HAL

archives-ouvertes.fr

Controlled precipitation of an inorganic compound in solution using a polymeric matrix

Martha Gellner, Ana Cameirão, Eric Serris, Frédéric Gruy

▶ To cite this version:

Martha Gellner, Ana Cameirão, Eric Serris, Frédéric Gruy. Controlled precipitation of an inorganic compound in solution using a polymeric matrix. Nicolas Roche. XII Congrès de la Société Française de Génie des Procédés Pour relever les défis industriels du XXI siècle A la croisée des Sciences et des Cultures, Oct 2009, Marseille, France. Société Fançaise de Génie des Procédés, 98, 2009, Récents Progrés en Génie des Procédés. <hal-00460275>

HAL Id: hal-00460275

https://hal.archives-ouvertes.fr/hal-00460275

Submitted on 26 Feb 2010

Controlled precipitation of an inorganic compound in solution using a polymeric matrix

GELLNER Martha[1], CAMEIRAO Ana[1] *, SERRIS Eric[2], GRUY Frédéric[1]

[1] *Ecole Nationale Supérieure des Mines de Saint Etienne, Centre SPIN – Département GENERIC ; LPMG -UMR CNRS 5148, 158 Cours Fauriel - 42023 Saint-Étienne Cedex 2, France*

[2] *Ecole Nationale Supérieure des Mines de Saint Etienne, Centre SPIN – Département ProcESS; LPMG -UMR CNRS 5148, 158 Cours Fauriel - 42023 Saint-Étienne Cedex 2, France*

Abstract:

Precipitation of strontium molybdate was performed from aqueous solutions of sodium molybdate and strontium chloride in presence of hydroxypropylmethylcellulose. Three experiments were conducted: without cellulose, with dissolved cellulose and with a tablet containing cellulose and strontium chloride powder. The first one results in agglomerates of bipyramidal crystals, the second one in smaller monosized bipyramidal crystals and the last one in a mixture of bipyramidal, spherical, ellipsoidal particles and their agglomerates. Explanations based on the effect of solution viscosity are proposed.

Keywords:

Release ; dissolution ; precipitation ; morphology

I. Introduction

Precipitation is an important industrial operation. Within precipitation, the processes of nucleation and crystal growth take place (Mersmann, 1994). The morphology of the particles, which appears finally as precipitates, is determined by the shape (shape of a cube, octahedron, needle or plate) of the single crystals and their assemblage. These properties depend on various aspects. There are the chemical and thermodynamical aspects which have an impact, the hydrodynamic one during the synthesis, interactions between crystal and medium and interactions between crystal and crystal. Furthermore, kinetics of different phenomena and the mass and energy transfers also have an influence.

Among the different steps leading to particles, mixing of reactants is the most important one. Following the mixing conditions, supersaturation heterogeneity in the precipitator can occur. As a consequence, wide particle size distribution and different particle shapes are observed at a given time in the reactor. Attempts in order to reduce the effect of mixing involve:

❖ optimized geometry of the vessel and reactants inlet system

❖ change of the precipitating chemical system: one of the two reactants is produced by a slow thermal decomposition of a third reactant. This ensures homogeneity in the reactor for the concentrations of the two reactants (Sugimoto, 2000).

Since two decades, pharmaceutical industry produces tablets enabling drug delivery (Uchegbu and Schaetzlein, 2006). These consist of a mixture of the drug crystals and a polymer matrix. During the transport of the tablet in the alimentary canal, the polymer matrix absorbs water or solution, polymer is swelling, drug crystals dissolve in the polymer-water system and drug

---

* Auteur à qui la correspondance devait être adressée : cameirao@emse.fr

molecules slowly diffuse to the border of the matrix and then in the solution containing the tablet.

This paper presents an application of this procedure to precipitation. In case of aqueous precipitation the control of supersaturation is possible via encapsulation of one of the reactants by a polymer matrix. The corresponding tablet is introduced in an agitated vessel containing the other reactant. The release time of the encapsulated reactant being much larger than mixing time, small supersaturation, and then small nucleation and growth rates are expected. Thus, homogeneity of reactants in reactor and control of precipitation could be reached. Tests about this procedure will be realized about precipitation of strontium molybdate. Cameirao (2008) studied its precipitation by a classical way: rapid mixing of reactants in a batch reactor with mechanical agitation. Morphology of strontium molybdate particles depends on the initial supersaturation. If the initial $SrMoO_4$ concentration is equal to $8 \, mol.m^{-3}$, $SrMoO_4$ particles are composed by agglomerates of $5 \, \mu m$ sized bipyramidal crystals. The purpose of this work is the study of the morphology of $SrMoO_4$ particles when the release of one of the reactants is controlled by the mass transfer through a polymeric matrix (cellulose).

II. Experimental apparatus and procedure

II.1. Materials

The precipitation of $SrMoO_4$ is generated by the reaction of a solution of sodium molybdate (Na_2MoO_4) with a solution of strontium chloride ($SrCl_2$) (or a tablet including strontium chloride).

The solutions were made with 1l of deionised water for the solution of sodium molybdate (Sigma-Aldrich®, Strontium molybdate dihydrate, 99+%, A.C.S. reagent) and according to the respective experiment with 500ml or 1l of deionised water for the solution of strontium chloride (Aldrich®, Strontium chloride hexahydrate, 99+%, A.C.S. reagent). To obtain the initial concentration of $8.10^{-3} \, mol.l^{-1}$ of each reactant for all experiments, the required amount of substance is either added to the deionised water or to the tablet.

The selected polymer is an Hydroxypropylmethylcellulose (905HYM, Seppic, France) and is used as a solute or as part of a tablet. The amount of polymer is dissolved in 500 ml deionised water. The polymer does not take part in the chemical reaction. It has just an impact on the kinetics of the reaction.

II.2. Experimental apparatus

The reaction was realized in a 2l open glass crystallizer mixed by a three-bladed paddled stirrer, a Mixel®TT. The stirrer generates an axial flow and was powered by a EUROSTAR digital IKA®-Werke motor. The regulation of the temperature at constantly 25°C was accomplished by a thermostat of the type LAUDA Saturateur ecoline RE306.

II.3. Procedures and method

The kinetics and the degree of precipitation at the end of experiments were determined by means of conductivity measurements performed on-line with a conductimetric cell of the type Consort 831, Bioblock.

Table 1: Experimental conditions

Initial Concentrations [$mol.m^{-3}$]	Temp. [°C]	Stirring rate [rpm]	Conditions	Viscosity [Pa.s]
$c_{Na2MoO4} = 8{,}01$ $c_{SrCl2} = 8{,}02$	25	350	solution of Na_2MoO_4 solution of $SrCl_2$	10^{-3}
$c_{Na2MoO4} = 7{,}95$ $c_{SrCl2} = 8{,}00$	25	350	solution of Na_2MoO_4 solution of $SrCl_2$ + cellulose	4
$c_{Na2MoO4} = 8{,}00$ $c_{SrCl2} = 7{,}79$	26	350	solution of Na_2MoO_4 tablets of $SrCl_2$ + cellulose	$[10^{-3}, 2]$

Particle size distribution (PSD) of the strontium molybdate particles suspension was measured with a Malvern Master Sizer 2000 immediately after sampling and dilution. Suspensions were filtered and analyzed with a scanning electron microscope (MEB Jeol JSM 6500F).

All experiments were realized with sodium molybdate solutions (Table 1). In the first experiment, the precipitation was achieved by a reaction between the solutions of sodium molybdate and strontium chloride. For the second experiment, the solution of strontium chloride was enriched by cellulose (4g). Finally, for the last experiment, the strontium chloride powder and the cellulose were compressed into a tablet. To ensure uniform mixing in the reactor, the stirrer speed was about 350 rpm.

For each experiment, the reaction duration of the precipitation was different. Experiments run without a tablet were started after the addition of the two solutions and completed sooner (after 3 hours) than those with a tablet. Additionally, the reaction did not start immediately in the experiments made with a tablet. In these cases, the precipitation generally started within 1-5 hours and was considered as completed after about 22 hours. The tablets were never completely dissolved at the end of the experiment, although a different degree of dissolution was visible after splitting their recovered remains.

III. Experimental results

The conductivity during the three experiments was measured and is shown in Figure 1.
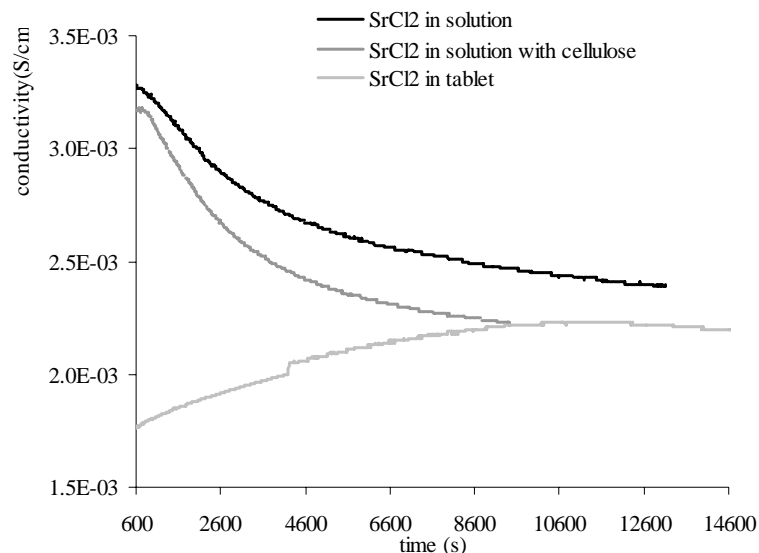

Figure 1: On-line measured conductivity during experiments.

In the first and second experiments, *i.e.* without tablet, conductivity decreases during precipitation (Figure 1) as observed in the work of Cameirao (Cameirao, 2008). In the case of the experiments realized with tablets the conductivity of the solution increases at the beginning of the experiment until a constant value (Figure 1) and then slowly decreases: the transfer of strontium chloride from the matrix to the solution is faster than the precipitation during the first stage whereas the opposite begins to happen during the second stage.

The particle size distributions obtained during precipitation for these three precipitations are presented in Figure 2.
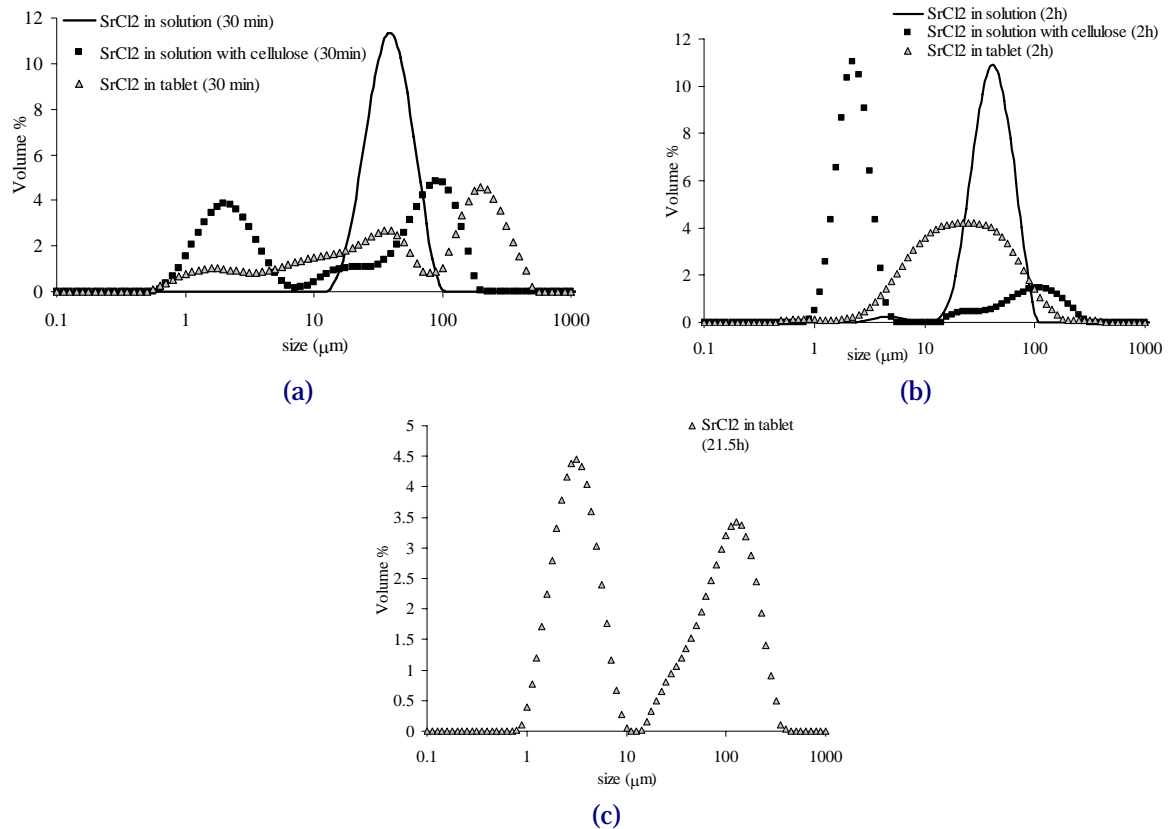
(a)

(b)

(c)

Figure 2: Particle Size Distribution of the suspension obtained at different times of the precipitation: (a) 30 min, (b) 2h and (c) 21.5h.

The particles obtained in the first experiment are agglomerates with sizes between 20-100 μm (Figure 3) They are composed of smaller sharp-edged bipyramidal particles with size equal to 5-6 μm according to the work of Cameirao (Cameirao, 2008) for a concentration less than 8 mol.m^{-3}. The surface of these bipyramidal particles is smooth (Figure 3). The precipitation is very rapid so that the final sizes and morphology are obtained after 30 minutes (Figure 2(a) and (b)).
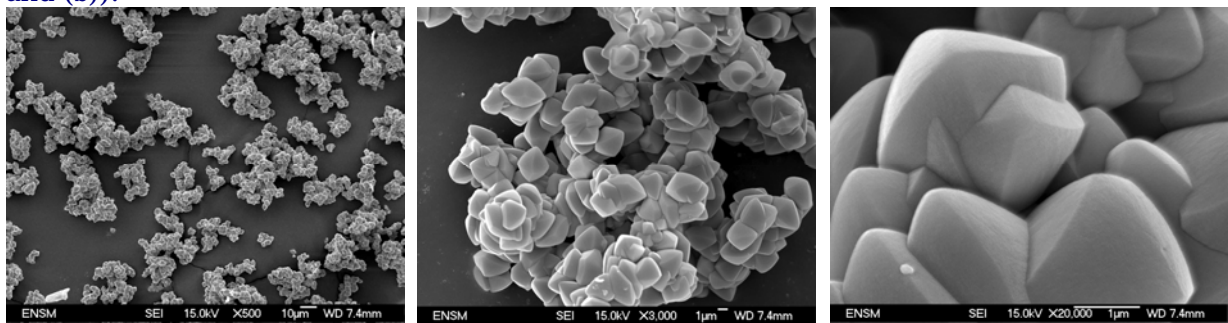

Figure 3: Micrographs of the dried powder of strontium molybdate obtained at the end of the precipitation reaction performed with two solutions

The presence of dissolved cellulose (4g) during the precipitation with initial concentration of SrMoO$_4$ equal to 8 mol.m^{-3} leads, like in the experiment without the cellulose, to bipyramidal particles all with the same size (~3 μm) and shape (Figure 4). In opposition to the first experiment, particles are not agglomerated. The surface of the particles is smooth and the edges are round. It can be observed, on the micrographs, cellulose adhered to the bipyramids surface (Figure 4).
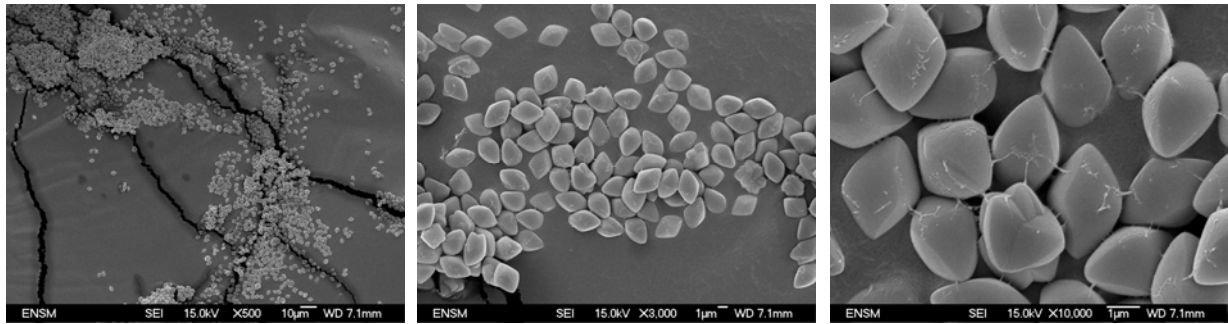
Figure 4: Micrographs of the dried powder of strontium molybdate obtained at the end of the precipitation reaction performed with the solution of strontium chloride and the solution of sodium molybdate and 4g of dissolved cellulose

In Figures 2(a)-2(b) the PSD shows initially (30min) two populations, one in the range 1-10 μm and the other in the range 10-200 μm almost with the same matter volume. At the end of precipitation (2h) the population with smaller sizes is the most important in volume as it can be seen in Figure 4 too. The population with sizes in the range 10-100 μm was not observed in micrographs.

The experiment run with polymer matrix (tablet) leads to particles sized in the range 0.9 - 9 μm and 20 - 500 μm (Figure 5). The micrographs show particles with various shapes: bipyramids, spheres, ellipsoids and agglomerates of them. The surface of the bipyramids is smooth and their edges are sharp. The ellipsoids have either a smooth or a rough surface, whereas the sphere surface is rough (Figure 5).

In Figure 2, three populations, 1-10 μm, 10 –100 μm and 100 –800 μm, can be observed at the beginning of precipitation (30 min); after 2h there is just one population between 5 and 200 μm and at the end two populations.
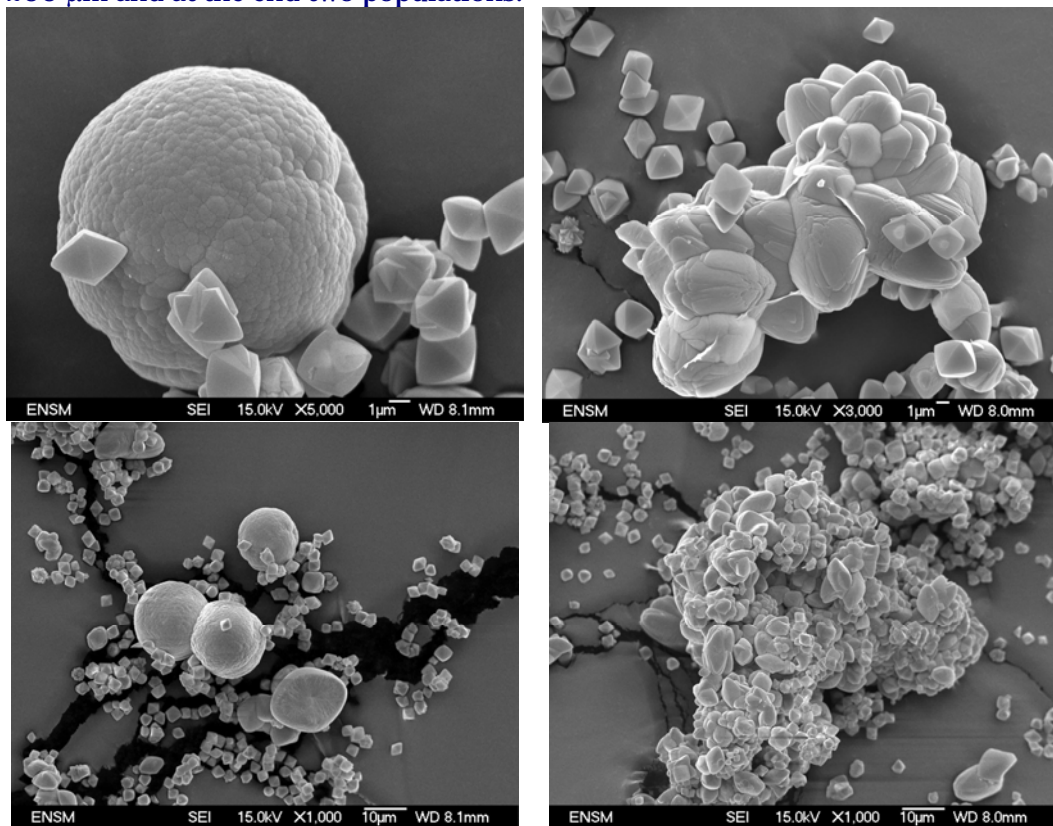

Figure 5: Precipitated particles for precipitation with polymer matrix (tablet)

5

Cameirao (2008) observed such a mixture of different shapes and sizes in the case of classical $SrMoO_4$ precipitation for initial reactant concentration higher than 8 mol.m^{-3}.

IV. Discussion and conclusion

The results show that the morphology and the size of $SrMoO_4$ particles are modified by the presence of polymer. Solutions with dissolved polymer are much more viscous than solutions without polymer. The increase of the dynamic viscosity of the solutions decreases more strongly the growth rate than the macromixing rate. Thus, the supersaturation is more homogeneous in the reactor. As a consequence, growth rate and particle size are smaller in presence of polymer, particle size distribution is narrower.

Moreover, hydroxypropylmethylcellulose seems be an anti-agglomerant additive for $SrMoO_4$ particles. The addition of cellulose to the initial solutions increases the viscosity, avoids agglomeration and produces bipyramidal round-edged and monosized particles.

Several experiments were performed by using wrapped tablets in order to reduce the transfer of cellulose to the solution. The value of the viscosity is consequently similar to that of the experiment without any tablet or cellulose. In both cases agglomerates of sharp-edged bipyramids arise. The only difference can be found in the size of these agglomerates which seem in general bigger for the experiment with the wrapped tablets.

The presence of one reactant inside a tablet leads to particles with four different shapes. The viscosity is higher than in the experiments without tablet or wrapped tablet but smaller than in the experiments with the dissolved cellulose. In all the experiments with tablets, sharp-edged bipyramids, spheres, ellipsoids and agglomerates of these are present. The size of the bipyramids was about the same in all these experiments. This was also the case for the spheres and ellipsoids. Thus, one observes different particle shapes, but each kind of particle is monosized.

At the beginning of the precipitation, high supersaturation may occur close to the tablet because of the high reactant concentration inside the tablet. Thanks to the low viscosity of the solution, this leads to large spherical or ellipsoidal particles (figure 5) according to Cameirao (2008). During the swelling of the matrix and its erosion due to the shear stress, there is a transfer of cellulose from the matrix to the solution. The consequent increase of viscosity reduces the effect of local high supersaturation. Strontium chloride may be spread into the reactor. This results in a slow precipitation of non agglomerated bipyramids as observed for high concentration of cellulose.

At this stage, the polymer leads to a morphology control, through the effect of viscosity. However, the precipitation by using tablets is a complex phenomenon, which needs to be sharply studied.

Experimental protocol must be improved in order to monitor the solution viscosity and the supersaturation. The experimental results found in this work are promising to the control of morphology and shape.

References

Dos Santos Nicolau Esteves Cameirao A. A., 2007, Etude expérimentale et modélisation d'une précipitation avec agglomération entre cristaux de morphologies différentes : application au molybdate de strontium, PhD Thesis, Institut National Polytechnique de Toulouse, France.

Cameirao A., Espitalier F., Gruy F. David R., 2008, Effect of precipitation conditions on the morphology of strontium molybdate agglomerates, Journal of Crystal Growth, 310.

Demopoulos G.P., 2008, Aqueous precipitation and crystallization for the production of particulate solids with desired properties, Hydrometallurgy 96.

Mersmann A., 1994, *Cristallization Technology Handbook*, Marcel Dekker, New York.

Sugimoto T., 2000, Fine particles: synthesis, characterization and mechanisms of growth, surfactant science series, 92, CRC Press.

Uchegbu I.F., A.G. Schaetzlein, 2006, Polymers in drug delivery, CRC Press.