

# Physical properties of NaCl-free cucumber fermentation cover brine containing $\text{CaCl}_2$ and glycerin and apparent freezing injury of the brined fruits

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## Abstract

Use of glycerin and  $\text{CaCl}_2$  to reduce the freezing point and improve quality of bulk stored fermented cucumbers brined without NaCl, was explored. The incidence of pre-freezing injury on the fruits, caused by deposition in tanks containing cushion brine prepared with 2.5%  $\text{CaCl}_2$ , was excluded by determining the liquid and fruits densities and buoyancy force. The NaCl-free cover brine thermal properties and freezing point, and the frozen fruits water loss were determined to estimate freezing damage. Cover brines supplemented with 14.5% glycerin, 18%  $\text{CaCl}_2$ , or 14% glycerin and 5%  $\text{CaCl}_2$  were needed to match the freezing point of the 6% NaCl cover brine, typically used for fermentation. Thermal properties of the NaCl-free cover brine were insignificantly affected by temperature or composition. Water loss was the main freezing injury in brined cucumbers. Supplementation of  $\text{CaCl}_2$  and/or glycerin in fermentation cover brines helped minimize fermented cucumbers water loss associated with freezing.

## Practical applications

This study presents an assessment of brine composition that can prolong processed pickle quality and bulk storage at temperatures below zero. Fermented cucumbers stored in cover brine containing 14.5 vol % glycerin, 18 wt %  $\text{CaCl}_2$ , or 14 vol % glycerin and 5 wt %  $\text{CaCl}_2$  have a reduced freezing point, which theoretically extends the window for acceptable product quality. The use of 14% glycerin above the cover boards to reduce the freezing point and, consequently, ice formation on the surface of the open-top tanks is to enable the removal of fermented fruits during winter with minimal tissue injury.

## 1 | INTRODUCTION

Utilization of fermentation cover brines containing 6–18% sodium chloride (NaCl) in cucumber processing generates a massive volume of waste water containing the deriving ions, which affects fresh water quality and aquatic life. Developing strategies to reduce the NaCl in pickling waste water includes the substitution of fermentation brines containing sodium salt with cover solutions containing 100 mM (1.1%) calcium chloride ( $\text{CaCl}_2$ ) (Pérez-Díaz et al., 2015). The relatively high density of 6% NaCl cushion cover brines, added in fermentation tanks prior to loading the fresh cucumbers, aids in preventing processing induced damage during the deposition of the fruits. Brine composition also affects the buoyancy force and hydrostatic pressure acting to

restrain the cucumbers submerged in the brine. The restraining force needed to submerge cucumbers in salt brine depends on the specific gravity which is related to the salt content (Humphries & Fleming, 1991). Thus, adapting the salt content of the NaCl-free cover brines containing  $\text{CaCl}_2$  to levels that can minimize deposition injuries of cucumbers during loading is of interest.

Concentrations of NaCl in cucumber fermentation cover brines are frequently increased to saturation levels during bulk storage in geographical regions with intense winters to ameliorate freezing damage on the fermented stock and facilitate their recovery from tanks at sub-zero temperatures. The complete removal or the reduction of NaCl from fermentation cover brines requires the development of alternate strategies to prevent freezing injury on the fermented stock during

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cold bulk storage in heavy winters, unloading associated injuries and damage induced during further processing.

Previous studies have proposed time–temperature profiles for the use of hot-air (Mao, Wang, Zhu, & Pang, 2007) and hot-water treatments to reduce chilling injury and preserve texture of whole fresh cucumbers (McCollum, McCollum, Doostdar, Mayer, and McDonald, 1995) and sliced pickles (Buescher, Cho, & Hamilton, 2013). Chilling injury is defined as a physiological alteration that negatively affects the quality of fruits and vegetables causing pitting, surface discoloration, water soaking, internal breakdown, susceptibility to fungal attack, loss of cell membrane semipermeability, decay, and increase in electrolyte leakage at temperatures above the freezing point (Aghdam & Bodbodak, 2014). Conditioning of freshly pickled cucumbers by submersion in warm water (50°C) for 45–60 min prevented softening of the tissue and the progress of curing in refrigerated sliced pickle products for up to 1 year at 7°C. Fresh cucumber fruits prewarmed with hot air at 37°C for 24 hr showed less visible signs of injury and a decrease in electrolyte leakage after 9 days storage at 2°C (Mao et al., 2007). There is a knowledge gap in understanding the nature of freezing injury of fermented cucumbers. Strategies to mitigate freezing injury in fermented cucumbers stored in bulk in outdoor open top tanks are lacking. Determining the extent of freezing on matter or a system demands the definition of thermal properties. Although a number of studies have been conducted to determine the thermal and rheological properties of cover brines from fermented and sulfite-preserved cucumbers (Fasina, Fleming, & McFeeters, 2002), limited data relates to freezing conditions. An estimate of heat loss associated with different insulation strategies in bulk storage at temperatures below the freezing point was recently documented (Diaz, Pérez-Díaz, Simunovic, & Sandeep, 2017).

The specific aim of this study was to determine if a reformulation of the NaCl-free fermentation cover brine containing CaCl<sub>2</sub> was necessary to prevent or ameliorate deposition and freezing injuries. The approach taken included studying the changes in the density of the cushion cover brines as a function of CaCl<sub>2</sub> supplementation to various concentrations. Density measurements were used to calculate buoyancy force on the free fall of the fresh cucumbers. Thermal properties of fermentation cover brine containing 1.1% CaCl<sub>2</sub> instead of NaCl and 0–20% glycerin, a food grade anti-freezing agent, were evaluated to further understand the freezing injuries on the fermented stocks during bulk storage in cold conditions. We attempted to define freezing injury for fermented cucumbers brined with CaCl<sub>2</sub> instead of NaCl when subjected to cold storage. The results provide crucial information for processors regarding the effect of brine composition on the quality of cucumbers preserved in fermentation cover brines during winter storage.

## 2 | MATERIALS AND METHODS

### 2.1 | Chemicals, sample preparation, and instruments

Calcium chloride anhydrous pellets (94–97%; Occidental Chemical Corporation, Dallas, TX), potassium sorbate anhydrous (99%; Nantong Acetic Acid Chemical Co., Ltd., Jiangsu, China), and glycerin anhydrous

(99.5%; Humco, Arlington, TX) used in freezing point determination were of USP grade.

Size 3A pickling cucumbers harvested in Mexico and exposed to the standard transportation system in the USA were kindly provided by processors. Fruits free of defects were washed and used in the freeze damage and density experiments.

A KD2 pro thermal analyzer (Decagon Devices, Inc., Pullman, WA) equipped with a KS-1 single needle sensor (operating environment range: –50 to +150°C, sensor range: 0.02–2.00 W/(m K) [thermal conductivity], 50–5,000°C cm/W [thermal resistivity], and accuracy: ±5% from 0.2 to 2 ± 0.01 W/(m K) and 0.02 to 0.2 W/(m K)) was used to determine the thermal properties of whole fermented cucumbers and cover brine. Size 3A fermented cucumbers and cover brine samples were kindly provided by processors.

### 2.2 | Density of cushion cover brines supplemented with varied CaCl<sub>2</sub> concentration

Two CaCl<sub>2</sub> concentrations (1.1 and 2.5%, wt/vol) were selected for this experiment, representing the recommended values for the full strength and equilibrated cover brines for the NaCl-free fermentation system (Pérez-Díaz et al., 2015). The marked reduction in salt content in the cover brines used, if compared to the generally used 6% NaCl solution, was selected to understand the effect of low salt content levels on cucumber injury during deposition. Cucumber density was determined using the displacement method with a volumetric cylinder. The quantity of cover brine displaced upon immersion of a fresh cucumber in the liquid was recorded as the fruit volume. The density of the cucumber was calculated using the following equation (Sartorius, 1999):

$$\rho_{\text{cucumber}} = \frac{m_{\text{cucumber}}}{V_{\text{cucumber}}} \quad (1)$$

where  $m_{\text{cucumber}}$  is the weight in grams of the cucumber (g) and  $V_{\text{cucumber}}$  is the volume of the cucumber (mL). Average density was obtained from the individual density of 30 fresh cucumbers.

### 2.3 | Buoyancy force determination

Buoyancy force ( $F_B$ ) was determined by depositing the cucumbers of known weight in a graduated five gallon measuring bucket filled with twelve liters of cover brine prior to measuring the quantity of cover brine displaced. Buoyancy force (weight of displaced volume) was calculated using the following equation (Sartorius, 1999):

$$F_B = (\rho_{\text{brine}})gV_{\text{displaced}} \quad (2)$$

where  $\rho_{\text{brine}}$  is the density of the brine (kg/mL),  $g$  is the gravitational force (N/kg), and  $V_{\text{displaced}}$  is the volume of the cover brine displaced (mL) and measured in the graduated bucket.

### 2.4 | Determination of freezing points for cucumber fermentation cover brines containing CaCl<sub>2</sub> and glycerin at various concentrations

Cover brine freezing points were defined by adjusting the CaCl<sub>2</sub> concentration from 1.1 to 20% (wt/vol) in individual solutions and

recording their temperature as a function of time during cold storage ( $-20^{\circ}\text{C}$ ). The recommended  $\text{CaCl}_2$  content for NaCl-free cucumber fermentations is 100 mM (1.1%) (Pérez-Díaz & others, 2015). The impact of the inclusion of 2–20% (vol/vol) glycerin in fermentation cover brines on the freezing point of the solution was also studied. The selection of these concentrations was based on the theoretical freeze point of the solutions in pure water (Occidental Chemical Corporation, 2017). A saturated NaCl solution (23 wt %) or a 21%  $\text{CaCl}_2$  cover brine would be theoretically needed to drop the freezing point of the cover brine in the tanks to  $-20^{\circ}\text{C}$  (Diaz et al., 2017). Glycerin solutions were prepared in the experimental cover brine solutions containing 2.5%  $\text{CaCl}_2$  and in cover brines containing NaCl as the control. Each solution was prepared using well water and mixed with a magnetic stirring bar at room temperature. Each experimental treatment was completed in duplicate in 16 oz pathology containers (ES3702; Azer Scientific, Morgantown, PA) with 350 mL of solution and stored at  $-20^{\circ}\text{C}$ . The temperature of all solutions was monitored using an Omega microprocessor thermometer (model HH21A; Omega, Stamford, CT) equipped with a type K thermocouple (NiCr-NiAl, range:  $-200$  to  $0^{\circ}\text{C}$ , resolution:  $0.1/1^{\circ}\text{C}$ , accuracy:  $\pm(0.3\% \text{ rdg} + 0.6^{\circ}\text{C})$ ). The temperature was measured every hour for 7 hr and twice a day for the three subsequent days. Temperature profiles were elaborated for each treatment and freezing points defined by recording the temperature at which ice crystallization occurred.

## 2.5 | Impact of glycerin supplementation on freezing injury of fermented pickles

Fresh size 3A pickling cucumbers were brined with 1.1 and 2%  $\text{CaCl}_2$  (wt/vol) with or without 14.5% glycerin (vol/vol) to visually assess the freezing injury induced by cold storage at  $-20^{\circ}\text{C}$ . The effect of 4.5 or 6% glycerin (vol/vol) on freshly pickled cucumbers brined with 6% NaCl was also studied as a control. Fruits and cover brine (50:50, wt/wt) were packed into a five gallon buckets and the containers stored at  $-20^{\circ}\text{C}$  for 24 hr. Pitting and surface discoloration of brined frozen cucumbers was visually assessed after thawing. Water loss of the thawed fruits was determined as described below.

## 2.6 | Average cucumber weight and water loss

Moisture content of cucumbers was determined using an oven drying method at  $105^{\circ}\text{C}$  for 24 hr (ASTM International, 2008), and samples were analyzed in triplicate using the following equation:

$$\text{water loss} = \frac{(M_0 - m_0) - (M - m)}{m_0} \quad (3)$$

where  $M_0$  and  $m_0$  are initial cucumber mass and dry mass before freezing (g), respectively and  $M$  and  $m$  are the cucumber mass and dry mass after freezing (g), respectively.

## 2.7 | Confirmation of calcium chloride concentration in cover brines and precipitate mineral content

Calcium content in the cover brines was determined by titration with EDTA using the dye binding method described by Gindler and King

(1972). Mineral content ( $\text{Ca}^{2+}$ ,  $\text{P}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Fe}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^+$ , and  $\text{Cu}^+$ ) in brine and dry solid precipitate were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using a Perkin Elmer ICP-OES Optima 5300 DV and completed by Cumberland Valley Analytical Services (CVAS, Inc., Waynesboro, PA). The dry solid precipitated was obtained by oven drying the precipitate at  $105^{\circ}\text{C}$  for 24 hr.

## 2.8 | Measurement of thermal properties

Cover brine samples (Table 3) were equilibrated to  $-20^{\circ}\text{C}$  in a refrigerated circulating bath to measure thermal conductivity and resistivity using a KD2 thermal analyzer probe. The same thermal properties along with volumetric specific heat were measured from intact fermented cucumbers at  $25^{\circ}\text{C}$ . The experiments were completed in duplicates and the average values reported.

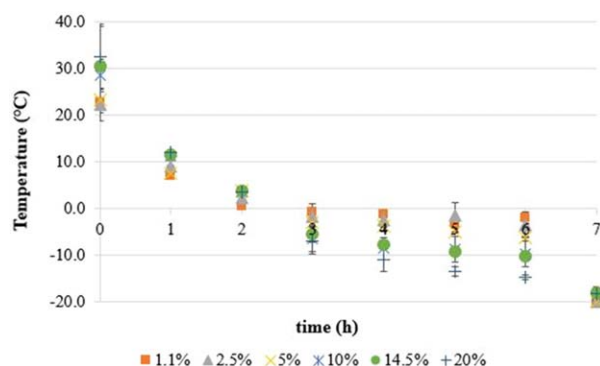
## 2.9 | Statistical analysis

Collected thermal properties data were evaluated using analysis of variance (ANOVA) with PROC MIXED in SAS 9.4 software (SAS®, Inc., Cary, NC). Statistical significance was made at an  $\alpha$  value of 0.05.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Effect of $\text{CaCl}_2$ concentration on the density of the cushion cover brines

Buoyancy force of the recommended cover brine for NaCl-free fermentations, containing 2.5%  $\text{CaCl}_2$  prior to equilibration with the fresh cucumbers, was found to be greater than the force of gravity on the fruits. The average density of 30 fresh size 3A cucumbers was 0.92 g/mL, about 0.04 g/mL lower than that previously reported ( $0.96 \pm 0.0025$  g/mL) for fresh cucumbers (Fasina & Fleming 2001). The difference observed can be attributed to the size of the cucumbers and the calculated volume method used in the present study (water instead of ethanol displacement). Density of cover brine containing 6% NaCl was reported as 1.04 g/mL by Humphries and Fleming (1991), which is similar to the density of a 1.1%  $\text{CaCl}_2$  solution ( $\sim 1.01$  g/mL) reported in the literature (Romankiw & Chou, 1983). Such density values were applied to make buoyancy force calculations. The buoyancy force for the 1.1 and 2.5%  $\text{CaCl}_2$  solutions (wt/vol) was 10.2 and 12.7 N, respectively, using 10 cucumbers (1.2 kg) for each solution. Thus, the buoyancy force at 2.5%  $\text{CaCl}_2$  (wt/vol), representing the full strength cover brine (12.7 N), was greater than the force of gravity on the fruit (12.1 N), allowing the cucumbers to rise up through the cushion cover brine upon deposition in the fermentation tanks. Such observation suggests that fresh cucumbers float in the cushion cover brine as the fermentation tanks are filled, which minimizes deposition injuries. The buoyancy force gradually diminishes as a function of time, due to the equilibration of the system (Fleming, Thompson, Bell, & Monroe, 1977), which aids in the settling of the cucumbers under the cover brine in the tanks prior to the active fermentation period and during bulk storage in the tanks (Humphries & Fleming, 1991).



**FIGURE 1** Temperature threshold for solutions containing different  $\text{CaCl}_2$  concentrations

### 3.2 | Freezing points of $\text{CaCl}_2$ solutions

Figure 1 shows the temperature profile for various  $\text{CaCl}_2$  solutions during 6 hr of freezing. The freezing point for solutions containing 1.1, 14.5, or 20%  $\text{CaCl}_2$  (wt/vol) was  $-2.0$ ,  $-8.8$ , and  $-14.0^\circ\text{C}$ , respectively. Solutions with  $\text{CaCl}_2$  concentrations above 10% (wt/vol) consisted of a mixture of water and ice during the 7 days of storage. However, solutions containing less than 10%  $\text{CaCl}_2$  crystallized after 6 hr of storage. Based on these observations it is estimated that 18%  $\text{CaCl}_2$  (wt/vol) is needed to match the freezing point of a 6% NaCl (wt) cover brine solution at  $-10^\circ\text{C}$ . Together, these observations suggest that a cover brine solution containing 2.5%  $\text{CaCl}_2$  prior to equilibration is prone to freezing in a short period of time in open top fermentation tanks at below zero temperatures. It has been observed that cover brine solutions containing either 6% NaCl (wt) or 1.1%  $\text{CaCl}_2$  (wt) form an igloo structure in commercial cucumber fermentation tanks, which forces the fermented cucumbers to concentrate in the center of the vessel. The thickness of the crystallized layers seems to be dependent on the salt concentration used, exposure time, and ambient temperature.

Even though it is known that the solubility of anhydrous  $\text{CaCl}_2$  is 74.5% at ambient temperature ( $20^\circ\text{C}$ ) and that solid phase separation in pure  $\text{CaCl}_2$  solutions occurs at temperatures below  $-50^\circ\text{C}$  when using the same percent by weight use for the study (DOW, 2003), solutions containing more than 10% salt developed a precipitate upon cooling, of about 7% solids (wt). The average percentage of  $\text{Ca}^{2+}$  that precipitated was 3.5 and 2.3% (wt/wt) for the 10 and 20%  $\text{CaCl}_2$  solutions (wt/vol), respectively (Table 1). It is hypothesized that  $\text{CaCl}_2$  interacted with other minerals present in the well water used for this experiment, given that

**TABLE 1** Percent of mineral precipitated per initial mineral weight

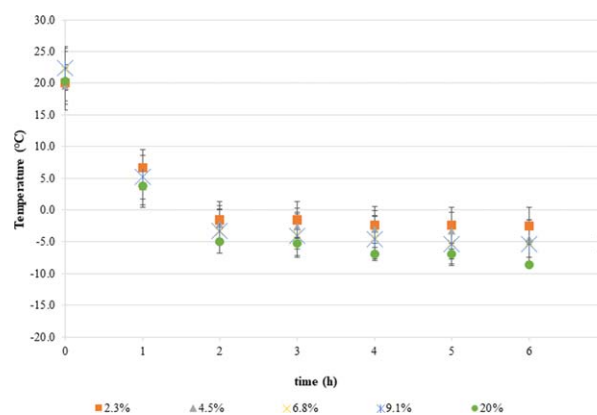
Mineral	wt % precipitated/initial wt (dry matter basis)	
	10% (wt/vol) $\text{CaCl}_2$ with 6 mM potassium sorbate	20% (wt/vol) $\text{CaCl}_2$ without potassium sorbate
$\text{Ca}^{2+}$	$3.53 \pm 0.64$	$2.3 \pm 0.28$
$\text{K}^+$	$15.5 \pm 2.30$	$9.39 \pm 1.34$
$\text{Na}^+$	$9.11 \pm 1.53$	$6.47 \pm 0.86$

Data shown represent the average and standard deviations of three independent replicates.

precipitates were not apparent in any of the studies performed with deionized water. A mineral content analysis of the precipitate showed that calcium, potassium, and sodium were present in significant fractions (Table 1). Potassium and sodium salts are part of the impurities in the pelleted anhydrous  $\text{CaCl}_2$  used for the experiment (2.5% potassium chloride, 1.6% NaCl, and 0.9% calcium bromide) and are also present in the well water (7.35 ppm  $\text{K}^+$  and 13.3 ppm  $\text{Na}^+$ ), which may have affected solubility and reflected in the minerals analysis. Calcium precipitation can also be attributed to the presence of dissolved organic matter in the water (Sindelar, Brown, & Boyer, 2015). Subsequent studies with cover brines containing  $\text{CaCl}_2$  and 0.1% (6 mM) potassium sorbate after equilibration with the fruits revealed that  $\text{CaCl}_2$  concentrations above 10% (wt/vol) reduced the solubility of the preservative. The average percentage of potassium precipitated per initial potassium content was 15.5 and 9.4% (wt/wt) for the 10 and 20% (wt/vol)  $\text{CaCl}_2$  solution, respectively. Potassium sorbate is commonly used in the pickling industry as a preservative and processing aid in fermentation tanks.

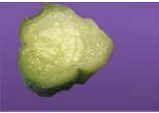





### 3.3 | Freezing points of $\text{CaCl}_2$ solutions containing glycerin

Figure 2 shows the temperature-concentration profile during a period of 7 hr for cover brines supplemented with glycerin. While glycerin reduced the freezing point and ice formation of the solutions; concentrations below 20% (vol/vol) in the 2.5%  $\text{CaCl}_2$  cover brines studied resulted in completely frozen solutions after 4 days of storage. The freezing point for solutions containing 2.5%  $\text{CaCl}_2$  (wt/vol), resembling full strength cover brines used for NaCl free fermentations, supplemented with 4.5 or 12.5% glycerin (vol/vol) was  $-3.2$  and  $-6.3^\circ\text{C}$ , respectively. Such freezing points are a couple of degrees lower than those observed for the comparable glycerin free solutions ( $-1.6^\circ\text{C}$ ). Adding 20 and 6% glycerin (vol/vol) to the cover brines containing 2.5%  $\text{CaCl}_2$  and 6% NaCl, respectively, resulted in solutions that remained a mixture of ice and water after a week of storage at  $-20^\circ\text{C}$ , with freezing points of  $-13.9$  and  $-10.9^\circ\text{C}$ , respectively. It is estimated that the 2.5%  $\text{CaCl}_2$  cover brines would have to be supplemented with 14% glycerin for it to match the freezing point of the 6% NaCl (wt) cover brine solution. While supplementation of the  $\text{CaCl}_2$  cover brines with 14% glycerin would be cost



**FIGURE 2** Temperature profile for a 2.5%  $\text{CaCl}_2$  cover brine containing different glycerin concentrations

TABLE 2 Description of freezing injury in cucumbers stored at  $-20^{\circ}\text{C}$ 

Treatment	Freezing injury in cucumber fruit	Description
1.1% $\text{CaCl}_2$ (wt/vol)		Green color mushy appearance
1.1% $\text{CaCl}_2$ (wt) and 14.5% glycerin (vol)		Translucent firm appearance
2% $\text{CaCl}_2$ (wt/vol)		Green/brown firm appearance
2% $\text{CaCl}_2$ (wt) and 14.5% glycerin (vol)		Translucent firm appearance
6% NaCl (wt)		Green color shriveled skin mushy appearance
6% NaCl (wt) and 6% glycerin (vol)		Translucent firm appearance

prohibitive for pickling operations, there is an opportunity to use the supplemented solution as insulating cover brine, if localized on the surface of cover boards, and separated from the fermentation cover brines with a food grade plastic cover, similar to those used for sauerkraut processing. A previous study has shown that the minimum localized temperature in fermentation tanks occurs near the surface, where insulation is needed to reduce ice formation (Diaz et al., 2017).

### 3.4 | Freezing injuries observed

Average cucumber weight loss and water loss were 16.3 and 5.9%, respectively, when brined with 1.1%  $\text{CaCl}_2$  (wt/vol). Slightly lower

values for weight and water loss (14.4 and 3.8%, respectively) were observed for cucumbers brined with 2.5%  $\text{CaCl}_2$  (wt/vol). Cucumbers exposed to a 10.6% NaCl cover brine containing 0.32% glacial acetic acid and 0.20% sodium benzoate have been reported to have a weight loss of 6.15% (Corey, Pharr, & Fleming, 1983). Visual inspection of the cucumber fruits submerged in cover brines for 3 days at  $-20^{\circ}\text{C}$  detected damage of the tissues similar to that described by Fukushima, Yamazaki, and Tsugiyama (1977). External wrinkles, internal pits, and change in color were observed in all the conditions studied (Table 2). However, the main injury observed as the result of this experiment was water loss. Interestingly, cucumbers submerged in cover brines supplemented with 14.5% glycerin had reduced tissue damage

TABLE 3 Thermal properties of cover brines as a function of composition and temperature

Solution	Composition of the solutions tested	Temperature ( $^{\circ}\text{C}$ )	Thermal conductivity, $\lambda$ ( $\text{W/m } ^{\circ}\text{C}$ )	Thermal resistivity, $R$ ( $\text{m } ^{\circ}\text{C/W}$ )
1	18% glycerin (vol), 2.5% $\text{CaCl}_2$ (wt), 0.1% potassium sorbate	22	$0.49 \pm 0.02$	$2.23 \pm 0.11$
		$-20$	$0.51 \pm 0.03$	$1.96 \pm 0.09$
2	6% glycerin (vol), 5% NaCl (wt), 0.1% potassium sorbate	22	$0.53 \pm 0.0$	$1.88 \pm 0.09$
		$-20$	$0.53 \pm 0.03$	$1.42 \pm 0.71$
3	1.1% $\text{CaCl}_2$ (wt), 0.1% potassium sorbate	22	$0.53 \pm 0.0$	$1.43 \pm 0.07$
		$-20$	$0.51 \pm 0.0$	$1.4 \pm 0.07$
Fasina et al., (2002)	6% NaCl	22	$0.50 \pm 0.03$	–

Data shown represent averages of duplicate and standard deviations.

(Table 2). Previous research showed that waxing and coating are effective in reducing transpiration and freezing injury in fruits and vegetables stored at low temperatures (Wang, 1993). Glycerin, the main component of triglycerides found in animal fat, vegetable oil, and crude oil, is used as a cryoprotectant in different products and industries (Coronado, Carvalho, Quispe, & Sotomonte, 2014) due to its noticeable freezing point depression when mixed with water. These observations suggest that cover brines supplemented with glycerin can serve as a strategy not only to reduce the cover brines freezing points but also to reduce freezing injuries during winter bulk storage.

### 3.5 | Influence of cover brine composition and temperature on thermal properties

Thermal properties data for the different cover brine solutions tested as a function of temperature are shown in Table 3. A thermal conductivity of 0.51 W/m K at  $-20^{\circ}\text{C}$  was observed for a solution containing 18% glycerin (wt), 2.5%  $\text{CaCl}_2$  (wt), and 0.1% (6 mM) potassium sorbate and for 1.1%  $\text{CaCl}_2$  with 0.1% (6 mM) potassium sorbate. The results showed that thermal property values were not significantly different ( $p > .05$ ) and similar to those published for cover brines with either 2 or 6 wt % NaCl ( $\sim 0.51$  W/m K at  $20^{\circ}\text{C}$ ) (Fasina et al., 2002). The concentrations used in this study (5% NaCl and 1.1 and 2.5%  $\text{CaCl}_2$ ) were at levels too low to obtain appreciable differences. Similarly, thermal resistivity values in this study were not significantly different ( $p > .05$ ) among the solutions tested.

Thermal conductivity, resistivity, and volumetric specific heat of fermented cucumbers were measured at 0.62 W/m K, 0.285  $\text{mm}^2/\text{s}$ , 1.73 m K/W, and 2.144  $\text{MJ}/\text{m}^3$  K, respectively. The thermal conductivity value reported for whole cucumbers within a temperature range of  $20$ – $95^{\circ}\text{C}$  is 0.61 W/m K (Fasina & Fleming, 2001), identical to that measured in this study. The thermal property results obtained in this study indicate that heat transfer during storage of fermented cucumbers in  $\text{CaCl}_2$  cover brines will behave similarly to bulk-stored fermented cucumbers brined with NaCl.

## 4 | CONCLUSIONS

The density of the full strength cover brine solution containing 2.2%  $\text{CaCl}_2$ , used for NaCl-free cucumber fermentations, was found to be sufficient to counteract the buoyancy effect of free falling fresh cucumbers into tanks. The freezing point for cover brines was dependent on the  $\text{CaCl}_2$  and glycerin concentration. Solutions containing 20%  $\text{CaCl}_2$  (wt/vol) remained as slush after several days of incubation at  $-20^{\circ}\text{C}$ . However, supplementation of cover brines with 20%  $\text{CaCl}_2$  would be counterproductive in regard to the reduction of  $\text{Cl}^-$  in waste waters and would present the difficulty of precipitate formation. Glycerin was able to diminish the ice formation and can be a viable alternative in reducing the freezing point of cover brine solutions. Less saturated  $\text{CaCl}_2$  solutions supplemented with glycerin may be used to top off cover brines over cover boards isolated by a food grade plastic to prevent the formation of ice on the surface of the tanks and facilitate the removal of the fermented stocks during winter. Thermal

properties of cover brines and fermented cucumbers at low temperature storage were also defined and found to agree with previously published data. Water loss was the main injury observed in cucumbers stored in cover brines at sub-zero temperatures. Fruits developed symptoms of freezing-injury in all cases studied except when 14.5% glycerin was added. Additional studies are needed to evaluate the utilization of glycerin as a component of cucumber fermentation cover brines, its potential role in preventing water loss associated with freezing injury and to develop strategies for its efficient use in tank yards.

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