SPINEL CRYSTAL DISTRIBUTION AND SETTLING IN A HIGH-LEVEL WASTE MELTER WORKING AS A PERFECT MIXER

PART 1. THEORETICAL RELATIONS

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The mathematical and laboratory modeling of the high-level waste vitrification process is able to reveal the mechanism of spinel crystal formation, their interaction with a melt and settling. This enables to find conditions for higher waste loading into vitrification facility. A model of a perfect mixer has been developed by authors with the aim to examine the crystal settling and to compare results with the numerical mathematical model. This model is based on the mass balance of inputted, outputted, nucleated, growing or dissolving and settling crystals in the melting space. To complete the description of possible melter behavior, similar relations were derived and are presented for the piston flow in the melter.

INTRODUCTION

The crystal settling in vitrification spaces is frequently a life determining factor of vitrification facilities. The first crystalline phase precipitating from the melt of HLW glasses below liquidus temperature are solid solutions of spinels containing Fe, Cr and Ni [1,2]. The extremely slow dissolution of spinels in the melt at temperatures above liquidus [3] brings about the spinel crystal settling on the melter bottom and oblique sides and growing of a sludge layer of high viscosity [4]. The sufficiently thick sludge layer may interfere with the melter operation mainly by blocking channels, thus the lifetime of the facility may be drastically shorten. To avoid this phenomenon, the waste loading is kept on the low level and consequently, the volume of produced glass is high. Nevertheless the mathematical and laboratory modeling of vitrification space, involving the spinel settling and sludge layer growth, could reveal the mechanisms of spinel formation, interaction with the melt, as well as settling and thus to find acceptable conditions for higher waste loading even under these unfavourable conditions.

The 3D mathematical model developed recently for this purpose involved the glass flow and heat transfer in the melter space coupled with temperature dependent properties of glass [5] and with spinel crystal kinetics [6,7]. Using this model, the calculations were performed to reveal the influence of temperature, initial size and amount of crystals, as well as melt liquidus temperature on the spinel distribution in the space and the thickness of the sludge layer. The first results have shown that the melt in the space is intensively stirred owing to electrical heating of the melt and consequently, the spinel crystals are almost homogeneously distributed in the space. Under these conditions, the behavior of the melter approximately simulated the perfect mixer with constant and homogeneous particle concentration inside. That is why a model of perfect mixing was derived by the authors of this work with the aim to examine the spinel settling and sludge layer grow in the perfect mixer under different process and material parameters and to compare acquired results with values coming from the complete mathematical model. The considerable shortening of calculations can be expected when applying this model for extended parametric studies of vigorously mixed vitrification spaces, as well as independence of results on concrete facility. The application of results from the ideal mixer as initial conditions of the numerical mathematical model could substantially decrease the calculation times of the numerical model.

THEORETICAL

When balancing the crystals in the melter, two monodisperse sources of crystals (a balance including entering polydisperse crystals may also be considered) are taken into account: crystals coming from the batch (cold cap), entering the melter through the top level, and nucleated crystals. The crystal sources are active simul-

taneously only when the melt temperature is lower than glass liquidus temperature, $T < T_L$, and $C_{in} < C_o$, where C_{in} is the concentration of crystals entering from the batch and C_o is the equilibrium concentration of crystals in the melt. Under mentioned conditions, all crystals present in the melter will grow. The total change of crystal concentration in the melter by crystal input is expressed as

$$dC(in) = \frac{\dot{V}\left(C_{in} + C_{No}\right)}{V} d\tau \qquad (1)$$

where C_{in} is the input concentrations of crystals coming from the cold cap and C_{No} is the input concentration of nucleated crystals, V is the melter volume and $\dot{V}$ its melt throughput.

For C_{No} we have

$$C_{No} = N_{No} a_{crit}^3 \rho_s \qquad (2)$$

where N_{No} is number density of nucleated crystals, a_{crit} is the critical size of nucleated crystals, and ρ_s is the spinel crystal density.

The mass flow of crystals entering the melt through the cold cap is

$$\dot{m}_{CCo} = C_{in} \dot{V} \qquad (3)$$

Similarly, the mass flow of nucleated crystals, which are formed instantly after the glass has entered the melter, is

$$\dot{m}_{No} = N_{No} \dot{V} a_{crit}^3 \rho_s \qquad (4)$$

The number of crystals entering the melter from the cold cap per time unit is

$$\dot{N}_{CCo} = \frac{\dot{m}_{CCo}}{a_o^3 \rho_s} = \frac{C_{in} \dot{V}}{a_o^3 \rho_s} \qquad (5)$$

Similarly, the flow of nucleated crystals is

$$\dot{N}_{No} = \frac{\dot{m}_{No}}{a_{crit}^3 \rho_s} = N_{No} \dot{V} \qquad (6)$$

As the all crystals in the melter grow (no crystals are lost by dissolution because $T<T_L$) and the amount of settled crystals is small, the initial ratio between numbers of crystals from the cold cap and nucleated crystals is constant:

$$\frac{\dot{N}_{CCo}}{\dot{N}_{No}} = \frac{N_{CC}}{N_N} = \frac{C_{in}}{a_o^3 \rho_s N_{No}} \qquad (7)$$

where N_{CC} and N_N are the number densities of crystals from the cold cap an nucleated crystals, respectively.

The concentration of crystals in the melter, coming from the cold cap, can be approximately expressed as:

$$C_{CC} = N_{CC} \bar{a}_{CC}^3 \rho_s \qquad (8)$$

where $\bar{a}_{CC}$ is the average size of crystals from the cold cap. Similarly,

$$C_N = N_N \bar{a}_N^3 \rho_s \qquad (9)$$

where $\bar{a}_N$ is the average size of nucleated crystals.

The constant ratio between both concentrations is obtained by combining equations (8), (9), and (7):

$$\frac{C_{CC}}{C_N} = \frac{C_{in}}{a_o^3 \rho_s} \quad \frac{1}{N_{No}} \quad \frac{\bar{a}_{CC}^3}{\bar{a}_N^3} = \frac{C_{in}}{a_o^3 \rho_s N_{No}} \quad \frac{\left(a_o + \dot{a}\bar{\tau}_{Age}\right)^3}{\left(a_{crit} + \dot{a}\bar{\tau}_{Age}\right)^3} \qquad (10)$$

where $a = a_o + \dot{a}\bar{\tau}_{Age}$, $\dot{a}$ is the average value of crystal growth rate and $\bar{\tau}_{Age}$ is the average age of crystals in the melter. The $\bar{\tau}_{Age}$ is the half of the average residence time of glass in the melter, if crystal grows.

As all the crystals present in the melter are coming from the cold cap or are nucleated in the melter:

$$C = C_{CC} + C_N \qquad (11)$$

where C is the total crystal concentration in the melter.

Both crystal concentrations may be expressed separately by using equations (10) and (11):

$$C_N = C \frac{1}{\dfrac{C_{in}}{a_o^3 \rho_s N_{No}} \dfrac{\left(a_o + \dot{a}\bar{\tau}_{Age}\right)^3}{\left(a_{crit} + \dot{a}\bar{\tau}_{Age}\right)^3} + 1} \qquad (12a)$$

$$C_{CC} = C \left[1 - \frac{1}{\dfrac{C_{in}}{a_o^3 \rho_s N_{No}} \dfrac{\left(a_o + \dot{a}\bar{\tau}_{Age}\right)^3}{\left(a_{crit} + \dot{a}\bar{\tau}_{Age}\right)^3}} \right] \qquad (13a)$$

If the expression coming from equations (12a) and (13a) is designated as A, we have

$$C_N = C.A \qquad (12b)$$

$$C_{CC} = C\left(1 - A\right) \qquad (13b)$$

The concentration change of crystals coming from the cold cap is then

$$dC_{CC}\left(\dot{a}\right) = N_{CC} 3 \bar{a}_{CC}^2 \dot{a} \rho_s d\tau \qquad (14)$$

and

$$dC_N\left(\dot{a}\right) = N_N 3 \bar{a}_N^2 \dot{a} \rho_s d\tau \qquad (15)$$

The actual number of crystals from both sources is given by equations (8) and (9). When applying equations (12b) and (13b), equations (14) and (15) can be written as

$$dC_{CC}\left(\dot{a}\right) = \left(1 - A\right) \frac{3 C \dot{a}}{\left(a_o + \dot{a}\bar{\tau}_{Age}\right)} d\tau \qquad (16)$$

and

$$dC_N\left(\dot{a}\right) = A \frac{3 C \dot{a}}{a_{crit} + \dot{a}\bar{\tau}_{Age}} d\tau \qquad (17)$$

The amount of settled crystals can be expressed as follows

$$dC_{CC}(settling) = -\frac{\bar{v}_{CC} S}{V} C_{CC} d\tau \qquad (18)$$

$$dC_N(setling) = -\frac{\bar{v}_N S}{V} C_N d\tau \qquad (19)$$

where v_{CC} and v_N are the settling velocities of crystals coming from the cold cap and nucleated crystals, respectively.

After applying the Stokes´ law for settling velocity and equations (12b) and (13b), we obtain:

$$dC_{CC}(settling) = -\frac{0.205 g \Delta\rho}{\eta}\left(a_o + \dot{a}\bar{\tau}_{Age}\right)^2 \frac{S}{V} C(1-A) d\tau \qquad (20)$$

and

$$dC_N(settling) = -\frac{0.205 g \Delta\rho}{\eta}\left(a_{crit} + \dot{a}\bar{\tau}_{Age}\right)^2 \frac{S}{V} CA d\tau \qquad (21)$$

where $\Delta\rho$ is the density difference of crystals and glass, η is the glass viscosity and S is the surface of the melter where crystals settle. Finally, the concentration change brought about by glass output is

$$dC(out) = -\frac{\dot{V}C}{V} d\tau \qquad (22)$$

Adding equations (1), (16), (17), (20), (21), and (22), and solving the resulting equation for $\tau \to \infty$ (stationary state), we obtain the total crystal concentration in the melter:

$$C_\infty = \frac{\dot{V}\left(C_{in} + N_{No}a_{crit}^3 \rho_s\right)}{\frac{0.205 g \Delta\rho}{\eta}\left[\left(a_o + \dot{a}\bar{\tau}_{Age}\right)^2 (1-A) + \left(a_{crit} + \dot{a}\bar{\tau}_{Age}\right)^2 A\right] S + \dot{V} - \frac{3(1-A)\dot{a}V}{a_o + \dot{a}\bar{\tau}_{Age}} - \frac{3A\dot{a}V}{a_{crit} + \dot{a}\bar{\tau}_{Age}}} \qquad (23)$$

If the crystal nucleation is negligible, $N_{No} \to 0$, then $A \to 0$ and only the crystals from the cold cap play the role:

$$C_\infty = \frac{\dot{V}C_{in}}{\frac{0.205 g \Delta\rho}{\eta}\left(a_o + \dot{a}\bar{\tau}_{Age}\right)^2 S + \dot{V} - \frac{3\dot{a}V}{a_o + \dot{a}\bar{\tau}_{Age}}} \qquad (24)$$

If, on the contrary, $C_{in} \to 0$ and $T < T_L$, and we get from Equation (23)

$$C_\infty = \frac{\dot{V}N_{No}a_{crit}^3 \rho_s}{\frac{0.205 g \Delta\rho}{\eta}\left(a_{crit} + \dot{a}\bar{\tau}_{Age}\right)^2 S + \dot{V} - \frac{3\dot{a}V}{a_{crit} + \dot{a}\bar{\tau}_{Age}}} \qquad (25)$$

For the thickness of the layer of settled crystals on the melter bottom, we have:

$$m_{sCC} = \bar{v}_{CC} . C_\infty (1-A)\tau \qquad (26)$$

where m_{sCC} is the amount of crystals settled on the bottom surface unit.

Similarly,

$$m_{sN} = \bar{v}_N . C_\infty A \tau \qquad (27)$$

The total layer thickness is

$$h_{Cr}(\tau) = \frac{m_{sCC}}{C_{layer}} + \frac{m_{sN}}{C_{layer}} = \frac{\left[\bar{v}_{CC} C_\infty (1-A) + \bar{v}_N C_\infty A\right]}{C_{layer}}\tau \qquad (28)$$

where C_{layer} is the mass concentration of crystals in the sludge layer.

Substituting $\bar{v}_{CC}$ and $\bar{v}_N$ from equation (20) and (21), we obtain

$$h_{cr}(\tau) = \frac{0.205 g \Delta\rho}{\eta C_{layer}}\left\{\left(a_o + \dot{a}\bar{\tau}_{Age}\right)^2 C_\infty (1-A) + \left(a_{crit} + \dot{a}\bar{\tau}_{Age}\right)^2 C_\infty A\right\}\tau \qquad (29)$$

where C_∞ comes from equation (23).

Similarly, as for C_∞, h_{Cr} expresses the thickness of a layer consisting of crystals coming from the cold cap if $A \to 0$ and nucleated crystals if $A \to 1$.

If the crystals inputting the melter from the cold cap are polydisperse, the procedure is similar to that applied for monodisperse crystals. The ratio between number densities of inputting crystals is assumed constant also in the melter.

If the melter temperature is higher than T_L, or the crystal input concentration from the cold cap is sufficiently high, $C_{in} > C_o$, crystals dissolve and no crystals can be nucleated in the melter ($N_{No} = 0$; $A = 0$; see equation (24)). In this case, the average residence time of crystals in the melter, $\bar{\tau}_{Cr}$, may be lower than the average residence time of glass, as some crystals completely dissolve. The value of $\bar{\tau}_{Cr}$ can be calculated from the equation:

$$\bar{\tau}_{cr} = \int_0^{\tau_{diss}} f(\tau)\tau d\tau + \int_{\tau_{diss}}^{\infty} f(\tau)\tau_{diss} \, d\tau \qquad (30)$$

Here, $f(\tau)$ is the probability density function for the distribution of glass residence times in the melter.

Thus, the first term on the right side of equation (30) expresses the portion of the average residence time of undissolved crystals (crystals in glass with low residence time), the second term expresses the portion of the average residence time of dissolved crystals (glass melt residence times are $> \tau_{diss}$).

The half of the value of $\bar{\tau}_{Cr}$ expresses the age of present crystals and should be therefore put into the mass balance in equation (24). In this case, the average crystal size, $a = a_0 + a\bar{\tau}_{Cr/2}$.

To get the values of $\bar{\tau}_{Cr}$ for the perfect mixer, the mass balance of crystals can be also used but no crystal nucleation, growing or dissolution, and settling can be considered. In this case, $C_\infty = C_{in}$ and the filling of the mixer volume by new glass is expressed as

$$C = C_{in}\left[1 - \exp\left(-\frac{\dot{V}}{V}\tau\right)\right] \qquad (31)$$

As the probability density function of glass residence times in the mixer is given by $\frac{1}{C_{in}}\frac{dC}{d\tau}$, the $f(\tau)$ function of the perfect mixer has the form

$$f(\tau) = \frac{1}{C_{in}}\frac{dC}{d\tau} = \frac{\dot{V}}{V}\exp\left(-\frac{\dot{V}}{V}\tau\right) \qquad (32)$$

By applying equations (30) ($\tau_{max} \to \infty$) and (32), we get for $\bar{\tau}_{Cr}$:

$$\bar{\tau}_{Cr} = \frac{V}{\dot{V}}\left[\exp\left(-\frac{\dot{V}}{V}\tau_{Diss}\right)\left(-\frac{\dot{V}}{V}\tau_{Diss} - 1\right) + 1\right] + \tau_{Diss}\exp\left(-\frac{\dot{V}}{V}\tau_{Diss}\right) \qquad (33)$$

Because $\tau_{\max} \rightarrow \infty$ for the perfect mixer, the inequality $\tau_{Diss} < \tau_{\max}$ is always valid when using equations (31) to (33). The polynomial expressions for the melter space filled by glass can be used as an alternative to rigorous mathematical modeling of the glass flow.

To compare the behaviour of an actual vitrification furnace with theory, the equations expressing the initial space filling by particles (crystals) for the perfect mixer and the piston flow should be presented.

The neglection of crystal nucleation in the case of the ideal mixer (equations (17) and (21)) and application of constant values of $\dot{a}$ and $\overline{\tau}_{Age}$ during space filling leads to the simplified differential equation for the instant particle concentration in the melter, C:

$$C = \frac{A}{B}\left[\exp\left(B\tau\right) - 1\right] \qquad (34)$$

where:

$$A = \frac{\dot{V}C_{in}}{V} \qquad (35)$$

and:

$$B = \frac{3\dot{a}}{a_0 + \overline{\tau}_{Age}\,\dot{a}} - \frac{0.205g\Delta\rho}{\eta}\left(a_0 + \dot{a}\,\overline{\tau}_{Age}\right)^2 \frac{\rho}{V} - \frac{\dot{V}}{V} \qquad (36)$$

For small crystals, the settling (second term) can be neglected.

If $\dot{a} \rightarrow 0$ and $\Delta\rho = 0$, the solution of equation (34) is given by (31).

For the piston flow, similar equations may be derived when neglecting crystal settling and starting from the mass balance of crystals in the melter.

The mass element of crystals in the piston flow melter is given by:

$$dm_{scc} = N_{cc}\rho_s \dot{V}a^3\left(\tau\right)d\tau \qquad (37)$$

And therefore:

$$dC = \frac{N_{cc}\rho_s \dot{V}}{V}a^3\left(\tau\right)d\tau \qquad (38)$$

Applying $N_{CC} = C_{in}/a_0^3\rho_s$ (see equation (5)), we get:

$$\frac{dC}{d\tau} = \frac{C_{in}\dot{V}}{Va_0^3}a^3\left(\tau\right) \qquad (39)$$

The Hixon-Crowell equation is applied to calculate $\dot{a}$ for both perfect mixer and piston flow [8]:

$$\dot{a} = k_H\left(C_0 - C'\rho_s\right) \qquad (40)$$

Where k_H is the mass transfer coefficient, C_0 is the equilibrium volume fraction of crystals and C' is the concentration of present crystals in the given part of the melter filled already by crystals. Inserting the instant crystal concentration in the melter, C', into equation (40), then gives:

$$\dot{a} = k_H\left(C_0 - \frac{C_{in}}{a_0^3\rho_s}a^3\left(\tau\right)\right) \qquad (41)$$

If $\dot{a} = 0$, we get from (39):

$$C = \frac{C_{in}\dot{V}}{V}\tau$$

(42)

which means that the average concentration of crystals of constant size grows linearly with time. This behaviour simulates the melter filling by a new glass melt.

To get the melter filling by dissolving or growing crystals, equations (39) and (41) are simultaneously solved.

CONCLUSION

Presented equations provide a chance to evaluate qualitatively the character of glass flow and expected particle distribution in glass melting and vitrification spaces. If the apparent similarity between a melting space and one of the presented models is found, the derived relations make it possible to calculate the concentrations and particle distribution (piston flow), as well as particle settling in the space. Thus, the numerical mathematical model requiring longterm calculations can be substituted for one of simplified models or by their combination. This is especially needed when extensive parametric studies of a melter are intended to find optimum conditions for melter operation or information about the overall character of glass flow when it is needed. The results of the simplified model can also serve as initial conditions for calculations made by the numerical mathematical model to shorten substantially the calculations. The second part of this work will provide the comparison of a HLW vitrification space with the proposed models and results of a parametric study examining the influence of temperature, melt liquidus temperature, initial spinel crystal size and concentration, as well as the impact of the value of mass transfer coefficient and melter pull rate on the crystal concentration in the melter and crystal settling on the melter bottom.

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KONCENTRACE SPINELOVÝCH KRYSTALŮ A JEJICH USAZOVÁNÍ V TAVICÍM ZAŘÍZENÍ PRO VITRIFIKACI VYSOCE RADIOAKTIVNÍCH ODPADŮ

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Matematické a laboratorní modelování procesu vitrifikace vysoce radioaktivních odpadů pomáhá nalézt mechanismy tvorby spinelových krystalů a popisuje interakce krystalů s taveninou i jejich usazování v tavicím prostoru. Pomocí výsledků modelů lze nalézt podmínky vhodné pro vyšší vitrifikační výkon příslušných zařízení. Vycházejíce ze zkušeností s numerickým matematickým modelem, autoři připravili zjednodušený model procesu založený na hmotové bilanci vcházejících, odcházejících, nukleovaných, rostoucích nebo rozpouštějících se a usazujících se krystalů v ideálně míchaném tavicím prostoru. Uvedené vztahy pro výslednou koncentraci krystalů a rychlost tvorby vrstvy usazených krystalů na dně tavicího prostoru byly doplněny odpovídajícími vztahy pro případ, že v tavicím prostoru existuje pístový tok.