



Solver documentation of Ni-Mn-Co hydroxides
co-precipitation

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1 Introduction

The present document provides a full description of the developed solver for the analysis of the Ni-Mn-Co co-precipitation in the presence of aqueous ammonia.

In the next sections all the features of the solver will be explained, e.g., the micromixing model adopted, how the chemical equilibrium is evaluated and how the population balance equation is solved. Following a short description of other features will be given and, in conclusion, a different approach, i.e., the compartment model, will be described.

2 Solver description

This solver is able to simulate the Ni-Mn-Co co-precipitation process in continuous reactors coupling Computational Fluid Dynamics (CFD) and Population Balance Modelling (PBM); the CFD solves the flow and total concentrations fields, while the PBM describes the formation and the size evolution of particles considering all particle processes, i.e., nucleation, growth, aggregation and breakage.

The Ni-Mn-Co hydroxide synthesis is performed in aqueous solution by reacting metal sulphates with sodium hydroxide in presence of ammonia as chelating agent. Chemical reactions cause an increase of the supersaturation, the driving force of the co-precipitation process; the supersaturation indicates if the metal hydroxide activities are higher, equal or lower than their solubility product. When a solution is supersaturated, nucleation and growth rates increase, and the formation of particles take place. Considering that the size of the precipitated particles is on the order of tens micron, it's possible to solve first the flow and turbulence fields because is reasonable to say that particles are passive and not influence the flow field.

The particle size distribution that characterizes the particle population is described by the Population Balance Equation that in turn is approximated by the quadrature method of moments, so the governing equations of moments are solved [1].

The simulation workflow is the following: after performing the CFD of the system in a decoupled manner, the solver starts to simulate the co-precipitation process solving the chemical equilibrium in order to determine the supersaturation of the system. Then, using a quadrature approximation, it will find the weights and abscissas to evaluate nucleation, growth, aggregation and breakage of particles and the precipitation rate. Finally, all the governing equations are solved; these steps are looped until the convergence is reached.

2.1 Micromixing model

In systems where the reactants are fed from different inlets, if the reactions are fast, it is possible that the solution is segregated at the molecular scale slowing the reaction rate. To take into account this phenomenon, a multi-environment micromixing model was implemented: this approach treats the segregation defining environments that interact together and that are described, at each time and spatial position, by a probability of the corresponding composition probability density functions [2]. Each feed is associated to an environment that mix together to form a reacting environment in which occurs the precipitation. The local concentrations of the species involved in a specific environment remain constant, but their probability decrease to the detriment of the reacting environment. The probabilities are tracked by the following equation:

$$\frac{\partial p_i}{\partial t} + \mathbf{u}_f \cdot \frac{\partial p_i}{\partial \mathbf{x}} = \frac{\partial}{\partial \mathbf{x}} \cdot \left(\Gamma_t \frac{\partial p_i}{\partial \mathbf{x}} \right) - r_i \quad \text{for } i \in \{1, 2, 3\} \quad (1)$$

where p_i is the probability of i -th environment, \mathbf{u}_f is the velocity of the fluid

that is equal to the one of the particles, Γ_t is the turbulent diffusivity and r_i is the probability flux from an environment to the reacting one, whose probability p_4 is the complement to 1 of the summation of the first three environments.

The flux $r_i = \gamma p_i (1 - p_i)$ that gives the rate at which the i -th environment is transformed into the reacting one is function of the probability of the i -th environment and of γ , variable depending on the turbulent properties, i.e., the turbulent kinetic energy κ and the dissipation rate ε , and that is expressed by the following equation:

$$\gamma = C_f \frac{C_\phi}{2} \frac{\varepsilon}{\kappa} \quad (2)$$

where C_f and C_ϕ are modelling coefficients. The former one is a correction factor used to match the scalar dissipation rate predicted by the model and that evaluated assuming a fully developed scalar spectrum in turbulence flows (see the Supplementary Material of our previous work [3]), while the latter is a parameter that depends on the local turbulent Reynolds number. The correlation used can be found in the work of Liu and Fox [4].

2.2 Chemical equilibrium

As mentioned before, the supersaturation of the systems, that is useful to evaluate the particle process rates, depends on the metal hydroxides activities in the precipitation environment. To determine the supersaturation, it's necessary to solve the chemical equilibrium that is characterized by all the reactions of complexation between metals and ammonia and the dissociation reaction of water and ammonia. All the reactions taking into account to describe the process can be found in the work of Van Bommel and Dahn [5] and are showed in Table 1. The effect of temperature is also considered implementing temperature dependencies for the dissociation constants of water and ammonia.

Table 1: Equilibrium reactions involved in the co-precipitation of $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ and the logarithmic of their constants [5]

Reactions	Ni	Mn	Co
$\text{M}_i^{2+} + \text{NH}_3 \rightleftharpoons [\text{M}_i(\text{NH}_3)]^{2+}$	2.81	1.00	2.10
$\text{M}_i^{2+} + 2 \text{NH}_3 \rightleftharpoons [\text{M}_i(\text{NH}_3)_2]^{2+}$	5.08	1.54	3.67
$\text{M}_i^{2+} + 3 \text{NH}_3 \rightleftharpoons [\text{M}_i(\text{NH}_3)_3]^{2+}$	6.85	1.70	4.78
$\text{M}_i^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{M}_i(\text{NH}_3)_4]^{2+}$	8.12	1.30	5.53
$\text{M}_i^{2+} + 5 \text{NH}_3 \rightleftharpoons [\text{M}_i(\text{NH}_3)_5]^{2+}$	8.93		5.75
$\text{M}_i^{2+} + 6 \text{NH}_3 \rightleftharpoons [\text{M}_i(\text{NH}_3)_6]^{2+}$	9.08		5.14
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$-0.0000422 T^2 + 0.0038 T - 4.82$		
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$-0.000113 T^2 + 0.0371 T - 14.8$		

Considering that the co-precipitation process occurs at basic pH, is reasonable to assume that ammonia is negligible dissociated at equilibrium conditions and the self-ionization of water has an insignificant contribution to the amount of OH^- in solution, so the activity coefficients are not considered in the chemical equilibrium calculations but only in the evaluation of the supersaturation. The equilibrium concentrations are calculated by solving a system of non-linear equations adopting the Newton-Raphson method.

The total concentrations of nickel, manganese, cobalt, ammonia, sodium and sulphates are tracked by the following governing equations:

$$\frac{\partial s_\alpha^{(4)}}{\partial t} + \mathbf{u}_f \cdot \frac{\partial s_\alpha^{(4)}}{\partial \mathbf{x}} = \frac{\partial}{\partial \mathbf{x}} \cdot \left(D_{\text{eff}} \frac{\partial s_\alpha^{(4)}}{\partial \mathbf{x}} \right) + \sum_{i=1}^3 r_i c_{T,\alpha}^{(i)} - Q_\alpha^{(4)} \quad (3)$$

where $s_\alpha^{(4)} = p_4 c_{T,\alpha}^{(4)}$ is the volume-weighted total concentrations of the chemical species mentioned before, $c_{T,\alpha}^{(4)}$ is the total concentration of species α in the react-

ing environment, D_{eff} is the summation of molecular and turbulent diffusivity, $\sum_{i=1}^3 r_i c_{T,\alpha}^{(i)}$ is the flux of species from the feed environment to the reacting one and $Q_\alpha^{(4)} = p_4 k_v \frac{\rho_{cry}}{MW_{cry}} h_3^{(4)}$ is the source term for the species consumed by the co-precipitation and it's equal to the generated volume of precipitate (see Eq. (9) in Section 2.3.1 to understand how it is calculated), where k_v is the shape factor and ρ_{cry} and MW_{cry} are respectively density and molecular weight of the crystals. Note that the $^{(4)}$ superscript is only used to tell the reader that the quantity is evaluated in the reacting environment and therefore weighted by its probability p_4 .

2.2.1 Newton-Raphson method

The equation considered to solve the chemical equilibrium with the Newton-Raphson method are mass balances for Nickel, Cobalt, Manganese and ammonia, and the electro-neutrality equation. From the definition of reaction constants, the concentration of the metal-ammonia complexes, NH_4^+ and H^+ are determined and substituted in the system of non-linear equations mentioned before. In this way we obtain a set of equations in terms of five unknowns that depend on the solution of transport equations. The five unknowns are: pNi^{2+} , pMn^{2+} , pCo^{2+} , pNH_3 and pOH^- . The set of equations can be represented in a vector (\mathbf{x}) form that is used in the iterative Newton-Raphson method to solve the following system of equations:

$$J(\mathbf{x}^n) \Delta \mathbf{x} = f(\mathbf{x}^n) \quad (4)$$

where $J(\mathbf{x}^n)$ is the Jacobian matrix of the set of equations $f(\mathbf{x}^n)$, $\Delta \mathbf{x} \equiv (\mathbf{x}^{n+1} - \mathbf{x}^n)$ is the unknown vector and n is the iteration number. The iterative calculation is performed until the error vector is lower than a threshold pre-fixed and the final version of the vector \mathbf{x} is the solution vector. A more

detailed explanation of the equilibrium calculation can be found in the Supplementary Material of our previous work [3].

2.2.2 Activity coefficients

As mentioned before, the activities of metal hydroxides are taken into account to determine the supersaturation in order to consider the deviation of the process from the ideal solution. They are calculated with the following equation:

$$a_{M^{2+}}(a_{OH^-})^2 = [M^{2+}][OH^-]^2\gamma_{\pm}^3 \quad \text{for } M \in \{Ni, Mn, Co\} \quad (5)$$

where γ_{\pm}^3 is the mean molal activity coefficient between the cation metal and hydroxide ion that is evaluated adopting the method of Bromley [6], considering that the reacting medium is a multi-component solution.

After evaluating the activity coefficients, they are used to determine the supersaturation, driving force of the co-precipitation, through the following equation:

$$S = \sqrt[3]{\frac{(a_{Ni^{2+}})^{0.8} (a_{Mn^{2+}})^{0.1} (a_{Co^{2+}})^{0.1} (a_{OH^-})^2}{\left(k_{sp}^{Ni(OH)_2}\right)^{0.8} \left(k_{sp}^{Mn(OH)_2}\right)^{0.1} \left(k_{sp}^{Co(OH)_2}\right)^{0.1}}} \quad (6)$$

that can be expressed in function of the metal concentrations by replacing the activity coefficients with the previous equation. The final form is the following:

$$S = \sqrt[3]{\frac{\left([Ni^{2+}]\gamma_{Ni\pm}^3\right)^{0.8} \left([Mn^{2+}]\gamma_{Mn\pm}^3\right)^{0.1} \left([Co^{2+}]\gamma_{Co\pm}^3\right)^{0.1} [OH^-]^2}{\left(k_{sp}^{Ni(OH)_2}\right)^{0.8} \left(k_{sp}^{Mn(OH)_2}\right)^{0.1} \left(k_{sp}^{Co(OH)_2}\right)^{0.1}}} \quad (7)$$

2.3 Population Balance Equation

The evolution of the PSD in the spatial domain and time is described, as mentioned before, by the Population Balance Equation (PBE) and to solve it, a quadrature method of moments is employed. In this way the PSD is approxi-

mated by a summation of N (normally $N = 2$ or $N = 3$) weighted Dirac delta functions each located at a quadrature abscissa; the weights and abscissas obtained by the quadrature approximation of the problem are described by the moments of lower order and they are used to determine particle processes rates, i.e., nucleation, growth, aggregation and breakage, source terms of moment governing equations, completing the closure of the problem. Weights and abscissas are calculated by a 1-D adaptive quadrature technique based on the Chebychev algorithm.

This approximation allows to solve the PBE tracking $2N$ moments of the PSD by the following equation:

$$\frac{\partial \langle m_k^{(4)} \rangle}{\partial t} + \mathbf{u}_f \cdot \frac{\partial \langle m_k^{(4)} \rangle}{\partial \mathbf{x}} = \frac{\partial}{\partial \mathbf{x}} \cdot \left(\Gamma_t \frac{\partial \langle m_k^{(4)} \rangle}{\partial \mathbf{x}} \right) + p_4 h_k^{(4)} \quad \text{for } k \in \{0, \dots, 2N - 1\} \quad (8)$$

where $m_k^{(4)}$ is the volume weighted moment of order k in the reacting environment and $h_k^{(4)}$ is the source term of the k -order moment, function of nucleation, growth, aggregation and breakage rates.

2.3.1 Source terms

The term $h_k^{(4)}$ in the governing equations of the moments represents the source term, that is defined in the following way:

$$h_k^{(4)} = J L_c^k + k G m_{k-1}^{(4)} + \overline{B}_k^a - \overline{D}_k^a + \overline{B}_k^b - \overline{D}_k^b, \quad (9)$$

where J is the nucleation rate, L_c is the size of the nuclei and G is the growth rate. \overline{B}_k^a and \overline{B}_k^b are the particle birth rates due respectively to aggregation and breakage, while \overline{D}_k^a and \overline{D}_k^b are the death rates always due to the same particle processes. A detailed explanation of the expressions used to model the different particle processes and all the relative references can be found in our previous

work [3].

Nucleation and growth Nucleation and growth rates are function of the supersaturation. The first one is described by the classical nucleation theory, taking into account both contributions due to homogeneous and heterogeneous nucleation, while the latter depends linearly on the supersaturation, assuming a diffusion-controlled growth. The expressions employed are the followings:

$$J = k_1 \exp\left(\frac{-B_1}{(\ln S)^2}\right) + k_2 \exp\left(\frac{-B_2}{(\ln S)^2}\right) \quad (10)$$

$$G = k_G(S - 1) \quad (11)$$

where k_1 , k_2 , B_1 , B_2 and k_G are modelling coefficients.

Aggregation and breakage Aggregation and breakage rates depend on the physical and turbulence properties of the fluid, but also on the particle sizes. When a method of moments is employed, the contributions of these two particle processes can be expressed by the following equations:

$$(\overline{B_k^a} - \overline{D_k^a}) = \sum_{i=1}^N \sum_{j=1}^N w_i^{(4)} w_j^{(4)} \beta_{ij} P_{ij} \left[\frac{1}{2} (L_i^3 + L_j^3)^{k/3} - L_i^3 \right] \quad (12)$$

$$(\overline{B_k^b} - \overline{D_k^b}) = \sum_{i=1}^N w_i^{(4)} a_i \left[b_i^{(k)} - L_i^k \right] \quad (13)$$

where w_i and L_i are respectively weights and abscissas calculated by the adaptive quadrature technique, β_{ij} is the aggregation kernel that consider the contributions of both, Brownian motion and turbulence fluctuations, P_{ij} is the aggregation efficiency, a_i is the breakage kernel and $b_i^{(k)}$ is the fragment distribution functions for the moment of order k .

The aggregation kernel is expressed by the following equation:

$$\beta_{ij}^{Br} = \frac{2k_B T}{3\mu} \frac{(L_i + L_j)^2}{L_i L_j} + \beta_{ij}^{Turb} = C_T \pi \sqrt{\frac{8}{15}} \left(\frac{\varepsilon}{\nu}\right)^{0.5} (L_i + L_j)^3 \quad (14)$$

where k_B is the Boltzmann constant, T is the temperature, μ and ν are the respectively the liquid and the kinematic viscosity and, in the end, C_T is a modelling parameter.

Instead, the aggregation efficiency $P_{ij} = \exp\left(-\frac{t_c}{t_i}\right)$ is function of the ratio between the time required by two colliding particles to form a stable link between them and the interaction time of these particles (function of kinematic viscosity and dissipation rate). The time required to create a stable bridge ($t_c = \frac{D_b}{f(\delta)G}$) is function of the dimension D_b of this bridge, which can be expressed by the following equations:

$$D_b = \frac{\sqrt{\rho}(\varepsilon\nu)^{1/4}}{\sqrt{A_p}} \frac{L_i L_j}{\sqrt{L_i^2 + L_j^2 - L_i L_j}}, \quad (15)$$

where ρ is the liquid density and A_p is a modelling parameter. A better explanation of the expressions used can be found in our previous work [3].

The breakage mechanisms considered are the following: symmetric fragmentation, uniform fragmentation, parabolic distribution and erosion with a specific mass ratio between daughter particles. In the works of Marchisio and co-workers [7] can be found the expressions used to model the fragment distribution functions and the breakage kernel. The expression used to model the breakage rate is the following:

$$a_i = C_{br} \frac{(L_i/\eta)^{\gamma_{br}}}{\tau_\eta} \quad (16)$$

where $\tau = (\nu^3/\varepsilon)^{0.25}$ and $\tau_\eta = (\nu/\varepsilon)^{0.5}$ are respectively the length and the time of the Kolmogorov scale, while C_{br} and γ_{br} are modelling parameters.

3 Other features

The developed solver can find a lot of applications to simulate the co-precipitation in continuous reactor, even at industrial scale that are characterized by very large volume and high residence time. This results in very long computational times, so other features are implemented, in the OpenFOAM solver, in order to reduce the computational costs of the simulations.

3.1 Operator-splitting approach

The first implementation added is an operator-splitting approach that improves solver robustness increasing the time-step and reducing simulation instabilities, and also makes faster the solver. With this method, the governing equations are solving in different steps: first, the transport of variables, i.e., probabilities, concentrations and moments, is solved for a half of the time step, obtaining an intermediate solution that is used to evaluate the supersaturation and to perform the integration source over a time step. After updating the local variables, the transport is solved for the remaining half time step.

The integration of the source terms is performed by an appropriate ordinary differential equation (ODE) solver and, for this reason, the CVODE integrator of SUNDIALS package is coupled with the model to perform the source integration with high-order stiff methods.

However, there are some drawbacks using this method, as the load-balance issue. Indeed, adopting the operator-splitting approach is possible that some cores require more time to perform the integration source, due to the large supersaturation gradient inside the reactor, slowing down all the other cores used to perform the simulation. In order to limit this problem, an hybrid parallelization is implemented.

3.2 Hybrid parallelization

The implementation of the hybrid parallelization, using MPI and OpenMP, is employed with the aim of reduce the load-balance issue and speed up the simulations. As mentioned before, adopting the operator-splitting approach, when the number of cores is increased too much, a great discrepancy of the load between each cores occur. Implementing the hybrid parallelization, it is possible to use a large number of cores that are necessary to perform the source integration in short times and, at the same time, decompose the spatial domain in less parts improving the load-balance of the simulation. MPI tasks are used only for the domain decomposition, while OpenMP threads assigned to each task are employed only for the integration of the source terms. In this way, the load-balance issue is almost solved because, decomposing the reactor in less zones, and so the solver is faster, also because the communication time between each core is shorter.

4 Compartment Model

Despite the implementation of the operator-splitting approach and the hybrid parallelization, the computational time required by the solver to perform a simulation is very long, so a less demanding method was developed: the Compartment Model. This approach consists of dividing the reactor into different compartments which exchange mass with their neighbours; moreover, the compartments are completely mixed. They are a collection of adjacent cells characterized by a mean value of all the variable tracked by the model, from the flow and turbulence properties to species concentrations and moments.

The reactor division must be done following specific criteria and, to do so, an automatic python script was developed to compartmentalize the system based

on the dissipation rate (ε) and probability fields; indeed, the latter ones are used to take in consideration the zones of the reactor where the supersaturation of the process is high, while the former is used to divide the remaining part of the system.

In this way, the division of the reactor requires only a CFD simulation without the PBE. After that, by using the fields of the variables mentioned before, the compartmentalization of the reactor is made through an agglomerative clustering method; the advantages of this algorithm are that it can consider the connectivity between cells, essential to create compartment with contiguous cells, and moreover it can be extended to consider more than one criterion for clustering. The division of the reactor is performed by the sklearn (scikit-learn) module of python; the entries required by the algorithm are the number of regions in which you want to divide the reactor, the criterion on which the compartmentalization is based and the connectivity between the cells (this is a sparse matrix in which the element at row i and column j is equal to 1 if cell i and cell j are adjacent). The linkage criterion used to perform the compartmentalization is the Ward's method; the algorithm, at each step, find the pair of clusters (also considering the connectivity between cells) that leads to minimum increase of the variance of the variable on which is based the compartmentalization. The division consists of three steps:

1. The reactor is divided in 5 regions employing as criterion, the value of the summation between the probability of metal sulphates and sodium hydroxide environments ($p_1 + p_3$). All the cells with a value lower or higher than a threshold, are divided from the others; the cells with a value of $p_1 + p_3$ in the desired range are near the inlet and they are considered as 2 regions (it's not possible to consider them as a single compartment because they are not contiguous, unless the range is expanded). The other

cells are the one of the final parts of the inlet tubes of metal and NaOH and the remaining part of the reactor; they represent 3 different regions because all of them are not contiguous

2. After the first division, the zone far from the inlets is divided using the turbulent dissipation rate as criterion. The final parts of the inlet tubes of metals and NaOH are considered as 2 compartments.
3. In the end, the zones near the inlets are divided in different compartments using, as criterion, both probabilities and turbulent dissipation rate. The probability field is scaled employing the following expression:

$$p = \frac{1}{\sqrt[3]{1 - (p_1 + p_3)}} - \frac{1}{\sqrt[3]{p_1 + p_3}} \quad (17)$$

The governing equations solved by the compartment model are the followings:

$$\frac{dm_{k,i}}{dt} = \sum_j F_{j,i} m_{k,j} - \sum_j F_{i,j} m_{k,i} + S_{k,i}, \quad (18)$$

$$\frac{dC_{\alpha,i}}{dt} = \sum_j F_{j,i} C_{\alpha,j} - \sum_j F_{i,j} C_{\alpha,i} - S_{\alpha,i}, \quad (19)$$

where $m_{k,i}$ is the moment of order k in the i -th compartment, $F_{i,j}$ is the flux between the i -th compartment and the j -th one, $S_{k,i}$ is the source term of the moment of order k in the i -th compartment, $C_{\alpha,i}$ is the concentration of the species α in the compartment i -th and $S_{\alpha,i}$ is the source terms in the i -th compartment of the species α that consider both, the precipitation rate and the flux from the feed environment to the reacting one. The flux $F_{i,j}$ is the summation of the flux of the cells that are at the boundary between the compartment i -th and j -th. The information about which cells are adjacent and in different compartments are obtained by the compartmentalization script described before.

In order to make the solver faster and more stable, also for the compartment model were implemented the operator-splitting approach and the source integration is parallelized with MPI through the python package mpi4py.

The great advantage of the compartment model is that is possible to drastically decrease the computational time of the simulation because the governing equations are solved for a small number of compartments and not for all the cells of the mesh used in the full CFD-PBM simulations. It's important to underline that the solution obtained approximates the true solution of the process, but it can be very useful obtain a first result that is quite in agreement with the full CFD-PBM approach.

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