Crystal Growth and Crystallization Control Tactics in Industrial Sugar Crystallizers

Part 1. Crystal Growth

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Abstract

Crystal growth is a favorite subject of crystallization research. Due to the complexity of the process there are several more or less different approaches to its study. Most of the theoretical studies rely on mass, energy and population balance equations, kinetic correlations and model formulations sometimes based on questionable assumptions and simplifications. Combined methods (theoretical plus small scale laboratory experiments) can provide useful information on the effect of one or the other parameter on crystal growth, but they are usually restricted to the study of a single (or only a few) crystal in well controlled environments.

The problems of crystal growth in industrial scale crystallization, when there are billions of crystals in the massecuite are rarely studied, and if so, the validation of the findings is rare, or is completely missing. Production of good quality sugar however should be based on an in-depth knowledge of the processes which characterize mass production. The major difficulty of the study of crystal growth in large populations was the long-standing lack of appropriate instruments needed to monitor on-line the governing parameters of crystal growth.

With the introduction of the SeedMaster Instruments on-line data acquisition of the most important parameters of crystallization, including supersaturation, crystal content and mother liquor purity became reality in quite a few mills and refineries of the world. The acquired data can be used to check, refine and validate crystal growth rate models *in real industrial environments*. This can help us not only to have a better understanding of the process, but also to find better ways to its advanced control as well.

There are several attempts in the literature directed to formulate in an equation the effect of a single parameter, like supersaturation, temperature or mother liquor purity on crystal growth. In this paper a multi-component crystal growth rate model is formulated. It contains all of the governing parameters which can be measured by dedicated instruments or calculated by a SeedMaster Instrument on-line in industrial crystallizers in operation. The model is based on single-parameter components (correlated to a single parameter) selected from the literature. The components have been combined in a single equation. It is only natural that the model must be validated with data acquired during the normal operation of industrial crystallizers.

Validation of the growth rate model relies on the comparison of the important parameters
1. *directly calculated on-line* by a SeedMaster Instrument (reference data) and
2. *the same ones calculated by making use of the growth rate model* (model data).

In our case the validation was completed in two batch vacuum pans in two different locations: one in a well-known refinery in Europe and the other one in West Africa.

The validated growth rate model provides a better understanding of the process of crystallization and can be used to design and implement more effective control strategies.

Introduction

With about 200 million tons per year nowadays, crystallized and re-crystallized sugar is probably the product manufactured in the largest quantity in crystalline form. Its mass production began more than 150 years ago and after a long period characterized by the manual control of crystallization, since about the middle of the last century we are witnessing an increasing interest in helping and even replacing the pan-men with different types of instruments and with the automation of the process of crystallization.

The ideas on how to manufacture sugar in large quantities fascinated researchers and plant managers as well since a long time. Sugar manufacturing consists of a series of operations, all of which require special skill and know-how in several disciplines. This is true for the final major operation: crystallization, too. Besides sugar, there are a lot of products in different industries (for example: pharmaceutical), where crystallization is also a major step of production. This is why crystallization and its research became really important. Though there are a lot of similarities, in this paper our attention will be devoted only to sugar crystallization.

The process of crystallization is really complex: there are a large number of parameters which have considerable effect on it. Hundreds of scientific papers and a large number of dissertations and books of the industry have been devoted to the main subject of sugar crystallization: crystal growth. Its study can be characterized as

- theoretical (or academic),
- experimental (confined mostly to experiments in the laboratories), or
- a mixture of the above two methods.

These types of studies have found their justification in the complexity of the problem and in the long-lasting lack of instruments able to provide reliable on-line data on the complete set of parameters governing crystal growth. However, the results usually provide information on the effect of one or the other parameter on crystal growth. The often un-specified or completely neglected parameters and the sometimes inconsistent use of terms make the comparison and use of the results difficult.

Cost-effective mass production of any product, including sugar needs advanced instrumentation and automatic control. When confronted with the task to implement an effective automatic control strategy of sugar crystallization by up-to-date PLC-s or DCS-s, control engineers generally need an approach *different from the purely academic or small-scale laboratory type one.* They are less interested in the intricacies of single-crystal growth on the *molecular and microscopic* level, when the task is to produce good quality crystals *by billions in a single strike*. To be successful, it is vital to gain as accurate as possible insight into the inner workings of the process of *industrial-scale sugar* crystallization. Selection of a good control strategy needs

- good knowledge of the parameters governing the process,
- knowledge of the relative and combined effect of these parameters on crystal growth,
- that is a *control engineering approach.*

In this publication it is assumed that only crystal growth takes place during the process that is it is assumed that *full seeding* with slurry or footing magma is being practiced.

Publications on the subject in most cases were directed to study the effect of a single parameter on crystal growth. While these attempts are certainly useful, they alone are not able to provide a clear, proven and reliable picture on the *relative and combined effects of all of the parameters governing the process of crystallization.* However, development and implementation of good crystallization control strategy and practice *is very much in need of this kind of information.*

It is very well known that supersaturation is one of the parameters (often referred to as the "driving force") having considerable effect on the rate of crystal growth. Contrary to false claims there is no single instrument capable to provide reliable data on it in real time. With the introduction of the SeedMaster Instruments [1], [2], [3], [4] on-line calculation of supersaturation and quite a few other important massecuite parameters became reality and actual practice in an increasing number of mills and refineries.

Aided by the on-line data acquired by the SeedMaster Instruments while monitoring and controlling hundreds of strikes in batch pans (pans from 30 to 120 m3 volume) in dozens of different countries of the world, an attempt is being made to
- test in practice previous results documented in the literature on the effect of one or the other parameter on the rate of crystal growth and to
- *formulate and validate* in real industrial environments *a single equation of crystal growth.*

The main aim of the investigations is to help to develop an effective control strategy subject of another forthcoming publication.

1. CRYSTAL GROWTH

1.1 Crystal growth: terminology

In the studies related to crystal growth
- linear crystal growth (growth along the different axes of a crystal) and
- volumetric crystal growth

are the subjects of investigations. However, it is not always clearly defined which one is being studied. This may lead to inconsistent or even contradictory claims regarding crystal growth. In this paper our main objective is to determine and demonstrate the effect of the most important parameters on *linear crystal growth*. The results can be easily converted to its *volumetric equivalent*, if needed. In what follows, the term "crystal growth" is clearly related to *linear crystal growt*h specified as da / dt, where
- **a** is the characteristic length of a crystal and
- **da / dt** is the rate of crystal growth.

1.2 Crystal size (mean aperture MA), size distribution (CSD) and coefficient of variation (CV)

The main important parameters of product sugar crystals are mean crystal size (MA), size distribution (CSD characterized by the coefficient of variation (CV)) and color. Only the first two of these parameters will be briefly discussed here.

The MA of the product crystals should be as close to the target product size as possible. *It depends very much on the seeding and control practice in use.*

A large number of studies resulting in an equally large number of papers have been devoted to the subject of crystal growth. There are three major theories regarding growth rate with more or less supporters and opponents for each one.

The common growth rate (CGR) theory.

According to McCabe's ΔL law: *The total linear growth of all crystals in the massecuite over the same time interval and along similar axes is the same, if they have similar and invariant geometric shapes and supersaturation is the same for all crystals in all locations in the massecuite. The linear growth rate is independent of crystal size* [5].

As a direct consequence of this theory a crystal crop having a wide size distribution like the ones used in seed slurries (for example: CV=80) will grow by the same growth rate (da /dt) resulting in a *continuously improving (decreasing) CV if the requirements stated above are met.*

Size dependent growth rate (SDG) theory.

One form of the growth rate G [6] (G = da / dt) based on the SDG theory is expressed by Eq. 1

$$G(L) = G(0)*(1 + \alpha*L) \qquad \text{Eq. 1}$$

According to the equation large crystals grow faster (constant α is positive). This results in a widening size distribution.

Growth rate dispersion (GRD) theory.

Instead of differences in size, differences in the growth rates are due to random variations over time or crystal population. There are supporters and opponents of the theory as well. "GRD is a real phenomenon, whereas SDG is largely an artifact" [7].

A practical approach.

It is evident that with billions of crystals in a limited massecuite volume the strict requirements posted by McCabe's law cannot be met; only approximated to some extent. The approximation is the best when the crystals are small and separated far from each other due to turbulent flow: that begins *right after seeding has been completed*. This is the period during which a *fairly common growth rate prevails* and results in an improving (decreasing) CV value. Later on, as crystal content increases the distances among them become less and less, and meeting McCabe's requirements becomes more and more impossible. It can be proved that at about 30 to 34 % (by volume) crystal content (or 86 to 87 % massecuite solids content) the crystals begin to touch each other even when they are evenly distributed, resulting in increasing differences in the local parameters. On the other hand, with increasing crystal content vacuum pans can be less and less termed as "perfectly mixed vessels", the assumption so often taken for granted in theoretical studies. This means that as the crystals keep growing, there will be more and more locations in the massecuite where

the major parameters (mother liquor purity, concentration, temperature, flow velocity and crystal content) will not be exactly the same and the chances of providing fresh feed syrup to supply growth are different.
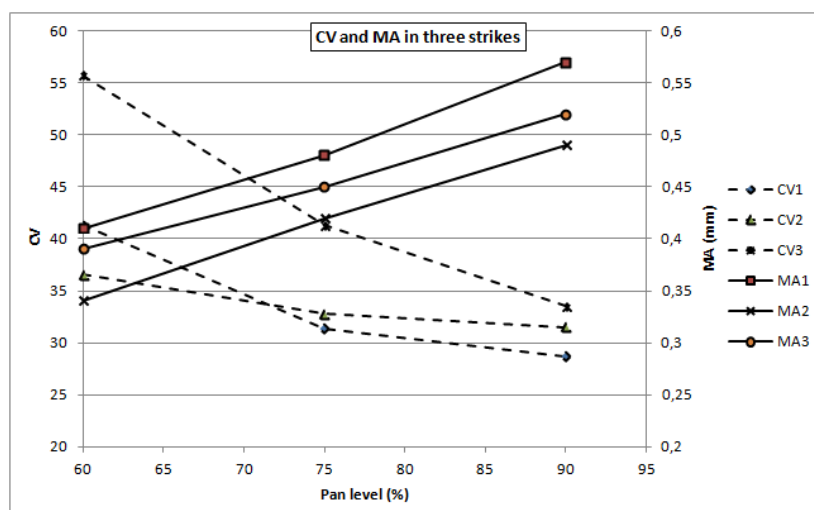

Fig. 1

In Fig. 1 the variations of CV and MA data versus pan level (60, 75 and 90 %) in three strikes are shown (the strikes were ended at 100 % level). The data were determined by the use of a laser diffraction size analyzer in a sugar mill in Brazil. Seeding of the pan was completed at 30 % level, but no data were available from that time. As can be seen, assuming seed crystal CV~ 80…90 in the slurry, there was already a considerable improvement in the CV value when level reached 60 %. *This is the period of crystal growth where the fairly common growth rate prevails.* The improvement continued, but slowed down after about 75 % level, the time when crystal content probably reached about 30 to 34 % by volume.

Lessons to learn: it is important
- to have high quality (small CV) seed crystals in the slurry when practicing full seeding, because right after seeding the improvement will start from the original CV value, and
- to have good, supersaturation-based control of the crystallization all over the strike in order to prevent nucleation or dissolution of the crystals.

2. THE MAJOR MASSECUITE PARAMETERS GOVERNING CRYSTAL GROWTH

It is a well known fact that crystal growth depends on quite many parameters of the massecuite, like
1. overall crystallization growth rate,
2. supersaturation,
3. temperature,
4. non-sugar concentration,
5. crystal content and
6. massecuite circulation,

Based on literature data the effect of these parameters on crystal growth will be discussed in a condensed form one by one.

Supersaturation (SS)

It is a well known and accepted fact that supersaturation (SS for short) is the most important parameter of crystallization. The multitude of its different definitions does not help to compare the results of research on its effect on crystal growth. The one which is most often used is as follows:

$$SS = \frac{\text{sugar in solution (g / 100 g water)}}{\text{sugar needed for saturation (g / 100 g water)}} \qquad \text{(both at the same temperature)}$$

It can be shown [1], [2] that SS is a function of several variables, namely:
- liquid concentration (C),
- mother liquor purity (P),
- temperature (T),
- liquid (feed syrup) quality parameters (m, b, c), which are different for feed syrups of beet or cane origin and should be determined locally.

It is clear that SS is a multiparameter function of several variables of the feed syrup or mother liquor (that is parameters of the technical sugar solution):

$$SS = f(C, P, T, m, b, c) \qquad \text{Eq. 2}$$

SS = 1,00 characterizes *saturation*. If SS is less than 1,00 fast dissolution of the existing crystals takes place, while above some limit (for example above SS = 1,15 depending on purity) spontaneous nucleation will be started. The normal area of control is in the range in between the two, close but safely below the nucleation limit.

As a rough approximation + / - 0 07 change in SS can be caused by:
+ / - 1 % change in liquid concentration (C), or
+ / - 5 °C change in temperature (T), or
+ / - 16 % change in feed syrup / mother liquor purity (P)

It is clear from Eq.2 that SS cannot be measured by any single instrument: *claims on the contrary are false and misleading.* On-line data on SS can only be provided by calculation, taking into account all of its governing parameters. In order to have reliable data on SS liquid concentration has to be measured *selectively,* that is undisturbed by crystal content, color and vapor bubbles with *at least + / - 0,1 % accuracy*. The only instrument capable to meet these requirements is the digital process refractometer pioneered by K-PATENTS Oy, Finland. It is to be noted that *purity (P) of the solution is not constant* during the process of crystallization; it has to be calculated on-line as well.

2.1. Overall crystallization growth rate (K; f0)

Crystal growth depends on two processes:
- mass transport of the sucrose molecules to the reaction layer at the surface of the crystals and
- integration of the molecules into the crystal lattice.

The process depends on quite many parameters, like:
liquid velocity (v) and width (δ) of the stagnant layer on the crystal surface, liquid density (ρ) and viscosity (η), coefficient of diffusion (D), temperature (T) and purity (P). Non-sugar composition (Nc) has also a   strong effect on crystal   growth   and shape as well [8]. Dextran gives the most important decrease in growth.

$$K = f0(v, δ, a, ρ, η, D, T, P, Nc) \qquad \text{Eq. 3}$$

As in many cases, when we do not have reliable and quantified information on different parameters governing a complex process, like in this case, all the variables (knowns and unknowns as well) are lumped in a *multivariable parameter K. Unfortunately enough, K is quite often regarded and treated in the simplified equations on growth rate as a constant, but it is anything, but constant.*

2.2 Crystal growth versus supersaturation (f1(SS))

The general and most often used, simplified equation of crystal growth is:

$$da / dt = K * (SS - b)^n \qquad \text{Eq. 4}$$

da/dt: growth rate (linear)
K: overall crystallization growth rate
b: constant
n: constant

Opinion on the value of "b" and "n" is fairly common: in most cases both are equal to 1,0, so

$$f1(SS) = SS - 1 \qquad \text{Eq. 5}$$

Based on experiments the authors in their paper [9] report on a somewhat different form:

$$f1(SS) = da / dt = 41,22*(SS - 1,038) \ (µm / min) \qquad \text{Eq.6}$$

According to Eq. 6 if SS = 1,138 the rate of crystal growth is 4,122 µm / min. *By using K=41,22 as a constant, this simplified equation hides the multitude of massecuite parameters which have considerable effect on the rate of crystal growth. This is certainly a gross simplification.*

2.3. Temperature (f2(T))

Keeping other parameters constant, increasing process temperature results in faster crystal growth (neglecting here the effect of temperature on the parameters listed in f0 and f1). It is generally accepted that the rate of growth increases exponentially with temperature and the general form of the equation is:

$$f2(T) = da / dt = A*EXP(B*T) \qquad \text{Eq. 7}$$

T: temperature ºC

The equation with actual data [10] and SS = 1,06 (constant) with flow velocity

v = 0 m/sec:
$$f2(T) = da / dt = 0,067*EXP(0,0586*T) \qquad \text{Eq. 8}$$
v = 5 m / sec:
$$f2(T) = da / dt = 0,0502*EXP(0,0495*T) \qquad \text{Eq. 9}$$

According to [11]:

$$f2(T) = da / dt = 0,277*EXP(0,0186*T) \qquad \text{Eq. 10}$$

2.4. Non-sugar concentration (f3(NS))

Increasing non-sugar concentration decreases the rate of crystal growth. The equation to be used is [10]:

$$f3(NS) = da / dt = EXP(-1,75*NS / 100) \qquad \text{Eq.11}$$

NS: non-sugar concentration (g / 100 g water)

2.5. Crystal content by volume (f4(y))

It is interesting to note that the effect of crystal content on crystal growth is rarely studied. It is even more so because it is evident that with increasing crystal content considerable changes in the process of crystallization take place, like:
- decreasing heat transfer coefficient between the calandria and the massecuite,
- increasing difficulties in supplying fresh feed syrup to the crystals,
- increasing differences in the important parameters (supersaturation, temperature, non-sugar concentration etc.) among different parts of the massecuite.

In experiments in the laboratories crystal to crystal interactions are in most cases carefully avoided. Crystal growth is mostly studied by growing a single, or only a very few (far away from each other) crystals in small crystallizers mostly in ideal conditions (constant temperature, syrup flow etc.). The rather simplified equations on crystal growth provide higher rate of growth than the one that can be really produced in an industrial crystallizer. "The rate of crystallization in supersaturated sugar solutions with a large number of crystals was less than that found with a single or only a few crystals under identical conditions. There is a strong correlation between the rate of crystal growth in supersaturated solutions and the volume of solution among the crystals" [13]. In a large number of laboratory experiments a coefficient h was determined defined as

$$h = (\frac{V_m - V_c}{V_m})^2 \qquad \text{Eq. 12}$$

V_m : massecuite volume $\qquad\qquad V_c$: crystal volume

It was found that depending on crystal content the rate of crystallization was decreased by the value of h compared to the rate valid for a single crystal under identical conditions. The reduction is quite considerable: the value of h changes in the 1 (no crystals) to 0,16 (crystal content = 60 % by volume) range. It does not depend on crystal size, temperature and supersaturation. Eq. 12 can be changed to

$$f4(y) = h = (1 - y)^2 \qquad \text{Eq. 13}$$

y : crystal content by volume (abs.)

2.6. Massecuite circulation

Opinions regarding the effect of stirring on crystal growth are varied.
"Opinions differ concerning the influence of stirring and agitation upon the crystallization velocity of sucrose. Experiments on this question have led different investigators to conclude that there is either a pronounced effect or relatively none". This is attributed to the fact that "conditions and circumstances are not uniform and comparable" [14]. The effect of flow velocity on crystal growth has already been demonstrated by Eq. 8 and Eq. 9.
Some studies regarding circulation in vacuum pans quite often rely on surprising simplifications:
- stirrers and their mode of operation (single speed, double speed, variable speed) are neglected,
- in most cases only the flow of liquid phase process medium (no crystals) is studied,
- syrup feed and location of feed entry into the pan are neglected.

Good circulation, however, has definite advantages like "thorough and unified distribution of feed, minimum variations of temperature, improved crystal formation,......however the stirrer does not show significant results in crystal size distribution or massecuite exhaustion" [15]. It is also well known that high supersaturation and bad massecuite circulation are made responsible for conglomerate formation.

3. MODELING CRYSTAL GROWTH IN INDUSTRIAL SUGAR CRYSTALLIZERS

3.1. The simple model of crystal growth.

The most often used model describing crystal growth is:

$$da / dt = K*(SS – 1) \qquad \text{Eq. 14}$$

It is evident from the above discussions that this model is a *very simplified* one. It neglects the effect of quite a few important parameters, or implicitly assumes that they are included in K, the overall crystallization growth rate, which is *certainly not constant*.

3.2 Complex models.

No.1.

An often quoted complex model of crystal growth rate is given by the expression [16]

$$da / dt = G = P1*(OS – P2)*EXP (P3*(I / W)*EXP (-FT) \qquad \text{Eq. 15}$$

where:
P1, P2, P3:	constants	
OS:	SS – 1	
FT:	(Eact / R)*(1 /(273,16 + T) – 1 / 333,16)	
Eact:	15,0 – 0,2*(T -60)	
R:	1,9872*E – 03	

This model relies on supersaturation (SS), non-sugar concentration (I / W) and temperature (T) data. All other missing parameters should be taken into account by the proper determination of constants P1, P2 and P3.

No. 2.

Another complex model based on mass, energy and population balances with constant K determined on the basis of data from eight strikes in an industrial crystallizer [17]:

$$da / dt = Ka*EXP[-57000/(R*(T+273))]*(SS-1)*EXP[-Kb*(1-P)]*(1+2*v/V) \quad (m / sec) \qquad Eq. 16$$

Ka	265
Kb	13,863
R	8,314 (gas constant)
T	temperature (C)
P	mother liquor purity (abs)
v	volume of crystals (m3)
V	massecuite volume (m3)
v/V	crystal content by volume (abs)

According to [18] the crystal growth rate:

$$da / dt = Ka*EXP[-57000/(R*(T+273))]*(SS-1)*EXP[-Kb*(1-P)]*(1+2*v/V) \quad (m / sec) \qquad Eq. 17$$

Ka	100
Kb	8

Notes:
- Eq. 16 and Eq. 17 have the same structure, but their two constants (Ka and Kb) and the results are quite different.
- This model contains all of the most important parameters, however, its last term (1+2*v/V) is certainly not correct: It is in direct contradiction with Eq. 13. *Increasing crystal content definitely will not increase the rate of crystal growth.*

4. FORMULATION AND VALIDATION OF A CRYSTAL GROWTH MODEL

There are not many attempts to be found in the relevant literature resulting in the *formulation and validation* of a model describing crystal growth: it is not easy even in a laboratory environment. One basic requirement, on-line monitoring of supersaturation, the most important parameter of crystallization *in industrial crystallizers* became available with the introduction and use of the SeedMaster instruments.
By making use of the model components discussed above, a complex model will be formulated and validated using all of the required data, including supersaturation acquired on-line in industrial batch vacuum pans in operation in two different countries of the world.

4.1 Model formulation.

The crystal growth model is based on the individual components discussed in Point 2. and has the following form:

$$da / dt = K*f1(SS)*f2(T)*f3(NS)*f4(y) \qquad or$$

$$da / dt = K*(SS – b)*0,277*EXP[0,0186*T]*EXP[-1,75*NS/100]*(1 – y)^A \qquad Eq. 18$$

where

da / dt	:	linear crystal growth rate (µm/min)
K	:	overall crystallization growth rate
SS	:	supersaturation (--)
b	:	constant
T	:	temperature (ºC)
NS	:	non-sugar concentration (g/100 g water)
y	:	crystal content (by volume, abs.)
A	:	constant

Crystal content by volume (abs.) depends on the number N and size "a" of crystals in a unit volume of massecuite. The volume of a single crystal depends on its size and shape. There are different shape and volume form factors in the literature for sugar crystals regarded "normal". In [6] data acquired by measuring the length along the 3 axes of a large number of crystals in a beet sugar factory L.b : L.c : L.a = 1,33 : 1,0 : 0,73 was found. The volume of a similar crystal with L.c = 1 mm is V1 = 0,971 mm3, while the volume of one of cubic shape with a = 1 mm is V2 = 1 mm3. For sake of simplicity cubic shape with crystal size "a" will be used here.

4.2 Model validation

4.2.1 Methodology

It is natural that the model of crystal growth as described by Eq.18 must be validated by using industrial-size sugar crystallizer(s) where mass production of sugar is practiced. In our case this meant monitoring crystallization on-line in a large number of batch pans already in use in different countries.

Our method of validation is based on the active on-line monitoring of (among others) the most important parameter of crystallization: supersaturation. This was made possible due to the development and active use of the unique SeedMaster Instruments.

4.2.2 Instruments.

It is clear from Eq.18 that supersaturation (SS) plays a very important role. There is no single instrument to measure it: it can only be calculated by taking into account all its governing parameters (see Eq.1). The SeedMaster 2 (and the newly introduced SeedMaster 3, manufactured by K-PATENTS Oy, Finland with even more features) can provide all of the required data on-line *every 10 second intervals* (Fig.2, Fig. 3).

Fig. 2.	Fig. 3
K-PATENTS refractometer and SeedMaster 2	SeedMaster 3
(Sugar mill in Brazil)	(Sugar Refinery, Middle East)
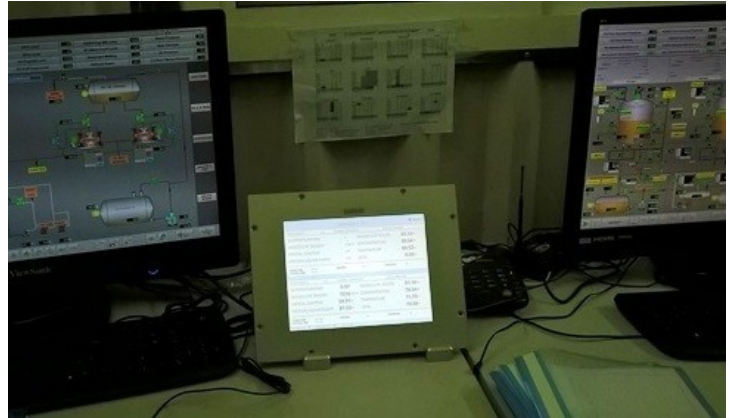
SeedMaster 2 (SM-2) or SeedMaster 3 (SM-3) inputs:
   a. syrup / mother liquor concentration (provided by a K-PATENTS process refractometer),
   b. temperature (provided by a K-PATENTS process refractometer),
   c. massecuite solids content (microwave transmitter), <u>OR</u>
   d. massecuite density (transmitter), plus
   e. massecuite level (transmitter).

Based on the above process data it is possible to calculate on-line the parameters which are really important in crystallization control:
SM-2 or SM-3 outputs (data are calculated on-line at 10 second intervals):
   • supersaturation SS
   • crystal content y (by volume, abs.)
   • mother liquor purity P (%)
   • mean crystal size (mm), (if no nucleation or dissolution of crystals takes place during the strike)
   • calculated massecuite solids content (%), or density (kg/m3), depending on the type of the selected instrument.

4.2.3 Method of model validation.

The basic process of model validation consisted of the following steps:
1. Selection of strikes characterized by:
   ✓ full seeding with slurry
   ✓ no nucleation all over the strike
   ✓ no dissolution of crystals all over the strike
   ✓ crystal size (MA) close to target (Case No.1: 0,65 mm; Case No.2: 0,25 mm)
   Monitoring of the strikes by a SM-2 or SM-3 from seeding till its end (time of crystallization), storing in a data archive every 10 seconds all of the input and calculated data.
2. Storing and trending data. All of the input and calculated data can be trended on the LCD of the SM-2 or SM-3 instruments. The same data can be downloaded and trended in Excel sheets as well. These are the "reference" or "SM-2" / "SM-3" data.
3. Calculation of the crystal growth rate da / dt according to Eq. 18 and its integral "a(n)" (crystal size) in Excel by using the SM-2 / SM-3 input data stored at 10 second intervals.

$$a(n) = a.s + \sum_{1}^{B} \left(da(n) / dt \right) \quad (mm) \qquad \text{Eq. 19}$$

   a.s: seed crystal size (mm)
   B: number of 10 sec intervals from seeding till the end of the strike
   time of crystallization: T.cryst = B / 6 minutes

With final crystal size (MA) and stored data on level, the number N of crystals in a unit volume (1 cm3) of massecuite can be calculated for every 10 second interval. Finally: using data on N and crystal size "a(n)", crystal content, solids content and

purity of the mother liquor can be calculated, too. *The calculated data are based on the simulation (modeling) of crystal growth represented by Eq. 18. and will be referred to as "SIMUL".*

4. Trending the data of the same selected reference ("SM-2" / "SM-3") and model ("SIMUL") parameter in a common Excel figure for comparison.
5. Eventual differences between the reference and calculated parameters are used to fine-tune the model equation (adjustable parameters K, b and A) accordingly.

5.   RESULTS

5.1 Case NO.1: Location: a well known refinery in West Europe

Instruments used: K-PATENTS PR-23-GP refractometer and SM-2

Strike parameters.
*   Feed syrup purity   : 98 %
*   Supersaturation when seeding   : 1,09
*   Time of crystallization (from seeding till the end)   : 141 min
*   Massecuite density (at the end of strike)   : 1499 kg / m^3
*   Product crystal size (MA)   : 0,65 mm
*   Massecuite volume ratio (V.max / V.seed)   : 2,51
*   Number of product crystals in 1 cm^3 of massecuite   : 1815
*   SS.max   : 1,145
*   SS.min   : 1,061

5.2 Measured data (data inputs) trended on the SeedMaster 2 display.
*   Mother liquor concentration (Fig. 4)
*   Temperature (Fig. 5)
*   Massecuite density (Fig. 6)

Fig. 4   Fig. 5   Fig. 6
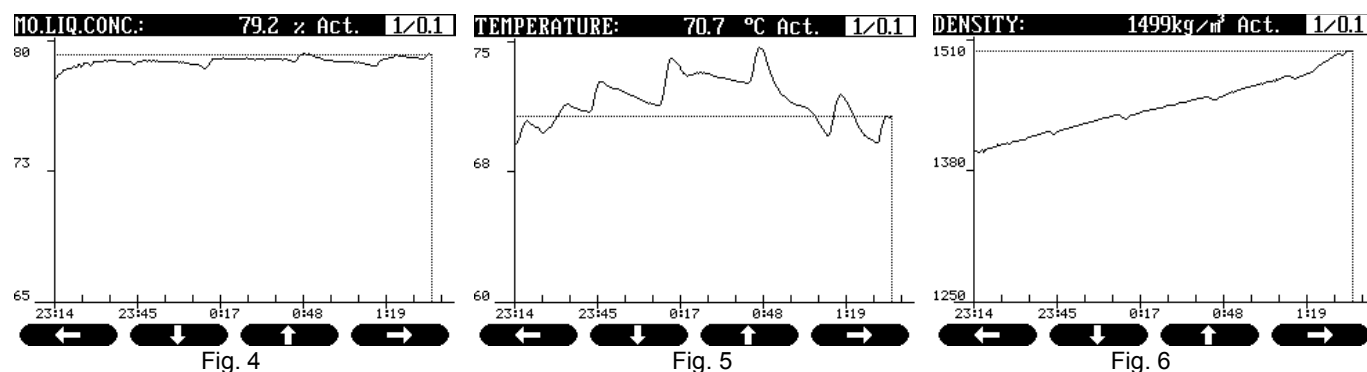
Notes:
1. Massecuite level was controlled as a function of massecuite solids content.
2. All trends were started when seeding was carried out and lasted till the end of the strike.

5.3 Comparing data monitored by the SM-2 with those calculated by making use of the model equation Eq.18.

Data are compared by showing the trends of the selected parameter. The trend window with white characters on black background shows *the original trend displayed on the SM-2 display*. The one beside it shows the same parameter displayed for comparison in an Excel diagram
*   with *solid line*, marked: SM-2 (exactly the same as the one on the SM-2 display) and
*   with *dotted line* marked: SIMUL: calculated after fine-tuning the K, b, A parameters of Eq. 18.

The horizontal axis is time expressed as a number (B). Actual Time = B / 6 minutes.
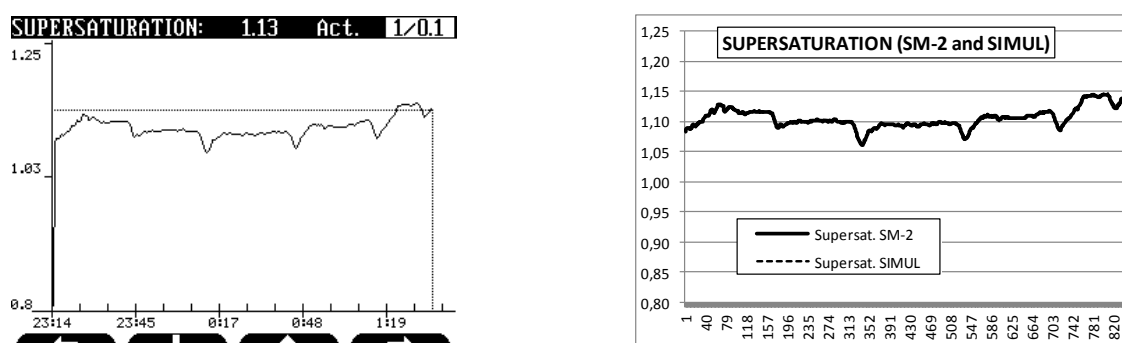
SUPERSATURATION:

Fig. 7.
NOTE: There is no noticeable difference between SM-2 and SIMUL data.
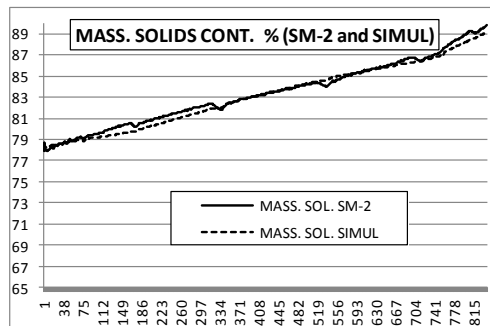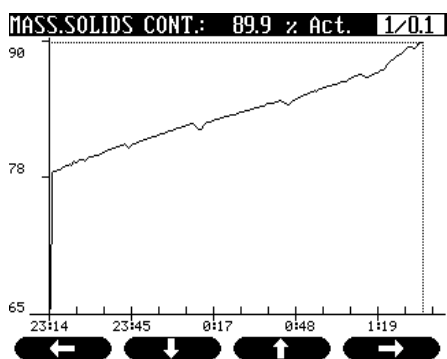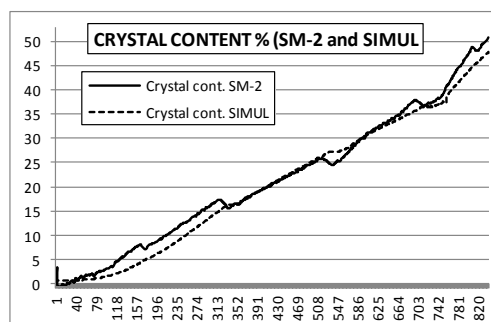
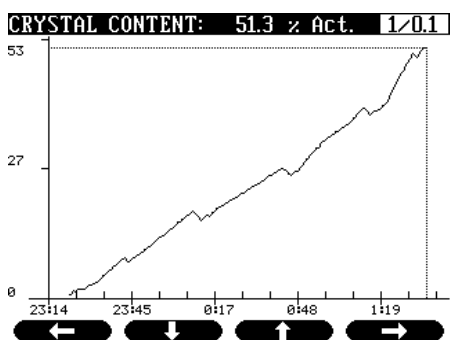*MASSECUITE SOLIDS CONTENT:*

Fig. 8

CRYSTAL CONTENT:

Fig. 9

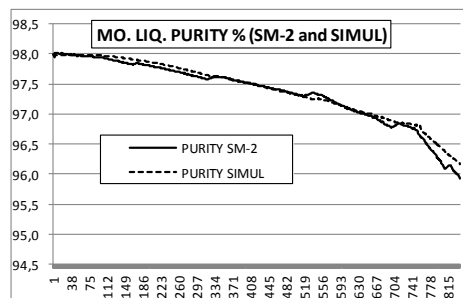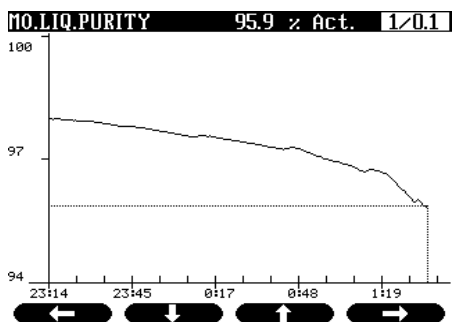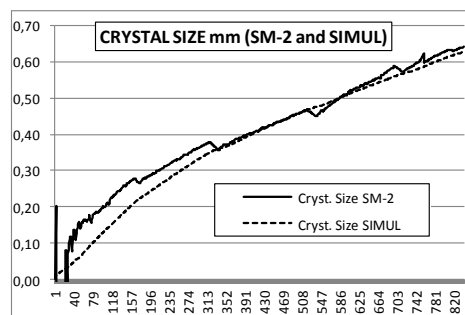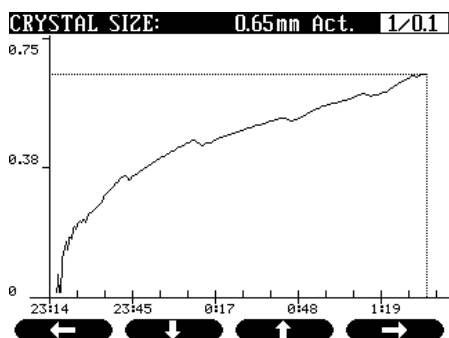*MOTHER LIQUOR PURITY:*

Fig. 10

CRYSTAL SIZE:

Fig. 11

NOTE: Considerable difference of crystal size data in the first 40 % or so of crystallization time. One of the possible causes: density probe calibration problem. The difference is fast reduced later on.
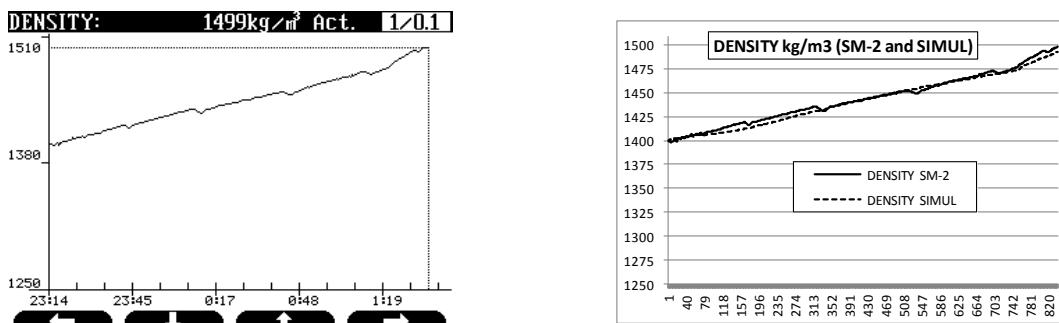
MASSECUITE DENSITY:

Fig. 12

5.4 The validated crystal growth equation.

Based on the process of validation it was found that the best fit was reached with parameters K, b and A as follows:

K: 0,0182   b: 1,035   A: 2

As already discussed, the overall crystallization growth rate K is a multiparameter function of several variables (see Eq. 3).
Using these data the (linear)crystal growth rate:

$$da / dt = 0,0182*(SS - 1,035)*0,277*EXP(0,0186*T)*EXP(-1,75*NS/100)*(1 - y)^2 \quad (\mu m / 10 \text{ sec}) \quad \text{Eq. 19}$$

Conversion of the equation in order to get the rate of crystal growth in the more accustomed engineering unit µm/ min can be done by multiplying K by 6. *However by doing so eventual changes in the values of the governing parameters during one minute will be neglected.*

$$da / dt = 0,1092*(SS - 1,035)*0,277*EXP(0,0186*T)*EXP(-1,75*NS/100)*(1 - y)^2 \quad (\mu m / \text{min}) \quad \text{Eq. 20}$$

where for completeness:
SS:	supersaturation (--)
T:	temperature (C)
NS:	non-sugar concentration (g/100 g water)
y:	crystal content by volume (abs)

NOTE: When using on-line data, most of all: supersaturation for crystallization control, it is *highly advised* to refresh all measured and calculated data at least every 10 seconds (it is a built-in feature of the SeedMaster Instruments). *Doing so only at 1 minute intervals will result in difficulties with control.*

5.5 Relative strength of the individual components (Eq.19).

Component: K

K is a function of quite many parameters of the process and the equipment used (Eq. 2).
The value of K determined validating the growth rate equation:

K = 0,0182 (sampling rate: 1 / 10 sec);   K = 0,1092 (sampling rate: 1 / minute)

Component: Supersaturation (SS) (Fig.13)

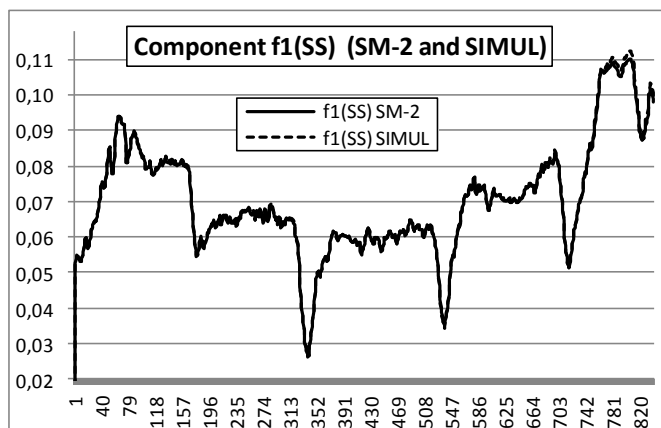$$f1(SS) = (SS - 1,035) \quad \text{Eq. 21}$$

Fig. 13

Eq.20 shows similarity to Eq.4 and it means that *there is no crystal growth if SS =< 1,035*. The effect of temperature T (see Fig. 5) on supersaturation is demonstrated.

Component: Temperature (T), (Fig.14)

$$f2(T) = 0,277*EXP(0,0186*T) \qquad Eq. 10$$

It was proved that Eq. 10 represents correctly the *direct effect of temperature* on crystal growth. However, while increasing the rate of crystal growth (Fig.14) it can only slightly compensate the large drop in supersaturation when temperature is increased (see Fig.13 and Fig.15). *Temperature has a complex effect on the overall rate of crystallization (K) as well.*
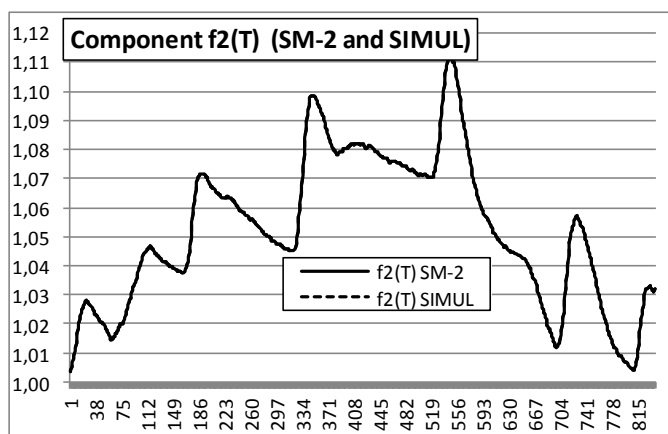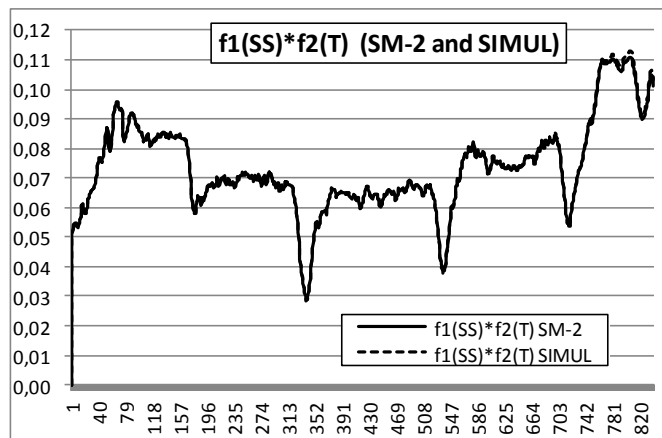

Fig. 14

Fig. 15

Component: Non-sugar concentration (NS), (Fig.16)

$$f3(NS) = EXP(-1,75*NS / 100) \qquad Eq. 11$$

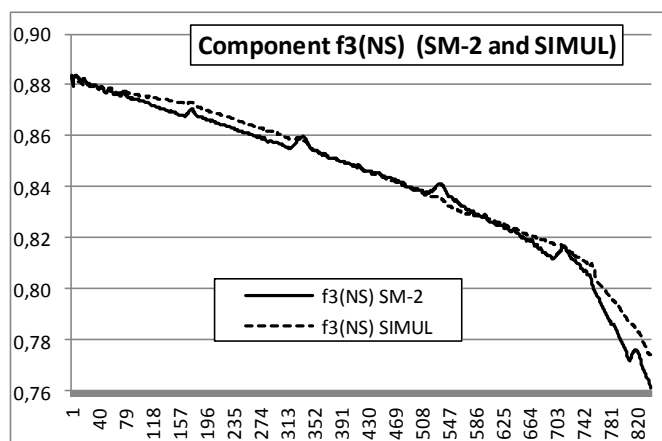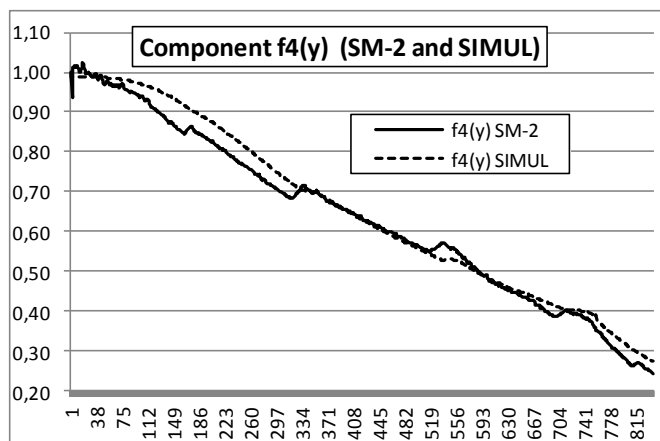Fig. 16

The effect of non-sugar concentration increases fast with low purity feed syrup, where the purity drop can be quite considerable.

Component: Crystal content by volume (y (abs.)), (Fig.17)

$$f4(y) = (1 - y)^2 \qquad Eq. 12$$

Fig. 17

It was proved that Eq.13 represents correctly the very strong effect of crystal content on the rate of crystal growth.

The combined effect of supersaturation, temperature, non-sugar concentration and crystal content on the rate of crystal growth is shown in Fig. 18.
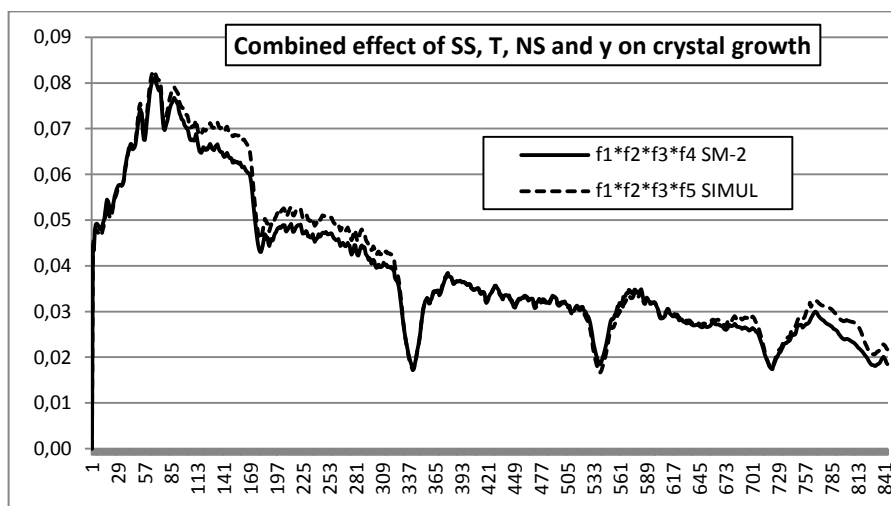

Fig. 18

Finally: when the data (Fig.18, vertical axis) are multiplied by 6000*K we get the rate of crystal growth in µm / min. The result is shown in Fig. 19.
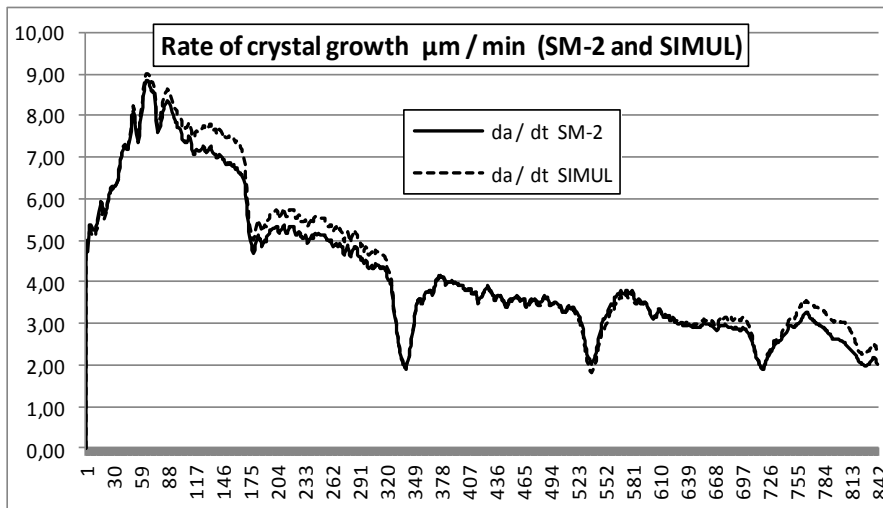
Fig.19

5.6 Case NO.2:   Location: refinery in West Africa

Instruments used: K-PATENTS PR-23-GP refractometer and SM-3

Strike parameters.

- Feed syrup purity   : 98 %
- Supersaturation when seeding   : 1,12
- Time of crystallization (from seeding till the end)   : 99 min
- Massecuite density (at the end of strike)   : 1495 kg / m³
- Product crystal size (MA)   : 0,28 mm
- Massecuite volume ratio (V.max / V.seed)   : 2,50
- Number of product (*footing magma*) crystals in 1 cm³ of massecuite   : 22400
- SS.max   : 1,14
- SS.min   : 1,09
- Full seeding with slurry

In this case only the major results of the model validation will be presented.

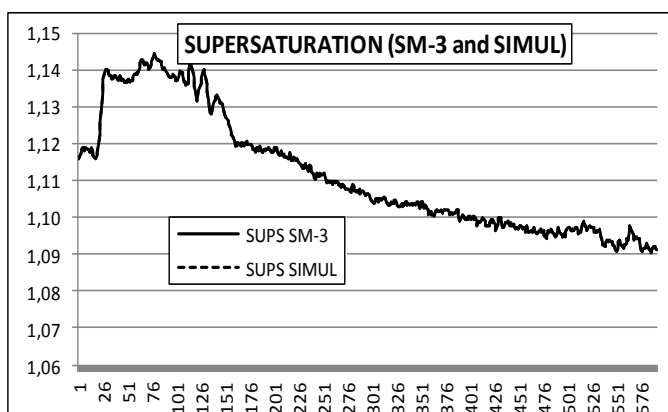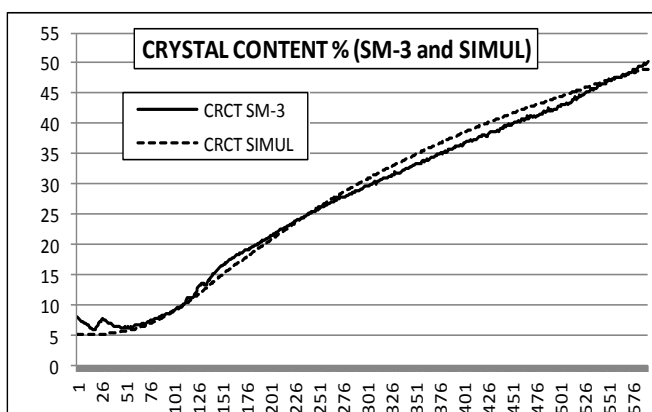Supersaturation and crystal content (% by vol.):

Fig. 20

Fig. 21

Supersaturation (Fig. 20): after keeping it almost constant at about SS=1,14 for a while after seeding, *due to increasing shortage of steam supply,* supersaturation began to drop considerably. No noticeable difference between the SM-3 and simulated data.

Crystal content (% by vol.) (Fig. 21): having fine-tuned the overall crystallization growth rate K, simulated crystal content tracks the one calculated by the SM-3 device.

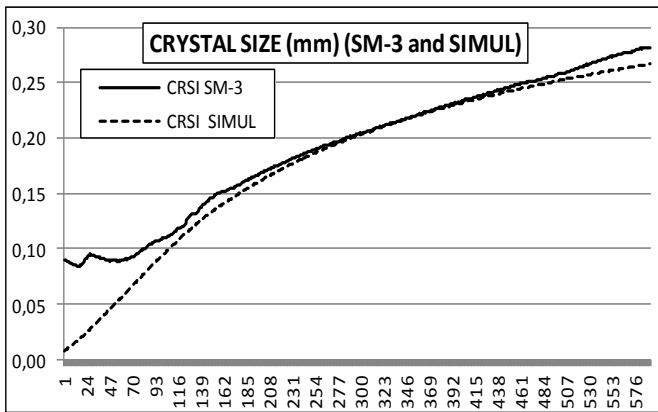*Crystal size (Fig. 22) and massecuite solids content (Fig. 23) (mm and %)*
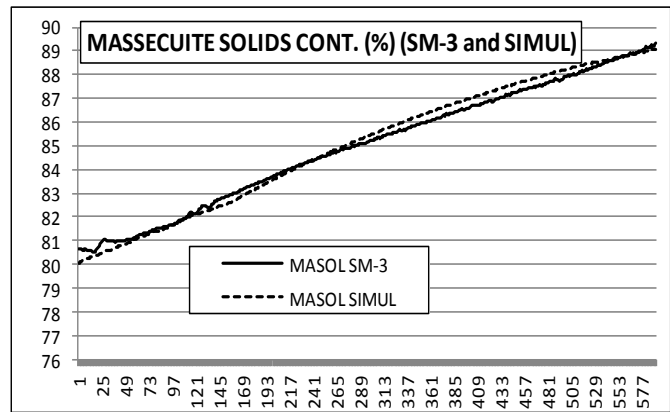

Fig. 22

Fig. 23

Crystal size (mm) (Fig. 22): the large (0,10 mm) crystal size calculated right after seeding by the SM-3 was due to calibration error of the microwave probe. There was probably a similar calibration problem towards the end of the strike.

Massecuite solids content (%) (Fig. 23): the same microwave calibration error just after seeding, followed by nice tracking later on.

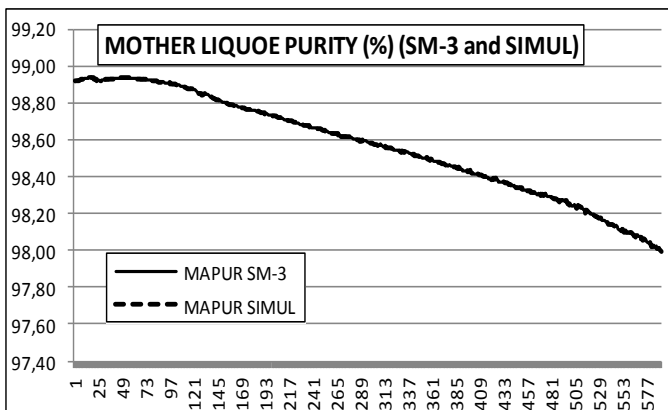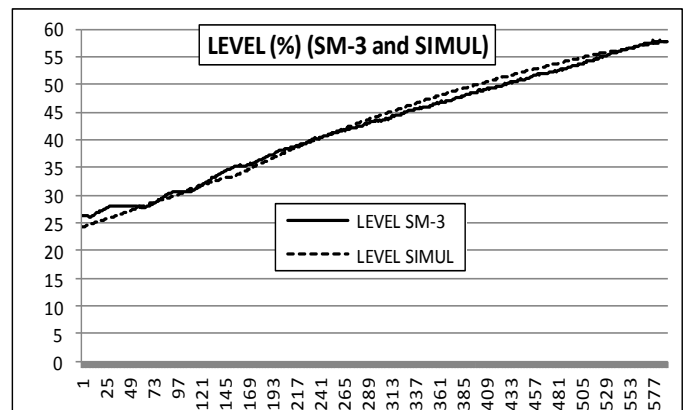*Mother liquor purity (Fig. 24) and level (Fig. 25) (%):*

Fig. 24

Fig. 25

Mother liquor purity (%) (Fig. 24): No noticeable difference between the SM-3 and simulated data.

Massecuite level (%) (Fig. 25): Small difference between SM-3 and simulated data.

Based on the process of validation in Case No. 2 it was found that the best fit was reached with parameters K, b and A as follows:
K: 0,0090   b: 1,035   A: 2

Comparing parameters of Eq. 18:

	K	b	A
Case No. 1	0,0182	1,035	2,0
Case No. 2	0,0090	1,035	2,0

Table 1.

5.7 Summary

As can be seen in Table 1, there is a *considerable difference in the values of K (ratio: 2:1), while the other 2 parameters (b and A) are the same.* The large difference in the overall crystallization growth rates (Eq. 3) could be expected: it lumps together the effect of all of the parameters which we are unable to measure or calculate. *K is certainly not constant during the strike but depends on quite many changing parameters.*
There are two considerable differences between the two cases:
1.   final (product) crystal size (0,65 and 0,282 mm, respectively), and
2.   the fact that there was not enough steam during most of the strike in Case No.2.
Remembering the effect of *liquid velocity v* and the *width of the stagnant layer δ* at the crystal surface it is logical to recall that the larger settling velocity of the larger size crystals (Case No. 1) has a positive (increasing) effect on K. Also, lack of steam supply (Case No. 2) to keep the rate of evaporation at the required (by the control system) level results in poor massecuite circulation and in a degrading effect on liquid velocity (*v*) and width of the stagnant layer (*δ*) *on the crystal surface*. These are only two of the many possible sources of the difference in the values of K in the two cases.

6. CONCLUSION

Crystal growth is a very complex process which depends on a large number of massecuite parameters, crystallizer designs and control practice. The process is highly nonlinear.
In this paper a multiparameter growth rate model and its validation was presented. The major findings are summarized below.

Supersaturation: its importance is widely acknowledged. Unwanted nucleation should be avoided all over the process of crystallization. The zone of control is very narrow: there is no crystal growth below SS <= 1,035 (see Eq. 20) and unwanted nucleation begins if SS > = 1,15…1,20, depending on mother liquor purity.
Fluctuations, like in Case No.1 (SS.max = 1,145, SS.min = 1,061) result in almost 3:1 change in crystal growth rate (Fig. 13). This certainly has a very strong effect on the time of crystallization (time from seeding to the end of the strike). Supersaturation should be kept constant and close, but safely below the nucleation limit all over the strike. This needs:

- good, undisturbed steam supply,
- well controlled (preferably: individual) vacuum system,
- reliable on-line data on supersaturation and.
- advanced crystallization control based on supersaturation [4].

Temperature: temperature has multiple effects on crystal growth: via supersaturation, directly and via the parameters affecting the overall crystallization growth rate (K).

Syrup / mother liquor purity: the effect of non-sugar concentration on crystal growth is considerable (Fig. 16) even with high purity syrups like in the two cases discussed here.

Crystal content: crystal content has a *very strong effect* on crystal growth (Fig. 17). Well designed level control is needed to find an optimal solution.

Overall crystallization growth rate (K): it is a multivariable parameter depending – among others – on equipment designs and control practice as well. It is a parameter to be determined locally.

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