Breaking the Ice: A Scientific Take on the Ice Melting Abilities of Household Salts

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Summary

Ice is formed in a very strict hexagonal pattern, causing it to be less dense than its liquid counterpart. Dissolved salt ions disrupt the formation of this crystal lattice structure, altering the equilibrium between water and ice. This property is crucial to road safety during winter conditions, when deicing salts are used to keep roads clear. In this study, we examined the melting abilities of several subtypes of salt, including calcium chloride, sodium citrate, magnesium sulfate, and sodium chloride. These common household salts were chosen because they differ in their chemical properties, environmental impact, and physical properties – including ease of spread and cost. To quantify the effectiveness of a salt at disrupting ice structure, increasing concentrations were added to standardized ice blocks in a 4°C cold room and the volume of melt-water was recorded. The properties of freezing point depression and enthalpy of dissolution were used to form hypotheses about the chemistry of melting. Additionally, they were used to predict the melting ability of novel salt mixtures. We discovered that calcium chloride is the most effective disrupter of ice structure. This result is important because it identifies a specific salt that can be purchased for home use as the most effective melter during the winter.

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Introduction

Icy roads account for 10% of annual fatalities while driving (1). In these dangerous conditions, one of the most important road safety tools is deicing salt. By investigating which salts are most effective at certain temperatures, roads can be deiced properly, reducing both winter fatalities and repair costs. Different commercially used road salts have different compositions and could have various levels of effectiveness. In addition to the chemical effectiveness of a particular salt, there are other factors to consider when designing a commercial road salt. Though salts have a chemical advantage over the sand that is also commonly sprayed on roads, there are long-term impacts of excessive salt use. When these ionic compounds dissociate into their respective ions, they are released into the environment and can wreak havoc on freshwater ecosystems (2). For example, chloride ions are highly mobile and toxic to aquatic life and sodium can displace important nutrients in soil (3). In addition to harming wildlife and vegetation, these salts can also directly impact human health. Similar to the salination of fresh water due to increasing sea levels, these changes can impair sources of drinking water and food production (4). Between 1983 and 2003, road salt contamination of private drinking wells cost the state of New Hampshire more than $3.2 million (3). This alone is a significant expenditure and doesn't even account for the hidden costs of long-term freshwater contamination.

The practical challenges of salt use such as cost, amount needed, and ease of application must also be considered. Identifying and utilizing the most effective salts could cut costs and limit the amount of salt that contaminates the environment each year. Using over 350,000 gallons of calcium chloride brine solution and over 186,000 tons of rock salt (sodium chloride) from 2015–2016, the New Jersey Department of Transportation (NJDOT) was able to keep its roads clear (5). A brine solution is preemptively applied to the roads using dump trucks that have a spreading mechanism, then the ice is treated with salt directly. In this study, we determined which deicing salt should be used on roads or purchased for home use. To rigorously examine this question in a controlled environment, we purchased chemically pure common salts and collected ice-melting data at both room temperature (23°C) and at a more realistic winter temperature (4°C). Sodium chloride, tri-sodium citrate dihydrate (sodium citrate), calcium chloride, and anhydrous magnesium sulfate were selected to test a range of salts that not only differ in chemical and physical properties, but also in their cost and impact on the environment.

One way to understand how salts melt ice is to consider the colligative property of freezing point depression. A colligative property is dependent only on the ratio of the number of solute particles to the number of solvent molecules in solution and not on the type of chemical species present. Freezing point depression can be predicted using the van 't Hoff equation:

$$\Delta T = i * K_f * m \qquad \text{[Eq. 1] (6)}$$

The solvent freezing-point constant (Kf) will be a fixed number, since only water was used in our experiment. This equation relates the freezing point depression to the van 't Hoff factor (i) of the solute and the molality of the solution (m). Molality is defined as the amount of moles of solute divided by the mass of the solvent in kilograms.

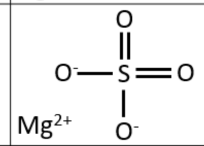
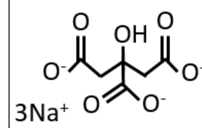
Salt	Sodium chloride	Calcium chloride dihydrate	Magnesium sulfate	Tri-sodium citrate dihydrate
Formula	$NaCl$	$CaCl_2 \cdot 2H_2O$	$MgSO_4$	$Na_3C_6H_5O_7 \cdot 2H_2O$
Chemical Diagram	Na^+ Cl^-	Ca^{2+} $2Cl^-$		
Solubility (g/L) (9-12)	357	1275	300	29.4
Molecular Weight (g/mol)	58.44	147.0	120.4	294.1
Saturated Molal Solubility (mol/kg H_20)	6.11	8.67	2.49	0.10
Van't Hoff Factor	2	3	2	4
Theoretical Saturated 1L H_20 Freezing Point Depression (°C) Kf=1.86 (13)	22.7	48.4	9.27	0.74
Heat of Dissolution (kJ / mol) (14)	3.9	-82.9	16.0	27.8
Price (USD /kg) (15-18)	76.2	103.4	45.8	58.0
Bulk Price (USD /kg) (19-22)	1.84	1.11	3.07	24.28

Table 1. Chemical descriptions and properties of the salts used.

Molarity, the more commonly used molar concentration unit, is defined as moles of solute per liter of solution. Molality does not change with temperature, as molarity does, making molality the more appropriate unit for the van 't Hoff equation (7). For ionic solutes, i is roughly equal to the number of dissociated ions per formula unit of solute. The actual van 't Hoff factor is always experimentally determined, with a more dilute solution having a van 't Hoff factor closer to the ideal factor for that solution (6). According to this formula, the more soluble a salt is in water and the more ions it produces, the greater the effect on freezing point depression.

When the molal solubility values for each experimental salt are substituted into the van 't Hoff equation, a saturated solution of calcium chloride is shown to have the greatest freezing point depression, with twice the value as the next salt, sodium chloride (**Table 1**). Although melting ice involves additional factors, this value does suggest that calcium chloride could be the most effective melter. If equivalent moles of the two salts are added, calcium chloride will generate more dissolved ions in a ratio of 3:2. If any excess salt is added, the high solubility of calcium chloride means it will remain effective for longer before saturating the water on the surface of the ice block.

Although freezing point depression is one way to think about melting ice, there are additional factors to consider in this system. When a salt comes in contact with ice, it undergoes the process of solvation, where electrostatic forces drive the neatly arranged water molecules to rearrange themselves around dissolved ions. The water molecules use their dipoles in order to counteract the charge of the ion, thus stabilizing the structure. This process of solvation is the determining factor of whether or not this process is exothermic or endothermic (8). The enthalpy of dissolution for a particular salt can be positive or negative, indicating that heat is either released in an exothermic reaction or absorbed in an endothermic reaction. This change in temperature might enhance or dampen the predicted effectiveness of a salt compared to using freezing point depression alone. Calcium chloride is the only salt used that has an exothermic enthalpy of dissolution, suggesting that it may have an enhanced effectiveness compared to the other salts (**Table 1**). We predict that a salt with a very endothermic enthalpy of dissolution, such as sodium citrate, would remove energy from the system and show a dampened ability to melt ice.

Results

As a preliminary experiment, 10 g of each salt was applied to the surface of a 250-g block of ice at a room temperature of 22.6°C. This amount of salt was chosen to approximately match the density of salt a person would apply at their home. After 25 minutes, the melted water was poured off and the volume recorded using a graduated cylinder. Volume rather than mass was used to minimize the error associated with dissolved salts. A no-salt control group was used to determine the effect of temperature alone and this value was compared to the average measured volume with each salt (**Figure 1**). For each salt, the standard deviation of four independent measurements shows a large variance at room temperature, necessitating a new set of experiments in a more controlled environment. However, as a baseline measurement, calcium chloride proved to be the most effective salt, melting on average about 24 mL more water than the no-salt control.

In order to simulate a more realistic winter condition, a 4°C cold room was used to collect the rest of the data. To more accurately represent the chemistry of freezing point depression, equivalent moles of each salt were added instead of grams. In these conditions, all no-salt control trays produced no melt water in 25 minutes, demonstrating a much more stable environment. For each salt, two independent measurements were taken at each .05-mole increment between 0 and 0.2 moles. The average melt values and standard deviations were then

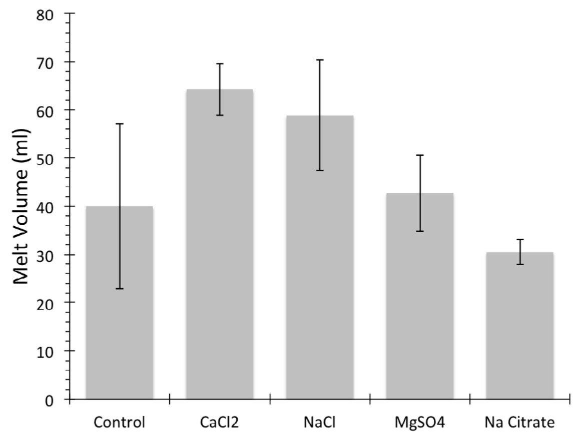


Figure 1. Volume of melted ice (ml) after the addition of 10 grams of each salt at 22.6°C. Error bars represent standard deviation of four independent measurements.

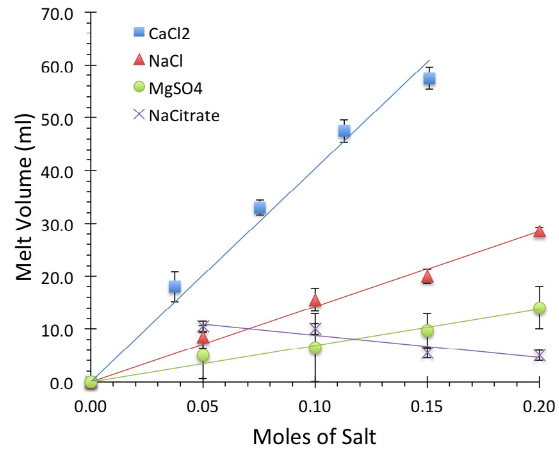


Figure 2. Volume of melted ice (ml) after treatment with increasing moles of each salt at 4°C. Error bars represent standard deviation of two independent measurements.

calculated and plotted and linear trend lines were fitted to the data (**Figure 2**). The data points for calcium chloride are at a slightly lower mole amount than the other salts due to a molecular weight correction to calcium chloride, which came as a dihydrate salt.

At 4°C, the standard deviation of each set of measurements was dramatically reduced, and the linear model was appropriate for all salts except sodium citrate, with an R^2 value greater than 0.97. Surprisingly, sodium citrate appeared to have a slightly negative trend, suggesting that this salt inhibits ice melting at high concentrations. For each of the other salts, the data shows that increased salt concentration positively correlates with the volume of melt water. This relationship can be quantified using the equation of the linear trend line and the slope of these lines can be used to compare the relative effectiveness of each salt. The data shows that calcium chloride, sodium chloride, and magnesium sulfate melt approximately 404, 142, and 69 mL/mole respectively at the concentrations used in this experiment (**Figure 2**). This information confirms and supports the reported use of calcium chloride and sodium chloride as common deicers during winter. To more closely examine the practical applications of these two salts, the data was re-plotted using the equivalent units of chloride ions, grams, and dollars per mL of water melted (**Figure 3**).

When equivalent moles of the two salts are compared, calcium chloride is more effective than sodium chloride in a ratio of 2.8:1 (**Figure 3a**). Although dissolving calcium chloride liberates two chloride ions per molecule of salt, the increased effectiveness of calcium chloride per mole is enough to offset this effect. Comparing equivalent moles of liberated chlorine gives a ratio of 1.4:1, suggesting that calcium chloride is also the more environmentally friendly salt (**Figure 3b**). An important practical consideration is the weight of salt required and calcium chloride has a greater molecular mass. When comparing equivalent grams used of calcium chloride and sodium chloride, the difference between the two salts narrows significantly to 1.2:1 (**Figure 3c**). A final crucial factor is the cost of the salt used in the experiment. The chemically pure calcium chloride was more expensive per gram than sodium chloride and when equivalent dollar cost is compared, give a ratio of 0.92:1 (**Figure 3d**). This suggests the effectiveness by cost is relatively similar and might help explain why both salts are widely used commercially.

The previous experiments generated data showing a linear relationship between salt added and melted ice. However, we predicted that at a certain point, the addition of extra salt would cease to show this relationship as the surface of the ice became completely saturated. This is an important consideration, as excessive use of salt would have an increased cost and environmental impact without efficiently melting additional ice. To examine this saturation point, 0.4 and 0.5 moles of calcium chloride and sodium chloride were spread on the same sized ice blocks and these data points were included on the plot (**Figure 4**). Although much more ice melted, the new data points fell below the value predicted by the linear trend line for both salts. In this molar range, the addition of calcium chloride appeared to retain a relatively linear relationship with the amount of ice melted. However, sodium chloride showed a much more abrupt saturation curve, generating only 30% more water with the addition of 150% as much salt.

Discussion

The goal of this experiment was to determine the most efficient deicing salt for both commercial and consumer applications. To do this, we rigorously tested the effectiveness of different common salts in a controlled environment. Our observations can help explain why a municipality might choose to use a mixture of different salt treatments and suggest a preferred salt to purchase for home use. From our data, calcium chloride and sodium chloride appeared to be by far the most effective at melting ice. This was expected, as these two salts are the most widely used commercial road salts (5). If

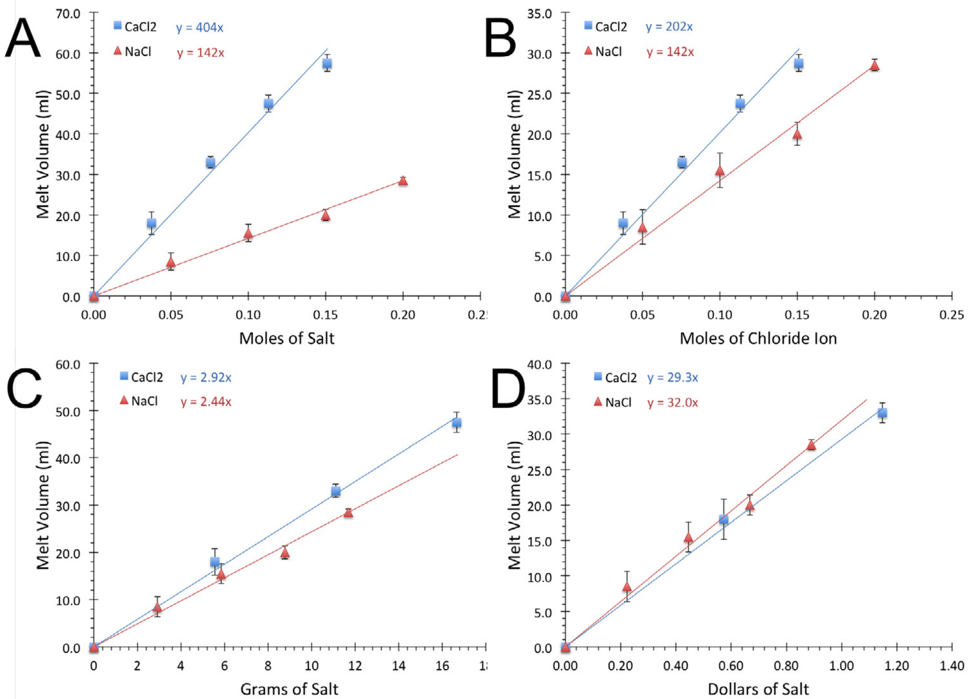


Figure 3. Volume of melted ice compared to increasing number of moles (A), chloride ions (B), grams (C), and dollars (D) of calcium chloride and sodium chloride. All linear trend lines fit with R2>0.98. Error bars represent standard deviation of two independent measurements.

equivalent moles of calcium chloride and sodium chloride are dissolved in water, the van 't Hoff equation predicts their effect on freezing point depression will occur with approximately a 1.5:1 ratio since they dissociate into 3 and 2 ions respectively (6). The equation further predicts that a saturated solution of these salts would depress freezing point with the ratio of 2.1:1 since calcium chloride has a greater solubility (**Table 1**). These dissolved ions interact with the dipole moment of the water, preventing it from forming the crystalline structure of ice. We hypothesized that freezing point depression could also help predict the relative effectiveness of deicing salts, as they dissolve and disrupt the ice lattice.

Although the predicted ordering by freezing point depression matched the experimental results, the magnitude of the difference was much greater than expected. Our data showed that calcium chloride was more effective than sodium chloride in a ratio of 2.8:1 (**Figure 3a**). This suggests that another factor, such as the enthalpy of dissolution, may be playing a large role in the relative effectiveness of these two salts. Calcium chloride has an enthalpy of dissolution of −82.9 kJ/mol while sodium chloride's enthalpy of dissolution is +3.9 kJ/mol (24). The energy released by calcium chloride could assist in the melting process, leading to a much larger difference between these two salts than predicted by van 't Hoff alone. Similarly, the large endothermic enthalpy of dissolution of +27.8 kJ/ mol (25) for sodium citrate might explain our observations for this salt. Although not statistically significant, our preliminary experiment at room temperature suggested that sodium citrate might be a melting inhibitor (**Figure 1**). Surprisingly, the same experiment repeated at 4°C also showed that increased concentrations of sodium citrate resulted in a negative slope (**Figure 2**). The endothermic enthalpy of dissolution could remove energy from the system, preventing additional ice from melting.

It is also important to consider our results in the context of the specific experimental setup. For example, these salts each had a different crystalline structure that impacted their effectiveness. Anhydrous magnesium sulfate was used in these experiments and was applied in the form of a dry, flaky powder. After 25 minutes, the salt appeared wet, but our measurements could not account

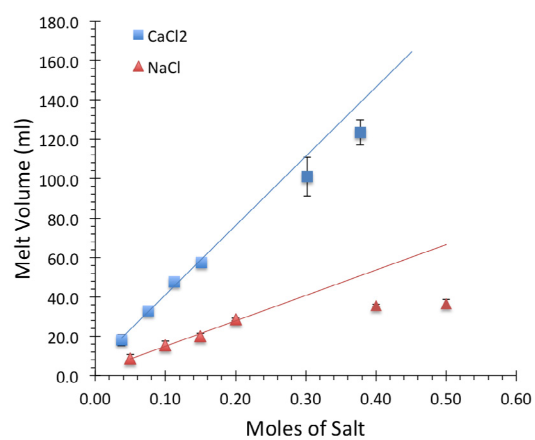


Figure 4. Saturation curve of calcium chloride and sodium chloride. Lines show linear trend in the absence of saturation. Error bars represent standard deviation of two independent measurements.

for any water that was absorbed by the magnesium sulfate to hydrate itself and thus could not be poured off. To fully hydrate 0.1 moles of magnesium sulfate to its natural heptahydrate form, 7 formula units of water for every formula unit of magnesium sulfate is needed (23). This would equate to 0.7 moles or 12.61 mL of water. This would suggest that our data underrepresented the ability of magnesium sulfate to disrupt the crystal lattice. In addition to salt hydration water loss, there is error in all of the melt-water measurements due to changes in density. Distilled water has a density of 1 kg/L, while saturated solutions of sodium chloride and calcium chloride are 1.2 kg/L and 1.4 kg/L, respectfully (26). However, due to the relative solubilities of these two salts, roughly four times the mass of calcium chloride will dissolve in the same original volume of water (**Table 1**). This means that saturated solutions of calcium chloride will have a greater total volume than saturated solutions of sodium chloride and this could cause us to overestimate the melting ability of calcium chloride.

To avoid issues such as salt hydration and density changes, we attempted to quantify the ability to melt ice by testing the tensile strength of the ice block after treatment. To do this, a 145-g ball was dropped from 17 centimeters above the surface and pictures taken of the cracks that formed. Using ImageJ image analysis software, the number and length of cracks could be quantified and compared. However, the results were too variable within even the control group, and no conclusions could be drawn. An additional study would have to be completed with compression testing machines in order to apply and measure direct force onto the ice.

Although calcium chloride was substantially more effective than sodium chloride per mole, to determine which salt is more effective in a practical sense the data must be looked at from a different perspective. In the real world, road salt is purchased, stored, and applied to ice in units of mass or cost. When moles are converted to grams, the difference between these two salts narrows substantially. In this context, calcium chloride is only more effective at a ratio of 1.2:1 and this difference is only significant if the concentration of salt used is quite substantial (**Figure 3c**). If the salts are compared in terms of volume melted per dollar spent, this difference disappears altogether and they appear essentially identical (**Figure 3d**).

If the effectiveness per dollar is the same, the choice might come down to delivery method. If loose crystal salts were used to fill a truck and spread on a road, the limiting characteristic would likely be weight. Our data shows that in the linear range there is only a 20% difference in effectiveness per gram used and that at the lowest concentrations, this difference is not statistically significant. Above the linear range, when the surface of the ice became saturated with salt, calcium chloride remained fairly effective while sodium chloride showed a much more abrupt saturation curve, generating only 30% more water with the addition of 150% more salt. However, the concentration used in our saturation experiments was an excessive amount. From personal observation during the winter, the amount of salt used in practice lies roughly within the linear range.

The NJDOT uses rock salt (sodium chloride) on their roads and our data confirms that this is an equally cost-effective decision (5). Bulk amounts of road grade salts might differ in price from the pure salts used in this experiment and this could determine the appropriate choice. When researching commercially available road salts online, sodium chloride often costed significantly more than calcium chloride (**Table 1**). The NJDOT also uses calcium chloride brine solutions and our data suggests that this is the best salt choice for brine (5). Calcium chloride is twice as soluble per gram as sodium chloride, allowing a tanker truck to carry double the melting capacity per load (**Table 1**). This would reduce the gas cost, the number of trucks required, and the time spent spraying the roads. However, if the brine solutions are prepared and then allowed to equilibrate to the same temperature, the differences between the enthalpies of dissolution will no longer apply. If our hypothesis about the impact of the exothermic dissolution of calcium chloride proves correct, one would expect to see the relative effectiveness of the salt decrease. This is an important consideration and would need to be tested further in a follow-up experiment using brines.

In addition to the practical and monetary considerations, the impact of road salt on the environment should be considered. As discussed, chloride ions are very mobile and extremely soluble in water. They are toxic to aquatic life and they have negative side effects to the surrounding vegetation (3). By comparing chloride ions released to melting ability, we propose that crystalline calcium chloride is the more environmentally friendly salt (**Figure 3b**). However, if calcium chloride brines are less efficient due to the loss of exothermic dissolution, these findings may not hold true. Calcium ions are necessary for growth in humans (27) and are even slightly beneficial to one's health (28). Due to the overall abundance of calcium in the Earth's crust (3.6% by mass) (29), the addition of calcium ions would not likely affect the soil greatly. However, the addition of sodium ions does change soil chemistry by replacing existing nutrients (3).

After careful consideration of chemical and physical factors, we conclude that, although calcium chloride is much more efficient than sodium chloride per mole, the practical considerations of salt use narrow the difference substantially. Our data suggests that the cost efficiencies of the salts are almost identical, which might explain why they are both widely used commercially. We hypothesized that both freezing point depression and enthalpy of dissolution of a salt impact its ability to melt ice and we observed this in our experiments. The potential impact of differences in enthalpy was greater than we predicted and this requires further testing. The characteristics of anhydrous magnesium sulfate powder prevented accurate measurements and sodium citrate seemed to inhibit melting, potentially due to its large endothermic dissolution. Salts that have a low solubility, but have an exothermic dissolution and salts that are highly soluble, but have an endothermic dissolution, such as sodium chlorate, can be compared to assist in further determining the balance of these two properties. Additionally, brine solutions of these salts can be used to simplify dissolution and gain a better understanding of why calcium chloride is predominantly used as brine. Further studies are also necessary to understand the full environmental impacts of each of these salts, including the positive and negative effects of chloride, sodium, and calcium ions in the environment. However, based on our data, we recommend purchasing calcium chloride for your front steps. For less money and less weight, it's sure to break the ice this coming winter.

Methods

Ice tray set up

Ten Newspring Pactiv black plastic disposable trays were filled with 250 mL of DI water each and frozen overnight at −20°C with lids. Each salt sample was weighed in a weigh boat on an electronic balance and set aside. Each sample was then applied evenly over the surface of each ice tray in intervals of 2.5 minutes. All other trays remained in the freezer before use. After spreading the salt, the lid was placed loosely back on top to limit the impact of airflow, and the tray was placed on a lab bench or in a 4°C cold room.

Data Collection

After all trays had been completed, the first tray was taken back out. The lid was removed, and the water that had been melted was poured into a graduated cylinder and recorded. The strict 2.5-minute interval ensured that each tray had melted for exactly 25 minutes. After the melt water had been removed, each tray underwent a drop test. A 145-g ball was dropped from 17 centimeters above the surface and pictures taken of the cracks that formed. Using ImageJ image analysis software, the number and length of cracks could be quantified and compared.

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