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# ACOUSTIC ON-LINE MONITORING OF SOLUTION CRYSTALLIZATION PROCESS IN PURE AND IMPURE MEDIA

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We show that acoustic emission (AE) is a very attractive non intrusive technique for monitoring crystallization processes. AE has been successfully applied in many fields of material sciences<sup>[1]</sup> and it was also used in the pharmaceutical industry for monitoring various chemical engineering processes<sup>[2]</sup> including fluidized bed granulation<sup>[3]</sup>, fluidized bed coating<sup>[4]</sup>, powder compaction<sup>[5]</sup>, etc. However, few studies deal with the use of AE to monitoring crystallization processes<sup>[6]</sup>.

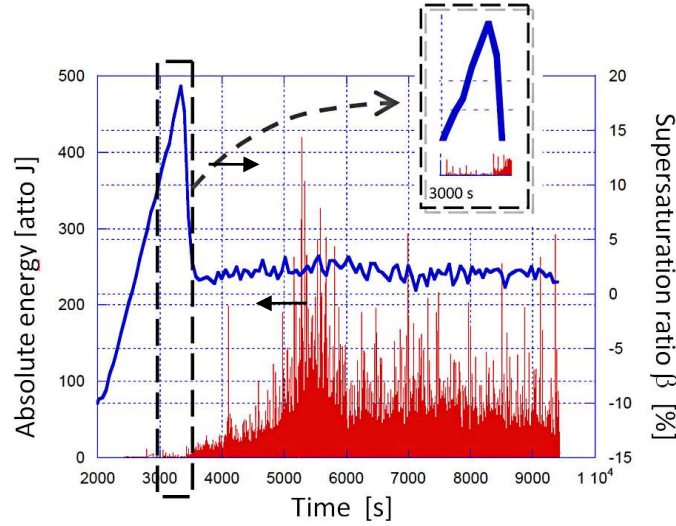
The objective of this work is to evaluate the potential for using acoustic emission to monitor polythermal batch crystallization in the absence and presence of impurities. The basic concept behind AE monitoring of crystallization processes is that the phase transitions occurring during crystallization in solution induce physicochemical changes in the suspension. Such changes release energy and therefore generate acoustic elastic waves propagating in the liquid medium<sup>[7]</sup>. Furthermore, as crystal particles are generated, the elastic properties of the dispersed phase also change. The latter changes affect the acoustic emission caused by the particle collision impacts and inter-particles and/or particles-wall frictions. The elasticity of crystals and their kinetic energy are also affected by many other properties such as size, shape, hardness, density, uniformity of composition which obviously depend on the presence of impurities during the process.

We report preliminary batch solution cooling experiments obtained with the model system Ammonium Oxalate/water (AO) in the presence of Nickel Sulfate as impurity. The experiments are monitored using AE, ATR FTIR measurement of supersaturation and CSD analysis performed thanks to *in situ* image acquisition. Complex but promising information is obtained thanks to AE monitoring.

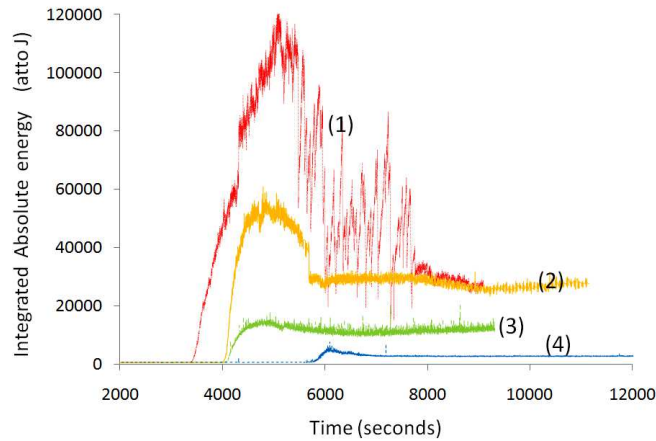
Two different studies are presented. The first study aims at understanding the origins of the different acoustic signals emitted during the cooling crystallization of AO aqueous solutions; the ability of AE technique to detect changes in physico-chemical properties of liquid and dispersed phases during crystallization is also evaluated. The AE data is put in contrast with the dynamic simulation of the crystallization process computed from Population Balance Equations (PBE)<sup>[8]</sup>.

It is shown that primary nucleation is early detected by AE, much before the end of the so-called induction period, as displayed in Fig.1a and highlighted in insert. Furthermore, the AE technique exhibits an interesting ability, contrary to *in situ* imaging and IR measurements, to detect switches in the nucleation and growth regimes of AO, the latter were found to depend on the applied cooling rate (not shown in this abstract)<sup>[9]</sup>.

The purpose of the second study is to establish how the AE technique can provide valuable information about the effect of impurities on the development of the crystallization process. Fig.2 shows that the absolute energy of the AE decreases with increasing impurity concentration. Basic crystallization kinetics and crystals morphology are indeed affected by impurities present in the suspension and despite the tremendous industrial importance of impurities, no successful study relating acoustic activity and effect of impurities on crystal nucleation and growth morphology was reported <sup>[10]</sup>.



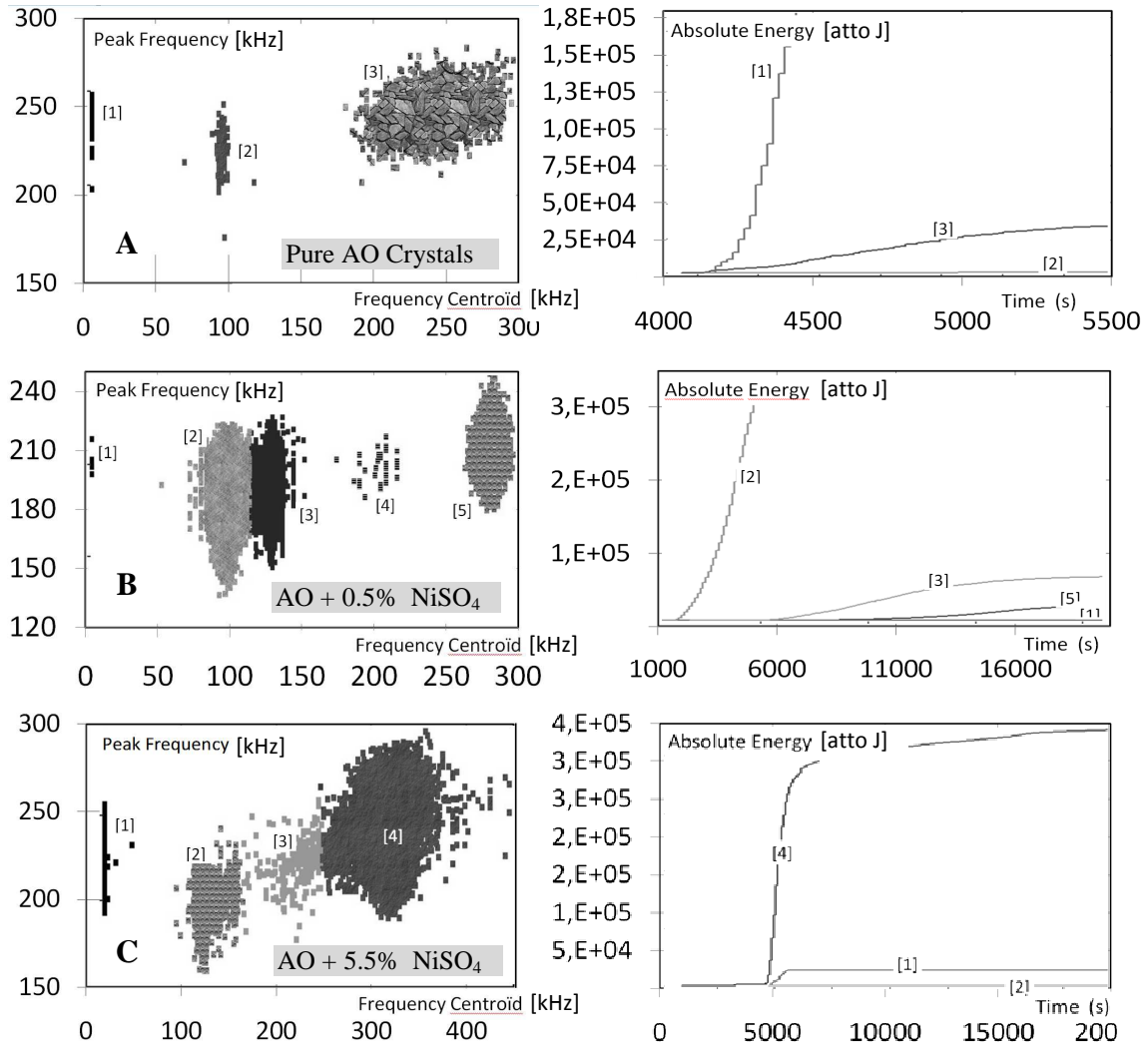
**Figure 1.** Cooling crystallization of AO in pure water: variations of the supersaturation ratio  $\beta(t)$  measured using ATR spectroscopy and absolute acoustic energy (normalized w.r.t the mass of solids).



**Figure 2.** Time variations of absolute acoustic energy for varying  $\text{NiSO}_4$  concentrations (1) pure water (2) 0.5 mol.% (3) 1% (4) 5%. The cooling rate was kept constant for all experiments:  $dT/dt = -30^\circ\text{C/h}$ .

Among the many acoustic parameters computed from EA raw data, several informative variables were identified as representative of the development of basic crystallization phenomena. The processing of relevant acoustic signals emitted during crystallization in pure and impure medium which were compared with experiments performed with suspensions of glass beads of calibrated size confirmed the hindering effect of increasing concentration of impurities on the growth of crystals together with increasing undesirable production (secondary nucleation and breakage) of smaller particles. From this latter point of view, the typical examples displayed in Fig.3 are interesting, even though the physics governing the AE of crystals remains to be investigated.

Roughly speaking, Fig.3 shows that the crystallization in pure water produces the highest level of acoustic energy release (note that curve 1 is cut) associated to a phenomenon located in a very narrow cluster (1 in Fig.3A). Two distinct phenomena also take place during the process that both reach a steady state value during the batch process (see curves [2-3] in Fig. 3A-right). On the contrary, it is clear that the amount of impurities reduces the energy released by AE, and that the dominant acoustic signals do not correspond to the same clusters (i.e. cluster 2 was negligible in pure water while it dominates with 0.5% impurity content). It is worth noting that absolute energy profiles related to the different –Frequency centroid/peak frequency– clusters always reach a steady-state before the end of the crystallization process. The results obtained with 5.5% impurity concentration illustrate the possibility of differentiating the intensity of impurity effects on the development of industrial crystallizations. For the latter experiment it is clear that the phenomenon related to cluster 4, which was marginal in pure solvent and with low impurity concentration, is now prevailing and could therefore be related to specific effects of impurities. Actually, preliminary investigations suggested that this cluster could be related to the fines content of the dispersed solid.



**Figure 3.** Clustering of acoustic variables and respective evolutions of the related energy during 3 batch processes. The 3 experiments were performed with  $dT/dt = -30^{\circ}\text{C/h}$

The recorded AE signal was put in contrast with both measurements and simulation results. This kind of comparison was not reported before, probably due to the difficulty of monitoring and describing the time evolutions of both continuous and solid dispersed phases: monitoring requires the use of advanced PATs and advanced PBE modeling cannot be developed without appropriate sensors like ATR FTIR and image analysis. The hypotheses drawn from the large and diversified set of experimental observations were thus partly validated using the PBE crystallization model.

For industrial batch crystallization monitoring purposes, due to its many advantages (i.e., the sensor is passive, non intrusive, non destructive and cheap), the AE technique therefore appears as a promising tool for industrial process monitoring. The assessment of the concentration of impurities and of their detrimental effects on the solid properties, the early detection of nucleation, and, in the near future, the monitoring of crystal nucleation and growth phenomena, could perhaps be developed thanks to the use of AE techniques.

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