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Food Chemistry 82 (2003) 61–71

Food Chemistry

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Water vapour sorption isotherms and the caking of food powders

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Abstract

Water vapour sorption isotherms describe the relationship between water content and water activity. Depending on the nature of food powder (crystalline or amorphous), the shape of isotherm is different. Mostly food powders have complex structures, including potentially crystallisable solutes such as sugars, which show changes in crystallinity during the adsorption of water. Even for such an apparently simple system as crystalline sugar, numerous factors affect the adsorption of water vapour and, as a consequence, the storage stability. The presence of a thin film of saturated solution at the surface of the crystal, grain size distribution and the inclusion of mother liquor droplets in the crystal are some of the factors which perturb the equilibrium relative humidity of sugar and its aptitude to caking. These conditions were carefully studied at the level of the laboratory and in a pilot silo. Conditions of "decaking" (recovering a flowing sugar after caking) were also established. In the case of noncrystalline powders, water activity, together with glass transition temperature, is important to determine if it is necessary to interpret the origin of the formation of bridges between food powder particles and the caking phenomenon.

Keywords: Sorption isotherm; Amorphous; Sucrose; Flowability; Jenike cell; Friability; Caking; Decaking; Pilot silo

1. Introduction

The behaviour of a food product towards the humid air which surrounds it, is described by the water vapour sorption isotherm which gives the relationship between water content and water activity at a given temperature. Adsorption of water at the surface of a food product may have physical or chemical origin and adsorbed water may occupy one or several layers. The best known mathematical model for interpretation of sorption isotherms is that of Brunauer, Emmett, and Teller (1938) based on multilayer adsorption. Five types of isotherms (Fig. 1) are described by Brunauer, Deming, and Teller (1940). Type 1 is the well known Langmuir isotherm, obtained by the monomolecular adsorption of gas by porous solids in a finite volume of voids. Type 2 is the sigmoïd isotherm, which is obtained for soluble products and shows an asymptotic trend as water activity tends towards 1. Type 3, known as the Flory-Huggins isotherm, accounts for the adsorption of a solvent or plasticizer like glycerol, for example, above the glass-transition temperature. The Type 4 isotherm describes the adsorption by a swellable hydrophilic solid until a maximum of hydration of sites is reached. Type 5 is the B.E.T. (Brunauer, Emmett, & Teller, 1938) multilayer adsorption isotherm, observed for the adsorption of water vapour on charcoal and related to types 2 and 3 isotherms. The two isotherms most frequently found for food products are Types 2 and 4 isotherms. Beside the 5 types of B.E.T. isotherms, one should mention the particular shape of adsorption isotherms obtained with crystals. Anhydrous crystals only contain traces of water at low and medium values of R.H.. The adsorption by anhydrous crystals corresponds to a saturation equilibrium (a vertical line on the adsorption curve) at a characteristic equilibrium relative humidity (E.R.H.) (for example ERH = 86% for sucrose; ERH = 76% for NaCl at 20 °C). The adsorption isotherm obtained with crystal hydrates is a stair like curve. The horizontal equilibrium of hydration (1 H_2O for LiCl, 2 H_2O for $CaCl_2$) is followed by vertical saturation equilibrium (ERH = 12% for LiCl). It also happens that, during the establishment of the adsorption or desorption isotherm, a polymorphic rearrangement (anhydrous $\leftrightarrows$ hydrate)

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doi:10.1016/S0308-8146(02)00534-4

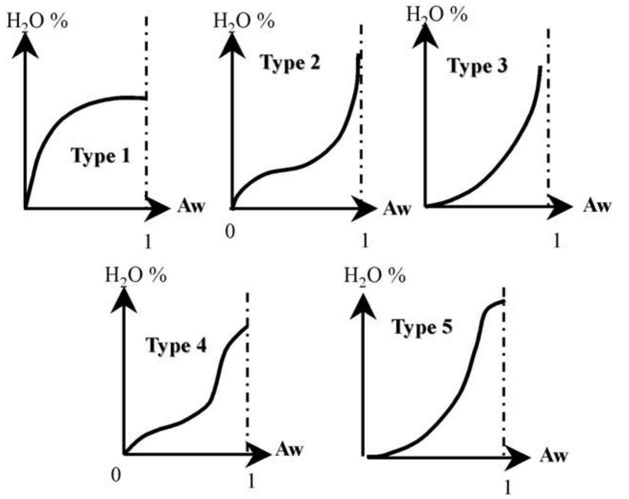

Fig. 1. Five types of isotherms (Brunauer, Emmett, & Teller, 1938).

occurs which is followed by a change in saturation equilibrium. This was observed for anhydrous betaine, which crystallizes as monohydrate during the establishment of sorption isotherm.

As a general rule, the amount of adsorbed water decreases at a constant water activity when temperature is increased. This trend can be explained using the equation of free energy ($\Delta G = \Delta H – T\Delta S$). As adsorption is a spontaneous phenomenon, ΔG is negative and adsorbed water is less free to escape in to the atmosphere which implies $\Delta S < 0$, then, $\Delta H < 0$. An increase in temperature is not favourable to the adsorption of water. This rule involves exceptions like the case of small sugars which become more hygroscopic when temperature is increased. The D-Glucose monohydrate sorption isotherm at 30 °C is composed of a plateau at 9% of moisture (1 H_2O/ glucose) and a vertical solubility equilibrium for $a_w = 0.91$. At 80 °C, crystallization water is removed and the saturation equilibrium is obtained at $a_w = 0.60$, which gives a higher amount of water adsorbed at $a_w = 0.60$ and $T = 80$ °C than that observed at 30 °C (Audu, Loncin, & Weisser, 1978). Hydrophilic food polymers, such as pectins, starch, casein or cellulose, have hygroscopicities which change as a_w is increased (Bandyopadhyay, Weisser, & Loncin, 1980) at 80 °C. Below the value of $a_w = 0.30$, potato starch is the more hygroscopic, whereas the hygrosocpicity of apple pectin is preponderant above this value. To account for the behaviour of different insoluble food products, mathematical models of sorption isotherms were proposed. A review of these models was proposed by van den Berg and Bruin in 1981. One of the best known models is that of Guggenheim, Anderson, and de Boer (GAB) (1966).

Water vapour sorption isotherms are useful for more than one purpose. In the special case of food powders, they may be used to predict caking. The lumping (or caking) of food powders can be considered as a spontaneous agglomeration phenomenon. It is generally caused by the wetting of the particle surface which causes its plasticization and sometimes dissolution. This happens especially for surfaces containing amorphous products. The plasticization may also be obtained by heating at a temperature above glass transition. The powder goes through different stages during the caking process. Four stages are reported by Gutman (1992):

- The pendular stage is that of free flowing powders,
- the funicular stage corresponds to the establishing of contact between particles
- the capillary stage is reached when moisture is high enough to provoke liquid bridges between particles
- the drop stage is obtained when dissolution of particles is predominant (see Fig. 2)

If drying occurs after wetting, the caking phenomenon is observed at a characteristic E.R.H. at which water is released from powder particles which form solid bridges and agglomerate. The physical conditions, such as 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 water content), plays a major role in the process of plasticization which leads to the agglomeration of food powders. The characteristic temperatures reported, in the literature, which characterize the viscous behaviour of food powders are T_s (sticking point), T_c (collapse temperature) and T_g (glass transition temperature). These transition temperatures are decreased when moisture content is increased and the Gordon-Taylor (1952) equation roughly works for different products, such as amorphous sugar, model fruit juice and freeze-dried orange juice (Aguillera, del Valle, & 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 et al., 1995).

We now propose the evaluation of caking of sugar samples with different grain sizes, amounts of amorphous particles, broken crystals or fine particles and surface impurities. Water vapour sorption isotherms, flowability angles and flow functions, determined with a Jenike cell, were the methods applied to study the caking phenomenon. Moreover, a method of ‘‘decaking’’ (removal of the lumping of sugar) was established using, varied relative humidity in a pilot silo.

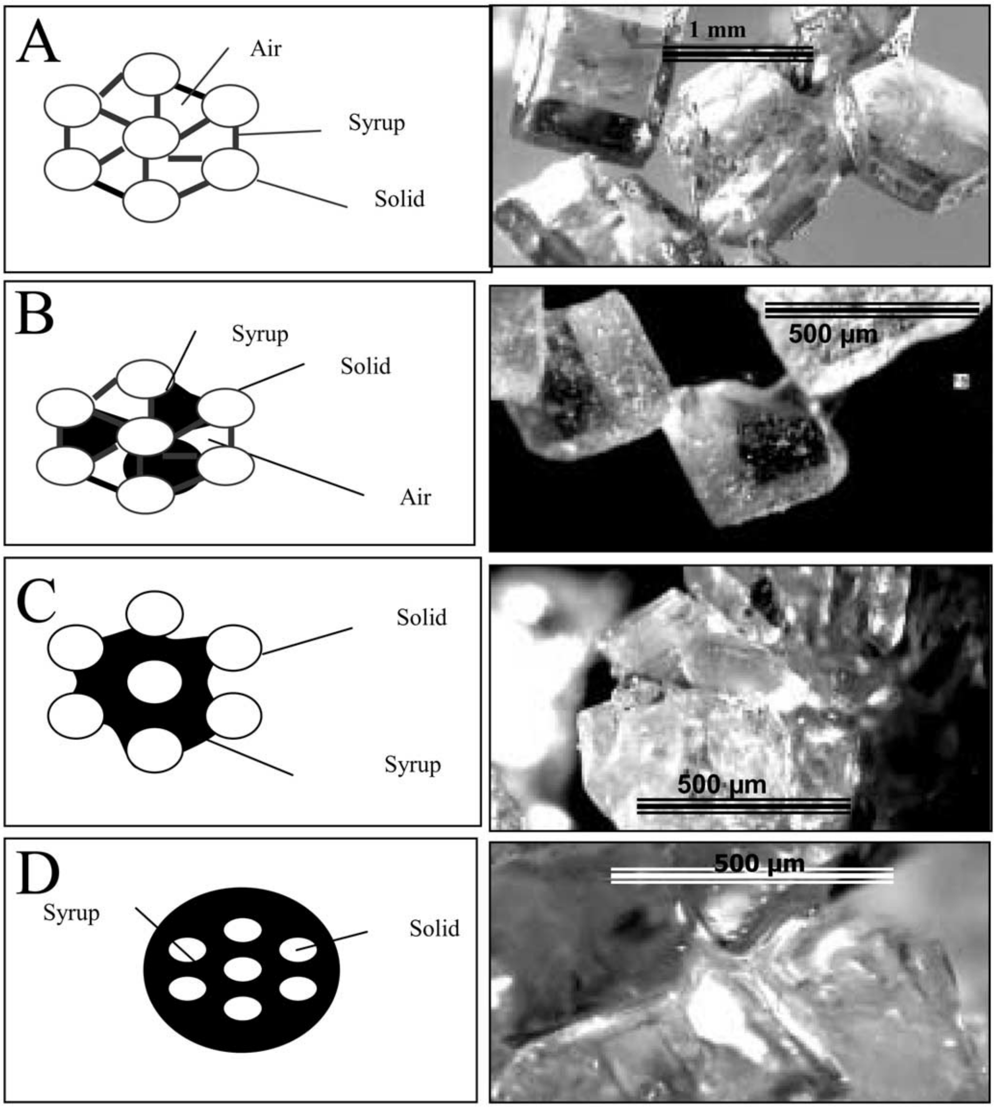

Fig. 2. Stages of wetting of sugar crystals (A pendular, B funicular, C Capillary, D drop).

2. Material and methods

2.1. Water vapour sorption isotherms

Water vapour sorption isotherms were established using the microclimate method. Equilibrium relative humidities (ERH) of gas-tight jars were fixed with saturated salt solutions (Greenspan, 1977). The analyses were carried out with sucrose samples previously dried (by oven-drying; 3 h, 105 °C). Sucrose was weighed in cupels (2 g) and maintained at 20 °C and different ERH until equilibrium was reached after 7 days (constant weight). At a given equilibrium relative humidity (ERH), water content was calculated and the sorption curve established as water content = *f*(ERH).

The investigated samples were crystalline sucrose with different grain sizes [mean aperture (M.A.)]. Estimations were made of the effect of fine particles on the behaviour of standard sugar. A moderate fraction (2, 5 and 10%) of fine crystals (<250 µm) or milled crystals was added to a standard sugar sample. The surface of the sucrose crystal is also sensitive to the presence of traces of impurities (ions, macromolecules, surface active agents). Also, established were the adsorption isotherms of sucrose crystallized in the presence of ionic impurities or surfactant to account for impurities effects.

2.2. Flowability characterization

2.2.1. Jenike cell

The Jenike shear cell (Fig. 3) was used for measuring angle of wall friction. The theory was developed by Jenike (1964). The measurement of yield stress of preconsolidated samples under various normal loads allows the establishment of flow functions of the studied sugars. The flow function is a plot which allows classification of

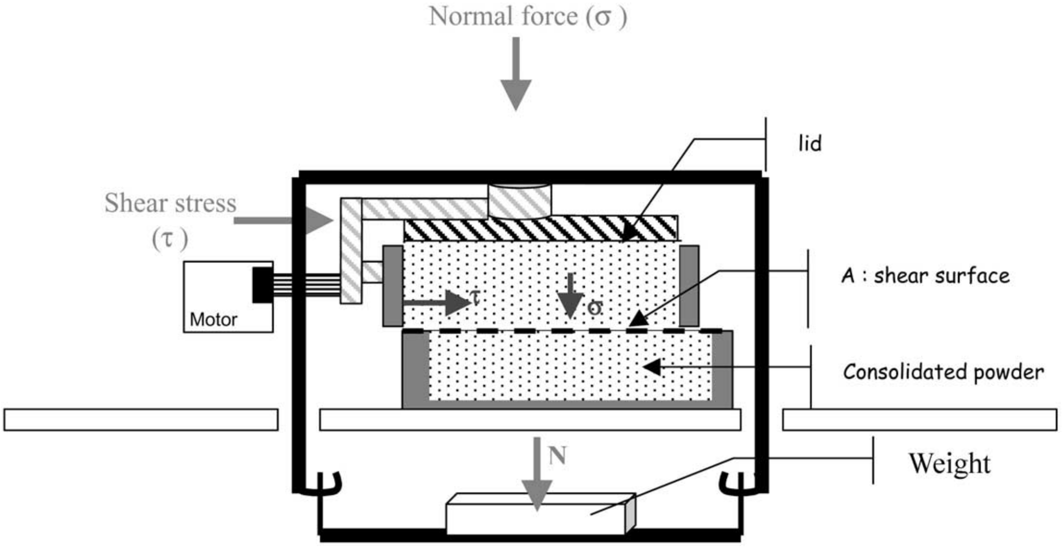

Fig. 3. Jenike Cell, experimental device.

powders as a function of their flowability. Flowability information is useful for predicting for example, mass flow in silo or caking index of sugars.

The procedure applied to measure the flow function of sucrose is that used by Teunou and Fitzpatrick (1999). Sugar samples were placed in the Jenike cell (200 g) 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, which are less important than the first one. The shear stress, corresponding to these points, was measured at a fixed shear rate of 6 mm/min. This procedure was repeated 4 times, with other consolidation stresses, in order to constitute the flow function (FF) of the tested powder.

2.3. Friability angle

To measure the friability angle, a Petri dish, containing the sugar sample equilibrated at a given relative humidity, was disposed on a inclined plane. The slope of the plane was manually changed. An abrupt flow of the sugar for a certain angle of the plane is the sign of cohesion rupturing between particles. Generally a free flowing powder does not exceed 90°. This relatively easy method makes it possible to evaluate the friability of the powder from the value of the angle.

2.4. Decaking of caked sugar

The pilot silo used for this study is a vertical stainless steel silo (Fig. 4). Its diameter is 60 cm, its height 80 cm, for an average capacity of 100 kg of sugar. The basis of the silo is made up with very fine stainless mesh and an empty conical bottom. This design ensures a perfect homogenization of air diffusing into the sugar. The walls of the silo are covered with an insulating polystyrene paperboard, which reduces the heat loss. Air fed into the pilot silo is generated by a dehydrator which can provide a flow at about 25 m^3/h. Dry air is humidified

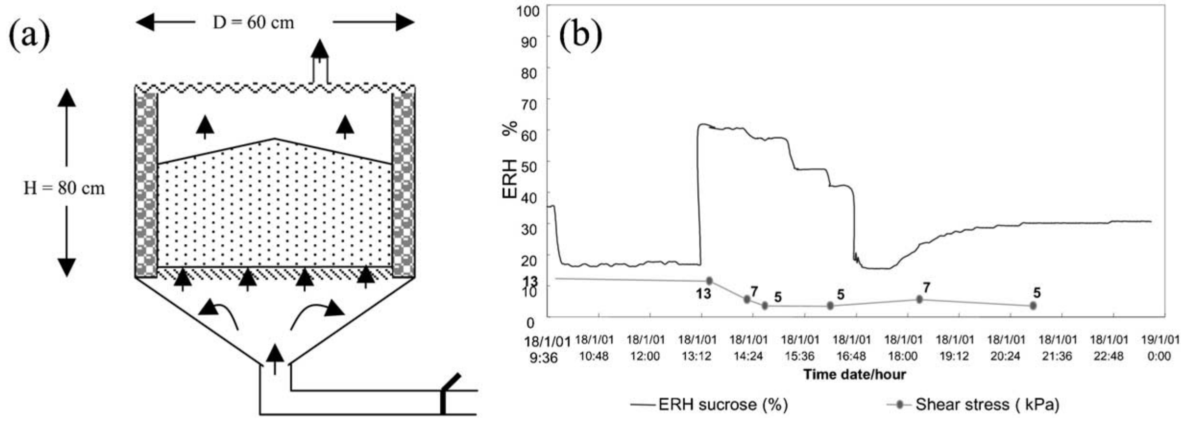

Fig. 4. Pilot silo (a) and decaking procedure (b) (humidification at 65% R.H. followed by progressive decrease in relative humidity).

using a controlled pulverization of water which allows relative humidities from 20 to 90%.

In order to approach the real conditions of storage, the sugar used for all these caking experiments was directly taken from the factory at the outlet of the dryer. Thus, our pilot installation was fed by sugar having the characteristics of that stored in the factories. Many studies undertaken on the subject of storage stability of sugar have been carried out with humidified sugar and revealed the complexity of the problem (De Bruijn & Marijnissen, 1996). Rearrangements of the film of syrup surrounding the crystal occurs during storage. Sugar is sampled directly in factories; it is still hot and has a thin layer of mother liquor at its surface. Relative humidity and the temperature of sugar are measured with autonomous sensors allowing aquisition of 8000 points. The sensors are placed in the sugar heap in order to control variation of these two parameters.

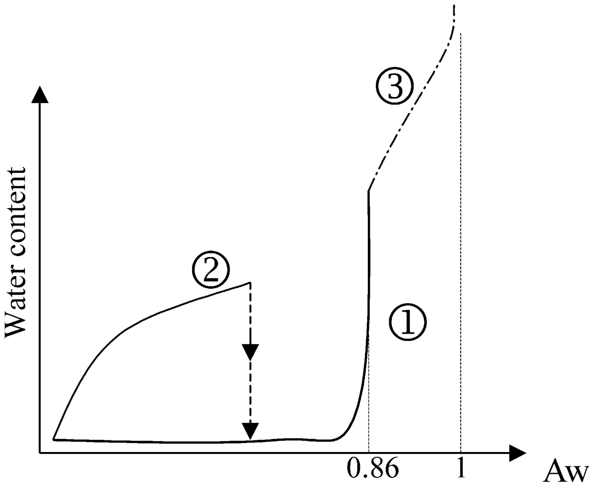

Fig. 5. General shape of adsorption isotherms of (1) crystalline sucrose, (2) amorphous sucrose and (3) saturated solution (→ recrystallization of amorphous sucrose).

3. Results and discussion

3.1. Water vapour sorption isotherms

To understand the behaviour of sugar samples submitted to water vapour adsorption, it is necessary to recall the general shape of adsorption isotherms of amorphous and crystalline sugar over the whole range of water activities (Fig. 5). What is characteristic of the crystalline state is the crystal/saturated solution equilibrium manifested by a constant a_w around 85–86%.

The size of sucrose crystals, as determined by the mean aperture (M.A.) of sieves, plays a major role in sorption behaviour. The presence of fine particles (<250 μm) in the sample induces a sorption isotherm between curve (1) and curve (2) in Fig. 5. This means that amorphous state of sucrose is dependent on particle size and that the amorphous state should be completed by the method of determination (Mathlouthi, 1994). Observation of Fig. 6, which shows the adsorption isotherms of sucrose at 20 °C and M.A. between 800 and 250 μm, allows characterization of samples with M.A. = 400–500 or 250 μm as partially amorphous to water vapour sorption. If fine particles (<250 μm) are added to standard sugar, the higher the amount of fine particles (2; 5; 10%) the more the behaviour of sugar

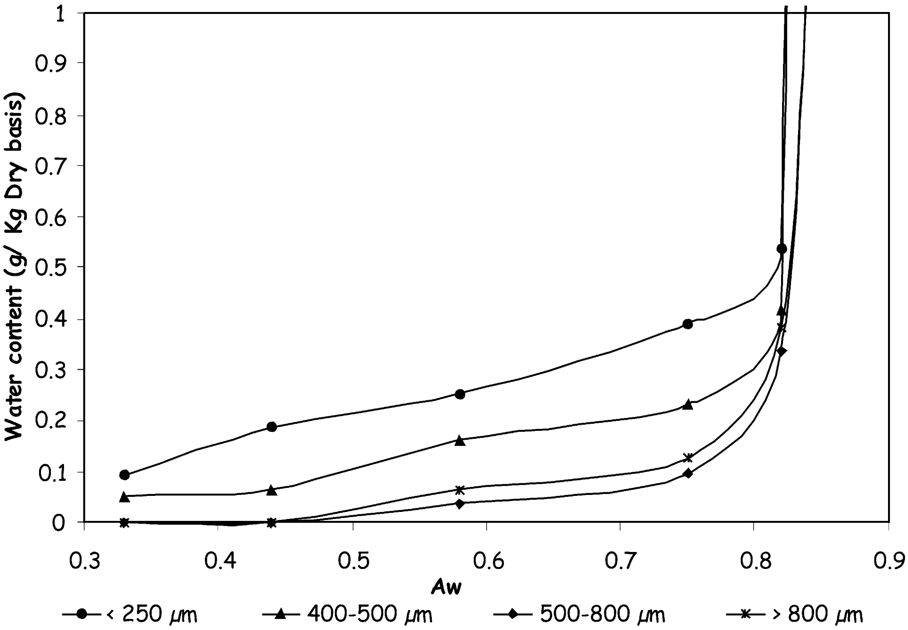

Fig. 6. Water vapour sorption isotherms as a function of crystal size distribution.

approaches that of amorphous state (see Fig. 7). In particular, the sorption isotherm of 100% of fine particles is comparable to that of amorphous milled sugar (Roth, 1976).

Size of particles is not the only parameter which characterizes their aptitude to cake. Their shape is also important. Comparison of the shapes of microcrystals (100 μm), obtained with a special crystallization process (Savarino and Génermont, 2000) with sugar dust from the sugar conditioning workshop in a factory, clearly shows their morphological differences (Fig. 8). The water vapour adsorption isotherms of these samples are also informative of their cristallinity (Fig. 9). Sugar dust from the factory is composed of the amorphous particles at the surface of sugar dried at high temperature in a short time, insufficient to allow crystallization in the film of syrup surrounding the crystals (Bressan & Mathlouthi, 1994). It also contains fine crystals (< 250 μm) and the broken particles obtained by attrition in the rotary dryer and elevator. Adsorption of water increases as the amount of ground sugar is augmented in a sample (Fig. 9). If microscrystals (250 μm), provided by Beghin-Say are taken as reference, it may be observed that adsorption of water vapour is increased as percentage of ground sugar increases from 21 to 70%. The fraction of standard sugar obtained by sieving (M.A. = 250 μm) very likely contains broken crystals; its adsorption isotherm is situated between those of 21 and 70% ground sugar (Fig. 9).

After crystallization of sucrose in a pilot crystallizer, in which relatively large amounts (1%) (w/w of syrup) of Na^+, K^+, Ca^{2+} and Mg^{2+} ions were added, the sugar obtained was washed, dried and submitted to water vapour sorption. Observation of the adsorption isotherms (Fig. 10) does not reveal any appreciable change in water vapour adsorption by the ions. On the other hand, the sugar crystals obtained in the crystallization boiler, with varied amounts of surfactants, seemed to behave differently towards water vapour adsorption. Results of water adsorption kinetics for sugar, crystallized in the presence of different amounts of surfactant (Fig. 11), show that the higher the dose of surfactant in crystallization medium, the lower is the adsorption of water vapour. This is understandable, as water is adsorbed by hydrophilic interactions (H-bonds), which are hidden as surface active molecules, which are hydrophobic, are spread on the surface of the crystals.

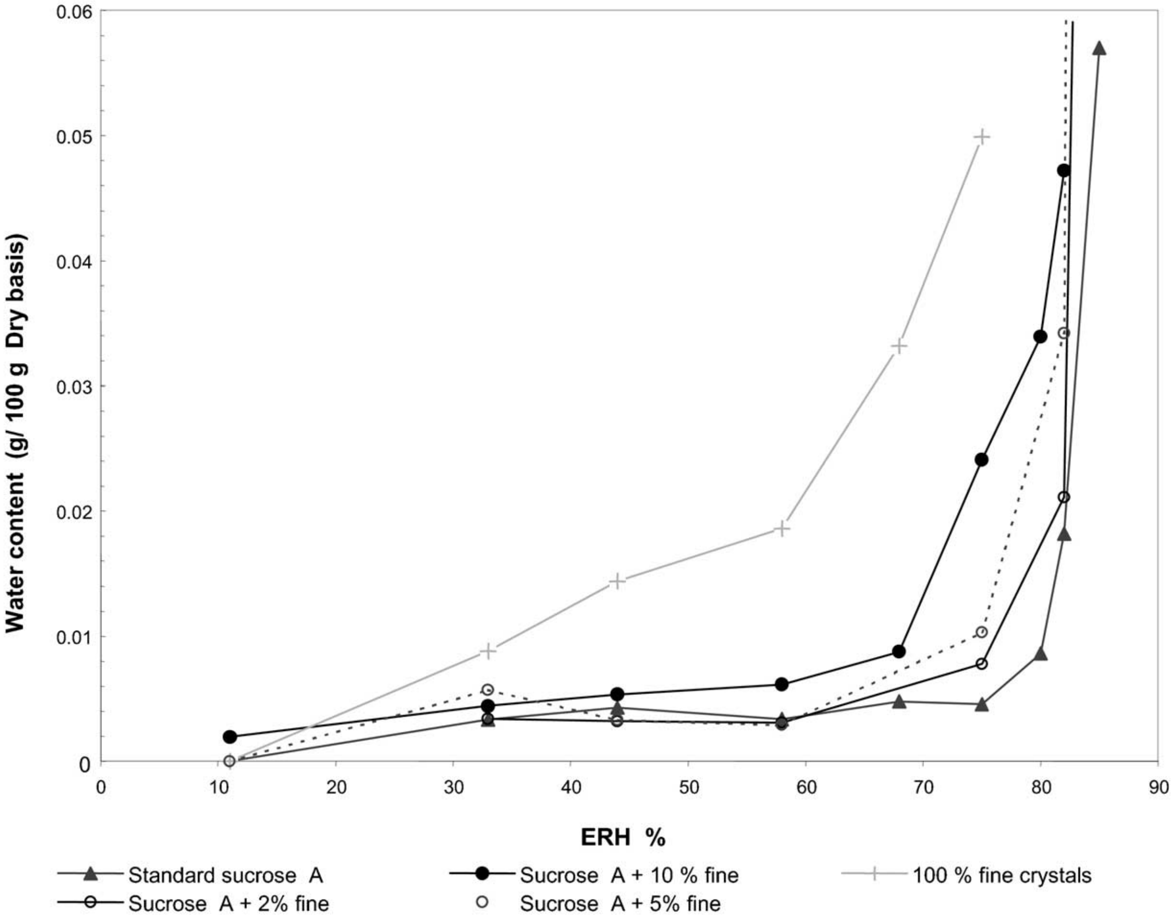

Fig. 7. Water vapour sorption isotherms of sucrose containing fine particles (2–5 or 10%) compared to water vapour adsorption of 100% of fine crystals.

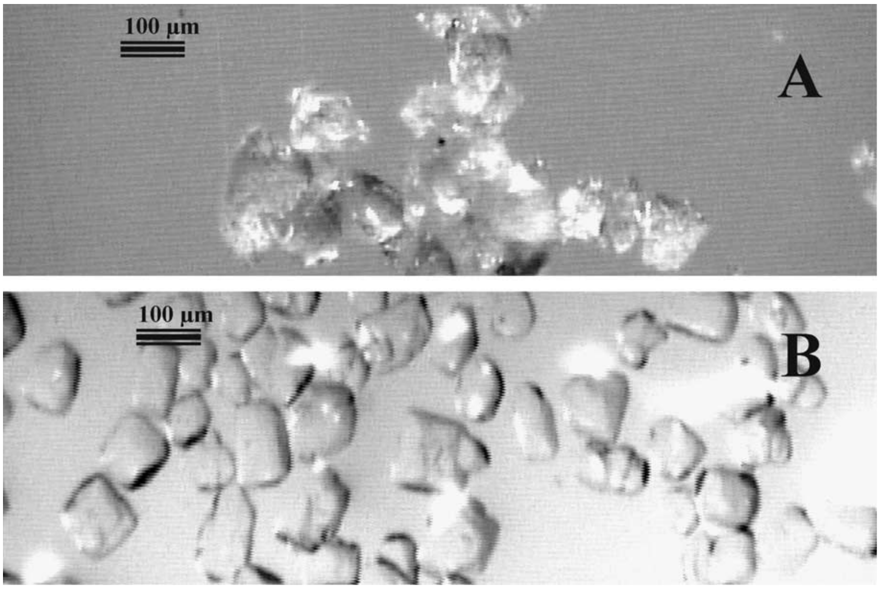

Fig. 8. Morphology of sugar dust (<100 µm) from factory (A) and sucrose microcrystals (Beghin-Say) (B).

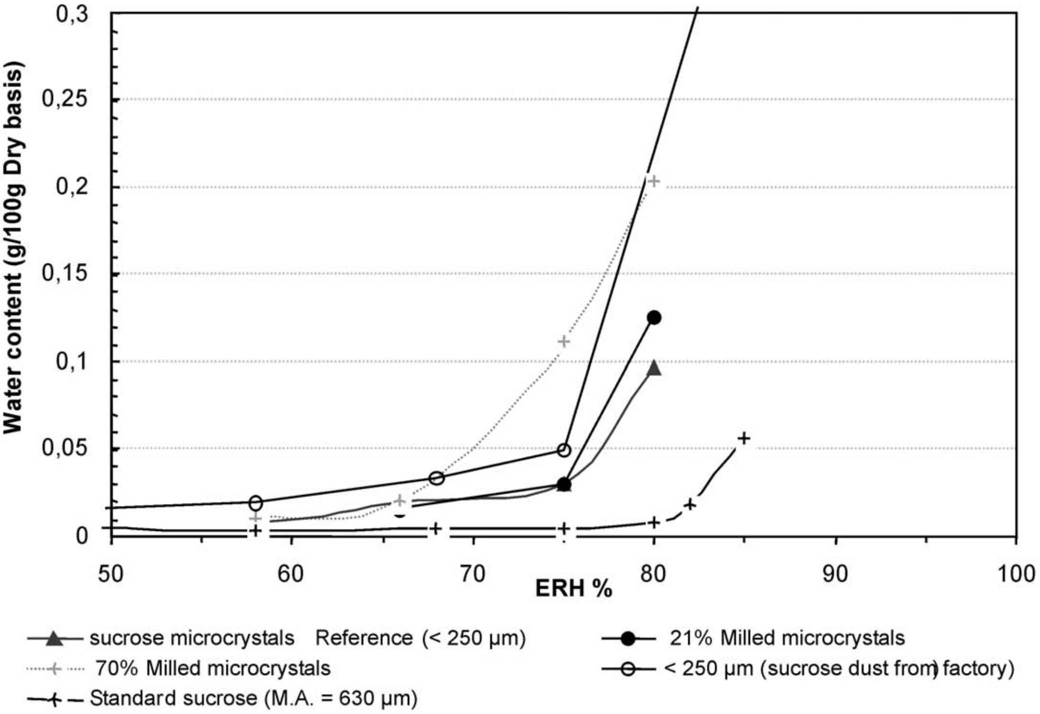

Fig. 9. Water vapour adsorption isotherms at 20 °C of sucrose microcrystals, sugar dust from factory, and 21 and 70% milled sucrose microcrystals.

3.2. Flowability and cohesiveness of sugar

Friability angle was determined using the experimental device described in Materials and methods. The different fractions of sieving, with M.A. varying > 800 µm to <250 µm, are equilibrated with different relative humidities and submitted to the friability test. Results (see Fig. 12) show that compaction of sugar manifested by a rapid increase in friability angle depends on the size of crystals. This is observed at $a_w = 0.40$ for fine particles (<250 µm) and at $a_w = 0.85$ for M.A. above 500 µm. The crystals with M.A. between 500 and 400 µm show an intermediate behaviour.

The flow function of sugar samples with grain sizes ranging from 50 to 100 µm to 1 mm, determined with a Jenike cell, are presented in Fig. 13. The flow index (i) given by the slope of the flow function (shear stress $(F_c) = f$(normal stress, σ_c), allows classification of the

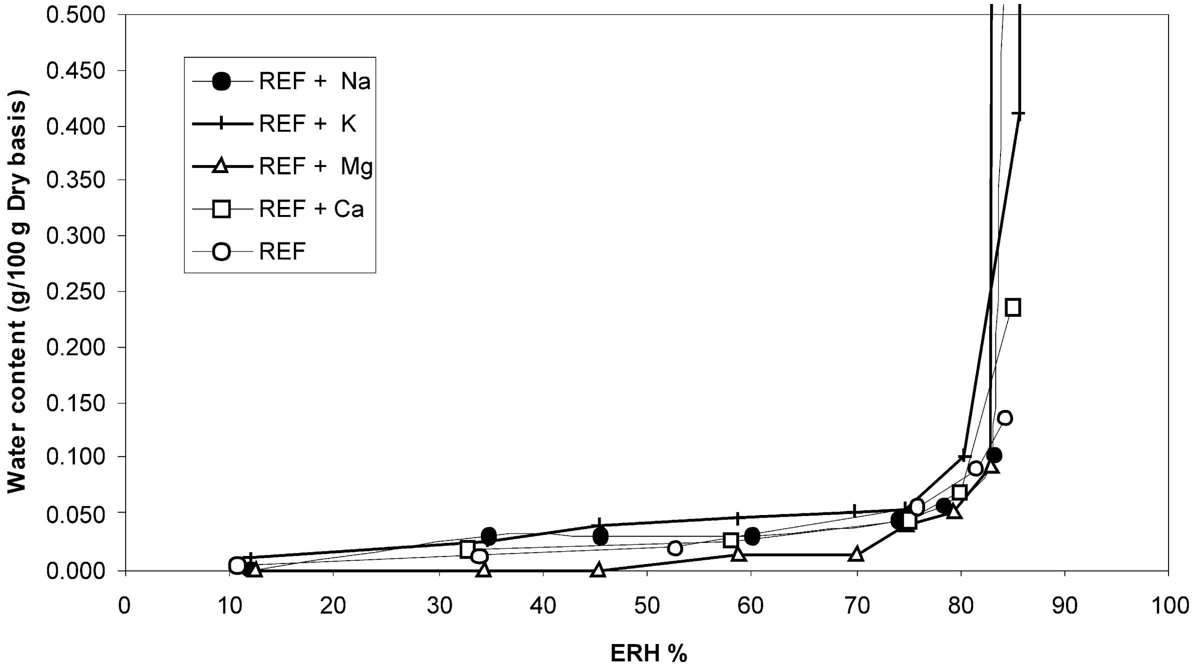

Fig. 10. Water vapour adsorption isotherms of sucrose crystallized in presence of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}).

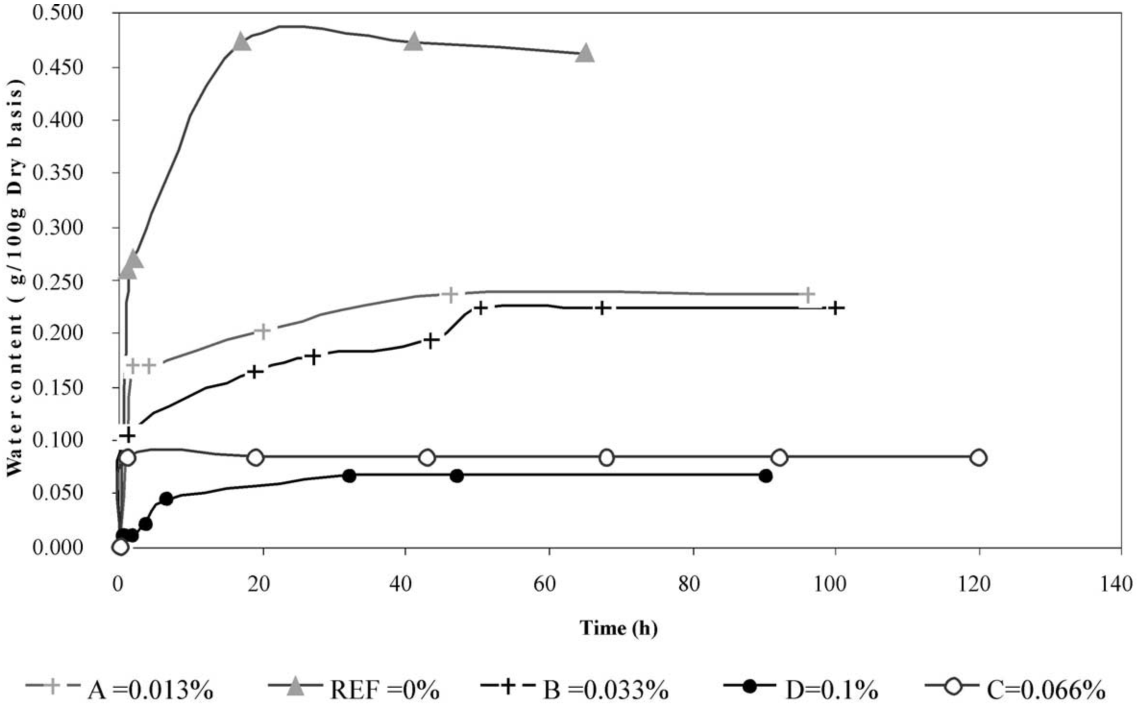

Fig. 11. Water vapour adsorption kinetics of sucrose crystallized in presence of different amounts of surfactant.

different sugar samples according to the ease of their flow. Table 1 summarizes the flow indices and classification of the different sugar samples tested. Below M.A. = 250 µm, the flow of sugar becomes difficult. The small size of particles together with their hygroscopicity, only allows moderate flow. Below 100 µm, compaction is reached.

3.2.1. *Decaking of caked sugar*

Caking is the result of a wetting followed by a drying. These stages were produced in the pilot silo. The more humid the air the more caking takes place (higher shear stress). Caked sucrose is more hygroscopic than uncaked sucrose. Fig. 14 presents water vapour sorption

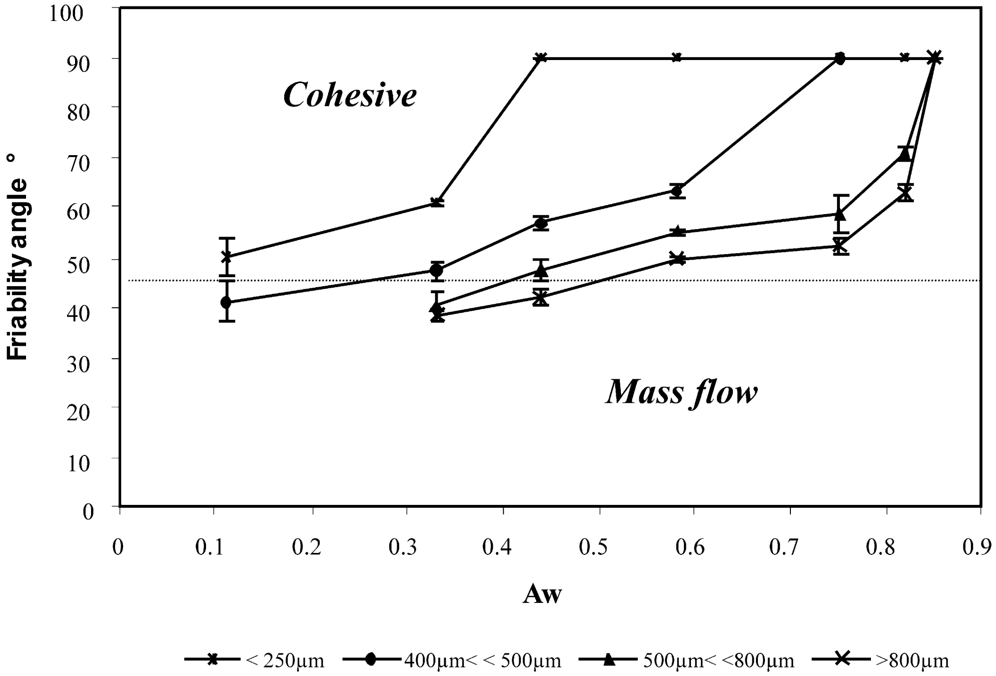

Fig. 12. Friability angle as a function of equilibrium relative humidity for different crystal sizes of sucrose.

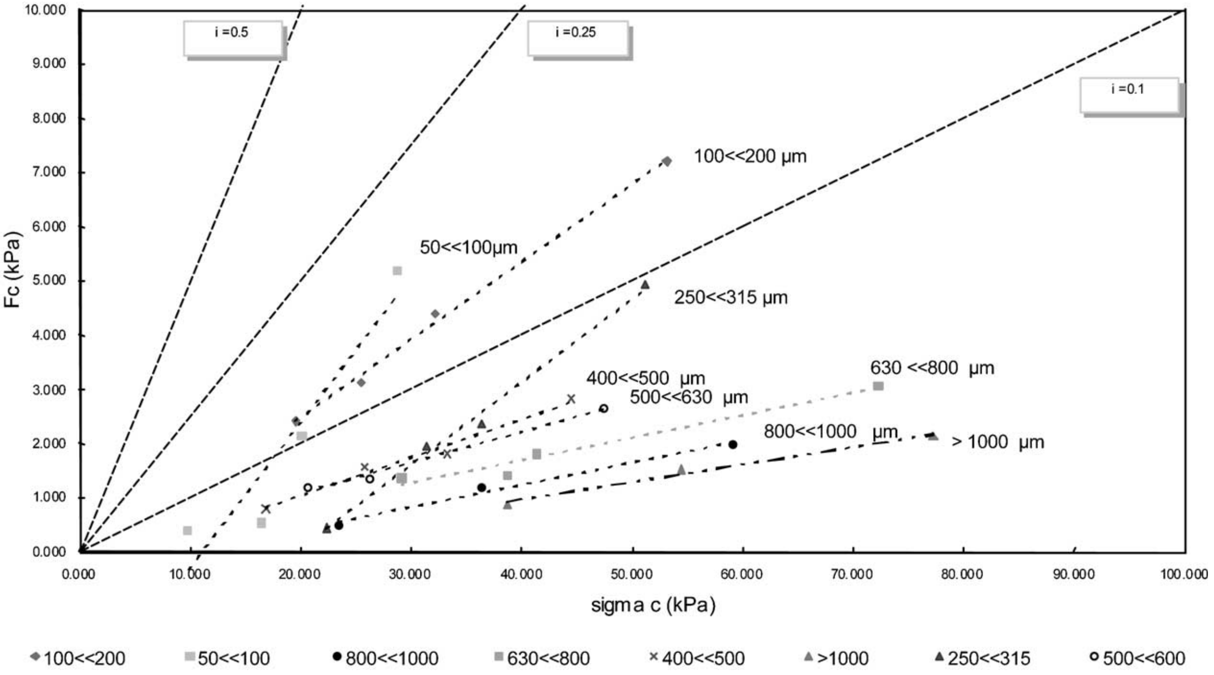

Fig. 13. Flow function (FF) of sugar samples with grain sizes ranging from 50 µm to 1 mm.

isotherms obtained for two samples of caked and uncaked sucrose crystals. Solid bridges, created during the caking procedure, make sucrose more hygroscopic. With the aim of avoiding all these problems linked to caking, we tried, in the pilot silo, to make caking reversible. Decaking is feasible by introducing humid air (ERH = 60%) into the silo, followed by a progressive decrease in air relative humidity in order to reach 40% relative humidity (see Fig. 4). In this case, the rate of water removal is less important than the rate of recrystallisation, which allows sucrose, contained in the interparticular bridges, to recrystallize. After this controlled relative humidity treatment, decaking is completed and sucrose flowability is regular (Mathlouthi & Rogé, 2001). Oppositely, an increase in air humidity (60%) followed by an abrupt decrease of the relative humidity

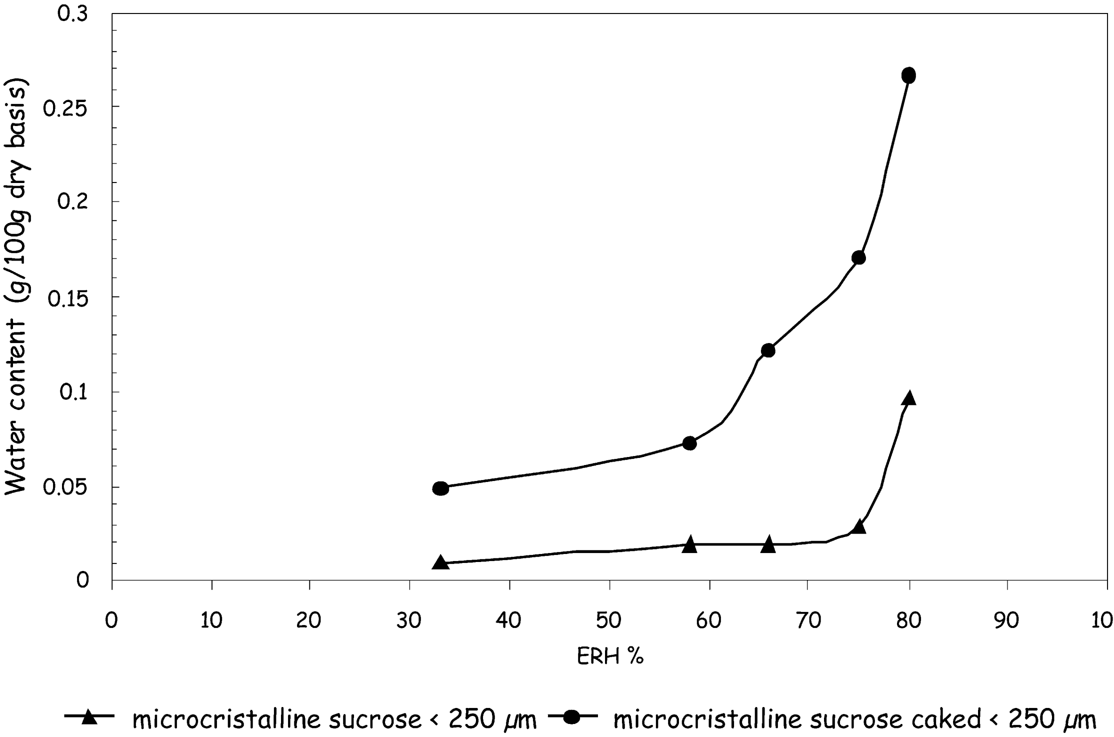

Fig. 14. Water adsorption isotherms of caked and non-caked sucrose microcrystals (<250 μm).

Table 1
Classification of sieved sugar fractions by flow index (i)

Sugar fraction	Flow Index (i)	Classification
> 1000 μm	0.0326	Free flow
800 << 1000	0.0412	Free flow
630 << 800	0.0417	Free flow
500 << 630	0.0568	Free flow
400 << 500	0.0708	Free flow
315 << 400	0.1087	Moderate flow
250 << 315	0.154	Moderate flow
100 << 200	0.1441	Moderate flow
50 << 100	0.2653	Cohesive

of air to 20% R.H., disallows the process of decaking. In this case, the rate of water removal is too fast compared to the rate of recrystallization and the compaction of sugar is irreversible.

To conclude, decaking is possible but it is detrimental to the morphology of sugar crystals. Observation, under microscope camera, confirms the presence of sugar crystal agglomerates in a free flowing sugar.

4. Conclusion

The study of some factors affecting the caking of white crystalline sugar shows that the presence of fine particles and the distribution of grain size are particularly important for control and prevention of the compaction of sugar.

Among the techniques used, the water vapour adsorption isotherm is an informative tool of determination of the critical relative humidity for a given sugar at a given temperature. An objective method of control of the flowability of bulk sugar consists in determining the flow functions of the different samples of sugars with the Jenike shear cell. Finally, a method of decaking (recovering of flowability) of a caked sugar is proposed. It consists in submitting sugar, in a pilot silo, to relative humidities above 60% and progressively deacreasing the relative humidity of air. Decaked sugar, although having free mass flow, is more hygroscopic than before caking.

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