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Effect of calcium in brine on salt diffusion and water distribution of Mozzarella cheese during brining

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ABSTRACT

A soft, pasty, high-moisture surface defect occurs with progressive brining of Mozzarella cheese. Addition of calcium is traditionally used to prevent this defect but the underlying mechanism is not clear. Mozzarella cheese was formed into a cylinder inside brine on its plane surface to ensure semi-infinite, unidirectional mass transfer and placed into brine containing 0, 0.1, or 0.25% (wt/wt) calcium chloride. To monitor the effect on cheese composition of calcium in brine, we measured calcium and water contents of the cheese during brining. The extent of calcium loss from the cheese decreased significantly with the addition of calcium. Addition of calcium to a final concentration of 0.25% decreased the loss of calcium from 94.13 to 18.22% from the outside region of the cheese after 30 d, and the water content of the cheese was decreased from 67.8 to 48.8%. To further elucidate the effect of calcium in brine, the Boltzmann method was used to determine the effective diffusion coefficient value, and low-field nuclear magnetic resonance was used to measure the cheese transversal relaxation time. The migration of calcium interfered with salt diffusion. At the end of brining, the amount of water bound to the protein of the cheese significantly increased. Addition of calcium to a final concentration of 0.25% diminished the proportion of bound water by 20.96%. In conclusion, addition of calcium hinders the diffusion of sodium and modifies the distribution of water in Mozzarella cheese during brining.
Key words: calcium, salt diffusion, water distribution, Mozzarella cheese

INTRODUCTION

Mozzarella is a moist, white, Italian curd cheese originally made from water buffalo (*Bubalus* sp.) milk. Mozzarella is typically salted in brine, which is critical for proper moisture control and contributes directly to the flavor, textural, and physical characteristics of Mozzarella cheese (Geurts et al., 1974, 1980). During brining, however, a soft rind defect occurs as the cheese develops a soft, moist, fragile surface layer that is difficult to shred (Kindstedt, 1994). Kindstedt et al. (1996) found that the concentration of calcium was significantly lower at the surface compared with the interior of the cheese. They suggested that calcium has a tendency to be leached from the surface of the cheese, solubilizing casein and causing swelling as water is bound to the protein.

The traditional solution to this problem is to add calcium to the brine in the form of $CaCl_2$. At the target calcium concentration, the risk of soft rind defects is minimized (Kindstedt, 1991; Kristensen, 1999). Kristensen (1999) reported that addition of sufficient calcium restores the equilibrium between the soluble and colloidal forms of calcium, thus preventing the protein from binding water. However, it is not clear whether calcium in brine affects salt diffusion in the cheese.

Salt diffusion, which is responsible for mass transport between the cheese and the brine, depends mainly on the composition of the brine (Guinee, 2004). Gerla and Rubiolo (2003) found that when several solutes diffuse simultaneously, in addition to the self-diffusion coefficient, cross-diffusion has to be included to account for the influence of one solute on the flow of another. Floury et al. (2009) used a modeling approach to investigate the transfer of salt and other ionic solutes and found that Na^+, Cl^-, and K^+ are present mostly in the soluble phase and facilitate salt diffusion. However, the mechanism by which calcium in brine affects salt diffusion is not clear. Further investigation is required to determine whether migration of ionic calcium causes synergy of salt diffusion or inhibition of salt diffusion.

The diffusion of salt is linked to changes in the water content of cheese (Payne and Morison, 1999). The distribution of water in Mozzarella is determined by the parallel protein fibers resulting from the stretching process (Kuo et al., 2003) and water undergoes a continuous rearrangement during ripening (McMahon et al., 1999). Kindstedt et al. (1996) reported that leaching

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of calcium induces solubilization of casein, which binds water and swells, causing the soft rind defect. However, no experimental details are available to monitor the hydration of protein during brining. Nuclear magnetic resonance (**NMR**) relaxometry is concerned with the quantitative determination of the most abundant components in a sample by evaluating decay rates and amplitudes of the NMR signal. Low-field NMR transverse relaxation has been used to quantify the changes in water distribution and mobility (Kuo et al., 2003).

The aim of the present study was to elucidate details of how calcium added to brine affects salt diffusion and reduces the risk of the soft rind defect for Mozzarella cheese. Mozzarella cheese was molded into cylindrical set to allow mathematical modeling of an effective diffusion process. Cheese was stored in brine containing 0, 0.1, or 0.25% (wt/wt) calcium chloride. The salt effective diffusion coefficient values during brining in different regions of the cheese were determined by the Boltzmann method, and water distribution was determined using low-field NMR spectroscopy.

MATERIALS AND METHODS

Mozzarella Cheese Making

Raw cow milk from the SanYuan Dairy Co. (Beijing, China) was pasteurized (63°C for 30 min, cooled to 4°C) and used at a casein:fat ratio of 0.75 (wt/wt). Milk was warmed to 37°C and 0.08 g/L of starter culture (FD-DVS ST-M5, Chr. Hansen, Hørshlom, Denmark) and 28.75 IMCU (international milk clotting units) of chymosin rennet (Stamix 1150, Chr. Hansen) were added. Curd was set and then cut at pH 6.15 ± 0.2, left for 5 min, and stirred gently to facilitate syneresis. When the curd pH reached 5.25 ± 0.1, the remaining whey was drained, and the curds were cooked and stretched for 3 min at 70°C. Duplicate batches of cheese were made.

Experimental Design

Brining Experiment. Brining experiments were carried out as described previously (Pajonk et al., 2003). After stretching, the cheese curd (pH 5.20 ± 0.1) was placed into plastic cylinders (length 2.5 cm, diameter 3 cm) and covered with food wax on one flat surface. Brine was prepared with food-grade sodium chloride at a concentration of 20% (wt/vol) in distilled water. Calcium chloride was added to reach 0, 0.1, or 0.25% (wt/wt), and the pH was adjusted to 5.18 using acetic acid. The brining containers containing cheese samples were covered with plastic film to prevent surface mass loss and stored for 3 h at 4°C. Therefore, the temperature of cheese and brine was 4°C during brining. The experimental brining apparatus is illustrated in Figure 1. Keeping the cheese cylinder inside the brine on its plane surface allowed a unidirectional transfer of ionic sodium and calcium mass. The brine was submitted to continuous slow agitation using a magnetic stirrer.

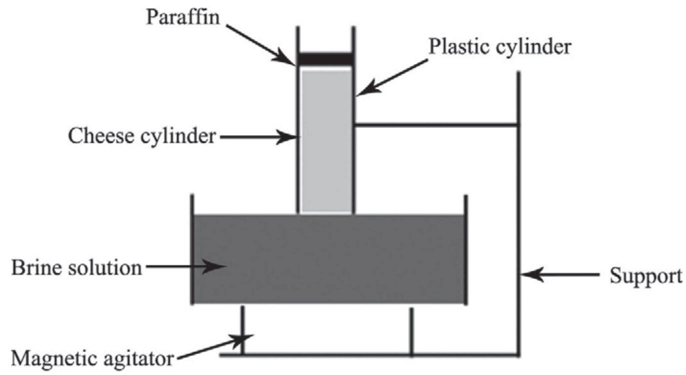

Figure 1. Diagram of the experimental brining device.

Sampling. After brining, cheese samples were rinsed with distilled water and the surface was dried on filter paper. Periodically, 2 cylindrical samples of cheese were removed simultaneously to duplicate physicochemical analyses. Cheese samples were cut from the cylinder as 5-mm-thick slices at 0 to 0.5 cm, 1 to 1.5 cm, and 2 to 2.5 cm along the length. The usual radius of Mozzarella cheese ball is ~2.5 cm; therefore, the chosen sites sampled the outer, inner, and central regions of the cheese, respectively. To understand the mechanisms of diffusion in cheese for an extended brining period, sampling was conducted at 1, 5, 9, and 24 h, and at 7 (168 h) and 30 d (720 h).

Compositional Analysis

Cheese samples were analyzed for water (ISO-IDF, 1982), fat (Marshall, 1992), and protein (ISO-IDF, 1986) contents. Ionic concentrations were measured by atomic absorption spectrometry (725-ES, Varian, Palo Alto, CA) as described (AOAC International, 2000) and were expressed in milligrams per 100 g of cheese.

Effective Diffusion Coefficient Values and Low-Field NMR

The Boltzmann method (Pajonk et al., 2003) was used for determination of the effective diffusion coefficient value. The diffusion coefficient represents the apparent diffusivity of sodium chloride, considering the solid cheese matrix and sodium chloride as the 2 components of the binary diffusion system.

A low-field NMR analyzer (MARAN-22 ultraresonance model with 2 MHz proton resonance frequency,