

Caking of white crystalline sugar

by Barbara Rogé and Mohamed Mathlouthi*

*Author for correspondence: mohamed.mathlouthi@univ-reims.fr

Université de Reims Champagne- Ardenne, laboratoire de Chimie Physique Industrielle, UMR FARE, B.P. 1039, F- 51687 Reims Cedex 2, France

Abstract

The parameters affecting sugar caking investigated in this study are moisture content, ERH (Equilibrium Relative Humidity) grain size, crystal shape, temperature and flow function. Water sorption isotherms describe the relationship between water content and water activity (or ERH). Depending on the structure of sugar particle (crystalline or amorphous), the shape of sorption isotherm is different. Even for crystalline sugar, numerous factors affect the adsorption of water vapor and as a consequence the storage stability. The presence of a thin film of saturated solution at the surface of crystal as well as crystal size distribution and the inclusion of mother liquor droplets in the crystal are some of the factors which affect the equilibrium relative humidity of sugar and characterize its aptitude to cake. Flowability is measured with Jenike cell for the shear stress determination in consolidated sugar sample. Flow functions are useful to predict mass flow in silo or caking index of sugars.

Introduction :

Caking of food powders, especially crystalline sugar may be considered as a spontaneous agglomeration phenomenon. It is generally caused by the wetting of particle surface which causes its plasticization and sometimes dissolution. This happens especially for surfaces containing amorphous product. The plasticization may also be obtained by heating above the glass transition temperature. The powder goes through 4 different stages during the caking phenomenon (Gutman, 1995) (Figure 1).

These 4 stages are:

- A. The pendular stage at which the powder is still free flowing,
- B. The funicular stage corresponding to the establishing of permanent contact between particles,
- C. The capillary stage reached when moisture is high enough to

provoke liquid bridges between particles,

- D. The drop stage obtained when dissolution of particles is preponderant.

If drying occurs after wetting, the caking phenomenon is observed for a characteristic equilibrium relative humidity (ERH) at which water is released from powder particles which form solid bridges and agglomerates. The physical conditions like surface tension, capillary pressure and interparticular forces at the origin of particular bridging are described by Downton, Flores-Luna and King (1983). Temperature together with water activity (or moisture content) plays a major role in the process of plasticization which leads to the agglomeration of food powders. The characteristic temperatures reported in literature which characterize the viscous behavior of food powders are T_s (sticking point), T_c (collapse temper-

ature) and T_g (glass transition temperature). These transition temperatures are comparable and decreased when moisture content is increased and the Gordon- Taylor (1952) equation roughly works for different products such as amorphous sugar, model fruit juice, freeze dried orange juice (Aguillera, del Valle and Karel, 1995).

Different methods have been used to account objectively for the flowability and cohesiveness of food powders. Among these methods are the flow rate through a funnel, the angle of repose, microscopical observation of particles, the flowability angle and the determination of flow function using a Jenike cell (Aguilera, del Valle and Karel, 1995).

We have studied caking of sugar samples with different grain sizes, amounts of amorphous particles, broken crystals or fine particles and surface impurities. Water vapor sorption isotherms, flowability angles and flow functions determined with a Jenike cell were the methods applied to inves-

tigate the caking phenomenon.

Materials and methods

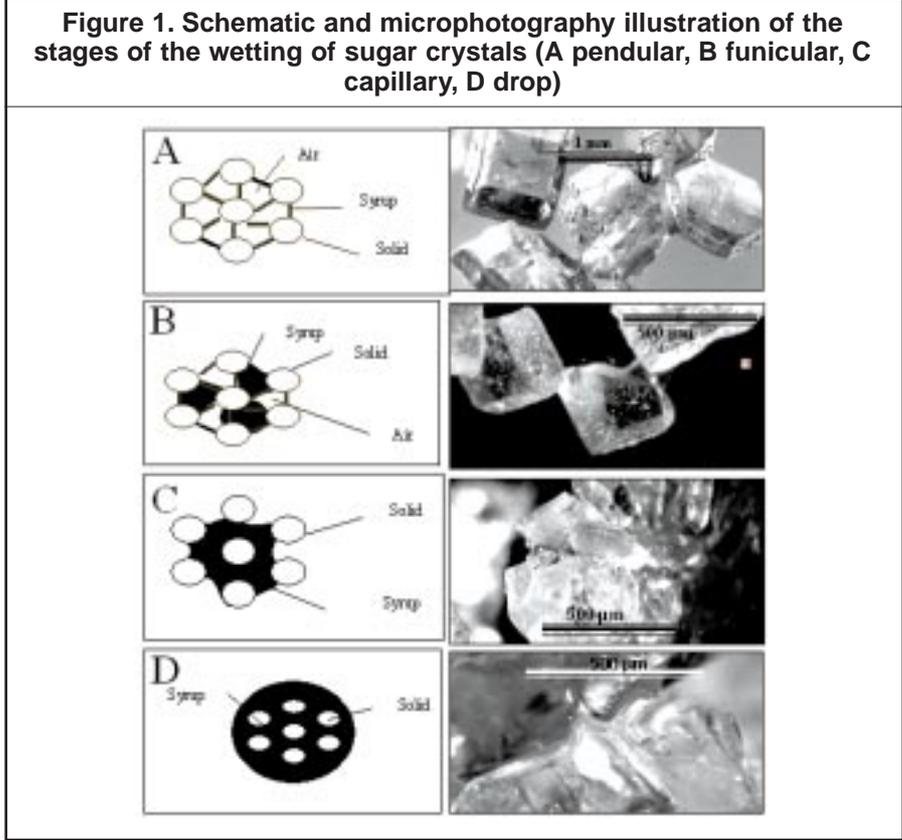
Water vapor sorption isotherms

Water vapor sorption isotherms were established using the microclimate method. Equilibrium relative humidity (ERH) atmospheres in gastight jars were fixed with saturated salt solutions (see Table 1) (Greenspan, 1977). The analyses were carried out with sucrose samples previously dried by oven drying (3 h, 105 °C). Sucrose was weighed in cupels (2g) and maintained at fixed temperature (4.5; 20; 25; 30; 35°C) and different ERH until equilibrium was reached after 7 days (constant weight). At a given equilibrium relative humidity (ERH), moisture content was calculated and the sorption curve established as moisture content = f(ERH).

The investigated samples were fractions of sugar with different grain sizes obtained by sieving. We also estimated the effect of fine particles on the behavior of standard sugar A (MA = 0.80; CV = 20; fines < 0.25mm = 0%). A moderate proportion (2; 5 and 10 %) of fine crystals (< 250 μm) was added to standard sugar A by weighing. We also milled part of standard sugar A and considered the fraction milled (21 %; 70 %) by a counting image analysis procedure. The EU grade of the standard sugar A used is 1 and the number of CEE points 6.68 (Aspect: 0.4; color : 2.21; Ash : 4.07). Moreover, it was found that ash doesn't have influence on sugar crystals hygroscopicity (Rogé, 2001).

Flowability characterization: Jenike cell

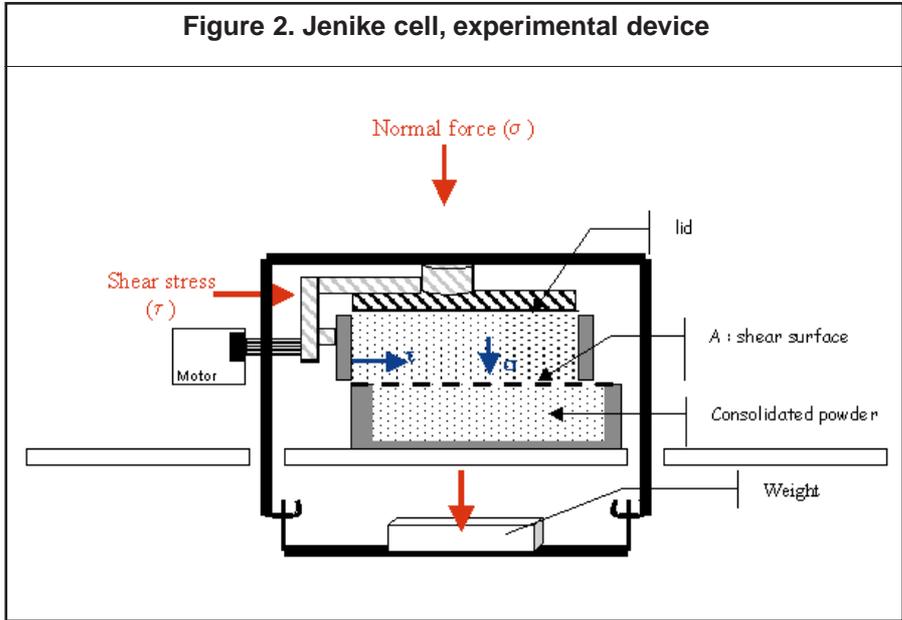
The Jenike shear cell was used for measuring powder flowability. Experimental device is presented in Figure 2. The theory was developed by Jenike (1964). The measurement of yield stress of preconsolidated samples under various normal loads allows establishing of flow function of the studied sugars. The flow function is a plot, which permitted to classify powders as a function of their flowability.



Flowability information is useful in order to predict for example, mass flow in silo or caking index of sugars.

The procedure applied to measure flow function of sucrose is that used by Teunou and Fitzpatrick (1999). Sugar samples are placed in the Jenike cell (200g) and consolidated under a known consolidation stress in order to reach the critical consolidation point. Then, the sample was sheared under

three new consolidating stresses, in order to measure shear stress required to cause the powder to fail. From the experimental values of shear stress obtained for the different normal forces applied a flow function is drawn which represents shear stress F_C as a function of normal force σ_c (Figure 3). The slope i of flow function allow identification of shear conditions under which the flow becomes difficult. For



comparison of real situation in an industrial silo, forces being exerted on sugar vary between 50 and 230 kPa when the silo height increases from 5m to 15m. A free flowing powder was characterized by a low flow index i_f , which is given by the slope of the flow function.

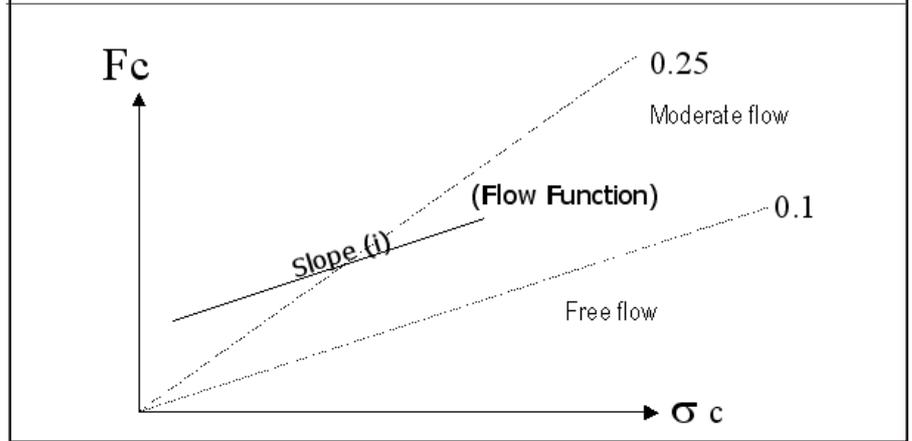
To study the influence of relative humidity (RH), we placed our samples at an appropriate relative humidity. During the procedure, we considered that RH is still constant. The shear stress corresponding to these points were measured at a fixed shear rate of 6 mm/min.

Results and discussion

Water vapor sorption isotherms

Effect of crystal size and the addition of fine crystals (< 250 μm) on caking

Figure 3. Schematic representation of flow function representing shear stress F_c as a function of normal force (σ_c). The slope of curve i_f is the flow index.



Particle size affects flowability of powders. The water vapor sorption curves allowed a quantification of the effect of relative humidity on the moisture content of powder. Flowability of powder depends on the water content. In addition,

visual observation proves to be qualitative information far from negligible.

Figure 4 shows water vapor adsorption isotherms for standard sugar (A) (OM = 0.80; CV = 20; fines < 0.25 mm = 0 %) containing different percentages of fine particles (< 250 μm). It is also shown on this figure, some pictures of sugar crystals at different stages of the water vapor adsorption curve. These results confirm that fine sugar crystals (< 250 μm) are the most hygroscopic as already mentioned by Werner (1963). It adsorbs increased amounts of water as relative humidity is increased. The shape of water vapor adsorption curve tends to be comparable to that of amorphous sugar (Roth, 1976). Oppositely, standard sugar shows the typical shape of adsorption isotherm obtained with a crystalline product (Figure 4). Between 0% and 82 % of relative humidity, standard sugar adsorbs only a negligible amount of water. Water adsorbed is almost constant and equal to 0.004 g per 100 g of dry substance. Above 82 % of relative humidity, adsorption of water by sugar increases rapidly to reach the adsorption curve of saturated sucrose solution. It should be recalled that the quasi-vertical line at about 82-83% R.H. is the equilibrium relative humidity of saturated solution at equilibrium with sugar crystal.

When fine particles (< 250 μm) are added to standard sugar (A), it is observed that the higher the amount of fine particles (2, 5, 10 %), the closer

Figure 4. Water vapor sorption isotherms of standard sucrose (A), and A with added fine particles (2-5 or 10%) compared to water vapor adsorption of 100% of fine crystals (M.A. < 250 μm) and to the behaviour of amorphous sugar (Roth, 1976)

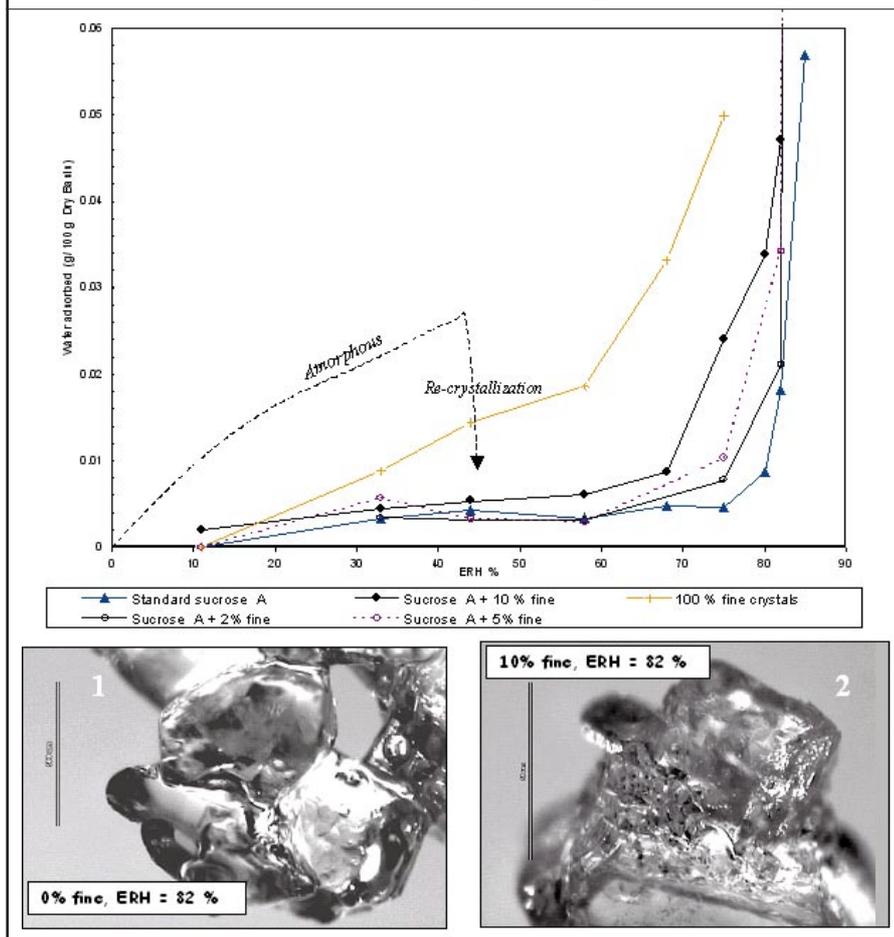
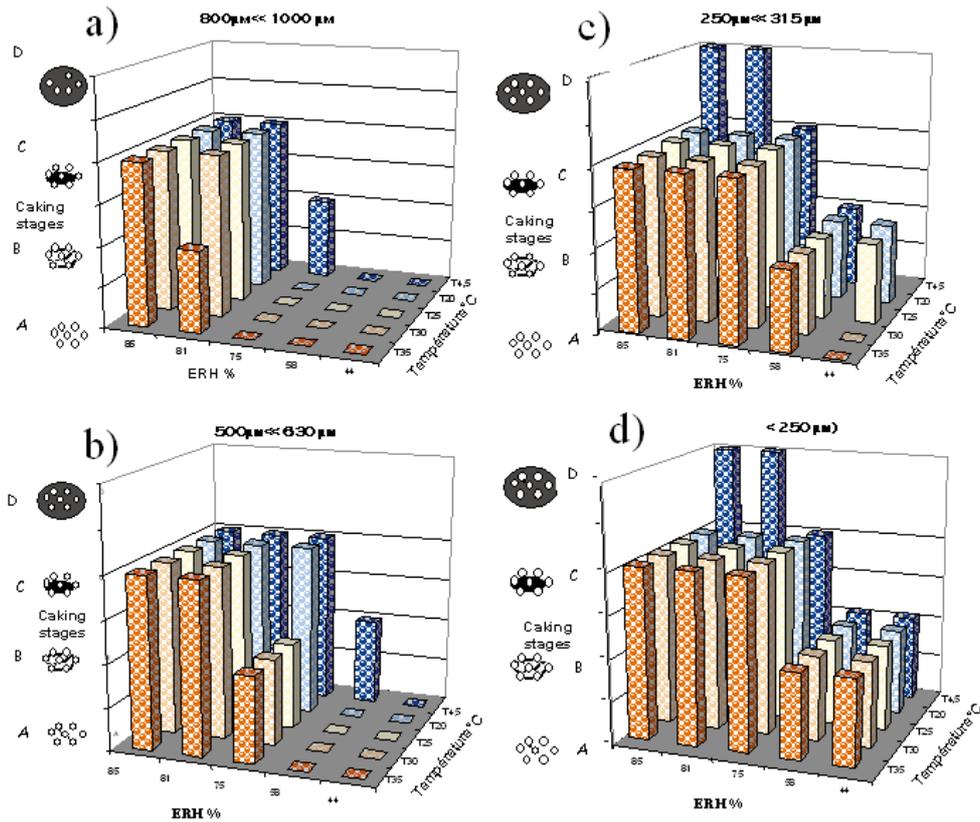


Figure 5. Variation of caking stages of sugar samples (fraction a, b, c, d are sieve refusal with M.A between 0 and 1000 μm) as a function of equilibrium relative humidity (ERH) and temperature



the behavior of the sample to that of amorphous sugar (see Figure 4). In particular the sorption isotherm of 100 % of fine particles is comparable to that of amorphous sugar. Increased amounts of adsorbed water cause the dissolution of amorphous sugar and tend to form liquid bridges between particles. However, sucrose in solution

tends to re-crystallize and to form solid bridges between particles. During this procedure of re-crystallization, free water is released and vaporized in the air, which leads to a decrease in water content (see Figure 4).

Microphotography pictures allow understanding of the mechanism leading to caking (Figure 4). Picture 1 in

the Figure 4 shows standard sugar A, as a reference, at the same equilibrium relative humidity (82 %). In picture 2, we notice that added fine crystals (10%) are welded and caked through solid bridges between crystals. Fine crystals ($< 250 \mu\text{m}$) play the role of binder between sucrose crystals. They contribute to increase the adsorption of water by standard sugar.

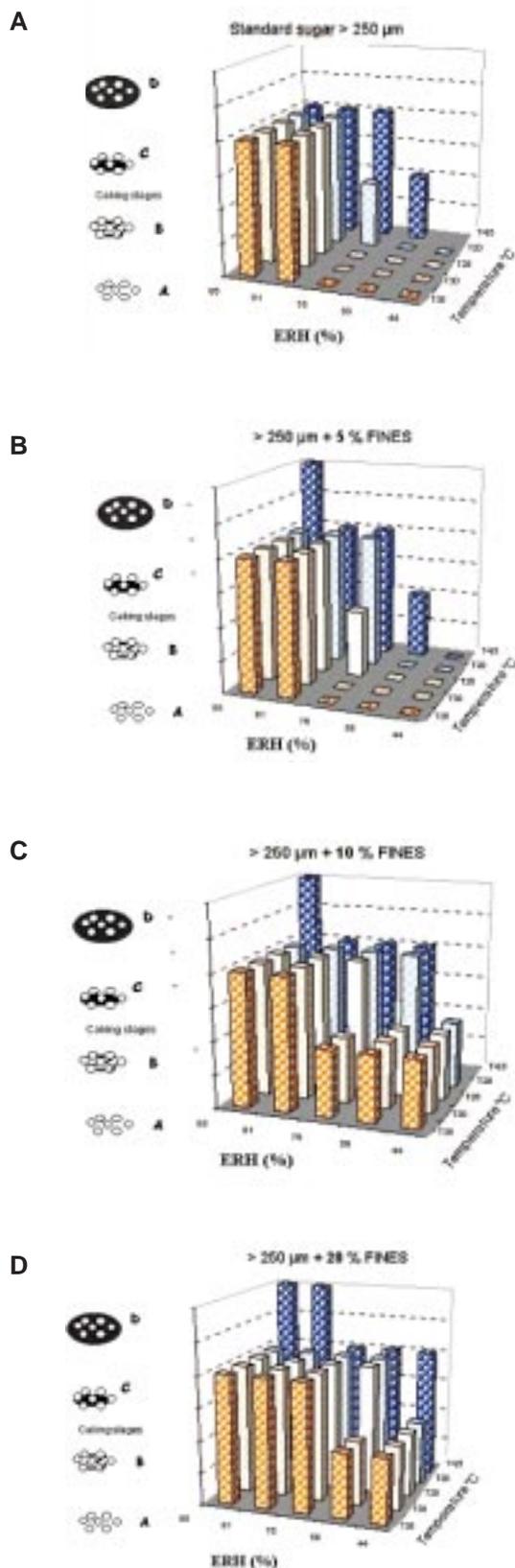
Table 1. ERH values for saturated salts solutions (Greenspan, 1977)

E.R.H. Values for saturated salts								
Temperature (°C)	LiCl	K ₂ CO ₃	NaBr	NaCl	(NH ₄) ₂ SO ₄	KBr	KCl	
5	11.26	43.13	63.51	75.65	82.42	85.09	87.67	
10	11.29	43.13	63.51	75.65	82.06	83.75	86.77	
15	11.3	43.14	62.15	75.67	81.7	82.62	85.92	
20	11.31	43.16	59.14	75.47	81.34	81.67	85.11	
25	11.3	43.16	57.57	75.29	80.99	80.89	84.34	
30	11.28	43.17	56.03	75.09	80.63	80.27	83.62	
35	11.25	43.17	54.55	74.87	80.27	79.78	82.95	

Effect of temperature and equilibrium relative humidity

To determine the behavior of sugar samples submitted to critical temperature and relative humidity, it is needed to establish water vapor sorption isotherms in the whole range of temperatures (5°C to 35°C) and relative humidities (33% to 90 %) to which sugar might be submitted. According to Teunou and Fitzpatrick (1999), we define critical temperature and critical ERH as being the starting point of caking mechanism, this point is called

Figure 6. Variation of caking stages of a standard sugar sample with added proportions (0; 5; 10 or 20%) of fine particles as a function of equilibrium relative humidity (ERH) and temperature



caking point. Sugar crystals stick together, become cohesive, and fluidity is nil. These isotherms were established for different crystal sizes (between 0 and 1000 μm). Variation of caking stages of sugar samples (Stages A; B; C and D) as a function of relative humidity and temperature are reported on Figure 5. Evaluation of caking is carried out by measuring water content, friability angle (Rogé and Mathlouthi, 2000) and finally by microphotography. These measurements are complementary and make it possible to classify sugars in 4 classes (ABCD, see Figure 1).

Figures 5 and 6 show a decrease in the amount of adsorbed water with an increase in temperature at constant relative humidity. As temperature is increased, the adsorbed water molecules gain more energy which tends to release them, thus the moisture content of the powder tends to decrease (Tenou and Fitzpatrick 1999). As can be seen in Figure 5, sugar crystals with sizes below 0.5 mm are more likely to cake than larger crystals. Moreover, the presence of fine particles (< 250 μm) in the sample

increases caking probability (Figure 6). Fine particles used for these experiences consist of dust collected in a factory. Figure 8a, shows these dust particles found in factories. An analysis by Differential Scanning Calorimetry (DSC), confirms their amorphous structure especially for sizes below 100 μm (Rogé 2001). These fine particles were composed of broken crystals obtained by attrition in the rotary dryer or in elevator for example. These results confirm those in the section relative to the quality of crystals. Fine particles seem to act as primers to the caking process. Moreover, the size of sugar crystals as given by Mean Aperture (MA) and CV plays a major role in sorption behavior. Table 2 presents the critical ERH and temperature for different MA and CV. It seems obvious that the more CV increases, the more sugar is hygroscopic, while Mean Aperture does not seem to have important effect.

Amorphous, fine particles and broken crystals

In order to validate the influence of amorphous sugar on water sorption properties of standard crystalline sugar, water vapor sorption isotherms (T = 20°C) were established on amorphous, milled and non-milled sugar with MA = 250 μm. Figure 7 reports water vapor sorption isotherms of microcrystalline sugar (< 250 μm) which was obtained according to a patented process by Beghin-Say (Savarino and Générmont, 2000). Sorption isotherm of microcrystalline sugar was compared to that of sugar sample with the same size (< 250 μm) collected as dust from a factory. As a general rule, sugar dust is not homogeneous in size and crystallinity. Visual and microscopical observations made on these two samples (Figure 8) clearly show the differences in shapes. The crystal shape of microcrystalline sugar was regular and the edges sharp whereas factory dust particles are irregular and opaque which characterizes amorphous particles.

Water vapor sorption isotherms of these two samples were different which shows that crystallinity has an

Figure 7. Water vapor adsorption isotherms at 20°C of standard sugar, sugar microcrystals (Beghin-Say) (B), sugar dust from factory (A) and 21% and 70% milled sucrose microcrystals.

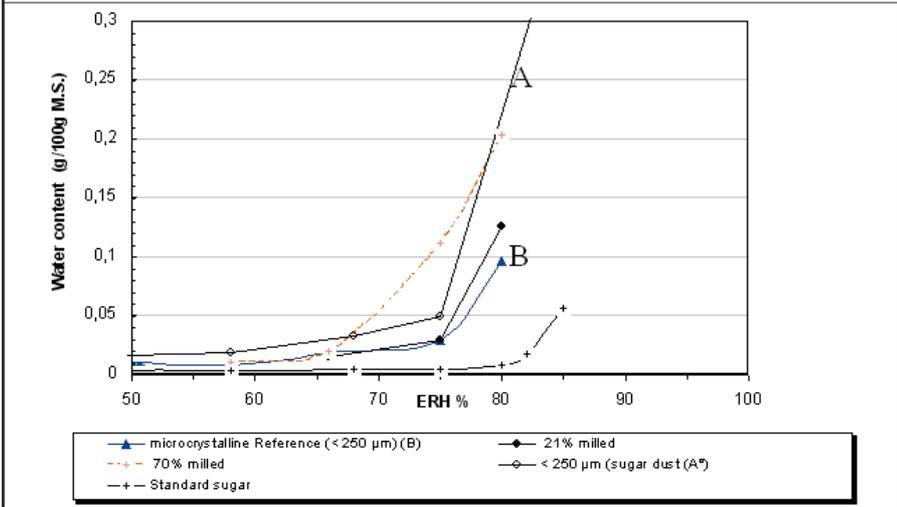


Figure 8. Microphotography; (A) sugar dust from factory. (B) sucrose microcrystals (Beghin_Say)

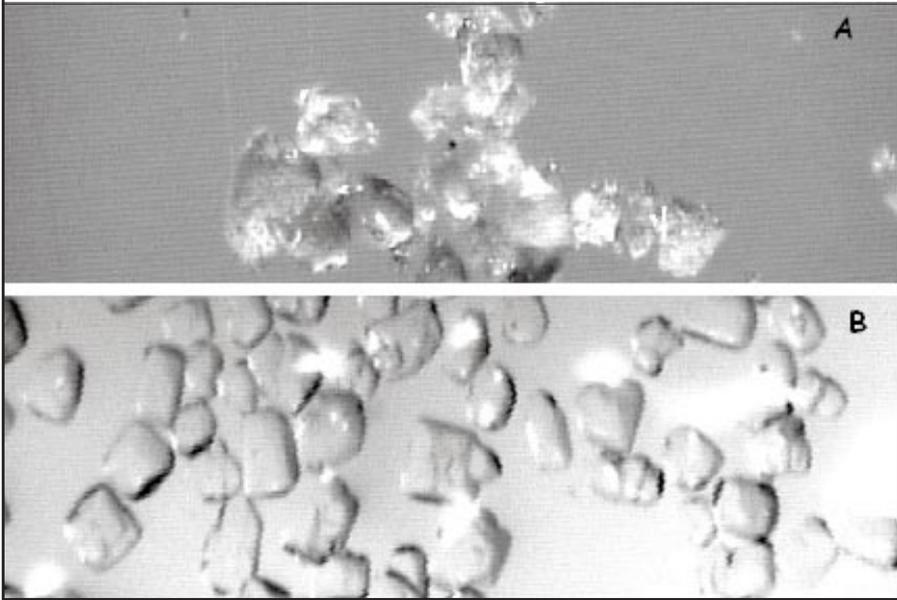
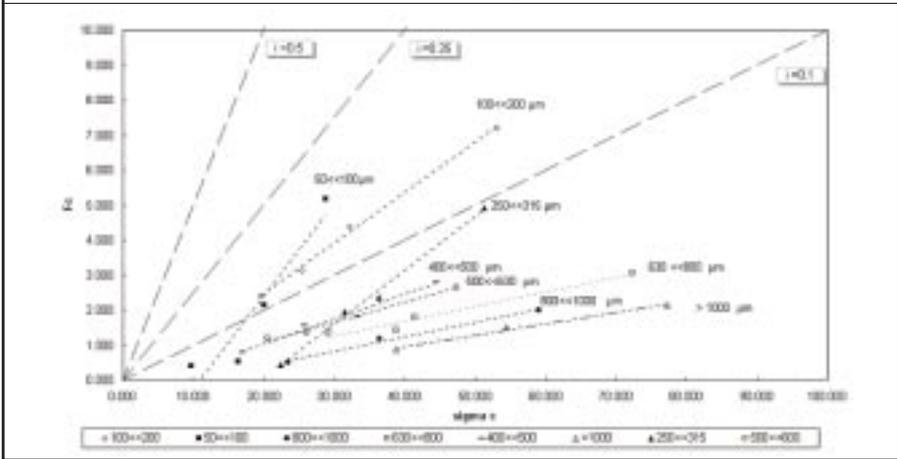


Figure 9. Flow function (FF) of sugar samples with grain sizes ranging from 50 μm to 1mm (Fc: 0 to 10 kPa; σc: 0 to 100 kPa) (i slope or flow index)



influence on final hygroscopicity of samples. To confirm this first observation, we have milled up to 21% and 70% (number percentage) of the microcrystalline sugar. This percentage was obtained by a counting procedure on 300 crystals with a microscopical technique. After this treatment, milled sugar was sieved in order to keep the same mean aperture (MA = 250 μm). This method of milling has been used by Roth (1976) to obtain amorphous material. With 21% of milled crystals in the sample, water vapor adsorption was comparable to that of non-milled sugar. When the percentage of milled sugar reached 70%, hygroscopicity is increased and the sample started caking at 66% RH instead of 75% for microcrystalline sugar.

Water vapor sorption isotherms indicated that hygroscopicity of sugar was dependent on its crystallinity. More than crystal size, the physical state of sugar (amorphous or crystalline) was found preponderant as regards hygroscopicity. Thus, it seems important to know the quantity of amorphous material present in industrial sugar. Accordingly, the shape of water vapor sorption isotherm as shown in Figure 4 proves to be a useful tool to reveal the influence of fine particles, or amorphous material.

Flowability characterization : Jenike cell

Crystal size and flow function

The only way to take into account the effect of powder physical properties (crystal size distribution (CSD)) and external conditions (T°, ERH) on powder flow properties as a function of storage time is the measurement of flow functions of the powder after its consolidation (Teunou and Fitzpatrick, 2000). This method, which is generally accepted for judging powder flowability, has the advantage of producing failure properties which can be used for quantitative design purposes and for qualitative comparisons of powders (Teunou *et al.* 1999). This technique allowed a good understanding of the behaviour of powder flowability in

Figure 10. Flow function (FF) of standard sugar sample with MA > 250 μm with added percentage of fine crystals (5-10 and 20%)

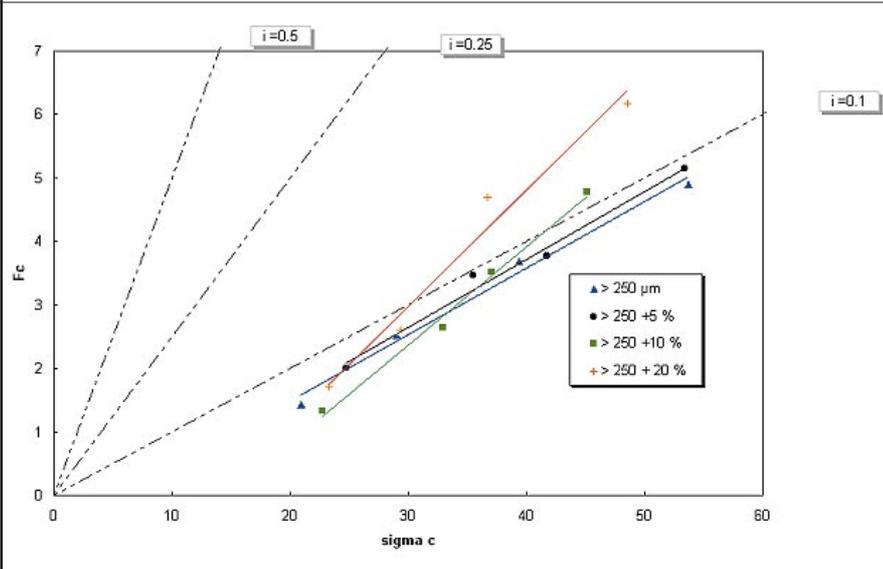


Figure 11. Flow function (FF) of sugar samples at different equilibrium relative humidity

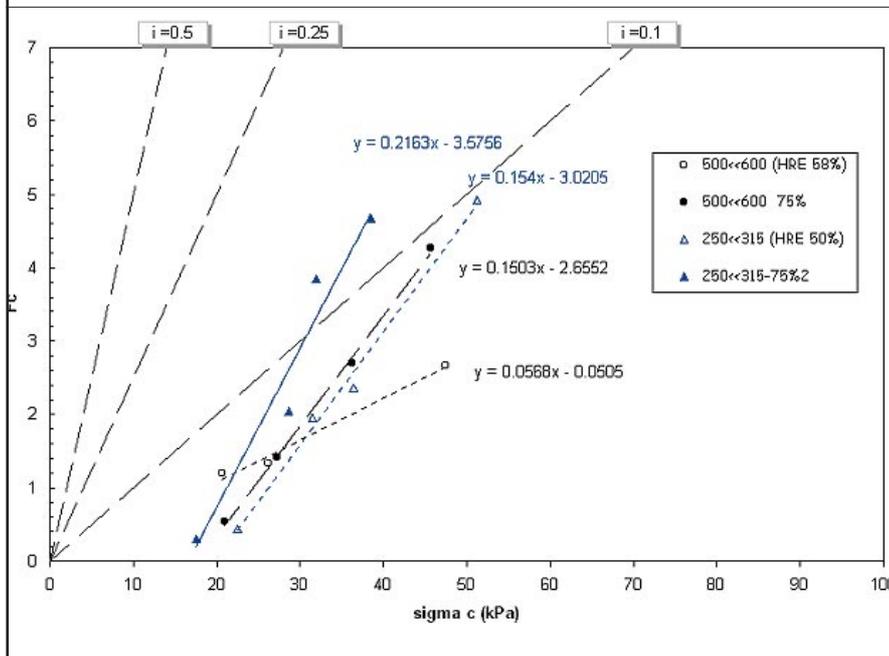


Table 2. Critical ERH for different crystal size distributions

T °C	critical ERH (ERH c) %		
	OM 0.56; CV 38	OM 0.56 ; CV 40	OM 0.59; CV 38
4.5	75	58	75
20	75	58	75
25	75	58	75
30	75	75	81
35	81	81	85

silos. The instantaneous flow functions of sugar with different sizes (from 100 μm < to < 800 μm), at 22°C and 55% ERH, are reported in Figure 9. Sugar used was the same factory sample with same CEE points. For sugar samples, it was possible to discriminate free flowing powder ($i < 0.1$) from the others. From Figure 9, we find that up to 20 kPa of shear stress flowability of sugar increases when crystal size decreases. Sugar is cohesive below a size of 400 μm which means that flow index i was higher than 0.1. This may change at lower shear stress. Teunou *et al.* (1999) state that only simple powders keep the same flowability at various shear stress ranges. Flow function measured at low consolidation stress reveals that the powders below 100 μm have a better flow than at high consolidation stress. This result underlines the complex role played by fine particles during caking. Figure 10 reports the flow functions at 20°C and 55% RH of a standard sugar added with different percentages of fine particles (5-10 or 20 %). As Figure 10 shows, above a consolidation stress of 25 kPa, and below 5 % of fine particles, the flow is similar to that of standard sugar and with 10 % of fine particles the flow is altered. The slope i is in the range 0.1-0.25 which is characteristic of medium flow. With 20% of fine particles, the flow is difficult. Below 25 kPa, sugar containing 20% of fine particles seems less cohesive than other samples (Figure 10). This behavior could be explained by an effect of ball bearing, which allowed, at low consolidation stresses, improvement of flow. At high consolidation stress, fine particles increased cohesion of the powder and reduced its flow.

Temperature, ERH and flow function

The flow functions of sugar samples at 20°C and at two equilibrium relative humidities (55% and 75%) were measured to quantify the effect of ERH on flowability. Results are summarized in Figure 11. The flow index (i) given by the slope of the flow function ($I = F_c/\sigma$) indicates that at high consolidation stress (> 30 kPa), flowability of sugar decreases as ERH is increased. Water

adsorbed onto the surface of sugar crystals will tend to form liquid bridges between particles making them more cohesive. This can lead to the caking at higher relative humidities or consolidations stresses. At consolidation stress below 30 kPa, it may appear surprising to find that "wet" sugar has better flow than "dry" sugar (see Figure 11). In this case water plays the role of a lubricant. This intriguing situation might happen in factory silo as there is no general rule governing the flow from silo. It is well known that "wet caking" is easier to handle than "dry caking".

Conclusion

The tendency of white crystalline sugar to cake was studied for different sizes of crystals under different conditions of storage such as varied temperature and relative humidity, added fine particles or dust. For this, we have used water vapor adsorption isotherms and shear stress Jenike cell as well as microphotography. From sorption isotherms, critical temperatures and ERHs of caking were determined for the different types of sugar samples studied. The samples with the lowest crystal size (below 0.5 mm) or with the highest proportion of added fine particles (> 10 %) were found the easiest to cake. It is particularly important to notice that the negative effect of fine particles (< 0.25 mm) on flowability is not only a matter of size, but mainly a matter of structure of the crystals. The sugar dust collected in the conditioning workshop of sugar factory is composed on fragments of crystals, very tiny powder particles originating from attrition of rapidly dried crystals and amorphous layers detached from bulk sugar. These different types of particles behave like amorphous sugar. Microscopic observation, differential scanning calorimetry and the hygroscopicity of sugar dust is comparable to that of amorphous sugar (milled, or freeze dried) rather than to well crystallized sugar crystals with sharp edges and 100 μm mean aperture (Beghin Say Patent).

Analysis of the effect of relative humidity and fine particles on the flow

function of a standard sugar was determined using a Jenike shear cell. Increased humidity was found to affect the flowability of sugar in silo as derived from shear stress. The most detrimental factor on the flowability proves to be the presence of a high amount of fine particles (above 10%). The illustration of the different stages of caking by microphotographies allows interpretation of each of the roles of moisture and fine particles on the caking mechanism.

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References

Aguilera J-M, del Valle J.M., & Karel M (1995). Caking phenomena in amorphous food powders. *Trends in Food Science & Technology*, 6, 149-155.

Downton G.E., Flores-Luna J.L., & King CJ (1982). Mechanism of stickiness in hygroscopic amorphous powders. *Ind. Eng. Chem. Fundamentals*, 21, 447-451.

Gordon M., & Taylor J.S. (1952) Ideal copolymers and the second order transition of synthetic rubbers, I. Non crystalline copolymers. *J. Appl. Chem.*, 2, 493-500.

Greenspan L. (1977). Humidity fixed point of binary saturated aqueous solutions. *J. Food Research*, 81 (1), 89-96.

Gutman S. (1992). Contribution à la connaissance physico-chimique des poudres : la notion d'humidité relative d'équilibre. *Thèse de Doctorat en Pharmacie*, UFR de Pharmacie Chatenay - Malabry :Paris XI.

Jenike A.W. (1964). Storage and flow of solids. In *Bulletin of the University of Utah*, 53 (26), Bulletin n°123 of the Utah engineering experiment station. Eleventh printing (1986), revised in 1980.

Mathlouthi M., & Rogé B. (2001). Water content, water activity and water structure, three approaches of water-food interactions : application to crystalline sugar stability.

Zuckerindustrie, 126 (51), 880-884.

Rogé B., & Mathlouthi M. (2000) Caking of sucrose crystals: effect of water content and crystal size. *Zuckerindustrie* 125 (5) 336-340.

Roth D (1976)., Amorphisierung bei der Zerkleinerung und Rekristallisation als Ursachen der Agglomeration von Puderzucker und Verfahren zu deren Vermeidung. *Ph. D. Thesis*, Universität Karlsruhe.

Savarino A., & Générumont G. (2000). Microcristal 120 : une innovation remarquable dans le domaine des sucres ultra-fins : propriétés et applications. *Industries Alimentaires et Agricoles*, 117, 22-24.

