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SIMULATION OF CONTINUOUS Ni-Mn-Co HYDROXIDE CO-PRECIPITATION BY COMPARTMENTAL POPULATION BALANCE MODELLING

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The layered lithium-nickel-manganese-cobalt oxides (NMC) is becoming the dominant cathode material in the lithium-ion battery market due to their attractive features, e.g., high capacity and thermal stability. Consequently, considerable efforts have been invested in studying the synthesis of precursor materials for NMC cathodes. The main precursor of these cathodes is Ni-Mn-Co hydroxide, $Ni_{1-x-y}Mn_xCo_y(OH)_2$, that is primarily produced in continuous stirred-tank reactors (CSTR). While many experimental works have been conducted to study the co-precipitation of $Ni_{1-x-y}Mn_xCo_y(OH)_2$, in particular the effect of operating conditions on the particle properties such as the particle size distribution (PSD), only few attempts have been made to simulate this process. Recently, we have proposed a coupled computational fluid dynamics-population balance modelling (CFD-PBM) approach to simulate the co-precipitation of $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ in an experimental vortex mixer [1]. However, the simulation of a typical industrial CSTR for the co-precipitation of Ni-Mn-Co Hydroxides becomes excessively long due to the large separation of timescales, i.e., very fast co-precipitation versus long reactor residence time (which is required to obtain spherical and compact particles). Thus, the present work is aimed at developing a compartmental PBM to reduce the computational time needed to simulate the co-precipitation of $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ in CSTRs, which is very useful for identifying the optimal operating conditions, scaling-up the process and adapting the product to fulfil the market demand.

Let us start with a brief process description. $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ particles are co-precipitated by injecting a 2M aqueous solution of metal sulphates (80% $NiSO_4$, 10% $MnSO_4$ and 10% $CoSO_4$) and a 5M NaOH solution into a baffled CSTR (see Figure 1) filled with 1 M ammonia solution. Table 1 lists the reactions taking place in the reactor [2]. Ammonia acts as the chelating agent that controls the molecular growth of particles. It is fed to the reactor by injection of a 10 M NH_3 solution. Most of the metal concentration is expected to precipitate near the metal injection tube through the nucleation and molecular growth. Subsequently, the formed particles undergo aggregation and breakage under turbulent conditions created by the agitator that rotates at 200 rpm. Eventually, the final particles are collected from the outlet at the top of the reactor.

A crucial step in developing the compartmental model is the definition of the compartment network, i.e., division of the reactor into a desired number of compartments based on suitable criteria. These criteria should reflect the gradient of fields used in the formulation of models for the nucleation, molecular growth, aggregation, and breakage, i.e., the supersaturation and turbulent dissipation rate (ε). The latter can be obtained by conducting a CFD simulation, however, the former requires a full CFD-PBM simulation, which is undesirable due to the high computational cost. It is noteworthy that the supersaturation is generated in regions close to the injection tubes where the mixing takes place. Since the co-precipitation reaction is very fast, it can be assumed that the micromixing is the controlling-step, hence the main factor in determining the supersaturation gradient. Thus, we employ a multi-environment micromixing model [3] that describes the segregation of the feed solutions (environments) near the injection points, and then, we use the environment volume fractions to define compartments there. The CFD and micromixing governing equations are solved by using Ansys Fluent v21R2. Next, we use the "*reactor network*" tool of Ansys Fluent to automatically separate cells with similar values of ε and environment volume fractions.

After defining the compartments, they are treated as completely mixed reactors that exchange mass with their neighbours (shown schematically in Figure 2). The mass fluxes between the neighbours and the average of the required fields (e.g., ε) in each compartment are extracted from the CFD simulation by writing a user-defined function in the Ansys Fluent software. Then, the population balance equation (PBE) and the species concentration balance equations are integrated in time by using an in-house parallel code developed in Python. It should be mentioned that a 2-node quadrature method of moments is employed for the solution of the PBE, meaning that, in fact, four moments of the PSD are integrated in time. Moreover, the supersaturation is calculated by using an equilibrium solver incorporated in the python code. More detail about the governing equations and equilibrium solver can be found in our previous work [1]. Figure 3 compares the time evolution of the Sauter mean diameter (SMD) predicted at the outlet of the CSTR by the CFD-PBM approach and by the compartmental PBM (using 20 compartments). These results are obtained by including only the nucleation and molecular growth. Moreover, the compartments are defined by using only the profile of the environment volume fractions. As can be seen from Figure 3, the SMD obtained by the compartmental PBM is in good agreement with that obtained by the full CFD-PBM. Thus, it can be concluded that the developed compartmental PBM can be a promising (relatively) cheap approach for the simulation of Ni-Mn-Co Hydroxide co-precipitation in CSTRs.

In the next steps, it is planned to consider the profile of both the turbulent dissipation rate and environment volume fractions in the definition of the compartments, and subsequently, include the aggregation and breakage of particles in the simulation. Finally, the predictions will be compared against the measurements obtained in a pilot-scale CSTR to identify suitable models and parameters for the nucleation, molecular growth, aggregation, and breakage of Ni-Mn-Co hydroxide particles.

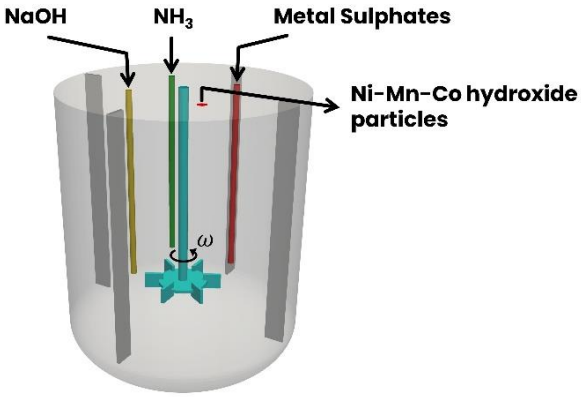

Figure 1: Co-precipitation of Ni-Mn-Co hydroxide in a CSTR. The metal sulphates solution contains $NiSO_4$, $MnSO_4$ and $CoSO_4$.

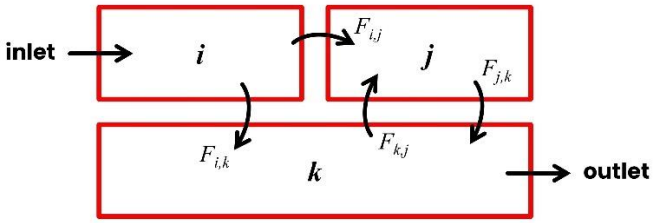

Figure 2: Schematic representation of a compartment network comprising three compartments

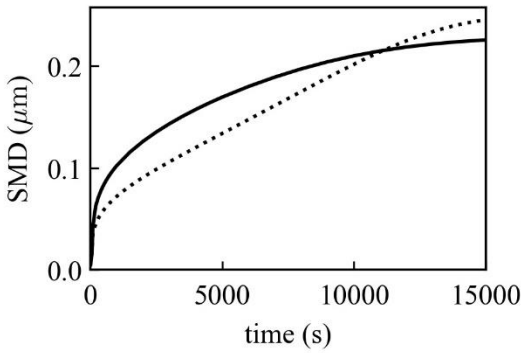

Figure 3: Sauter mean diameter of particles predicted at the CSTR's outlet by the compartmental PBM (solid curve) and the CFD-PBM (dotted curve)

Table 1: The equilibria of the Ni-Mn-Co hydroxide co-precipitation [2]. M denotes Ni, Mn, and Co.

Reactions
$M^{2+} + NH_3 \leftrightarrow [M(NH_3)]^{2+}$
$M^{2+} + 2\ NH_3 \leftrightarrow [M(NH_3)_2]^{2+}$
$M^{2+} + 3\ NH_3 \leftrightarrow [M(NH_3)_3]^{2+}$
$M^{2+} + 4\ NH_3 \leftrightarrow [M(NH_3)_4]^{2+}$
$M^{2+} + 5\ NH_3 \leftrightarrow [M(NH_3)_5]^{2+}$
$M^{2+} + 6\ NH_3 \leftrightarrow [M(NH_3)_6]^{2+}$
$M^{2+} + 2OH \leftrightarrow M(OH)_2$
$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
$H_2O \leftrightarrow H^+ + OH^-$

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