FREEZING POINT DETERMINATIONS OF SAFECOTE BRINE MIXTURES

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Executive Summary

Freezing points of Safecote admixed with 23% w/w sodium chloride brine, 20% w/w magnesium chloride brine and 20% w/w calcium chloride brine have been determined over a wide composition range.

The freezing point, measured for a 50:50 mixture of Safecote:NaCl, was -40.4 °C and the freezing points measured for 75:25 mixtures of $MgCl_2$ and $CaCl_2$ with Safecote were -45.3 and -46.9 °C respectively. The curves of composition versus freezing point for each of the three brines exhibit a smooth, non-linear, relationship between composition and freezing point. This will enable the end user to make a meaningful interpolation of required composition for a specified lower limit of operating temperature. The samples were all observed to be mobile liquids up to the measured freezing point but their viscosity increased as the temperature was decreased.

A sample of pure Safecote was also tested down to -72.5 °C and no presence of a solid phase (freezing) was observed. As with the Safecote:brine mixtures the viscosity of pure Safecote samples increased with decreasing temperature.

Experimental

Safecote was used as supplied and samples of sodium, magnesium and calcium chlorides were laboratory grade reagents from Aldrich chemical company. The brine solutions were prepared gravimetrically from the metal chloride and deionised water to the desired composition. Mixtures of Safecote and the brine solution were also prepared gravimetrically to the desired composition.

Freezing point data was logged down to -72.5 °C using a 'K' type thermocouple, recording temperature on a digital volt meter interfaced to a personal computer. The thermocouple was calibrated against various freezing mixtures of solid carbon dioxide and a variety of organic solvents. The temperatures recorded were found to agree to within ± 1% of accepted literature values for the relevant freezing mixture.

Results

Freezing point curves for three example compositions of Safecote with sodium, magnesium and calcium chloride brines are shown in figures 1 to 3.

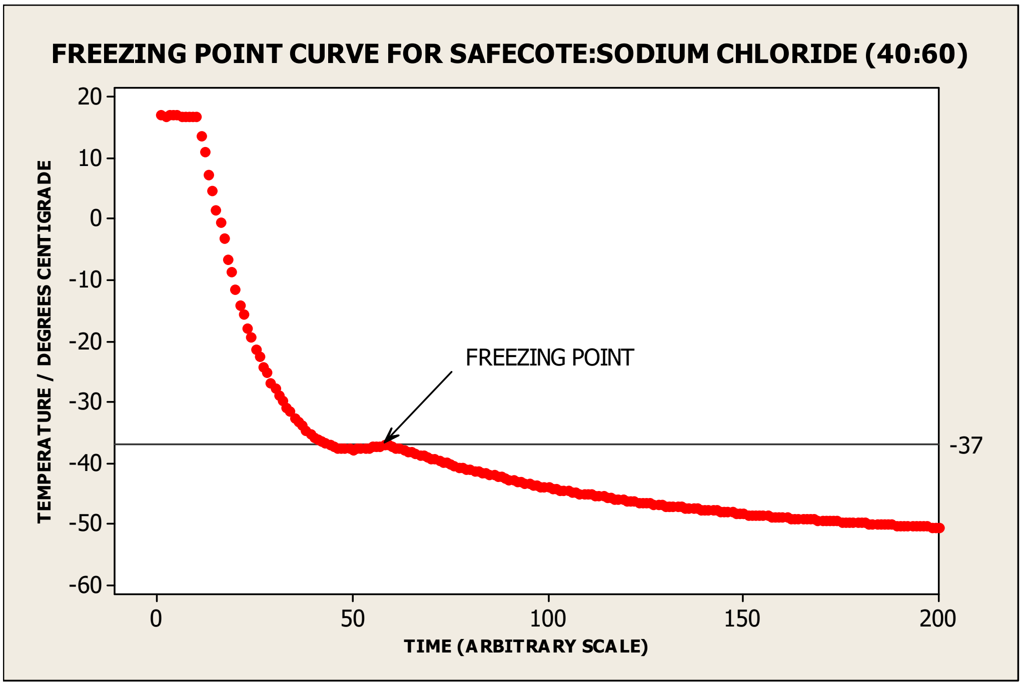

Figure1. Freezing point curve for 40:60 Safecote:23% sodium chloride.

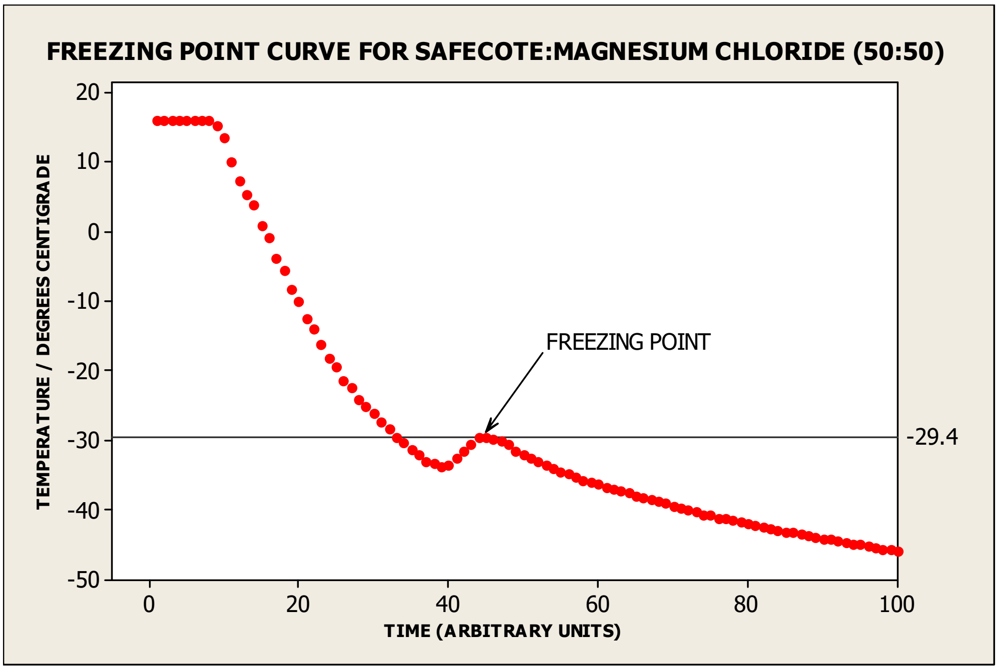

Figure 2. Freezing point curve for 50:50 Safecote:20% magnesium chloride.

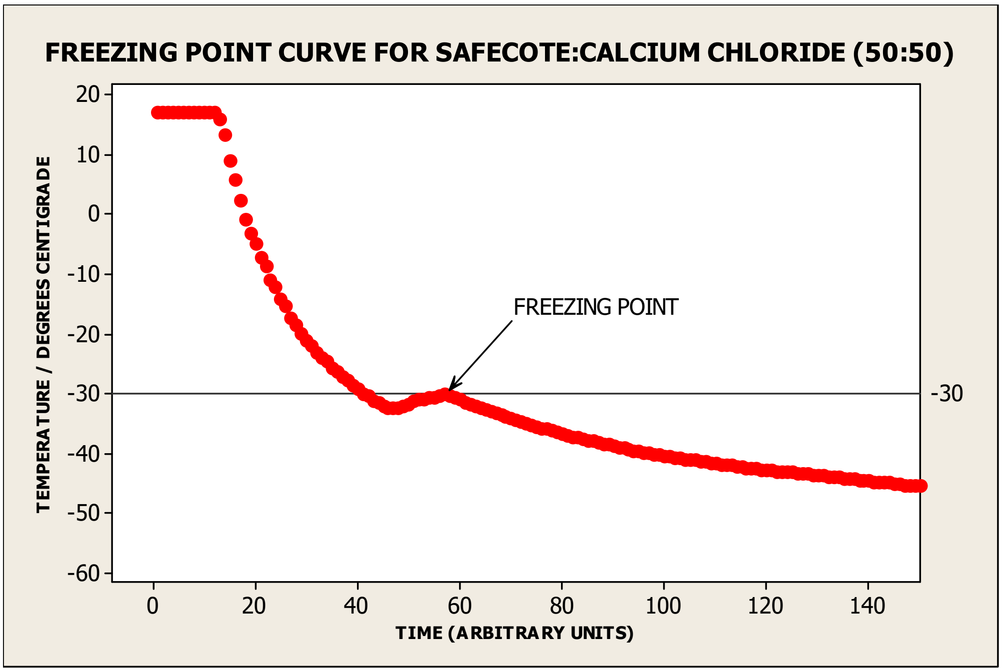

Figure 3. Freezing point curve for 50:50 Safecote:20% calcium chloride.

In figures 2 and 3 the phenomenon known as 'under cooling' or 'super cooling' is present in the cooling curves. Sometimes as a liquid or solution is cooled towards its freezing point the temperature will drop below the freezing point before any phase change occurs. This behaviour is enhanced by very clean or new equipment which lacks scratches or other irregularities that serve as sites for crystallisation to occur. Adequate stirring overcomes any excessive super cooling in a mixture although a slight super cooling depression may always be observed. Figure 1 illustrates a curve with an absence of super cooling and the freezing point is derived from the plateau in the cooling curve. The freezing point in the other mixtures in figures 2 and 3 is derived from the maximum, or plateau, in the discontinuity which follows the super cooling. The plateau or maximum at the freezing point is caused by the energy change occurring as the phase of the mixture changes from liquid to solid. Effectively the thermal energy being removed from the liquid is offset by the energy required for the phase change to occur and the temperature remains constant during the time taken for the sample to change from a liquid to a solid.

Tables 1 to 3 summarise the freezing points for the Safecote:Brine mixtures studied. Freezing points for all the mixtures were performed 6 times and the mean calculated. All determinations were within ±3% of each other and the recorded freezing points are considered to be a very accurate determination of the point at which the mixtures changed phase from liquid to solid. An additional freezing point determination was performed for a Safecote: 20% $MgCl_2$ mixture of composition 90:10 and as shown in table 2 no phase change was observed down to -72.5 °C.

Safecote: NaCl (23% NaCl w/w)	**Identification**	**Freezing Point / °C (mean)**
10:90	*NaCl 90*	**-27.1**
20:80	*NaCl 80*	**-30.8**
30:70	*NaCl 70*	**-32.3**
40:60	*NaCl 60*	**-37.1**
50:50	*NaCl 50*	**-40.4**

Table 1. Freezing points of Safecote:sodium chloride (23% w/w) brines.

Safecote:$MgCl_2$ (20% $MgCl_2$ w/w)	**Identification**	**Freezing Point / °C** (mean)
10:90	*$MgCl_2$ 90*	**-20.3**
25:75	*$MgCl_2$ 75*	**-24.2**
50:50	*$MgCl_2$ 50*	**-30.6**
75:25	*$MgCl_2$ 25*	**-45.3**
90:10	*$MgCl_2$10*	**No solid phase formed ≥ -72.5 °C**

Table 2. Freezing points of Safecote:magnesium chloride (20% w/w) brines.

Safecote:$CaCl_2$ (20% $CaCl_2$ w/w)	**Identification**	**Freezing Point / °C** (mean)
10:90	*$CaCl_2$ 90*	**-24.3**
25:75	*$CaCl_2$ 75*	**-26.1**
50:50	*$CaCl_2$ 50*	**-30.4**
75:25	*$CaCl_2$ 25*	**-46.9**

Table 3. Freezing points of Safecote:calcium chloride (20% w/w) brines.

A determination of the freezing point of 'as supplied' Safecote failed to detect any phase change in the liquid down to -72.5 °C. so although the liquid became very viscous at this temperature it was still a liquid, albeit with a very low mobility. This is shown in figure 4 and there is an absence of any plateau or discontinuity which would indicate a phase change.

Reference determinations of the freezing points of 20% w/w solutions of $MgCl_2$ and $CaCl_2$ were made and the results are summarised in table 4.

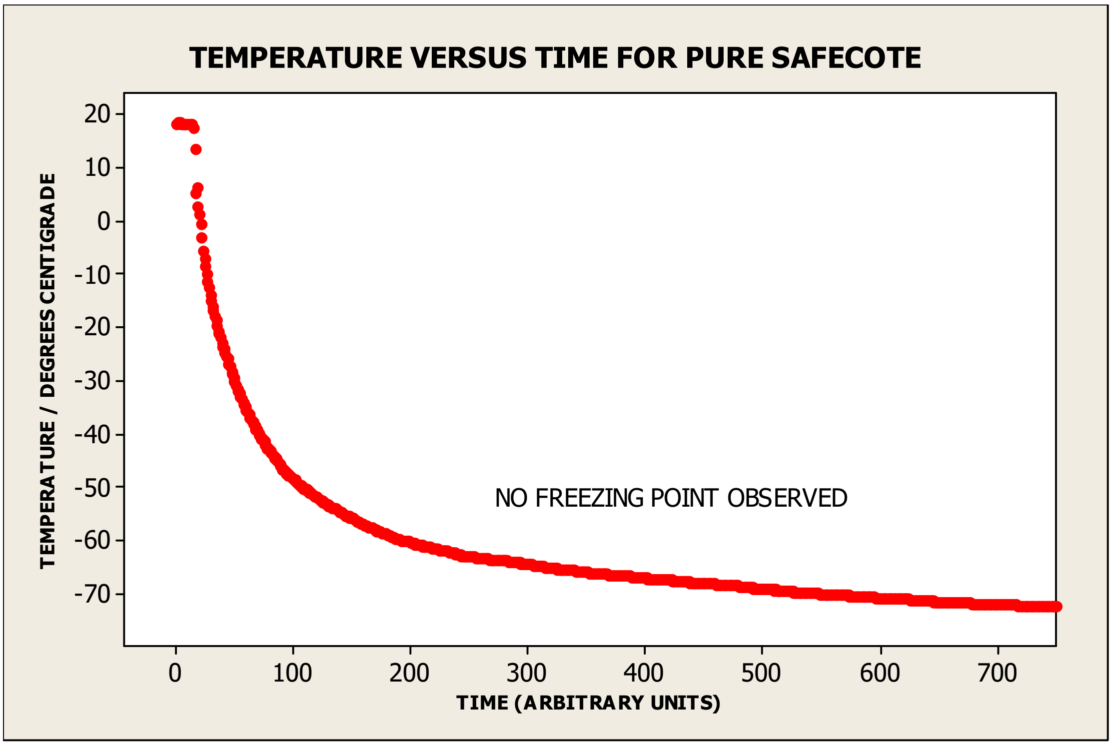

Figure 4. Freezing point curve 'as supplied' Safecote.

Brine solution	**Freezing Point / °C**
23 % w/w Sodium chloride	-20.9
20 % Magnesium chloride	-22.7
20% Calcium chloride	-25.5

Table 4. Freezing points of pure brine solutions.

Discussion

The measured freezing points for the three Safecote/brine mixtures indicates a satisfactory lower limit at the 50:50 or 75:25 Safecote:brine mixture of ≤ 40°C.

Graphs (figures 5 to 7) of composition versus freezing point for the three Safecote/brine mixtures exhibit a well defined functional relationship between freezing point and composition.

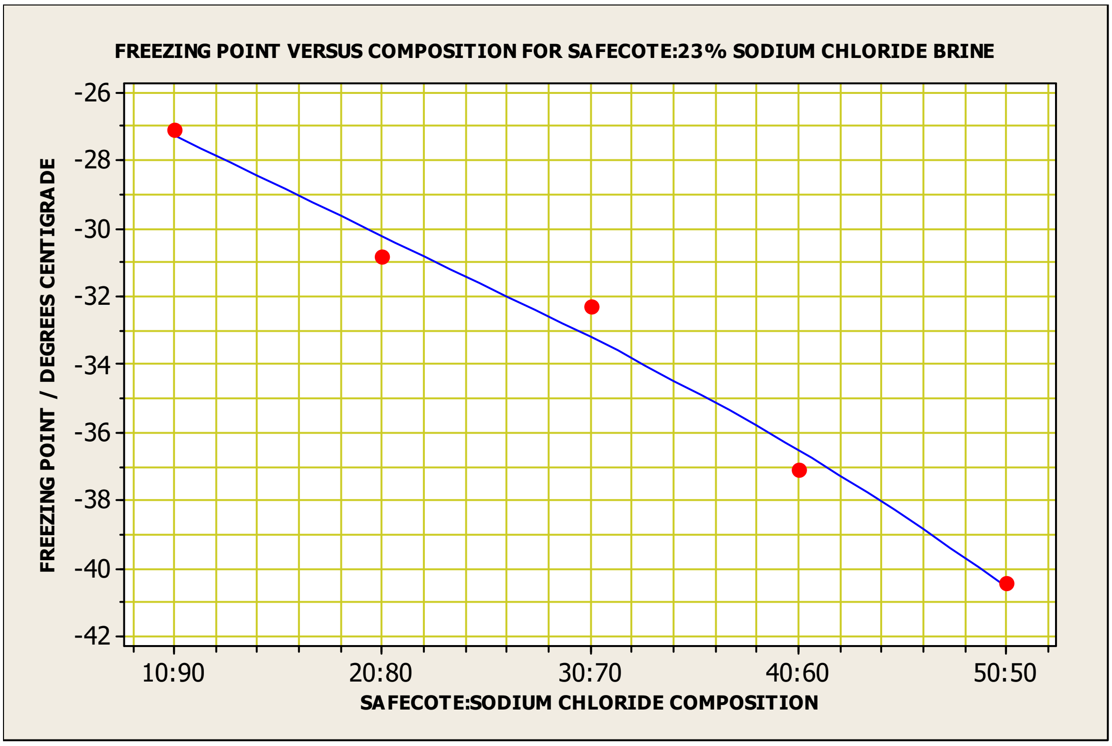

Figure 5. Relationship between freezing point and composition of Safecote/sodium chloride mixtures.

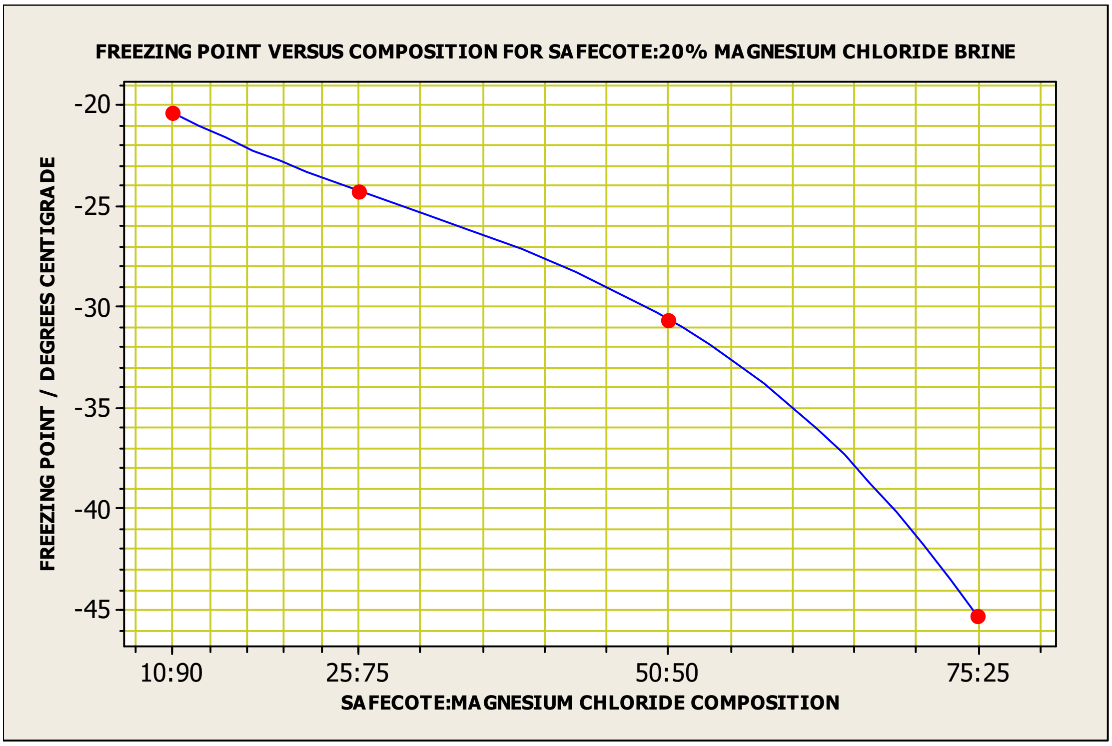

Figure 6. Relationship between freezing point and composition of Safecote/magnesium chloride mixtures.

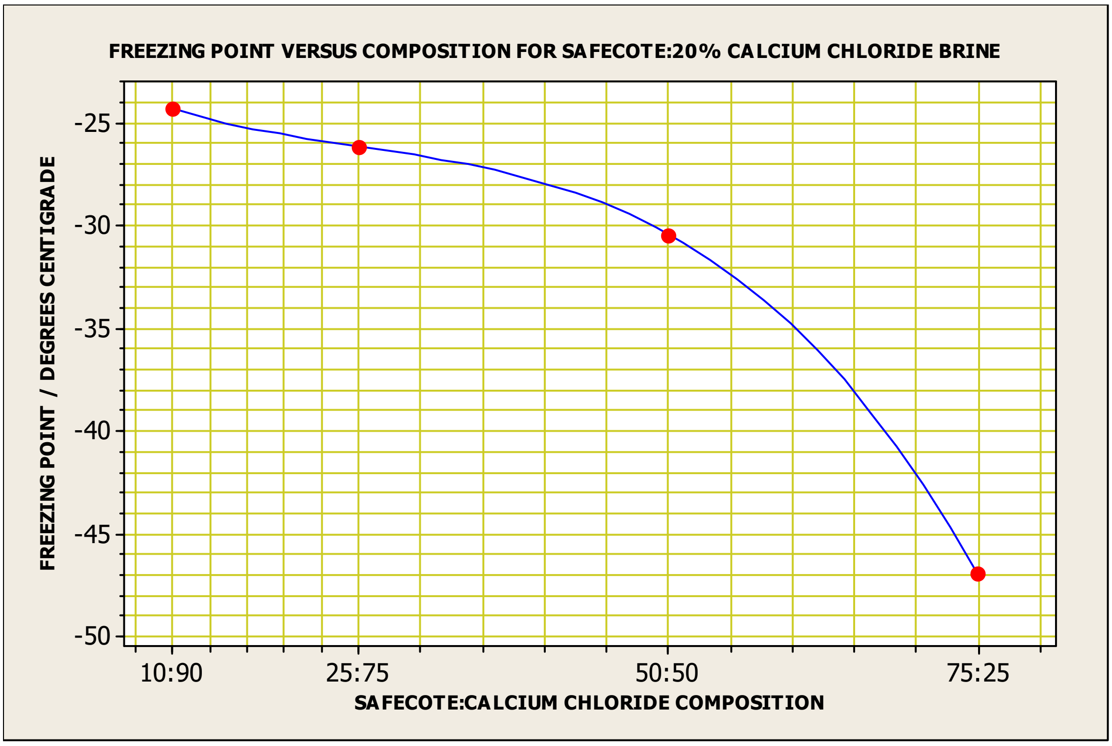

Figure 7. Relationship between freezing point and composition of Safecote/calcium chloride mixtures.

Clearly the well defined relationship between freezing point and composition will enable the end-user to produce a de-icing mixture suitable for their local winter temperature minima.

In all cases the viscosity of the mixture increased with decreasing temperature. Although the Safecote/Brine mixture is still, theoretically, a liquid at a temperature just above the freezing point it will be extremely viscous. Such a liquid will be quite capable of melting frozen water (ice/snow) at that temperature but the high viscosity will limit any tendency to spread over a surface and the material may not be economically viable as a de-icer.