Assessment of NIR *in-line* for monitoring and automatic management of crystallisation processes

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Introduction

The correct management of industrial crystallisation processes has represented up till now a relevant problem due to the lack of suitable measurement devices. In fact the optimization of the process would require the knowledge in *real time* of the exact value of the amount of the crystal present in the magma, the supersaturation of the growth solution and the growth kinetics, ^{1,2,3} but all these parameters are difficult to evaluate because the system is in continuous evolution, and they can change from one process to another. Therefore, nowadays, process management frequently derives from indirect considerations and/or back experiences rather than reliable and effective knowledge of the system. As a result, crystals seldom have predictable features, which often implies bad commercial quality of the final product.

As an alternative method to obtain supersaturation values and their variations during the process we propose the use of the NIR *in-line* technique using a fibre-optic probe submerged in the magma. NIR was tested as a completely automated crystallisation manager by setting up the interfacing of the NIR instrument with the PC-control unit of the crystalliser. As a model, we have used the cooling crystallisation of sucrose as it is undoubtedly significant from the agro-industrial point of view.

Materials and method

Experimental apparatus

A laboratory crystallizer with a working volume of 3 litres was equipped with a mechanical stirrer and a jacket for the heating/cooling water flow (Figure 1). The probe, directly immersed in the magma, was connected to a Foss NIRSystem[®] 6500 through a fiber-optic bundle. NIR spectra of the magma was collected, stored on the PC and then processed by means of Vision[®] software version 2.20, supplied with the instrument.

Samples

Samples of saturated sucrose solutions at different temperature and containing different amount of sucrose crystals were prepared. A total of 207 spectra were collected, in a wide range of sucrose crystals concentration (0-37%), temperature (80-30°C), agitation rate (300-700 rpm) and particle size (100-800 μ m). The concentration unit was expresses as grams of crystals per 100 grams of magma.



Figure 1. Experimental apparatus.

Development of calibration

Mahalanobis distance of 3s (probability threshold of 0.95) in the PC's space was taken to select the training set (157 samples). Calibration model to predict the amount of crystals in the magma was performed by PLS regression on first-derivative spectra. Statistics used to evaluate the equation were: the correlation coefficient (\mathbb{R}^2), the standard error of calibration (SEC), the F-value and the standard error of cross validation (SECV). In Figure 2 some of the spectra collected are reported; in Figure 3 the calibration curve for the evaluation of the percentage of the crystals in the magma is shown. In Table 1 the statistical parameters of the curve obtained are reported.







Figure 3. Calibration curve for the prediction of the percentage of crystals in the magma.

	Statistical parameters
\mathbb{R}^2	0.9924
SEC	0.9397
F value	2692.8035
SECV	1.0429

Table 1 – Statistical parameters of the model

Results

In the cooling crystallisation of a pure sucrose solution, a supersaturated solution at a relatively high temperature, is added with the suitable amount of seed and the cooling of the magma must start. We do not know in advance the correct cooling rate nor the optimum value of the supersaturation during the variation of the temperature which we have to maintain. Taking constant the characteristics of the seed (amount and size), the cooling rate should be not too great (so avoiding high values of supersaturation and, as a consequence, spontaneous nucleation phenomena and trapping of mother liquor) (line 1 in Figure 4), and not too low (so avoiding too long a time of crystallisation) (line 2 in Figure 4). The line 3, which represents a constant supersaturation during the whole crystallisation, could describe the correct profile of the supersaturation.



Figure 4. Schematic sucrose solubility diagram

If we want to maintain the supersaturation constant, the decrease in the temperature of the magma during the time 4,5,6 must follow the profile shown in Figure 5: a slow decrease at the beginning (due to a very low surface of the crystals) and at the end of the cooling (due to very low growth kinetics) and more rapid decrease in the middle. What is the correct slope of this curve during the decrease in the temperature? We considered that NIR has solved this problem by the continuous evaluation of the characteristics of the magma (amount of sucrose crystallised and supersaturation) transferring the data in *real-time* to the automatic system of cooling.



Figure 5. Temperature decrease overtime during a typical cooling crystallisation process.

After having calibrated the instrument, thanks to the interfacing between the NIR and the computer of the crystallizer (Figure 1), we set up several tests of process management in order to evaluate whether the system could automatically maintain in the magma, at each temperature, the planned value of supersaturation. In practice, the percentage of crystals in the magma determined in real time by the NIR, were automatically transferred to the computer of the crystallizer, where a suitable software transforms them in sucrose concentration of the growing solution and, based on the actual temperature of the magma, calculates the supersaturation value. If this supersaturation gets out of the planned value at that temperature, the system automatically start up the cooling or the heating device. This auto-regulation permitted us to optimize the cooling without knowing in advance the actual growth kinetics of the crystals, which, as already pointed out, depends on many parameters often difficult to determine.

Parameters	Value	
Starting temperature	66°C	
Starting supersaturation	1.05	
Planned supersaturation during the cooling	1.05	
Amount of solution	1687 g	
Amount of seed	25 g	
Size of the seed	60 µm	
Final temperature	30 °C	
Stirring	300÷800 rpm	

Table 2 Operative conditions of the lab test.

The results of one of the test (the condition of which are reported in Table 2) can be considered satisfactory. In Figure 6 the NIR-predicted values of the percentage of crystallised sucrose and the temperature trend during the automatic cooling are depicted; Figure 7 shows the concentration of the growing solution (Sucrose/Water ratio), the planned (solid line) and the actual (dots) value of supersaturation during the entire crystallisation.

Conclusion

Summing up, with this NIR-based system we have been able to determine the amount of crystals present in a magma, to evaluate the actual concentration of growing solution and the supersaturation value and finally to auto-regulate the cooling.

Even though so up to now at laboratory scale only, we have tried to set up a system able to maintain the optimal cooling profile without knowing in advance all the variations in the parameters which can influence the process and without any operators intervention except for choosing the supersaturation value at the beginning of the process. This control strategy and automatic management could make possible optimization of cooling crystallisation processes, both in the laboratory and in industrial plants, without the need for planning cooling profiles *a priori* based on parameters not always corresponding to the real evolution of the process.

This represent only a feasibility study for assessing NIR technique for the control and automatic management of crystallisation processes, but on the basis of the encouraging results achieved, several aspects will be studied in more details, with the aim to improve the calibration model going towards the complexity of industrial applications.



Figure 6. Variation of the percentage of crystals and temperature during the automatic management of the cooling.



Figure 7. Sucrose/Water ratio and supersaturation of the growing solution during the automatic management of the cooling.

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