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A Comparison of Simulation Techniques for Uranium Crystallization Process

Anton O. Ochoa Bique*[a], Alexey G. Goryunov[a], Flavio Manenti[b]

[a] Tomsk Polytechnic University, Dept. of Electronics and Automation of Nuclear Plants, 30 Lenina St, Tomsk, 634050, Russia
[b] Politecnico di Milano, Dept. di Chimica, Materiali e Ingegneria Chimica „Giulio Natta“, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
anthonob@tpu.ru

Developing a cellular automata model and discretized model are permitted to describe of the uranium crystallization process. The discretized model allows describing changing parameters of the crystallization process in the crystallizer active volume and choosing the most effective operating modes. The cellular automata model enables monitoring the evolution of crystal formation and the prediction of mother liquid recovery as well. The purpose of the work is to develop, describe and compare different mathematical models.

1. Introduction

The crystallization process is a complex multi-phase and multi-component process involving solid phase in the crystal form. Phase transformations and heat and mass transfer processes forming the conditions at the interface play a key-role in the formation of the material properties (Rossi et al., 2014). To properly grow crystals and operate uranium crystallization processes, it is important to carry out comprehensive studies of the phenomena involved in. For these reasons, many authors focused on crystallization process to improve controllability and operability for safety purposes. Crystallization of uranyl nitrate was studied in the literature (Chikazawa et al., 2008; Homma et al., 2008). In addition, the mathematical modeling of the crystallization process has been recently broached (Veselov et al., 2014) together with studies on the extraction processes (Goryunov et al., 2011). A novel promising approach to the simulation of crystallization processes is represented by the cellular automata, as described in Ochoa Bique and Goryunov (2014). The scope of the paper is to compare each other the existing techniques to simulate the uranium crystallization process. Due to the complexity in setting real experiments up and lack of process behavior as well, the focus of this research activity is on the use of the virtual experiment method to identify the unsteady regimes of process behavior.

2. Design and Function of a Linear Crystallizer

A linear crystallizer is a vertical metal tube with an external cooling jacket (Figure 1) as reported by Veselov(2014).

The unit can be roughly represented by three sections: a crystallization section, washing section, and crystal collection section. Uranium solution (melt), heated up to the proper operating temperature, is supplied to the crystallization zone from the top of the unit operation. The external surface of the unit is cooled by a jacket. Along the unit, the uranium solution is progressively cooled down and it becomes supersaturated and the growing process of the crystals starts in the mother liquid. Due to the difference of mass densities, the crystals acquire an additional vertical speed as compared to the mother liquid.

Nitric acid washing solution is supplied to the crystal washing zone. It rises up the working volume of the apparatus in countercurrent with respect to the precipitated crystals. It is fed to clean up the external surface layers of the crystals from the trapped impurities. The initial temperature of the washing solution and the initial concentration of the contained target product should be selected so as to have the partial dissolution of crystals in the washing solution. The countercurrent flow of nitric acid opposes to the velocity of crystals and

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their overall rate along the vertical axis of the apparatus is somehow reduced. The mother liquid and the washing solution are removed from the active volume of the crystallizer at the extremities of zones I and II.

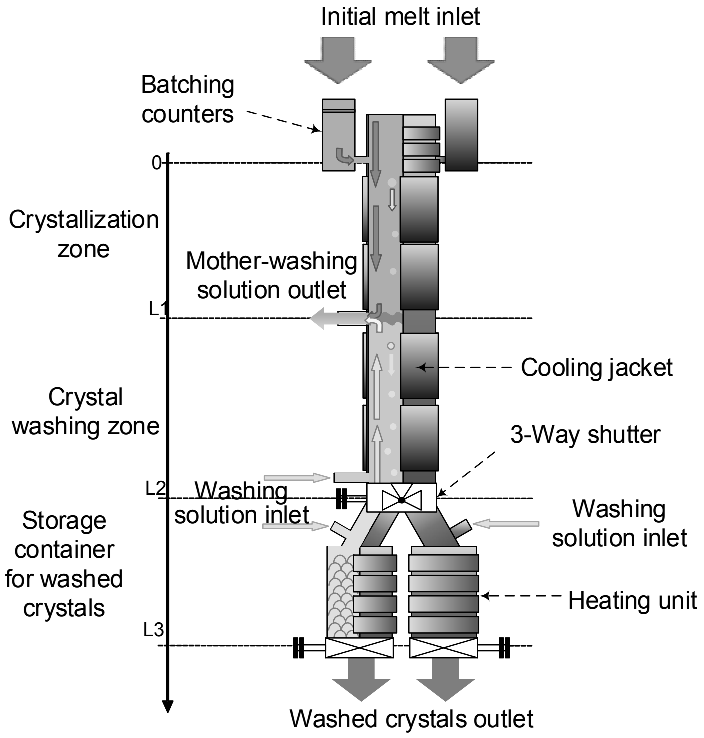

Figure 1: Diagram of a linear-type crystallizer

The design of the feed ports of the mother liquid and unloading of crystals allows to operate the crystallizer in continuous. The design of the cooling jacket of the apparatus provides independent cooling of several sections of the working areas. A conceptual model for the crystallization process is reported in Figure 2. In this work, the crystallization process is modeled by means of two different approaches: (1) the cellular automata model; and (2) the discretized model.

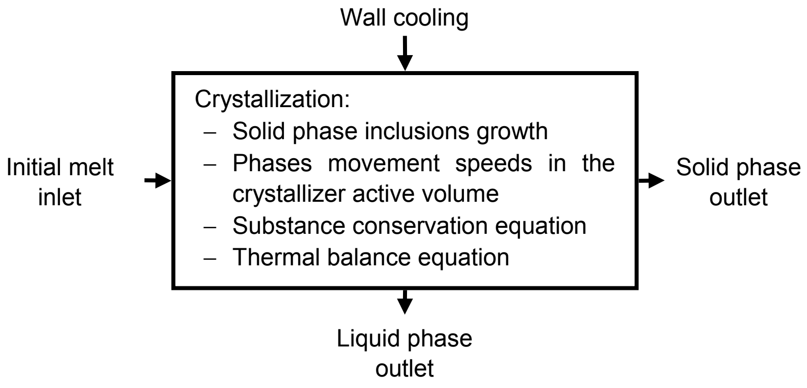

Figure 2: Conceptual model for the crystallization process

3. Mathematical model of the uranium crystal growth in the form of a cellular automaton

The process of crystal growth takes place according to certain rules and conditions (Hesselbarth and Göbel, 1991) of evolution.

Transformation of cells from the liquid state will be implemented, if the following conditions of the phase transition are fulfilled (Abasheva and Koltsova, 2007):

1. The process occurs only in the forward direction.

2. The cell can transform into the solid phase only if at least one of its neighbors is already at the solid state.
3. Cell is crystallized, if the following condition is satisfied:

$$\Delta_{ij}^{(n)} > \Delta^* - \lambda \left[\sum_{k,l \in O(i,j)} \Phi_{kl}^{(n)} - 4 \right] \tag{1}$$

where $\Delta_{ij}^{(n)}$ - supersaturation in (i,j)-cell; Δ^* - limiting supersaturation; $\Phi_{kl}^{(n)}$ - phase of (k,l)-cell of the nearest environment of (i,j)-cell; λ - parameter characterizing the effect of the local curvature of interphase surface on the condition of the phase transition. The effect of the local curvature of interphase surface is related to vertical sum of neighbor's phase states. When in the nearest environment there are exactly four solid cells, it indicates the absence of the effect of the curvature of the interphase surface.

Also, the phase transition of the cell is accompanied by an increase in cell temperature T_{ij} itself and a decrease in the concentration of the components in liquid cells of the nearest environment C_{kl} :

$$T_{ij}^{(n+1)} = T_{ij}^{(n)} + dT \tag{2}$$

$$C_{kl}^{(n+1)} = C_{kl}^{(n)} - q \cdot \Delta_{kl}^{(n)} \tag{3}$$

In addition, at each time step, the heat exchange and the diffusion of components is accounted for between the adjacent liquid cells:

$$C_{ij}^{(n+1)} \to C_{ij}^{(n)} + \frac{D}{m} \cdot \left(\left\langle C_{kl}^{(n)} \right\rangle - C_{ij}^{(n)} \right) \tag{4}$$

$$T_{ij}^{(n+1)} \to T_{ij}^{(n)} + \frac{a}{p} \cdot \left(\left\langle T_{kl}^{(n)} \right\rangle - T_{ij}^{(n)} \right) \tag{5}$$

where

$$\left\langle C_{kl}^{(n)} \right\rangle = \frac{1}{n_{liq}} \cdot \sum_{k,l \in O(i,j)} C_{kl}^{(n)} \tag{6}$$

$$\left\langle T_{kl}^{(n)} \right\rangle = \frac{1}{8} \cdot \sum_{k,l \in O(i,j)} T_{kl}^{(n)} \tag{7}$$

where n_{liq} - number of liquid cells in the nearest environment of (i,j)-cell ($n_{liq} \le 8$); $\left\langle C_{kl}^{(n)} \right\rangle$ and $\left\langle T_{kl}^{(n)} \right\rangle$ - respectively, the average concentration of the liquid cells and the average temperature in liquid and solid cells of the nearest environment of the (i,j)-cell;

D, a, m, p- parameters characterizing by the diffusion coefficient, thermal conductivity, as well as the discretization of space and time.

4. Mathematical model of the uranium crystallization process (discretized model) in the linear crystallizer

A liquid nitric-acid uranyl nitrate solution (liquid solution) is ideally considered as a three-component liquid:

$$C_{UN}^m + C_{HNO_3}^m + C_{H_2O}^m = \sum_{i=1}^{NC} C_i^m = 1 \tag{8}$$

where C_i^m is a mass content of the i-th component in the liquid solution. Mass content values of uranyl nitrate (UN) and nitric acid (HNO_3) are evaluated by initial conditions of uranium (U) and HNO_3 concentrations.

The dependence between C_{UN}^m and $C_{HNO_3}^m$ is described in (Veselov et al., 2014).

$$C_{UN}^m = A - \psi \cdot C_{HNO_3}^m, \quad A = 1/(1+\alpha) = 0.785 \tag{9}$$

where the parameter α is the ratio of six molar mass of water to the molar mass of UN (it needs six molecules of water per the one molecule of UN to get the one crystal of uranyl nitrate hexahydrate). $\psi = (A - C_{UN}^{m,\text{int}}) / C_{HNO_3}^{m,\text{int}}$ - the slope of the line, determined by the composition of the initial melt.

The growing rate of the crystal radius is stated as follows:

$$\frac{dR}{dt} = k(C_{UN}^{m} - C_{UN}^{m,sat}) \cdot \frac{L}{U_s} - R \tag{10}$$

where k - the growth rate of the crystal phase inclusions (in the general case k is the function of temperature and liquid phase composition); U_s - a speed of solid phase movement; $C_{UN}^{m,sat} = C_{UN}^{m,sat}(T,\psi)$ – concentration of UN saturation in liquid solution (the function of temperature and composition).

Liquid and solid phases in the crystallizer active volume move with different velocities owing to their mass densities difference. The velocity of solid phase movement $U_s(\text{t})$ can be written by the following expression:

$$U_s(\text{t}) = U_{liq} + \frac{2}{9}\frac{g}{\upsilon} R^2 \left[\frac{\rho_s}{\rho_{liq}} - 1 \right] \tag{11}$$

where U_{liq} - liquid velocity; g – gravity; υ - liquid phase kinematic viscosity (function of the temperature and composition); ρ_s and ρ_{liq} – mass densities of solid and liquid phases, respectively.

The density of the liquid phase is described according to Chikazawa et al. (2008): $\rho_{liq} = [1.023 + 2.936 \cdot 10^{-2} \cdot C_{HNO3} + 1.313 \cdot 10^{-3} \cdot C_U - (4.681 \cdot 10^{-4} + 3.475 \cdot 10^{-5} \cdot C_{HNO3}) \cdot T] \cdot 10^3$.

The conservation principle applied for UN and HNO3 leads to the Eq. (12) and Eq. (13).

$$\frac{dC_{UN}^{m}}{dt} = \frac{Q_0 \cdot C_{UN}^{\text{m,int}} - U_{liq} \cdot S \cdot (1 - 4/3 \cdot \pi R^3(t) n) \cdot C_{UN}^{m} - U_s \cdot S \cdot 4/3 \cdot \pi R^3(t) n \cdot A}{U_{liq} \cdot S \cdot (1 - 4/3 \cdot \pi R^3(t) n)} \tag{12}$$

$$\frac{dC_{HNO3}^{m}}{dt} = \frac{Q_0 \cdot C_{HNO3}^{m,\text{int}} - U_{liq} \cdot S \cdot (1 - 4/3 \cdot \pi R^3(t) n) \cdot C_{HNO3}^{m}}{U_{liq} \cdot S \cdot (1 - 4/3 \cdot \pi R^3(t) n)} \tag{13}$$

where Q_0 is an initial volumetric flow rate; S – sectional area; n - amount of crystallization centers.

The energy balance for the active volume of the crystallizer is stated as follows and provide the temperature variation due to enthalpic bulk contributions, internal heat exchange and external (cooling jacket) heat exchange contributions:

$$\frac{dT}{dt} = T_{in} - T - \frac{\pi \cdot D \cdot \chi \cdot (T - T_{cj})}{\rho_{liq} \cdot \mathrm{C}_{liq} \cdot Q_0 \cdot \left(1 - 4/3 \cdot \pi R^3(t) n\right) + 4/3 \cdot \pi R^3(t) n \cdot \mathrm{C}_s \cdot \rho_s \cdot S \cdot U_s} \tag{14}$$

where D – diameter of the cross section of the crystallizer active volume; C_s and C_{liq} – specific heat of solid and liquid phases; χ – heat conductivity of the media (solid + liquid phases) in the considered crystallizer working volume section; T_{cj} - temperature of the cooling jacket.

5. Virtual Experiments

Using the proposed model of crystal growth, different patterns of crystal growth were calculated. All computed numerical results are reported in Figure 3 and in Table 1.

Table 1: Numerical results of crystal point

-	Step of iteration (N)	Initial concentration (C)	Initial temperature (T)	Number of crystal point
Test 1	30	1.22	25	1068
Test 2	60	1.22	25	1356
Test 3	30	1.2	25	592
Test 4	30	1.21	25	1004
Test 5	60	1.22	27	908
Test 6	60	1.22	30	572

Figure 3 shows the growth pattern of the uranium crystal at different values of time (step of iteration), the initial concentration ($C = C_{UN}^{m} / C_{UN}^{m,sat}$) and the initial temperature. Increase of the uranium crystal rate, depending on reduction of the initial temperature (C = const) and on the increase of the initial concentration, (T = const), takes place, since in both cases there is an increase of the initial supersaturation. With higher initial supersaturation, the system results far away from the equilibrium condition and, consequently, the crystal growth rate is faster.

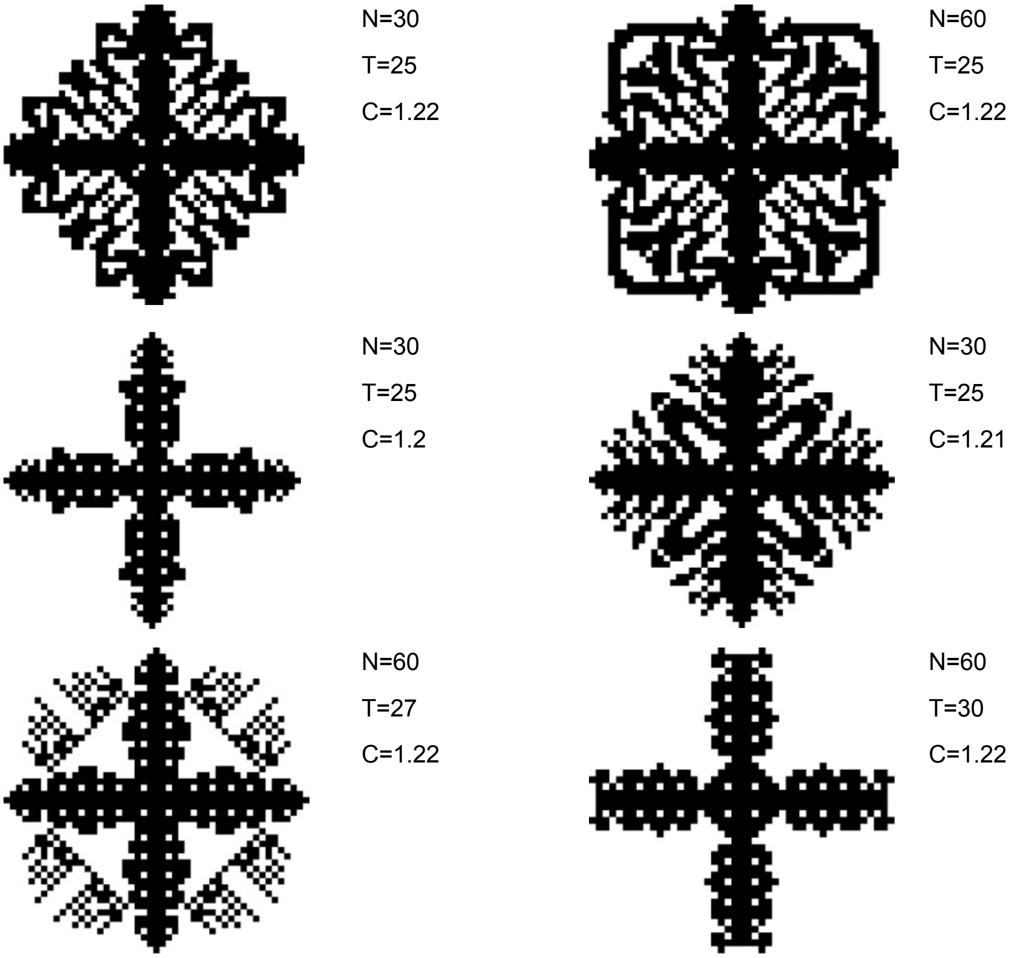

Figure 3: Effect of initial values on the crystal growth

The cellular automata model allows monitoring the evolution of crystal formation. In this case, it makes possible to detect of mother liquor catching. Cellular automata for crystallization are discrete in time, physical space, and orientation space and is used quantities such as dislocation density and crystal orientation as state variables. Cellular automata is defined on two-dimensional lattice. Physics of the process are taken into consideration in this approach. It is possible to set complex boundary conditions, consider the complex phase transitions with intermediates, and assume distribute values for the phase formation and concentration and temperature as well. This is not possible in case of differential equations, first-principles models.

However, the proposed discretized model of linear crystallizer allows analyzing different temperature modes with respect to the process optimization. It became possible when the active volume of the crystallization zone was split on 20 series-connected sections and the discretized model was used for the every section. Set of equations described in Section 4, reasonably determines the dynamics of growth / dissolution of the crystalline phase and the dynamics of liquid phase movement. Mass concentrations of uranium and nitric acid, the temperature and flow rate of the mother liquor entering the entrance of the crystallizer took by initial data.

Figure 4 shows the trends of UN concentration in the liquid phase (%wt) and the diameter of solid phase growth (in m) depending on time for the every section.

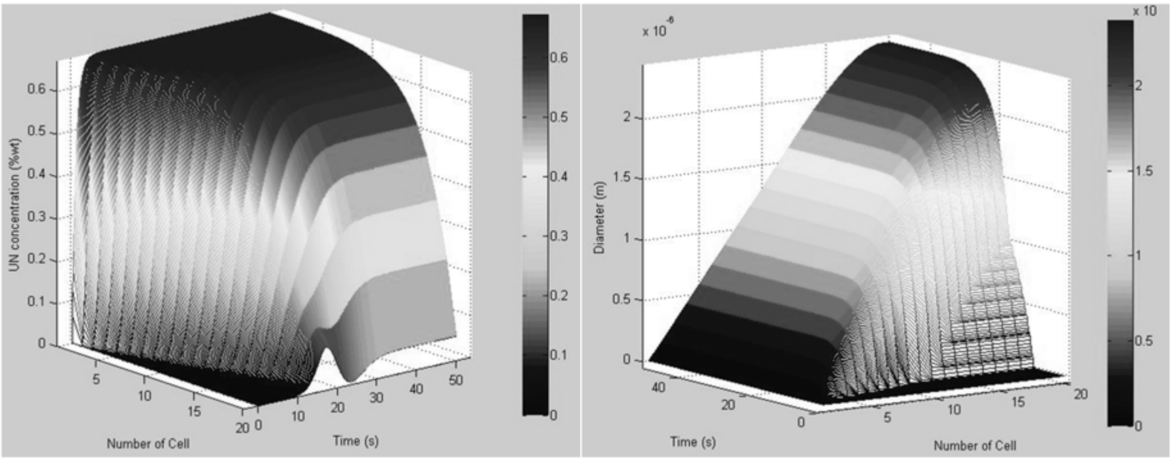

Figure 4: Dependence of UN concentration and the diameter of solid phase growth *on time*

6. Conclusions

On the basis of cellular automata model, different calculations of the patterns of crystal growth were carried out. An assessment of the effect of perturbations in the initial conditions on the rate of crystal growth was conducted. A discretized model described the main dynamics of the crystallization process. The model allows to properly analyze different temperature regimes of crystallization process, which allows choosing the most effective operating modes of linear crystallizer. Further, it is planned to test both models against real data.

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