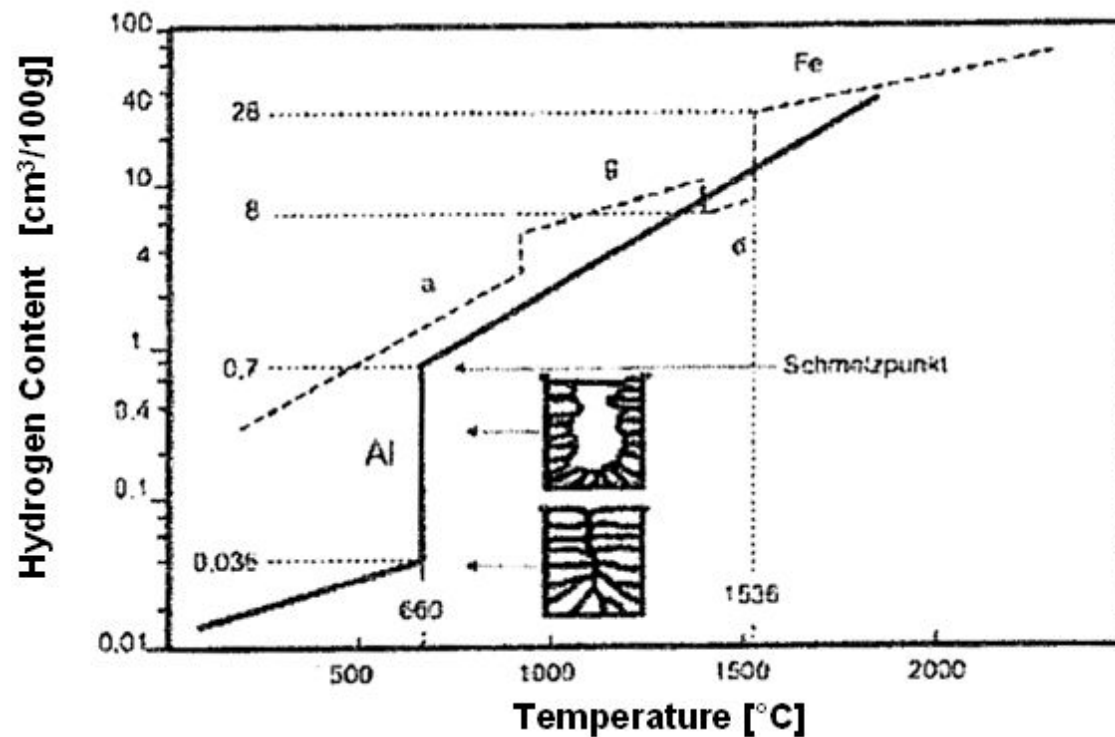
- The melt starts to boil, because at 800 °C only 2cm³/100g hydrogen are soluble in liquid Aluminium
- Boiling starts seriously during solidification, because then the solubility drops rapidly down to 0,04 cm³/100 g.
- The solidified metal contains a lot of blow holes, because the gas cannot escape quantitatively from the interdendritic area of the cast.
- Last, not least skins of Al₂O₃ are formed and may be spoiled into the cast resulting in inclusions.

Formation of hydrogen

Dissolution of hydrogen in aluminium (and Iron)

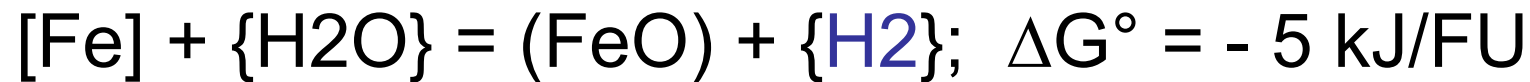
800°C: $3\text{H}_2\text{O} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{H}_2$. $\Delta G^\circ = -1.1 \cdot 10^6 \text{ J}$.

In connection with oxygen gas an **oxyhydrogen explosion** may result



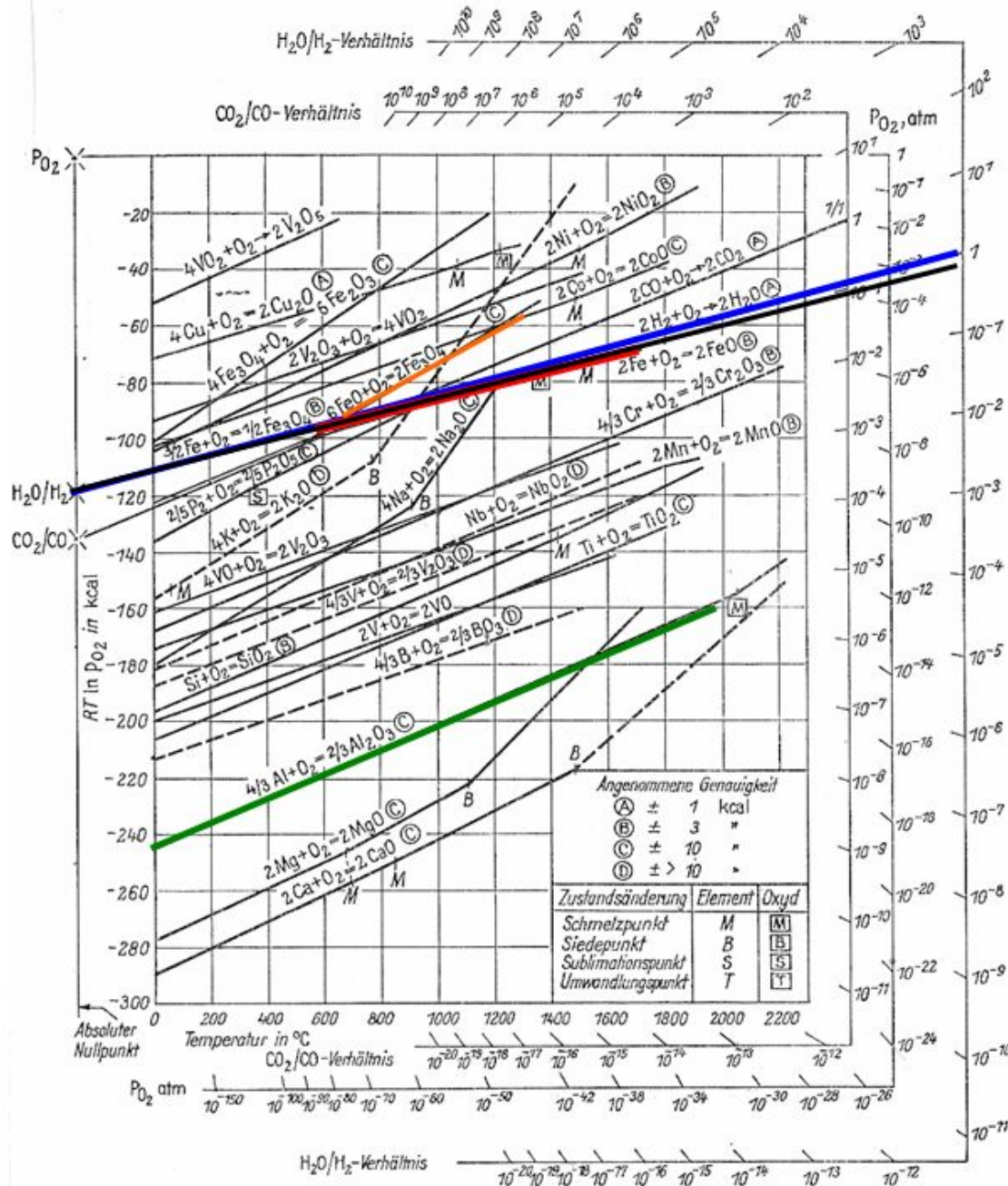
Dissolution of hydrogen in iron

at 1600 °C



$\text{H}_2/\text{H}_2\text{O} \approx 1$ (Richardson – Diagram)

In connection with oxygen gas an
oxyhydrogen explosion may result.

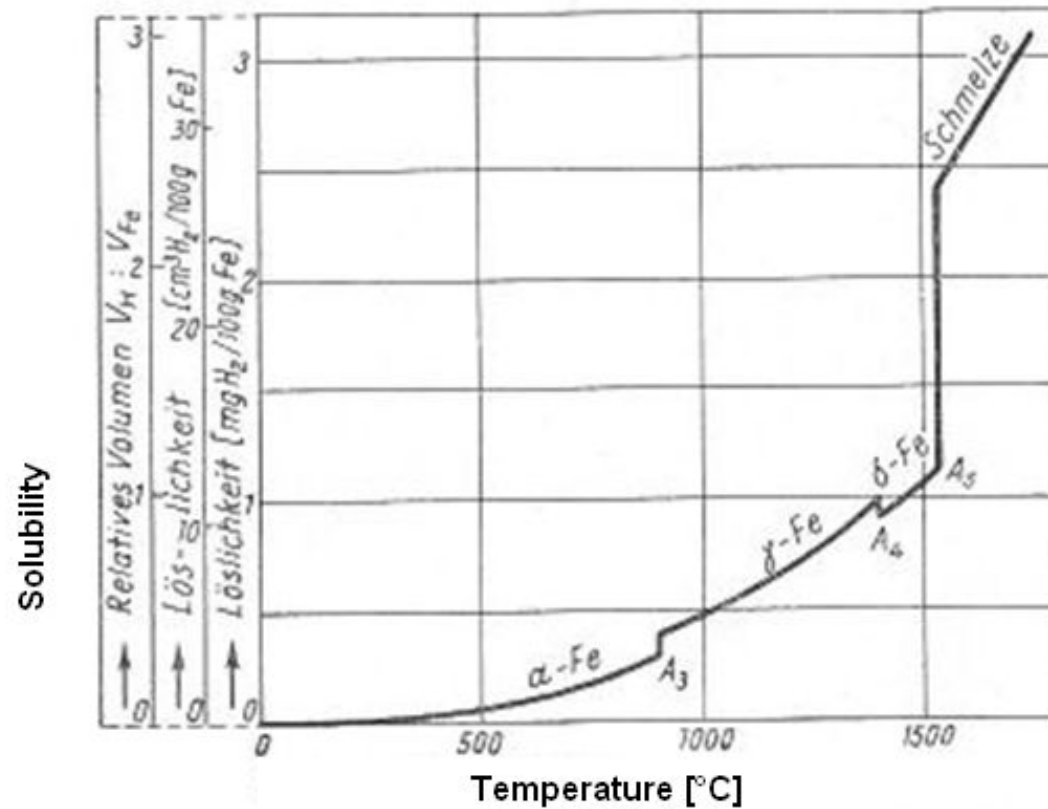


Richardson –
Ellingham – Diagram /3/

Hydrogen in iron:

The steam is partially reduced forming H_2 and liquid FeO (Comparison with the Richardson-Ellingham Diagram [3, 4] shows, that $H_2/H_2O \approx 1$). In connection with oxygen gas an **oxyhydrogen explosion** may result. Steam explosion can occur as well. All the other effects described for aluminium may occur as well. In addition the well known **hydrogen-brittleness** may occur. If, at about $100\text{ }^{\circ}\text{C}$, the atomic dissolved hydrogen forms molecular hydrogen, the structure may burst due to the high pressure of formation.

Hydrogen in iron



hydrogen-brittleness may occur: $2[H] \rightarrow \{H_2\}$

3.3 Formation of Brucite:

MgO materials, which comes in contact with moisture becomes decomposed, because brucite is formed.



$$K_{\text{H}_2\text{O}} = 1/P_{\text{H}_2\text{O}} = 1,57 \cdot 10^6, \text{ d.h. } P_{\text{H}_2\text{O}} = 6,37 \cdot 10^{-7} \text{ atm.}$$

$$P_{\text{H}_2\text{O}}, RT \equiv P_0 = 0,0354 \text{ atm} \quad (V_{\text{Mg}(\text{OH})_2} - V_{\text{MgO}}) = 13,3 \text{ cm}^3/\text{mol}$$

$$\Delta G = \Delta G^\circ + R_1 T \cdot \ln K_{eq} + (1 - \pi) \cdot \Delta V_C = 0$$

Gibbs Energy: standard + relative (gas) + relative (graphite)

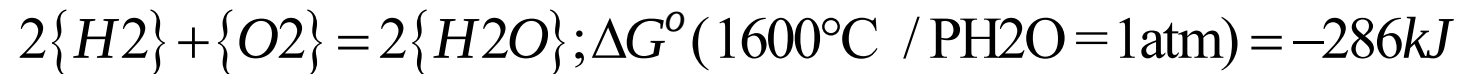
$$\pi - 1 = \frac{R_1 \cdot T \cdot \ln P_0 / P_{\text{H}_2\text{O}}}{(V_{\text{Mg}(\text{OH})_2} - V_{\text{MgO}}) \cdot R_1 / R_2} = \frac{8,3 \cdot 300 \cdot \ln(0,035 / 6,4 \cdot 10^{-7})}{13,3 \cdot 0,1} = 20 \cdot 10^3 [\text{atm}]$$

$$R_1 = 8.31 \text{ J/mol} \cdot \text{K}, R_2 = 84.8 \text{ atm} \cdot \text{ccm/mol} \cdot \text{K}$$

4. Infiltration

Is infiltration facilitated by water steam?

(Capillary forces + electromagnetic forces are acting)



It results $P_{O_2} = 10^{-8}\text{atm}$.

Oxygen content of liquid iron? The partial pressure of water at 25° is $P_{H_2O} = 0,035\text{atm}$. From this the partial pressure of oxygen in the atmosphere at $1600^{\circ}C$ results as

$$\begin{aligned}\Delta G_P^{\circ} &= \Delta G^{\circ} + RT \cdot 2 \cdot \ln 0,035 \\ &= -286000 + (8,31 \cdot 1873 \cdot 2 \cdot (-3,35)) \\ &= -390\text{kJ}\end{aligned}$$

Equilibrium constant

$$K_{H_2O} = \frac{P_{H_2O}^2}{P_{H_2}^2 \cdot P_{O_2}} = \frac{1}{1} \cdot \frac{1}{P_{O_2}} = \exp\left(-\frac{-390356}{8,31 \cdot 1873}\right) = 7,8 \cdot 10^{10};$$

$$P_{O_2} = 1,3 \cdot 10^{-11} atm.$$

oxygen content of liquid iron at 1600°C

$$\{O_2\} = 2[O]; \Delta G^o = -237 kJ / FU$$

$$K_{eq} = \frac{[O]^2}{P_{O_2}} = \exp\left(-\frac{-236610}{8,31 \cdot 1873}\right) = 4 \cdot 10^6;$$

$$[O] = \sqrt{4 \cdot 10^6 \cdot P_{O_2}} = 2 \cdot 10^3 \cdot 3,6 \cdot 10^{-6} = 0.0072 wt\% = 72 ppm.$$

Surface tension of liquid iron

$$\sigma_{\text{Fe-1600}^\circ\text{C}} = 542 - 464 \cdot \log[\%O] = 1536 \text{ mN / m}$$

$$\text{Th.Young(1804)} : \sigma_R - \sigma_{\text{Fe,li}} = \sigma_{\text{Fe,R}} \cdot \cos \theta_{\text{Fe,R}}$$

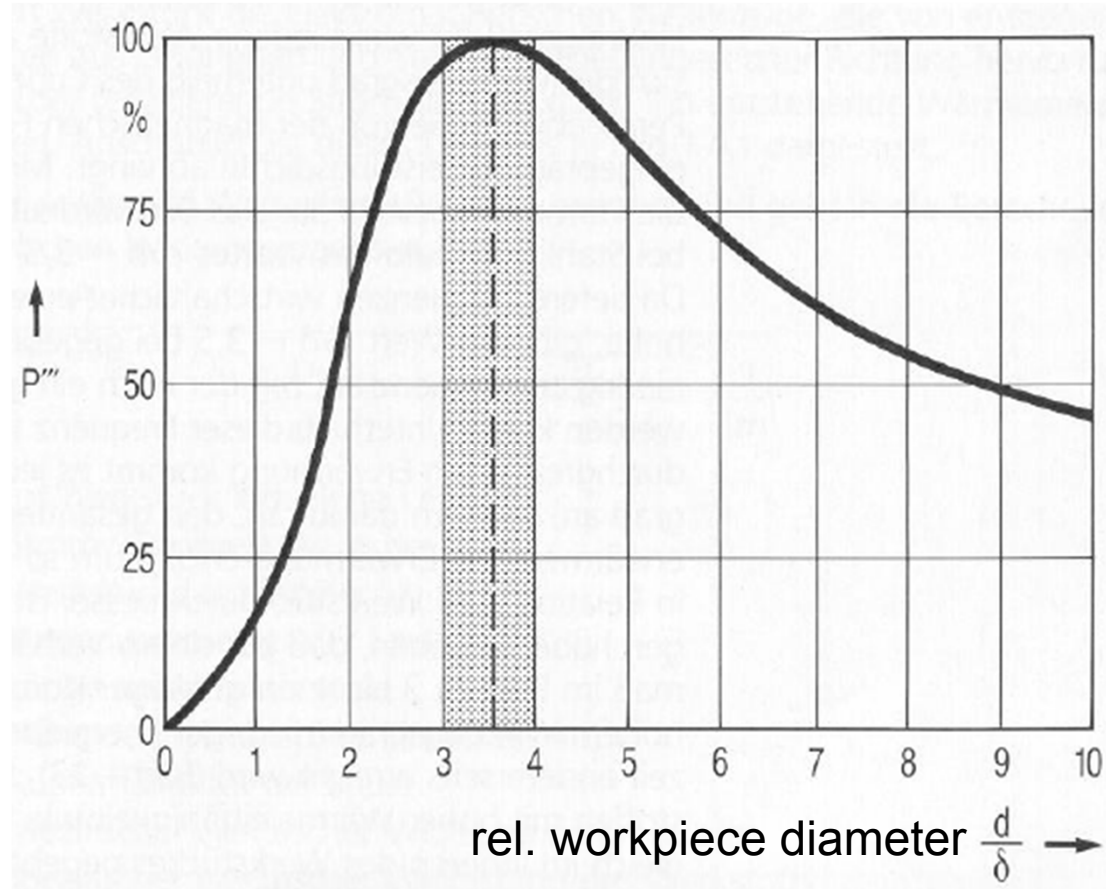
$$\theta_{\text{Fe,R}} \approx 110^\circ$$

The highest partial pressure of water vapour may be 1atm. Then the partial pressure of oxygen at 1600°C is 10^{-8} atm and the melt is saturated by 0,2wt% oxygen. The surface tension of the melt follows to be $\sigma_{\text{Fe}} = 866 \text{ mN/m}$ and $\theta_{\text{Fe/R}} = 89^\circ$. The melt wets the refractory. Therefore in general

Infiltration is facilitated by water steam.

Infiltration in an induction furnace

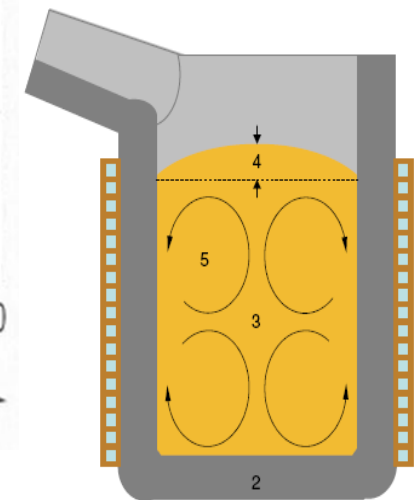
Induced volume power density P



Depth of penetration of el.-magn. field

$$\delta = \left(\frac{\rho_{el}}{\pi \cdot f \cdot \mu_r \cdot \mu_0} \right)^{1/2} [m]$$

Diameter d of thread $\ll \delta$



- 1 Induktionsspule (Kupfer, Wasser)
- 2 feuerfester Tiegel
- 3 metallische Schmelze
- 4 Badüberhöhung
- 5 Badbewegung

Infiltration in an induction furnace

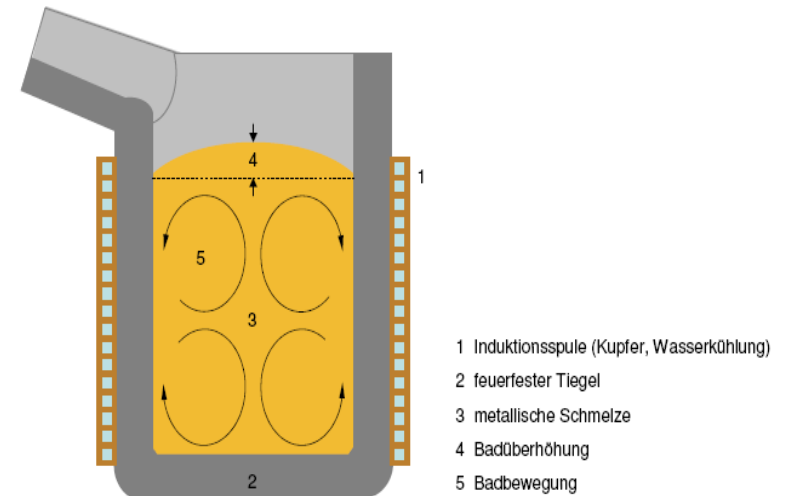
magnetic pressure $P_m = \rho \cdot g \cdot h_{\ddot{u}} \quad [\text{N/m}^2]$

$$P_a + \rho \cdot g \cdot (h + h_{\ddot{u}}) = -\frac{4 \cdot \sigma \cdot \cos \theta}{d} [N / m^2]$$

$$d = -\frac{4 \cdot \sigma \cdot \cos \theta}{P_a + \rho \cdot g \cdot (h + h_{\ddot{u}})} [m]$$

$$d = -\frac{4 \cdot 1.5 \cdot \cos 120^\circ}{98100 + 7 \cdot 10^3 \cdot 9.81 \cdot (2.7 + 0.5)} = 10^{-5} \text{ m}$$

$$l = \sqrt{\left(\frac{d \cdot \sigma_s \cdot \cos \theta}{4 \cdot \eta_s} + \frac{d^2 \cdot (P_a + \rho_s \cdot g \cdot (h + h_{\ddot{u}}))}{16 \cdot \eta_s} \right) \cdot t} [m]$$



Penetration depth:

The dynamic viscosity of steel is $\eta_s = 0.003$ Pa·s. The total ferrostatic height in our example is $(h+h_{\ddot{u}}) = 3,2$ m at the bottom of the furnace. With the very small diameter of the thread $d = 10^{-5}$ m and the external pressure $P_a = 98100$ N/m we can see, that in one minute 5 cm steel are infiltrated if the temperature remains sufficiently high. That is

$$l / cm \approx 5\sqrt{t / \text{min}}$$

Threads

The depth of **penetration of the electromagnetic field** in a middle-frequency induction plant (about 250Hz) in liquid iron is $\delta \approx 3 - 4 \text{ cm}$ /7/.

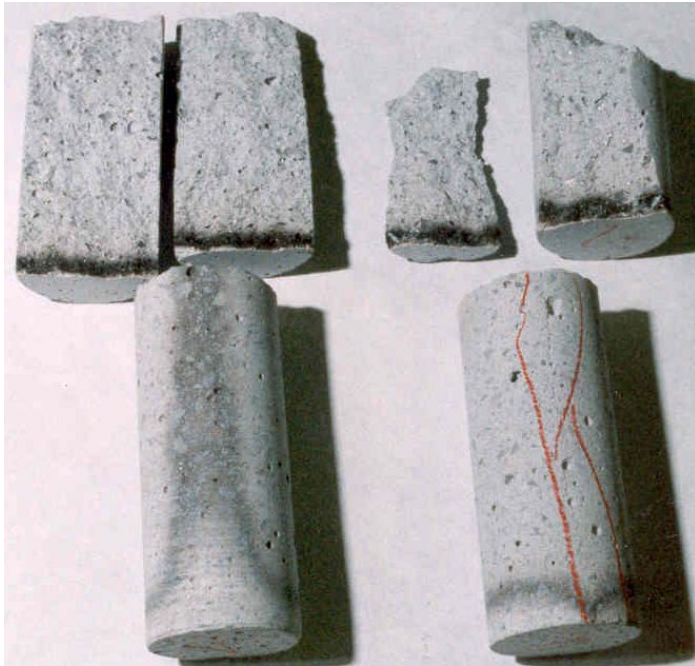
At $d/\delta < 0.1$ no power is transmitted anymore. Threads smaller than $d = 4 \text{ mm}$ are not heated any longer and will solidify if the temperature of the lining has decreased below the melting point. The higher the frequency, the smaller are the threads which can be heated up by the electromagnetic field and which then may infiltrate the lining.

Destroying of refractory by threads:

If the electromagnetic field couples the threads they may be heated up in a very short time to high temperature. The refractory may be destroyed by temperature shock and its melting.

In addition, the infiltrated metal has another coefficient of thermal expansion as the refractory, it may oxidise and it may form new compounds with the lining material. Therefore pressure may develop which destroys the lining resulting in the liquid metals breaking through.

5. Formation of Graphite



L: ULCC on basis „fused silica“; **R:** Ramming Mix ca. 1300°C,
Pers. Memo. R. Krebs (2012)

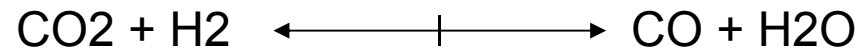
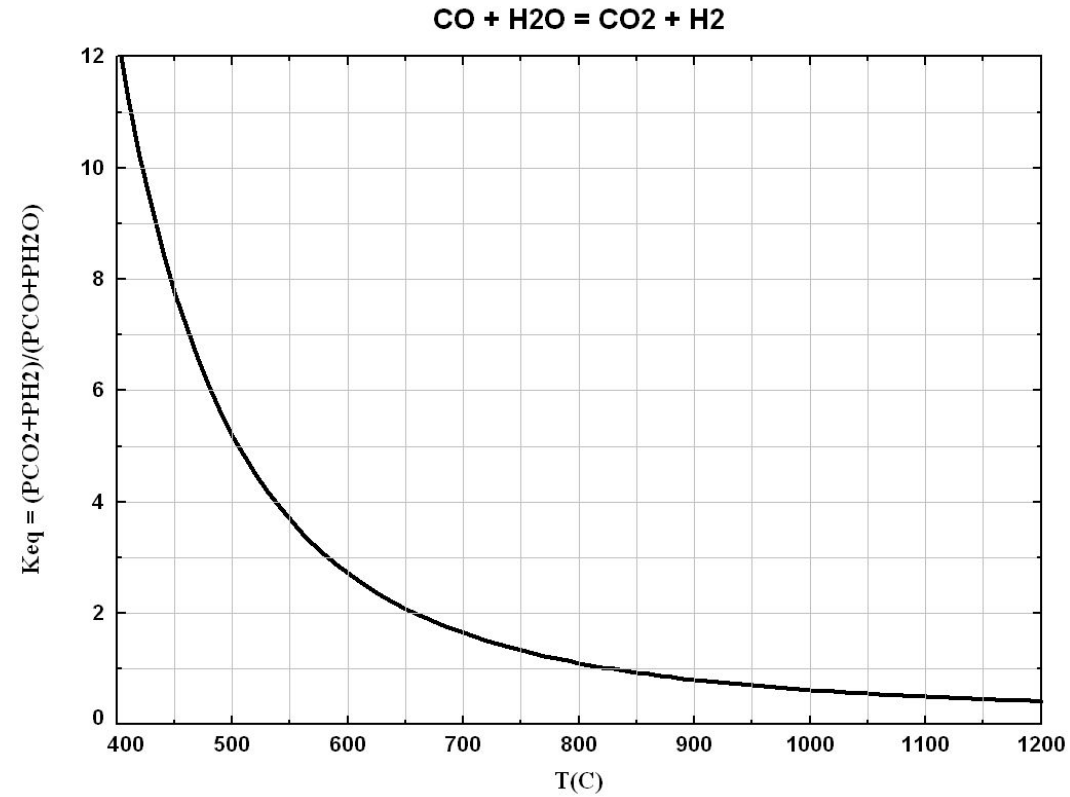
Ultra low cement castable

Preconditions:

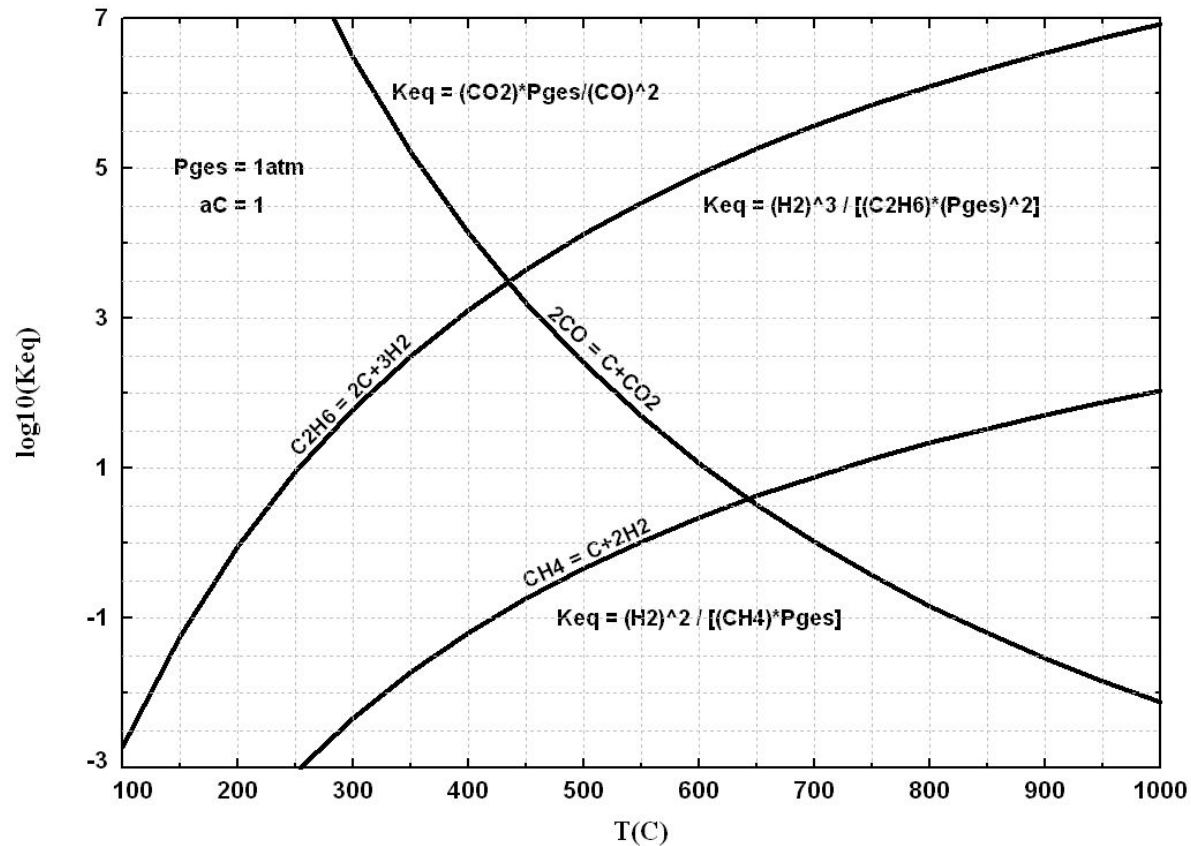
- High temperature
- Organic parts in the refractory material
- No aerially oxygen
- Impermeable closed surfaces, e.g. by rapid sintering

Precipitation of graphite without access of air :

- Water - gas equilibrium



Stability of the compounds C₂H₆, CH₄ and CO



- The stability of CO grows with T and P.
- The stability of hydrocarbon drops with growing M, T and P

Crystallisation pressure of carbon

$$\{CH_4\} = \langle C \rangle + 2\{H_2\}. \quad \Delta G^o(1000K, 1atm) = -19395 J / FU$$

$$K_{eq} = \frac{P_{H_2}^2 \cdot a_C}{P_{CH_4}} = \exp\left(-\frac{\Delta G^o}{R_1 \cdot T}\right) = \exp\left(-\frac{19395}{8.31 \cdot 1000}\right) = 10.3$$

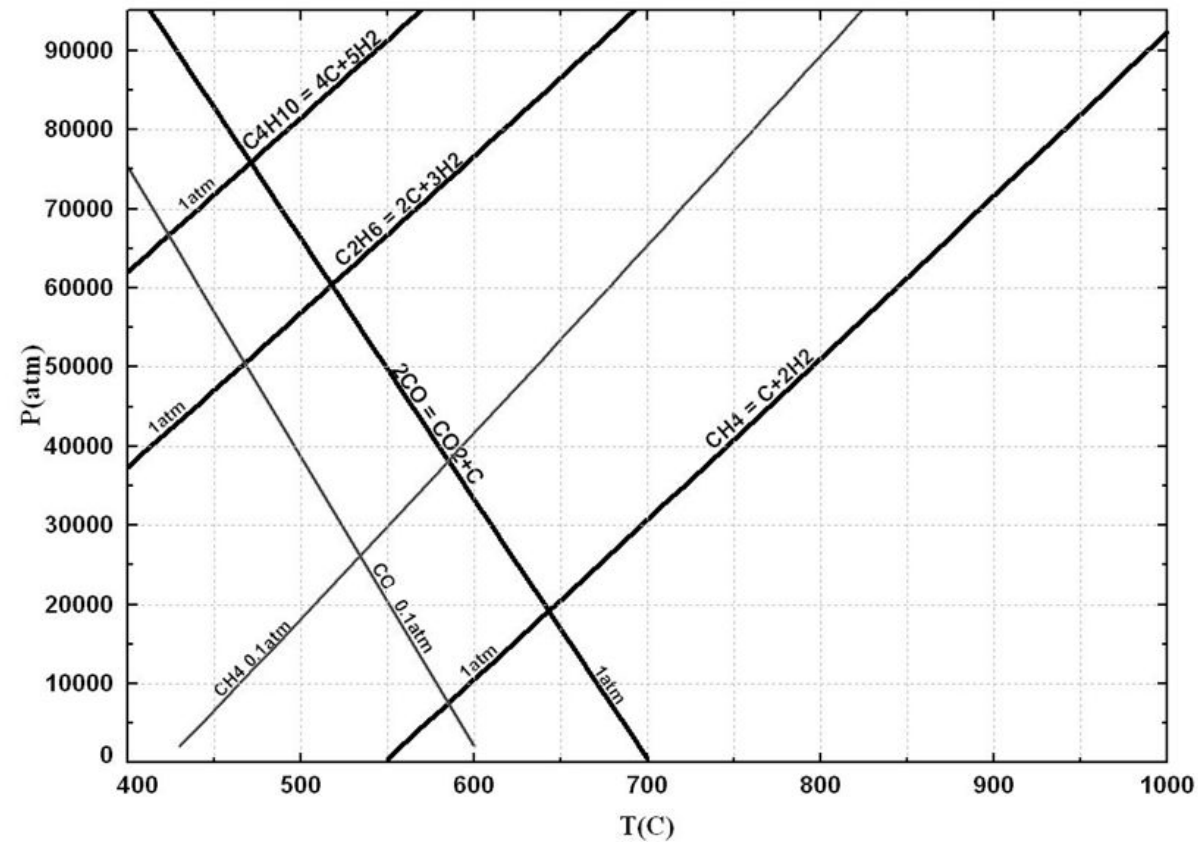
$$\Delta G = \Delta G^o + R_1 T \cdot \ln K_{eq} + (1 - \pi) \cdot \Delta V_C = 0$$

Free Enthalpie: standard + relative (gas) + relative (graphite)

$$K_{eq} = P_{H_2}^2 / P_{CH_4} = 1 \quad R_1 = 8.31 \text{ J/mol} \cdot K, R_2 = 84.8 \text{ atm} \cdot \text{ccm/mol} \cdot K$$

$$(\pi - 1) = \frac{-\Delta G^o - R_1 T \cdot \ln K_{eq}}{\Delta V \cdot R_1 / R_2} = \frac{+19395 - 8,31 \cdot 1000 \cdot \ln 1}{5,3 \cdot 0,1} = 36 \cdot 10^3 \text{ atm.}$$

Crystallisation pressure of graphite precipitation



The crystallisation pressure of C from hydrocarbon rises with M , T and $1/P$
The crystallisation pressure of C from CO drops with T and $1/P$

6. Drying of Refractory

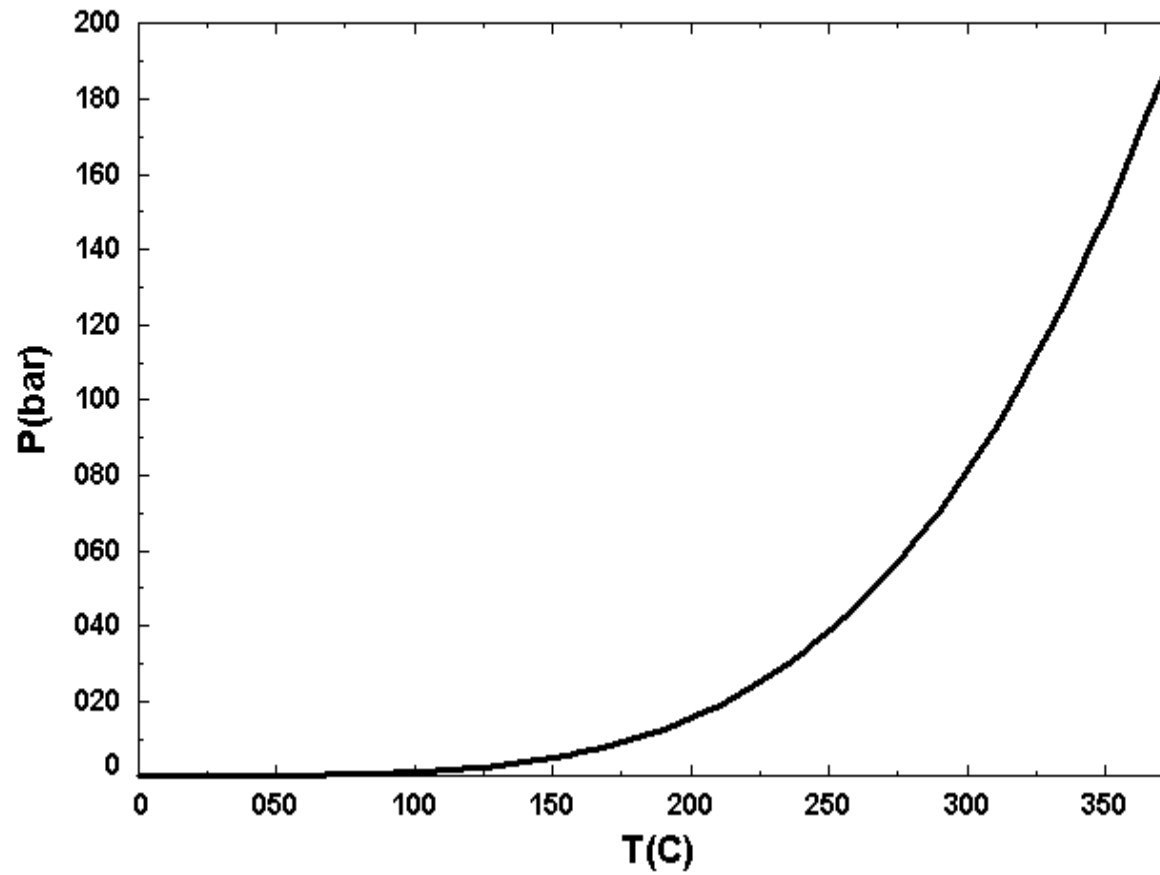


Damage of refractory wall due to evaporation pressure of water,
pers. memo. K.-E. Granitzki (2005)

Drying of Refractory

Real Vapour Pressure of Liquid Water

0 - 375°C



Drying of Refractory

6.1 Basic Information

Refractory material is heated to more than 600 °C.

Refractory castables consist of Al_2O_3 , CaO and SiO_2 + 5% water

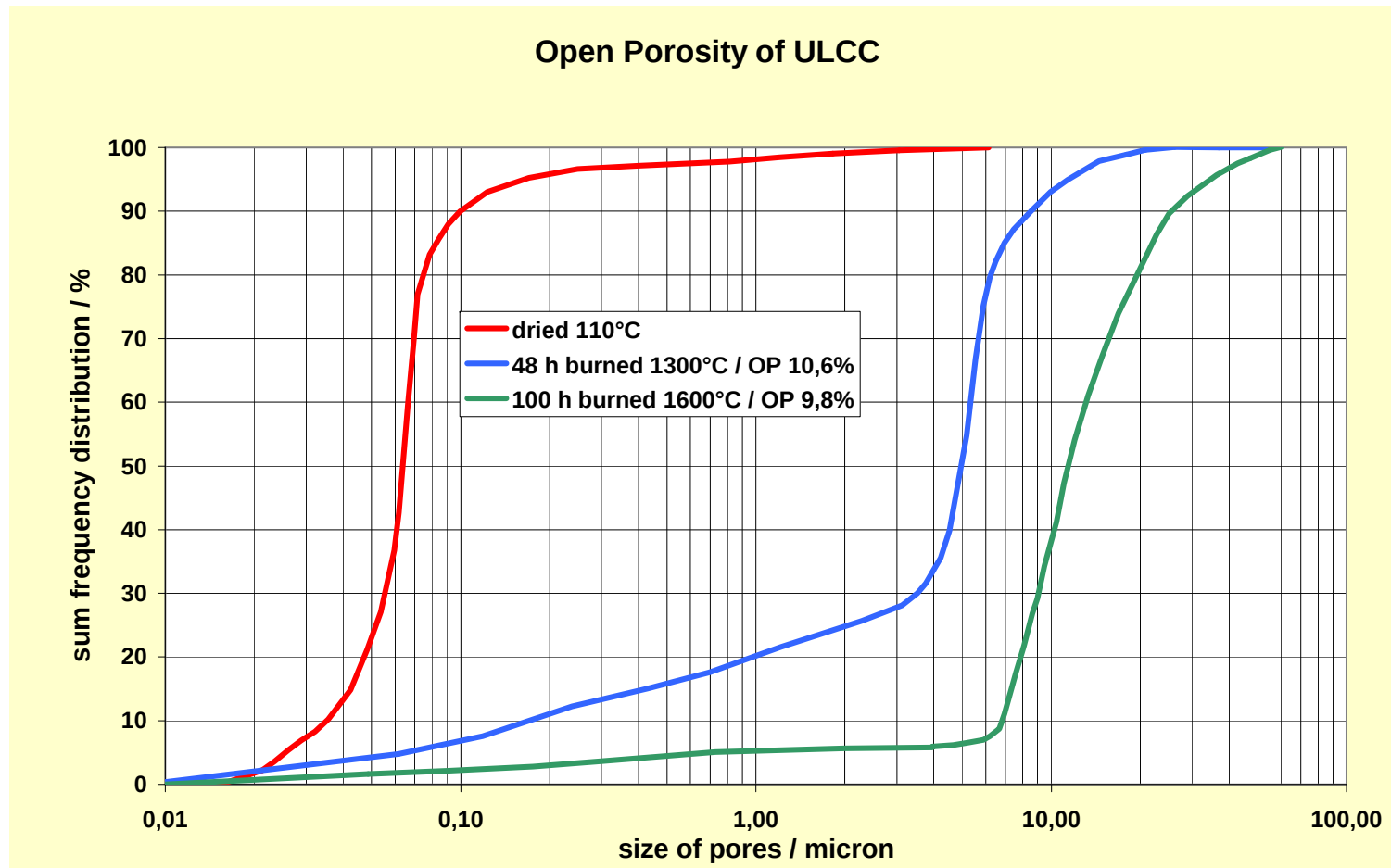
After mixing during a rests ≥ 24 h (curing), the hydraulic binder phases are formed

Around 50 % of the added water is bound as hydrate; the rest is present free in the microstructure

Decomposition of hydraulic phases (drying stages):

- 1) 1. Adsorbed water evaporates (≤ 110 °C).
2. Calcium aluminate hydrates liberate Water ($< 250^\circ\text{C}$)
3. Remaining hydrates, gibbsite ($\text{Al}(\text{OH})_3$), decompose (≤ 400 °C).

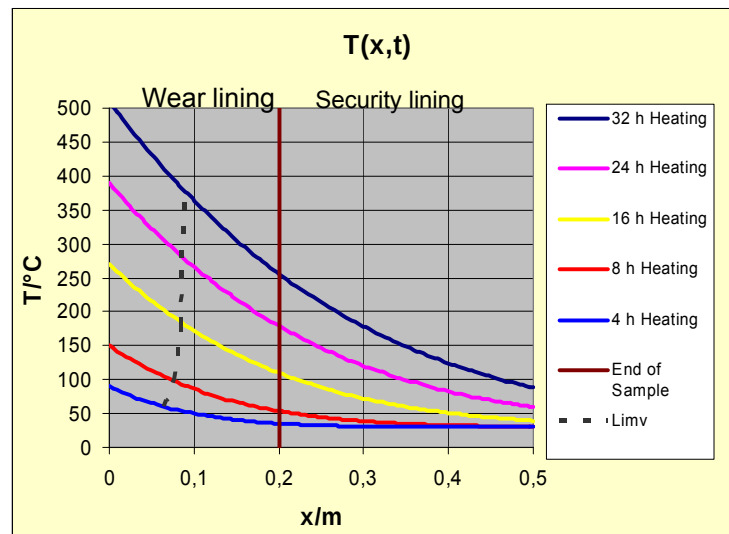
Pore size distribution of an ULCC (Calderys)



6.2 Drying Model

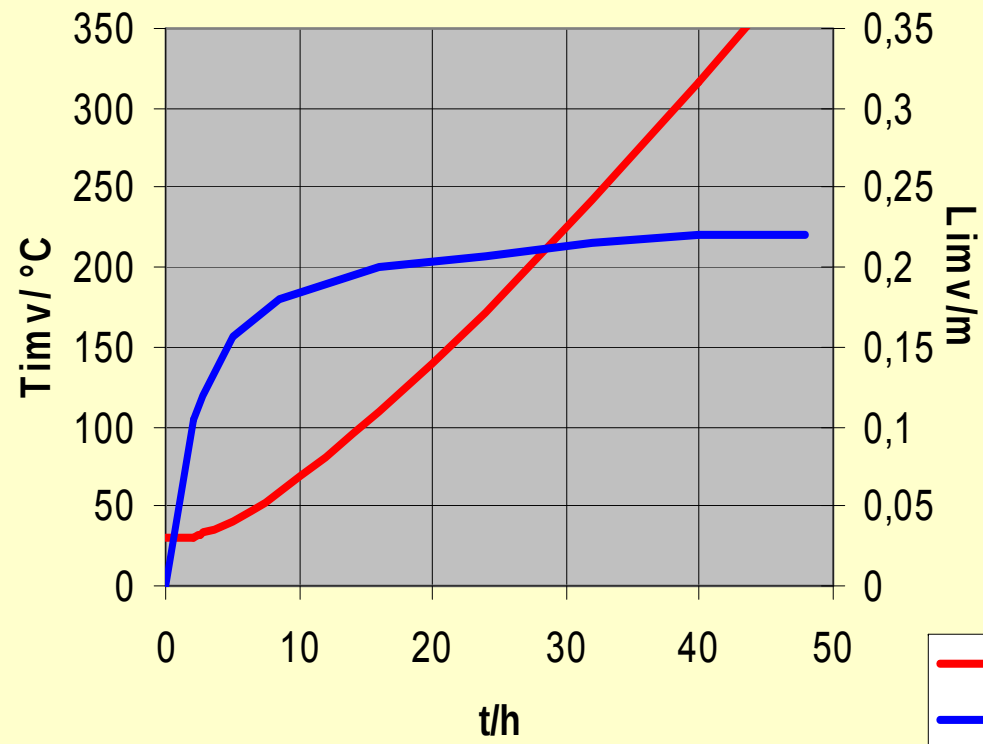
Four assumptions:

1. The temperature course defines the drying process
2. The first and the second drying stage can be treated the same
3. $> 350\text{ }^{\circ}\text{C}$ there is no danger of explosion for the castable during further increase of the temperature
4. The integral mean value of the temperature, formed over the total thickness of the castable layer, approximately replaces knowledge of the exact **location** of the drying plane



Temperature / time course
 $T_0 = 30^{\circ}\text{C}$, $k = 30\text{K/min}$
 $a = 9 \cdot 10^{-7} \text{ m}^2/\text{s}$

Integr. Med. Values T_{imv}/t and L_{imv}/t



$T_0 = 30^{\circ}\text{C}$,
 $L = 0.5 \text{ m}$;
 $k = 15 \text{ K/h}$;
 $a = 9 \cdot 10^{-7} \text{ m}^2/\text{s}$

Integral mean value of temperature T_{imv} and its location L_{imv}

Two approximations can be used:

$$1. \mathcal{G}_{IMV} = \mathcal{G}_a + 2,66 \cdot k \cdot t \cdot \sqrt{\frac{a \cdot t}{L}} [^{\circ}C] \quad t < 3h \quad k=\text{heating rate}$$

$\mathcal{G}_{IMV}$ =integral mean value of T

$$2. \mathcal{G}_{IMV} \cong \mathcal{G}_a + \frac{3 \cdot 10^3 \cdot a^{0,25}}{\sqrt{L}} \cdot k \cdot (3,7 \cdot 10^{-3} \cdot t - 33,5) [^{\circ}C] \quad t > 3h$$

$$\frac{\mathcal{G}_0 - \mathcal{G}_a}{\mathcal{G}_{IMV} - \mathcal{G}_a} = \frac{\sqrt{L}}{3000 \cdot a^{0.25}} \cdot \frac{t}{3,7 \cdot 10^{-3} \cdot t - 33,5} \quad t > 3h$$

$$k = \frac{\mathcal{G}_0 - \mathcal{G}_a}{t} [K / s]$$

Postulation:

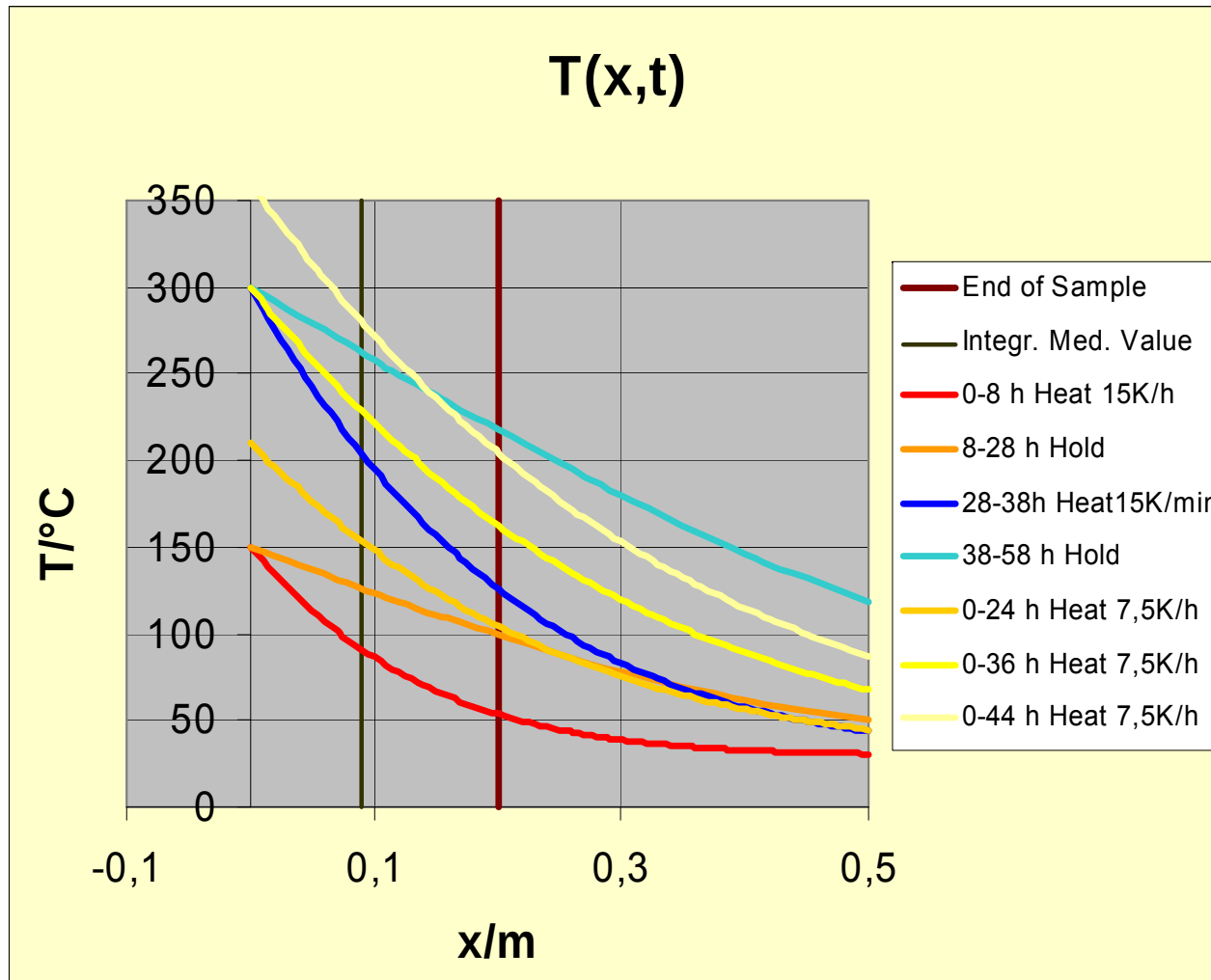
$\mathcal{G}_{IMV}$ remains < 200 °C, until the cold end of the castable exceeds 110 °C

Drying in field practice

One proposal for the drying of cured castable is as follows:

Heating at 15 K/h to 150°C
Holding over 1 h/0.01 m wall thickness
Heating at 15 K/h to 350°C
Holding over 1 h/0.01 m wall thickness
Heating to $\geq 600^{\circ}\text{C}$.

This approach avoids vapour explosion.



$T_0 = 30\text{ °C},$
 $L = 0.2\text{ m};$
 $L_{IMV} = 0,09\text{ m}$
 $k = 15 / 7,5\text{ K/h};$
 $a = 9 \cdot 10^{-7}\text{ m}^2/\text{s}$

Comparison: field praxis / model

6.3 Formation of Ice

Energy balance of evaporation of water: $n \cdot \Delta H_v = (1 - n) \cdot C_p \cdot \Delta T$

n = Mass fraction of vapour

$1-n$ = Mass fraction of water

$\Delta H_v = 2257 \text{ kJ/kg}$, evaporation enthalpy of water

$C_p = 4,3 \text{ kJ/Kg} \cdot \text{K}$, specific heat of water

ΔT = Change of temperature during adiabatic evaporation

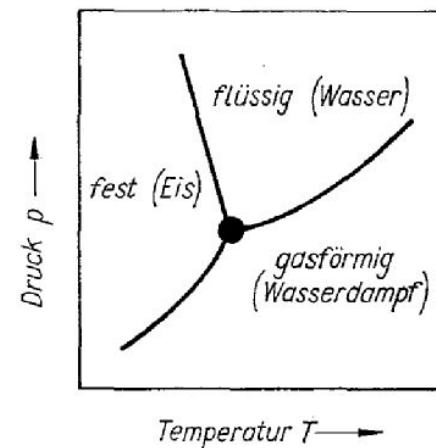
How much water evaporates adiabatically without forming ice?

$$n = \frac{1}{\frac{\Delta H_v}{C_p \cdot \Delta T} + 1} = 17\% \quad (\Delta T = 110 \text{ K})$$

Coexisting phases of water

triple point ($P = 6 \cdot 10^{-3} \text{ atm}$, $T = 7,5 \cdot 10^{-3} \text{ °C}$)

$$F = K + 2 - P = 1 + 2 - 3 = 0$$



Evaporation rate from the surface without pore diffusion:

$$\dot{m}_{\max} = F_{\text{eff}} \cdot 0,59 \cdot \sigma \cdot P_s \cdot \sqrt{\frac{M}{T}} \left[\text{kg} / \text{m}^2 \cdot \text{s} \right]$$

$F_{\text{eff}} = 0,05 \text{m}^2$ (5 % porosity)

$\sigma = 0,1$, condensation coefficient for boiling water is

$P_s = 500 \text{ Torr}$. Vapour pressure at 87°C .

$M = 18 \text{ kg/kmol}$.

$$\dot{m}_{\max} = 0,05 \times 0,59 \cdot 0,1 \cdot 500 (18 / 360)^{1/2} = 0,3 \text{ kg} / \text{m}^2 \cdot \text{s}.$$

Time to cool down adiabatically by evaporation:

$$t = \frac{\bar{m}}{F \left(\frac{\Delta H_v}{\bar{C}_p \cdot \Delta T} + 1 \right) \dot{m}} \left[\text{s} \right] = 1720 \text{s} \approx 0,5 \text{h}$$

$m_{\text{water}} = 26,2 \text{kg}$, $\bar{m} = 523 \text{ kg} / \text{m}^2$, $\bar{C}_p = 1,06 \text{ kJ} / \text{kg} \cdot \text{K}$.

$\Delta T = 110 \text{ K}$, $L = 0,2 \text{m}$, $F = 1 \text{m}^2$, $\rho_R = 2700 \text{kg/m}^3$,

Taking the **true evaporation rate** of the steam, given by the temperature course because the drying rate is governed by heat supply and not mass transport we get another result:

$$\dot{m}_g = 3 \cdot 10^{-4} / L_{IMV} \left[\frac{kg}{m^2 \cdot s} \right] \quad \text{Limv: location of Timv}$$

$$T_0 = 30 \text{ } ^\circ\text{C},$$

$$L = 0.2 \text{ m};$$

$$L_{IMV} = 0,09 \text{ m}$$

$$k = 15 / 7,5 \text{ K/h};$$

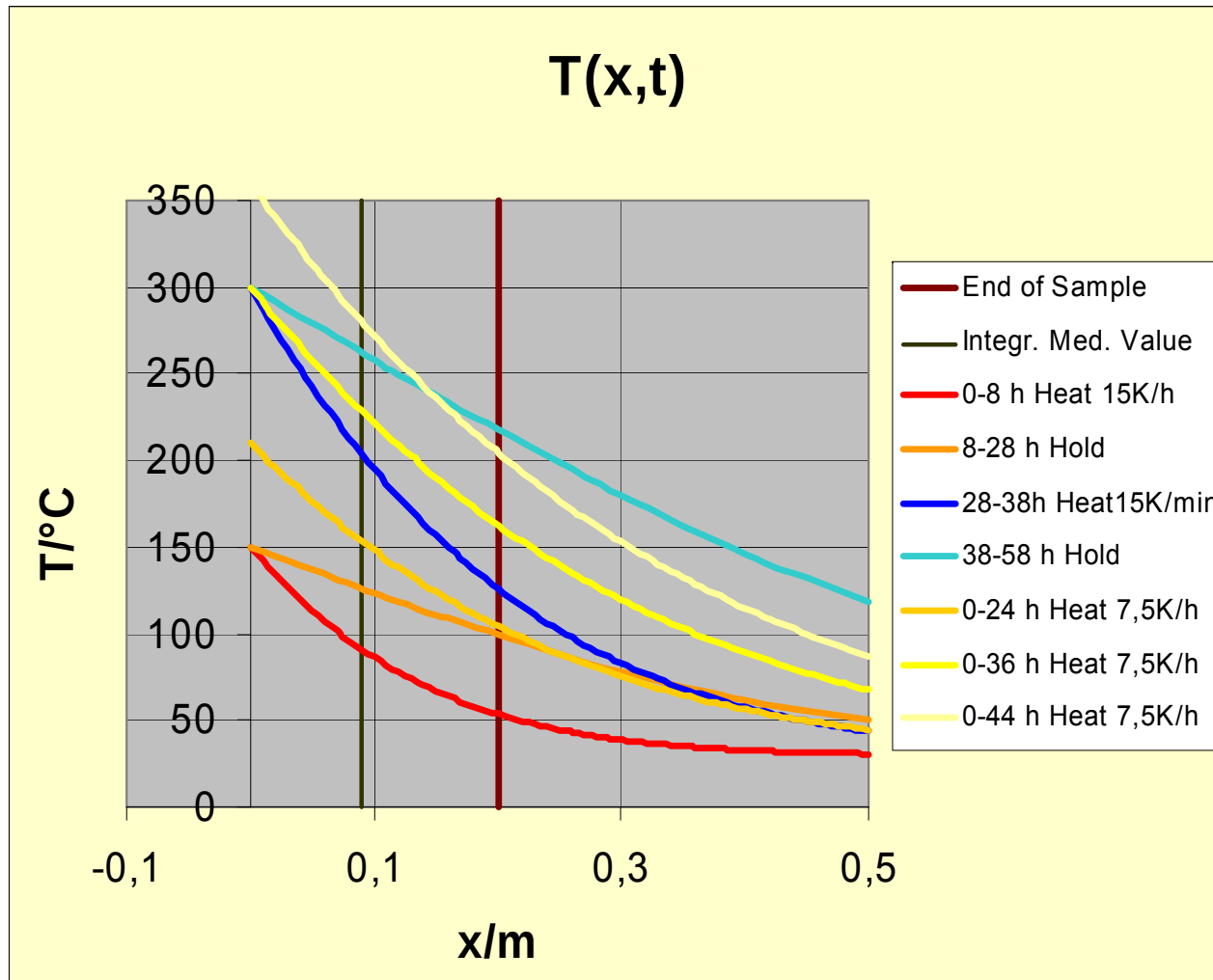
$$a = 9 \cdot 10^{-7} \text{ m}^2/\text{s}$$

$$\dot{m}_J = 3 \times 10^{-4} / 0,9 = 3,3 \times 10^{-4} \left[\frac{kg}{m^2 \times s} \right]$$

To evaporate $m_{H_2O} = 26,2 \text{ kg}$ water it takes the time

$$t_J = \frac{m_{H_2O}}{\dot{m}_J} = \frac{26,2}{3,3 \times 10^{-4}} = 7,9 \times 10^4 \text{ s} = 22 \text{ h}.$$

Drying has to be conducted slowly.



$T_0 = 30\text{ }^{\circ}\text{C}$,
 $L = 0.2\text{ m}$;
 $L_{IMV} = 0,09\text{ m}$
 $k = 15 / 7,5\text{ K/h}$;
 $a = 9 \cdot 10^{-7}\text{ m}^2/\text{s}$

Comparison: field praxis / model

7. Conclusion

- Water in a vessel of a vacuum – induction furnace has to be avoided.
- Two main “leaks” are humid refractory and hydrocarbon in the lining
- Water in contact with the melt may result in an oxyhydrogen explosion
- Infiltration is promoted by oxygen favouring the wetability melt/refractory
- Cleanliness of the melt becomes poor because oxides are formed
- Graphite formation results from cracking of hydrocarbons without air
- Drying is governed by the heat conduction and has to be conducted slowly to avoid the formation of steam explosions and of ice. Both are able to destroy the lining. A model is presented.

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