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Innovative precipitation in emulsion process: toward a non-nuclear industrial application

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Abstract

A precipitation in emulsion process has been proposed by Borda *et al.* in 2008 for the continuous precipitation of lanthanides or actinides as oxalate, in order to either increase the production capacity or allow the precipitation of long-life radioactive elements under optimum safety conditions. During R&D tests, a strong correlation between the emulsion's properties and those of the particles produced have been evidenced, thus enabling the size and morphology of the powder to be tuned by varying the droplets properties, the latter being controlled by the column operating conditions. This process thus appears as an attractive alternative to conventional processes for the synthesis of high-value precipitates; as it offers interesting intensification capabilities. In this context, the feasibility of the precipitation of bismuth subnitrate (BSN), for which the emulsion route for precipitation seems to be particularly attractive, has been studied. Indeed, the division of the reacting volume into droplets may allow efficient temperature regulation of the exothermic reaction. In addition, an improvement of the product appearance is expected. This first phase of the feasibility study focused on the choice of the organic phase and the sensitivity of the droplets and solid particles properties to the operating conditions. Following the encouraging results observed in stirred-tank reactor, we successfully tested the implementation in a pulsed column, at lab-scale.

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1. Introduction and context

1.1. Outline of the process

A precipitation in emulsion process has been proposed in 2008 for the continuous precipitation of lanthanides or actinides as oxalate, in order to either increase the production capacity or allow the precipitation of long-life radioactive elements under optimum safety conditions¹. The novelty of the process resides in the containment of the reactants to precipitate in droplets of aqueous phase dispersed in an inert organic phase and flowing counter-currently in a pulsed column. Nucleation is initiated by the coalescence of the drops containing the reagents. One of the major advantages of the process for nuclear applications, is the confinement of the sticky precipitates by the inert organic diluent (Tetrapropylene Hydrogen TPH), thereby limiting the risk of fouling of the device and its adverse consequences in terms of productivity, safety, etc. The emulsion route further addresses the problems of injection and micro-mixing, often the cause of lack of reproducibility in conventional precipitation process. At last, a first campaign of tests conducted in a lab-scale pulsed column has demonstrated the efficiency and the robustness of the process in a wide range of flow-rates and chemical conditions, for either the production of CeIII precipitates or the production of UIV+CeIII mixed precipitates². Moreover, these prior studies have shown a strong correlation between the droplets properties and those of the particles produced, thus enabling the size and morphology of the powder to be tuned simply by varying the column operating conditions. To get a better understanding of this coupling, a modelling approach is developed in parallel³.

1.2. Synthesis of bismuth sub-nitrate (BSN): the issues

Bismuth has a valence of III or V and can form up to fifty different salts⁴. Among the sub-nitrate species, the BSN produced by OCM, also known as bismuth oxohydroxonitrate in its monoclinic form, $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$, is industrially obtained by batch precipitation of bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$, in concentrated sodium hydroxide solution. The reaction is highly exothermic. BSN is intended for veterinary use and must meet the high standards of the pharmacopoeia⁵, including:

- Bi content between 71 and 74%
- Residual humidity below 3%
- White powder hardly soluble in water

As in many industrial wet-chemistry processes, recurring non-conformities are observed on BSN products. Particularly, although the reaction is highly exothermic, the temperature must remain below 40°C in order to obtain the desired sub-nitrate phase. Moreover, the product properties (especially density and color) are highly sensitive to the pH: a too high acidity of the reacting $\text{Bi}(\text{NO}_3)_3$ solution induces subsequent washing and grinding issues in the process.

In this context, OCM is interested in developing a more robust and flexible production chain, and the precipitation in emulsion process developed by CEA seems to be an attractive technology as it could offer efficient temperature regulation and flexibility in the product properties. The process in pulsed column would further increase the productivity through continuous operation.

In this work, the relevance of the emulsion route for the industrial production of BSN precipitates has been investigated.

2. Experimental

2.1. Methodology

To assess the feasibility of emulsion precipitation of BSN particles, the major differences between this chemical system and the reference one (e.g. cerium oxalate particles) have been considered first.

The main difference is the exothermic reaction. Hence, preliminary tests were dedicated to the choice of the organic phase, in order to address potential safety or operating issues.

The second major difference (see Tab. 1) lies in the density of the final product. Indeed, BSN is approximately twice as dense as cerium oxalate, which can significantly alter the flow of reactive droplets after coalescence. Hence, a prior parametric study was implemented in a stirred-tank reactor, involving small volumes and allowing easy cleaning in case of caking.

The implementation in a laboratory-scale pulsed column was considered in a third step, in order to assess the industrial implementation.

Table 1. Comparison of the relevant properties for both precipitating systems

Possible droplets content	Reference System	Case Study
Charge to precipitate	Ce(NO ₃) ₃ in 1.5M HNO ₃ solution	Aqueous solution of Bi(NO ₃) ₃
Complexing agent	0.7 M H ₂ C ₂ O ₄ solution	1.88 M NaOH solution
Typical surface tension with TPH	43 mN/m (Ce solution)	38 mN/m (Bi solution)
	32 mN/m (oxalic acid solution)	42 mN/m (NaOH solution)
Final product density	2,42 g.cm ⁻³	4,93 g.cm ⁻³

2.2. Material and methods

The drop-scale experiments were achieved in a glass cubic tank (10×5×10). Two droplets (10 μL each), each of them containing one of the reagents, are deposited on a Teflon substrate immersed in TPH (Fig. 1, left), thanks to two syringes. They are put into contact until their coalescence occurs and the precipitation reaction begins. The precipitation process is monitored by a camera.

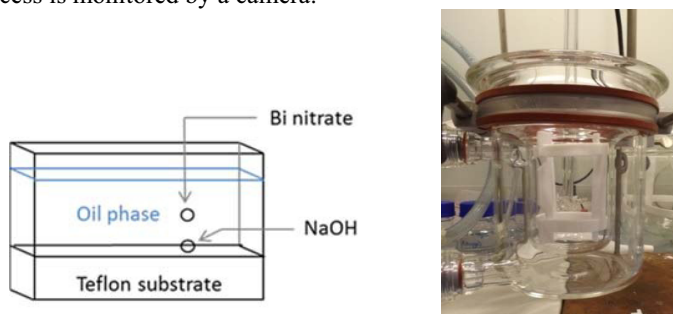


Fig. 1. Left: Sketch of the drop-scale experiments set-up. Right: Picture of the stirred-tank reactor

The batch precipitation tests were performed in a 250 mL jacketed stirred-tank reactor (Fig. 1, right). The glass reactor was silanized to avoid wetting issues. It was equipped with a 3-blades turbine, made of silanized glass, and 3 Teflon baffles to avoid vortex formation. Temperature was regulated at 25°C by a thermostatic bath. The stirring rate was adjusted between 700 and 850 rpm in order to reach a good emulsification regime and to ensure good circulation of the drops, even after the precipitation of dense solid particles occurs, and while avoiding overflow. Different tests were performed, at various volume fraction of the aqueous phase (from 2 to 16%). In each case, the solution of Bi(NO₃)₃ is introduced first, then after the emulsion has reached a steady regime, the required amount of NaOH is poured in the reactor. The experiments are stopped 20 to 30 minutes after the start of the reaction, by stopping the agitation. Once the emulsion had settled, the aqueous suspension was withdrawn and the particles filtered, washed with water then dried before proceeding to laser granulometer analysis, SEM observations and XRD measurements.

At last, a 15-mm inner diameter pulsed column, equipped with a Teflon packing consisting of alternated truncated disk, was used to carry on continuous precipitation experiments, representative of the industrial implementation of the process. The reciprocal up and down movement of the fluid is ensured by a pneumatic

pulsing device. The TPH flow, ranging between 3 and 12 L/h, is driven by a gear pump (ISMATEC). The reagents are injected through sampling holes located along the column, using DESAGA piston pumps. The suspension containing the solid particles is extracted from the lower settler by a peristaltic pump. More details on the column operation can be found in².

3. Results and discussion

3.1. Preliminary studies

In the emulsion process, the droplets containing the charge to precipitate and the complexing agent are dispersed in an inert oil phase. The first step was to verify the compatibility of the organic phase used in the reference system, TPH, with the reagents involved in the BSN process.

- Because an exothermic reaction occurs, an organic phase with a sufficiently high flash point must be considered for safety reasons. The oil phase should however exhibit a moderated viscosity in order to ensure good circulation of the fluids. TPH was observed to fit both requirements.
- It is essential that no reaction, and no mass transfer, occurs between the droplets and the continuous organic phase during the precipitation process. In this aim, various miscibility tests were made in test tubes by mixing TPH with concentrated sodium hydroxide solutions of various concentrations. No transfer of hydroxyl ions was evidenced after 2 months. Moreover, no reaction and no dissolution were observed between a dried BSN powder and the TPH after several days of contact. TPH is thus inert regarding the reagents of the BSN process.
- The emulsification process and the emulsion behavior are strongly dependent on the surface tension between the organic and the acid phase. As shown in Tab. 1, the surface tensions are quite similar for both systems and in each system for both considered aqueous phase. Hence, the emulsification process of the BSN system is not expected to deviate notably from the one of the reference system.
- Solid confinement is ensured, and fouling avoided, as long as the droplets do not wet the solid parts of the crystallizer. Contact angle measurements performed on various substrates have highlighted that the wetting issues can be avoided using Teflon-coated materials or glass after a silanization treatment.

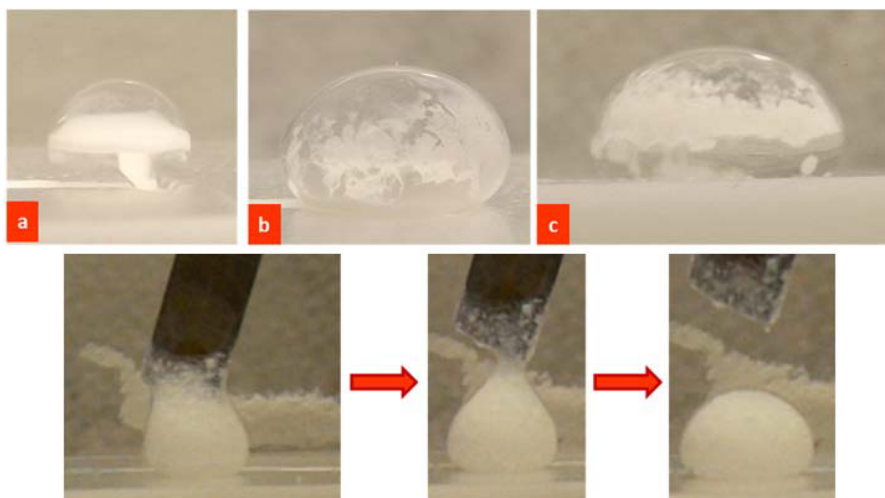


Fig. 2. Top: First moments of the coalescence of BSN after coalescence of two drops immersed in TPH and respectively containing $\text{Bi}(\text{NO}_3)_3$ and NaOH . Bottom: Adherence of the BSN precipitate on the – hydrophilic –stainless-steel spatula.

Preliminary precipitation tests in emulsion were achieved at the drop scale to check the feasibility and investigate whether the precipitated particles remain confined in the aqueous drop. As illustrated on the top of Fig. 2, the produced BSN is efficiently confined in the daughter droplet after coalescence and reaction are achieved. However, as can be observed on the bottom of Fig. 2, the solid particles tend to stick the tip of stainless-steel spatula, used to move and twist the drop, as soon as they get into contact with it. Stainless-steel is indeed efficiently wetted by the aqueous phase.

3.2. Continuously stirred-tank reactor (CSTR) results

The typical steady-state achieved in stirred-tank reactor, regarding the emulsion, can be observed on Fig. 3. The hydrodynamic behavior was satisfactory, except at high droplet volume fraction where the apparent density of the aqueous phase became too high to be efficiently pumped by the turbine. This limitation however is likely due to the reactor configuration.



Fig. 3. Batch experiments of BSN precipitation in emulsion. Effect of the droplet volume fraction, from left to right: 2%, 10% and 16%.

XRD results confirm that we synthesized the same BSN phase as in the OCM industrial process. However, as evidenced by the bimodal particle size distribution (PSD), and confirmed by the SEM pictures shown in Fig. 4, the particles growth was not completed at the end of the runs, and many small particles were still present.

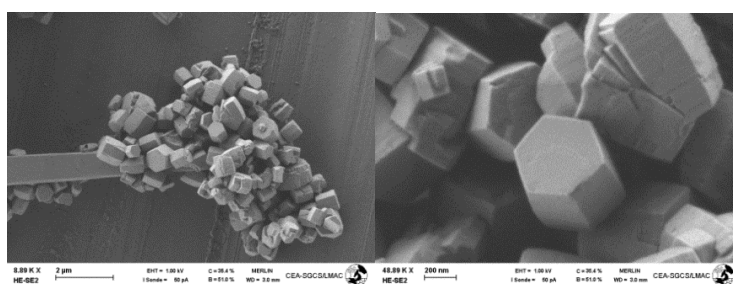


Fig. 4. Typical aspect of the particles produced in batch experiments in CSTR.

3.3. Pulsed column results

Following the encouraging results obtained in batch mode, first experiments were carried in continuous mode in the pulsed column. Regarding the hydrodynamic aspects, we used the same operating conditions as the one used for the reference system². Again, the results were very encouraging:

- A good circulation of the droplets was achieved, and the particles remain confined in the droplets (see Fig. 5). The evolution of the droplets mean diameter and hold-up with the flow-rate and pulsation intensity were in agreement with previous observations considering cerium oxalate.
- SEM observations (Fig. 6) revealed particles of similar shape (needle-like crystals) as in the batch experiments. Besides, agglomerated particles of size bigger than the one typical of the industrial process are evidenced.

Since no data were available regarding BSN solubility, it was not possible to evaluate the precipitation yield. However, most of the XRD patterns evidenced the presence of unreacted bismuth nitrate for these first and un-optimized trials, thus suggesting that equilibrium was not reached.



Fig. 5. Continuous BSN precipitation in a pulsed column

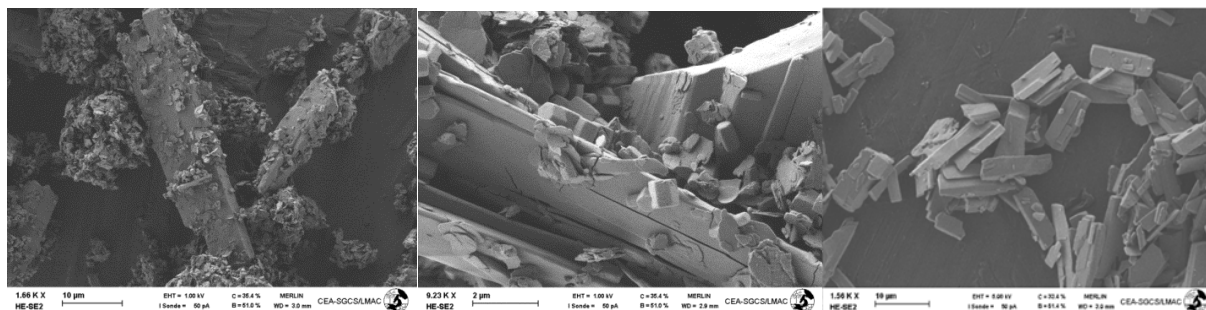


Fig. 6. Typical aspect of the particles produced in pulsed column (left and middle). Comparison with the industrial product (right)

As for oxalates², many ways can be explored in order to promote crystal growth. Indeed, these preliminary experiments were carried out considering the same chemical conditions as in the CSTR (in terms of NaOH excess), and the same procedure as for the cerium oxalate precipitation (upstream injection of the complexing agent before feeding the species to precipitate). Hence it could be interesting to change the reagents proportions (*e.g.* reduce the NaOH excess), to consider multiple feed lines (to establish a supersaturation profile) and of course increase the droplets residence time (to promote aggregation and growth).

4. Conclusion

The comparison between the reference CEA system (*i.e.* cerium oxalate) and the main features of BSN precipitation revealed no major inconsistency regarding the production of this veterinary product in emulsion, in pulsed column. The process was first tested in a stirred tank reactor, in batch mode, in order to address possible caking issues, due to either droplets wetting or massive settling of the dense drops of BSN suspension. For droplets volume fractions up to 10%, a satisfactory hydrodynamic behavior was observed. SEM analysis and XRD patterns revealed good similarities between the precipitated BSN and the industrial OCM product. However, the product obtained in emulsion exhibited a bimodal size distribution, with a significant amount of tiny particles (see Fig. 4), that are likely due to the short residence times considered in these batch reactor experiments (20-30 minutes).

Following these encouraging results, continuous precipitation tests in pulsed column were carried out. Different operating conditions were considered in order to vary the drops size and residence times (see⁶ for details on emulsification in pulsed column), and hence to promote crystal growth. Although chemical analysis of the mother liquors and XRD patterns suggested the reaction was not completed, large agglomerated particles were produced, even bigger than the commercial grade (see Fig. 6).

Through a comparative analysis of the OCM process and our reference system, and with a reduced number of tests, the feasibility of BSN precipitation in emulsion has been demonstrated and its relevance for industrial-scale production of the product was highlighted. The operating conditions have now to be optimized, which requires a comprehensive study of the chemistry of BSN precipitation, beginning by a comprehensive solubility study.

Acknowledgements

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