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Preliminary studies on in situ monitoring of lactose crystallization using focused beam reflectance measurement

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Abstract

Isothermal crystallization of lactose was studied at supersaturated concentrations (w/w) of 50%, 55%, and 60% at temperatures 20°C and 30°C using an in situ system, focused beam reflectance measurement (FBRM), and a refractometer. The FBRM data were compared with Brix readings taken over time using a refractometer during isothermal crystallization. Chord length distribution obtained from FBRM in the ranges of <50 >Î¼m (fine crystals) and 50 to 300 Î¼m (coarse crystals) were observed and evaluated in relation to the extent of crystallization and rate constant results deduced from the refractometer measurements. The measured fine crystal counts increased with supersaturated concentration and temperature during isothermal crystallization. On the other hand, coarse counts were observed to increase with decreasing supersaturated concentration and temperature. The total crystal counts (coarse + fine crystals) obtained from FBRM increased as the temperature increased at all concentrations. The robustness of FBRM in understanding isothermal lactose crystallization at various concentrations and temperatures was successfully evaluated in the study.; Dairy Day, 2014, Kansas State University, Manhattan, KS, 2014; Dairy Research, 2014 is known as Dairy Day, 2014

Keywords

Dairy Day, 2014; Kansas Agricultural Experiment Station contribution; no. 15-156-S; Report of progress (Kansas Agricultural Experiment Station and Cooperative Extension Service); 1111; Lactose crystallization; Focused beam reflectance measurement

Preliminary Studies on *In Situ* Monitoring of Lactose Crystallization Using Focused Beam Reflectance Measurement

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Summary

Isothermal crystallization of lactose was studied at supersaturated concentrations (w/w) of 50%, 55%, and 60% at temperatures 20°C and 30°C using an *in situ* system, focused beam reflectance measurement (FBRM), and a refractometer. The FBRM data were compared with Brix readings taken over time using a refractometer during isothermal crystallization. Chord length distribution obtained from FBRM in the ranges of <50 μm (fine crystals) and 50 to 300 μm (coarse crystals) were observed and evaluated in relation to the extent of crystallization and rate constant results deduced from the refractometer measurements. The measured fine crystal counts increased with supersaturated concentration and temperature during isothermal crystallization. On the other hand, coarse counts were observed to increase with decreasing supersaturated concentration and temperature. The total crystal counts (coarse + fine crystals) obtained from FBRM increased as the temperature increased at all concentrations. The robustness of FBRM in understanding isothermal lactose crystallization at various concentrations and temperatures was successfully evaluated in the study.

Key words: lactose crystallization, focused beam reflectance measurement

Introduction

Lactose is the most abundant carbohydrate present in milk. It is found in concentrations of 4.4 to 5.2% and is one of the major constituents in infant formulations, dried milk, and whey products. Commercial production of lactose involves concentration of whey or whey permeate by evaporation followed by batch crystallization. During the process, α-lactose crystallizes as tomahawk-shaped crystals. Crystal size distribution and lactose yield are the most important criteria to monitor during industrial crystallization of lactose and are influenced by the degree of supersaturation, rate of cooling, agitator speed, presence of impurities, and viscosity of supersaturated feed material.

The dairy industry currently is depending on refractometer measurements to follow lactose crystallization, but this approach provides no information on crystal size distribution during crystallization. *In situ* monitoring of lactose crystallization to meet the special requirements of crystal size distribution (CSD) is needed. Focused beam reflectance measurement (FBRM) could be used to monitor the CSD and chord length distribution (CLD) *in situ* from supersaturated lactose solution.

The FBRM uses a monochromatic laser (785 nm) rotating at a constant speed of 2 meters per second. As particles pass in front of the probe window, light is backscattered from the particles to the sapphire window. The duration of the backscatter is measured and particle chord length is obtained. Schematic representation of working principle of

FBRM is shown in Figure 1. The objective of the present study was to evaluate the applicability of FBRM for *in situ* monitoring of the isothermal crystallization of lactose.

Experimental Procedures

Experimental Design

A 2 × 3 factorial design was used in the study, with temperature and concentration as independent variables. Concentrations (50%, 55%, and 60%) w/w were randomly assigned to temperatures (20°C and 30°C) and resulted in 6 measurements. Experiments were conducted randomly and in two replications.

Preparation of Supersaturated Lactose Solution

Lactose solutions of desired supersaturation were prepared using 99.7% pure alpha lactose (Davisco Foods International, Inc., Le Seuer, MN). Desired concentrations of lactose (w/w) were obtained by dissolving 250, 275, and 300 g of α-lactose in 250, 225, and 200 g of distilled water to prepare 50%, 55%, and 60% (w/w) supersaturated solutions, respectively. The lactose and water mixture was heated to 87±3°C under continuous stirring to dissolve all the crystals. A lid was placed on the beaker to avoid moisture loss during heating. After ensuring the dissolution of all the crystals, the supersaturated lactose solution was rapidly cooled to the desired experimental temperature (20°C or 30°C) without agitation.

Isothermal Crystallization of Lactose

Isothermal lactose crystallization studies were carried out in a batch crystallizer specially designed for this work. The FBRM probe (Particle Track E25, Mettler-Toledo AutoChem, Inc., Columbus, OH) was immersed in a purpose-built batch crystallizer for *in situ* monitoring of the crystallization process as shown in Figure 2. The batch crystallizer was placed in a temperature-controlled water bath that could maintain a constant temperature. An overhead stirrer with a four-bladed propeller (Caframo, Georgian Bluffs, Ontario, Canada) was placed in the crystallizer to facilitate stirring. As shown in Figure 2, the propeller was maintained at 2.5 cm above the bottom of the beaker containing the supersaturated sample. The FBRM *in-situ* probe was fixed at a height of 5 cm from the bottom of the beaker and at an angle of 30 ± 5° to the vertical axis of the stirrer for all the crystallization experiments.

Crystallization Monitoring Using an FBRM Probe

Before the start of each experiment, the FBRM probe was cleaned thoroughly with distilled water to avoid interference from unwanted particles, as suggested by the manufacturer. The data from the FBRM probe were acquired using iC FBRM (version 4.3.391, Mettler-Toledo) every 3 minutes for the first 60 minutes and every 30 minutes thereafter during isothermal crystallization. Three categories of crystal chord length ranges, 0.5–50 μm, 50–300 μm, and 300–2,000 μm, were monitored and are designated fine, coarse, and large, respectively.

Determination of Extent of Crystallization and Rate Constant

At regular intervals, an approximately 1 ml of the crystal suspension was removed from the crystallizer using a dropper to measure the refractive index of the suspension. The refractive index, expressed in terms of °Brix, of lactose solution was measured using a

digital refractometer (Reichert Technologies, Depew, NY). A calibration curve was used to convert the °Brix reading to actual lactose concentration solution, and refractometer readings were subsequently used to calculate the mass of crystals and extent of crystallization at any time *t* during isothermal crystallization. Mass of crystals at any time *t* was calculated from the initial lactose concentration C(0) and lactose concentration C(*t*) at time *t* using Equation 1. Water was assumed to represent 5% of the total mass of lactose crystal.

$$M_{Crystal}(t) = M_{H_2O}(0)\ \frac{C(0) - C(t)}{95 - 0.050C(t)} \quad (1)$$

where $M_{Crystal}(t)$ is mass of crystals at given time *t*, $M_{H_2O}(0)$ represents 5% of the total mass of lactose crystal, C(0) is initial concentration, and C(*t*) is concentration at time *t*.

The extent of crystallization at time *t* was calculated using Equation 2 from the mass of crystals at time *t* obtained from Equation 1 and saturation concentration of lactose at temperature 20°C and 30°C.

$$\%Y(t) = \frac{M_{Crystal}(t)}{M_{Crystal}(t \to \infty)}\ X100 \quad (2)$$

where Y(*t*) is the extent of crystallization at time *t*, $M_{Crystal}(t)$ is the mass of crystals obtained from Equation 1, and $M_{Crystal}(t \to \infty)$ is the mass of crystals at lactose solubility at experimental temperature.

From the concentration difference ΔC, plotted against time *t,* it was observed that the curve shows best the first-order decay fit. The rate constant can be deduced from plotting Equation 3, the first-order decay equation, where $[A_0]$ is the initial concentration of lactose solution before crystallization and *k* is the rate constant. $[A]$ is the concentration difference ΔC, at a given time *t,* where ΔC = C(*t*) – C(t ∞), with C(t ∞) as lactose solubility value at the temperature of interest.

$$ln\left(\frac{[A]}{[A_0]}\right) = -kt \quad (3)$$

Results and Discussion

Determining Extent of Crystallization and the Rate Constant from Brix Values

The extent of crystallization was determined during the isothermal crystallization of lactose for 50%, 55%, and 60% concentrations at 20°C and 30°C. Figure 3 shows the extent of crystallization during isothermal crystallization of lactose for 50%, 55%, and 60% concentrations at 20°C and 30°C, respectively. Figure 3 shows that the extent of crystallization was higher at 30°C than at 20°C for all concentrations of lactose. The time required for isothermal crystallization to reach 90% was 300, 360, and 420 minutes for 60%, 55%, and 50% lactose solutions, respectively. On the other hand, the extent of crystallization at 20°C did not reach 90% even at 630 minutes for all the lactose concentrations studied. The extents of crystallization at 30°C were calculated to be 93%, 95%, and 96% for 50%, 55%, and 60% solutions, respectively. The extents of crystallization at 20°C were calculated to be 80%, 83%, and 86% for 50%, 55%, and 60% solutions, respectively.

Extent of crystallization increased with lactose concentration at a given experimental temperature. A maximum extent of crystallization was observed for the 60% supersaturated solution concentration followed by 55% and 50% lactose concentrations at 30°C. A similar trend was observed at 20°C.

Rate constants for the isothermal crystallization of lactose at 20°C and 30°C were calculated using Equation 3. For calculation purposes, it was assumed that the rate of mutarotation proceeded at a higher rate than crystallization of α-lactose. This assumption is based on the fact that mutarotation is not a limiting factor during crystallization of lactose. The rate constants obtained at different concentrations and temperatures are shown in Figure 4, which shows that the rate constants were higher at 30°C than at 20°C for the three lactose concentrations studied.

Overall, refractometry is a suitable technique to calculate crystal mass throughout lactose crystallization. Another advantage of this technique is that it can be implemented easily regardless of crystallizer design; however, refractometer readings do not provide information on crystal size distribution.

Evaluation of FBRM Data

Plots of fine crystal counts (<50μm) obtained from FBRM during the isothermal crystallization of lactose at various temperatures and concentrations against time are shown in Figure 5. A steep increase in the fine crystal count was observed during the initial phase of crystallization (first 15 minutes) and can be attributed to primary nucleation of lactose crystals. These findings were in agreement with the extent of crystallization and the rate constant as shown in Figures 3 and 4, respectively. A further increase in fine crystal counts after the initial rapid increase was due to secondary nucleation and disintegration of lactose crystals. The disintegration of lactose crystals was caused by attrition and collisions between crystals and the crystallizer walls and impeller.

The plot of coarse crystal counts (50–300 μm) obtained from FBRM during isothermal crystallization of lactose at various temperatures and concentrations is shown in Figure 6, which shows a substantial difference between coarse crystal counts of lactose at 30°C and 20°C. The growth of crystals at 20°C was also relatively higher than that of the lactose crystals obtained at 30°C. The number of coarse crystals increased as temperature and supersaturation decreased; in other words, isothermal crystallization at 20°C and a concentration of 50% were favored to produce the largest mean-squared crystals in the present study. In contrast, the count of fine crystals increased as temperature and supersaturation increased. These results suggest that growth of crystals was favorable as temperature decreased, whereas an increase in temperature favored nucleation and formation of finer crystals.

Counts of larger particles (300–1,200 μm) were found to be negligible and were not included in the analysis.

Evaluation of Chord Length Distribution

Chord length distributions obtained from FBRM at various time intervals during isothermal crystallization of lactose for all the treatments are shown in Figure 7. Crystal counts at 30 minutes at 30°C were clearly higher than at 20°C for all supersatu-

rated concentrations, which supports observations from Figure 5. Total crystal counts increased with time for the first 6 to 8 hours and decreased during the last few hours in 55% and 60% concentrations. At 50% concentration, however, counts were reported to increase more at 20°C than at 30°C throughout the experiment, which is also apparent in Figure 6. A decrease in total crystal counts can be explained as a combination of the breakage of crystals and the interference of smaller crystals. A prominent decrease in the number of coarse crystals at 30°C can be explained by the fact that, as the growth and density of crystals increases, the probability of the probe detecting particle width rather than particle length is high. Impeller speed, apart from enabling active crystallization by uniform supersaturation and mass transfer, also causes breakages, which could be an additional explanation for a decrease in coarse crystal count as time proceeds and was easy to track using FBRM.

Conclusion

The efficiency of FBRM in studying lactose crystallization with respect to operation parameters such as concentration and temperature was evaluated. FBRM is a powerful tool, and it can be used to follow secondary nucleation as a result of attrition and breakage apart from chord length distribution and crystal size. The results of this study imply that changes in concentration and temperature were well understood in terms of crystal size and counts over time using FBRM. The data obtained from FBRM supplements and strengthens refractive index data.

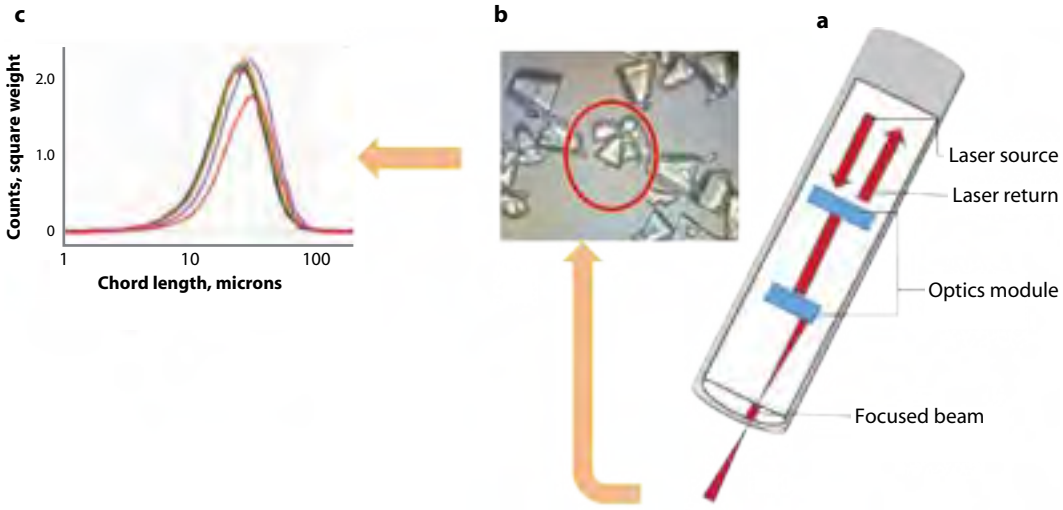

Figure 1. (a) Focused beam reflectance measurement (FBRM) probe design, (b) detection of particles by probe using a laser moving at constant velocity, and (c) chord length distribution graph obtained from crystal distribution.

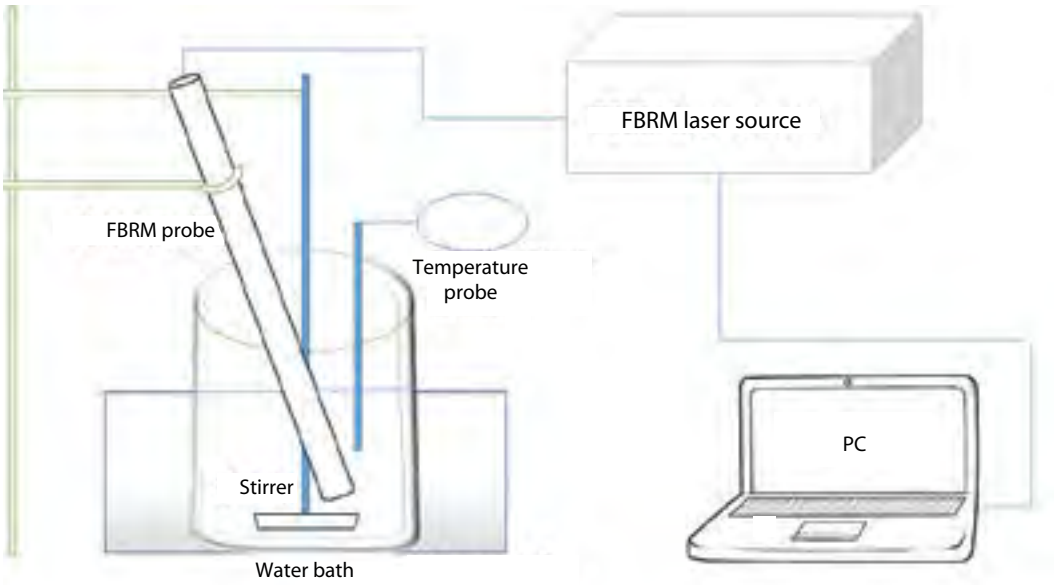

Figure 2. Experimental setup for evaluation of lactose crystallization using focused beam reflectance measurement (FBRM).

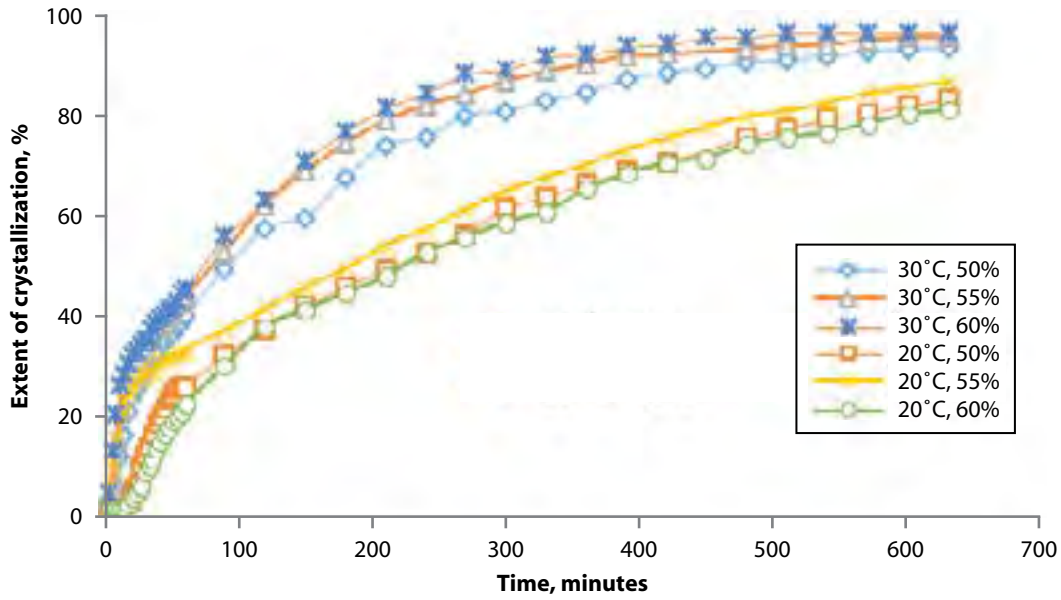

Figure 3. Extent of crystallization for 50%, 55%, and 60% at 20°C and 30°C.

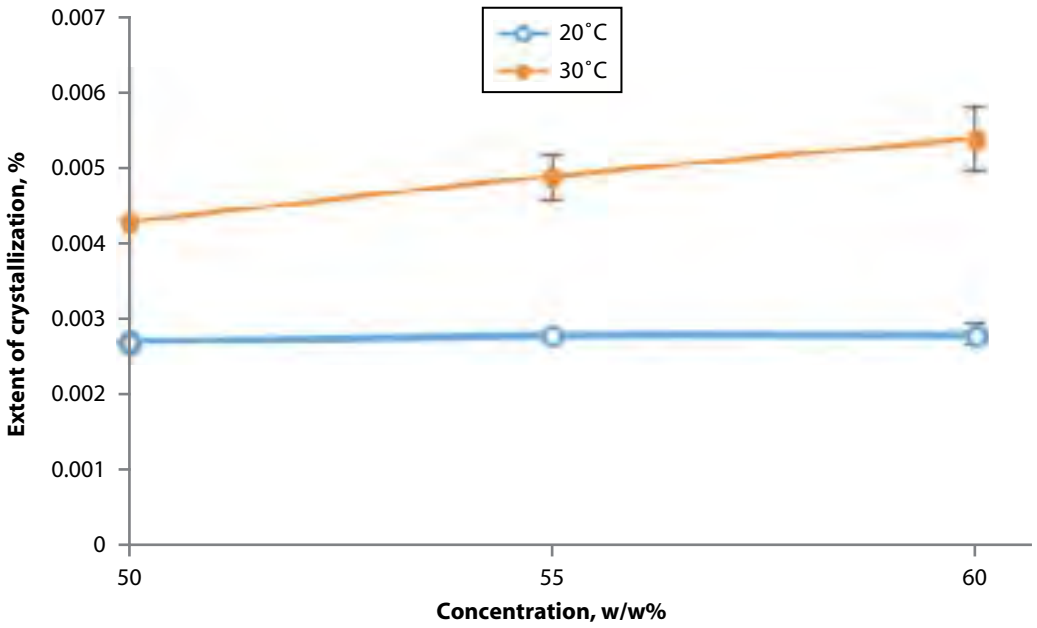

Figure 4. Rate constants of different concentrations at 20°C and 30°C.

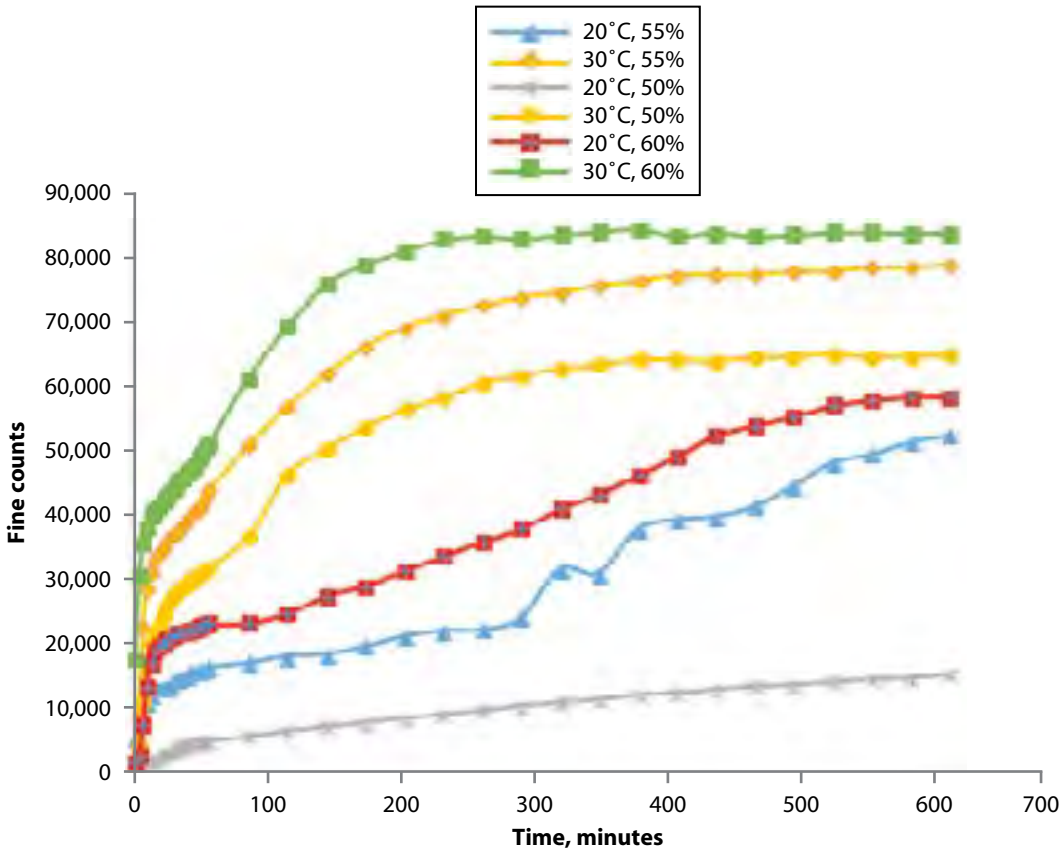

Figure 5. Count of fine crystals (<50μm) for 50%, 55%, and 60% concentrations at 20°C and 30°C.

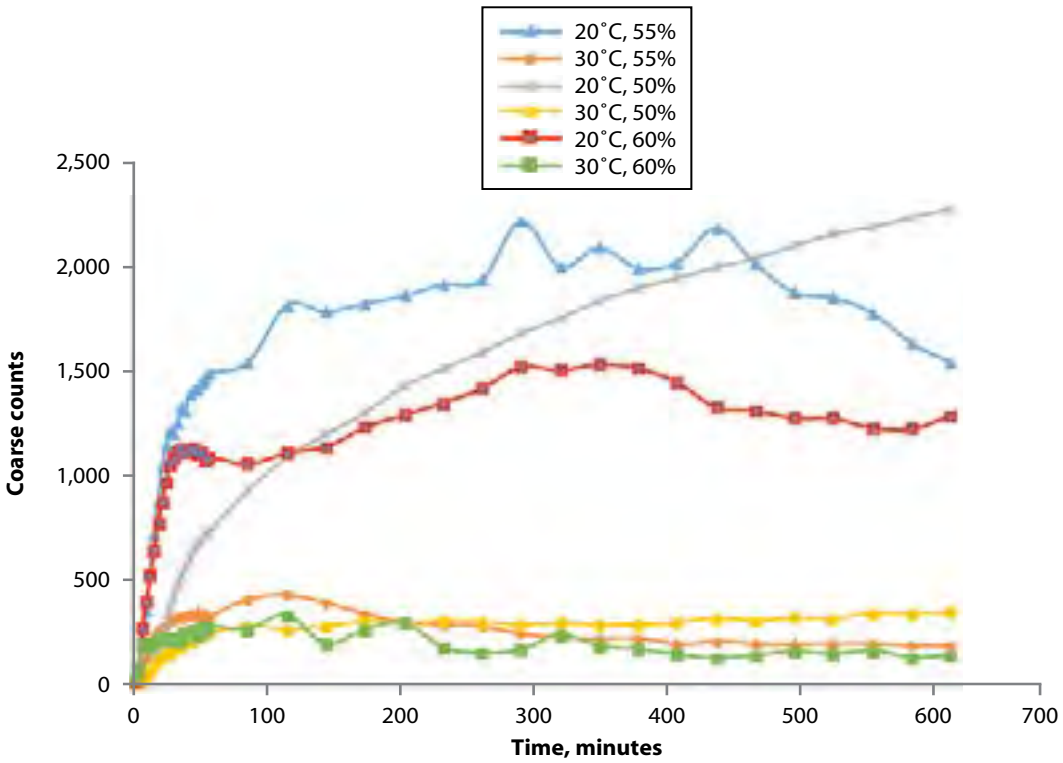

Figure 6. Count of coarse crystals (50–300μm) for 50%, 55%, and 60% concentrations at 20°C and 30°C.

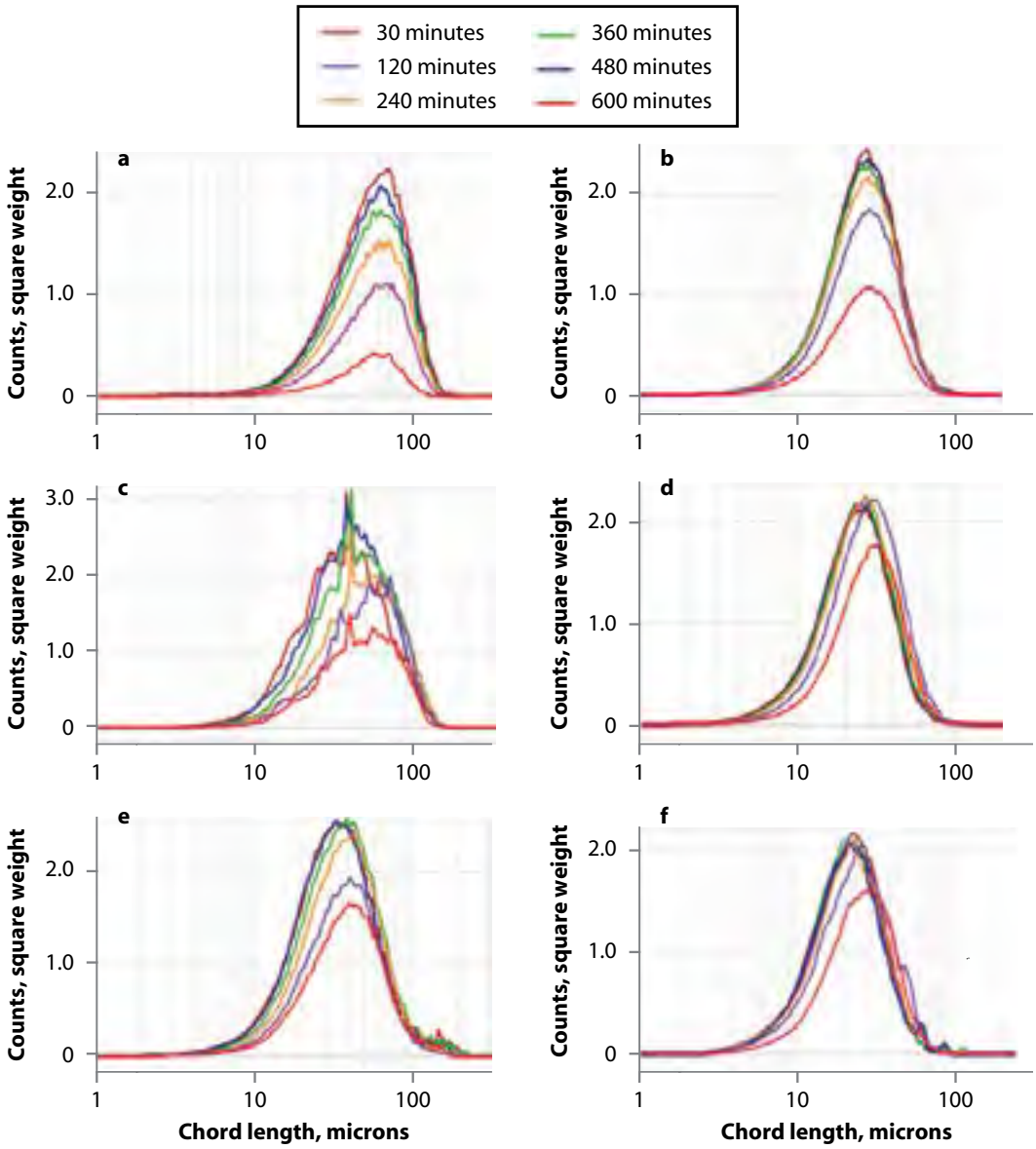

Figure 7. Chord length distributions of crystals obtained from focused beam reflectance measurement data at different time periods. (A) 20°C, 50%; (b) 30°C, 50%; (c)20°C, 55%; (d) 30°C, 55%; (e) 20°C, 60%; (f) 30°C, 60%.