PROPERTIES OF SALT AND SRA SOLUTIONS AS THEY RELATE TO THE DRYING AND WETTING OF CEMENTITIOUS MATERIALS

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Background

Deicing salts have been the subject of research over the years, with special attention to some durability issues (concrete degradation, absorption, hysteresis during drying and wetting, freeze/thaw or crystallization pressure). Few research was done instead on the influence of deicing salts on the mechanism of drying of cementitious materials.

Shrinkage Reducing admixtures (SRA) are known to minimize the potential of cracking by decreasing surface tension and by increasing viscosity of the pore solution. Research has focused mainly on their influence on cracking response, mechanical properties or fluid transport. Little information are available on their effect on fluid properties over a wide range of concentrations and at different temperatures.

Several studies have shown the importance of wetting and drying processes of cementitious materials for durability. This mainly refers to joints deterioration and freeze/thaw damages. Among these studies, however, very few explicitly consider the properties of the fluid in the wetting and drying mechanisms.

Research Significance

SALTS
SRA
→
Fluid Properties
Viscosity, Surface Tension, RH_{EQ}

Transport Processes
Wetting/Drying and Hysteresis, Rate of absorption of Salts and SRAs, DOS
→
DURABILITY
TRANSPORT MODELING
TRANSPORT TESTING
SPECIFICATIONS

Research Objectives

1. Show the influence of deicing salts and SRAs on fluid properties in terms of viscosity and surface tension;
2. Show the dependence of viscosity and surface tension on concentration of solute and on temperature;
3. Describe models able to predict viscosity and surface tension when the solution characteristics are known and when some parameters (concentration and temperature) are changed;
4. Show the influence of the properties of solution on drying mechanisms (non-linear moisture diffusion coefficient).

Materials

MORTAR

For desorption test 0.42 w/c mortar with 55% of fine aggregates by volume was used. Cylinders (34 mm of diameter and 50 mm tall) were cast and then cut in thin slices (0.80 ± 0.05 mm) using a water cooled diamond tipped wafer cut saw.

Figure 1: Porous ceramic

POROUS CERAMIC

Additional desorption tests were performed on porous ceramic samples commercially available (See *Figure 1*) with absorption of 22.5% by mass. Prior to testing, both mortar and ceramic samples were submerged for 24 hours in different solutions.

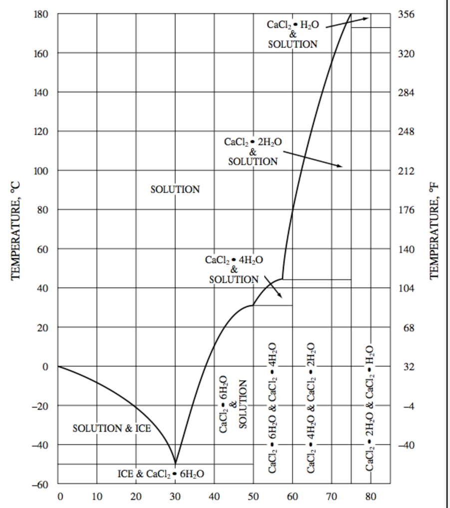


Figure 2: Phase diagram of calcium chloride solution

SALTS

Three common deicing salts were analyzed considering the following ranges of mass concentrations: 0.70% - 23% for NaCl, 0.96% - 32% $CaCl_2$ and 0.90% - 30% for $MgCl_2$.

SRAs

Two commercially available shrinkage reducing admixtures (SRA) were analyzed: SRA 575 (SRA_1) and TETRAGUARD® AS20 (SRA_2) both from BASF Chemical Construction. Water-SRA solutions were prepared in the range 0.5% - 100% by mass.

Methods

Three type of tests were performed in this study:

- Viscosity measurements (using an Anton-Parr rheometer, model Physica MCR 301);
- Surface tension measurements (using a Du Noüy Ring tensiometer, *Figure 4*);
- Desorption analysis using an automated sorption-desorption analyzer (TGA Q5000, *Figure 3*).

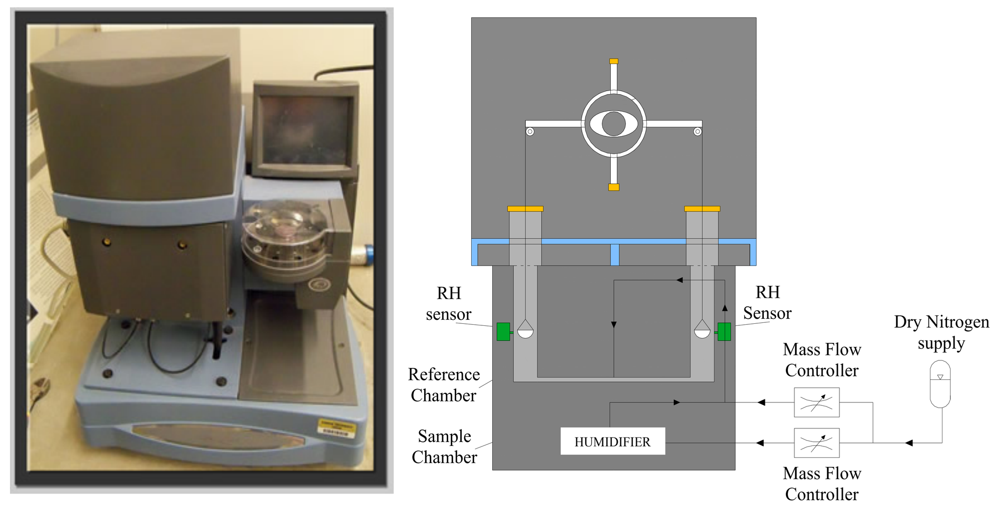


Figure 3: Automatic Desorption/Sorption analyzer and its schematic

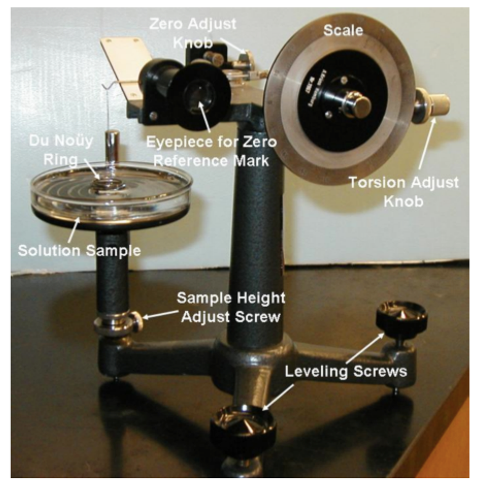
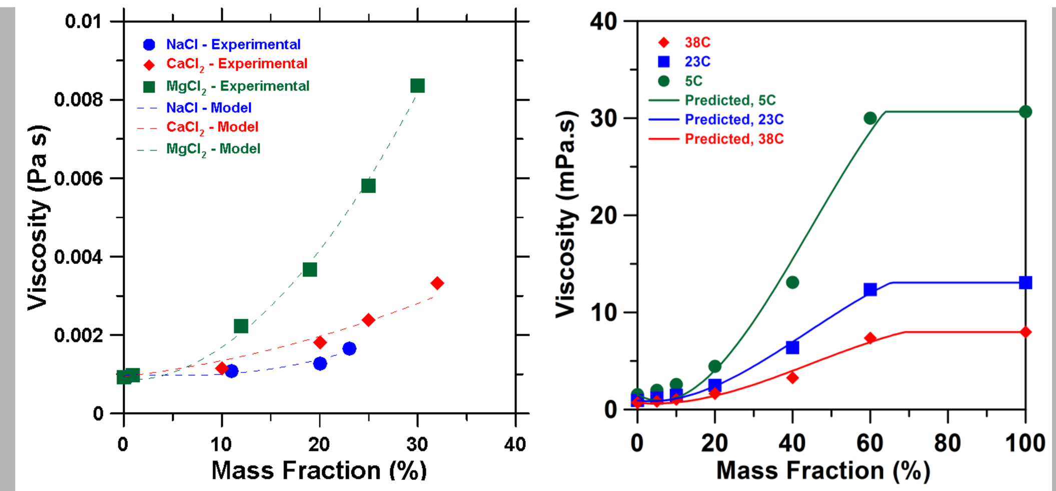


Figure 4: Du Noüy Ring tensiometer (Pease et al. 2005)

Modeling and Results

VISCOSITY 1 2 3

CONCENTRATION

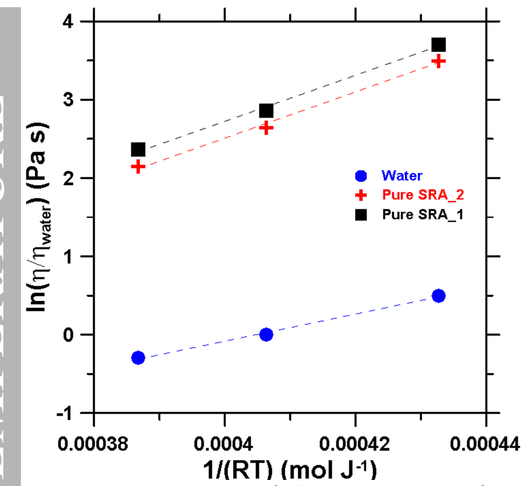


(a) $\eta = \eta_{water}(1 + C_1 \cdot V_{salt}^{1/2} + C_2 \cdot V_{salt} + C_3 \cdot V_{salt}^2)$

(b) $\eta = \eta_{water} + (\eta_{SRA} - \eta_{water}) \cdot (C_1 V_{SRA} + C_2 V_{SRA}^2 + C_3 V_{SRA}^3)$

Figure 5: Viscosity as function of concentration for a) deicing salt solutions and b) SRA solution

TEMPERATURE



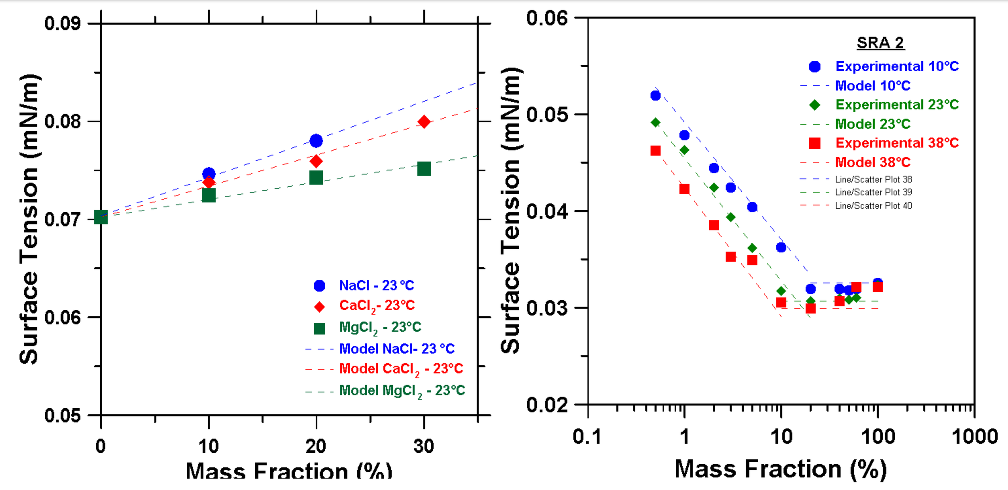
$\eta_{SRA-23} = \eta_{water-23} \cdot \exp\left(-\frac{E_A}{R}\left(\frac{1}{273° + T} - \frac{1}{296°}\right)\right)$

Figure 6: Viscosity as function of temperature for SRA solution

Deicing salts and SRA both lead to an increase in viscosity compared to pure water. Temperature increases cause viscosity to decrease (exponentially for deicing salts and according to an Arrhenius type of law for SRAs).

SURFACE TENSION 1 2 3

CONCENTRATION



(a) $\gamma = \gamma_{water} + \frac{\Delta\gamma}{\Delta C} C$

(b) $\gamma = \gamma_{water} - RT\Gamma^m \ln\left(1 + \frac{C}{b}\right)$ for $C \le C_{SRA}$; $\gamma = \gamma_{SRA}$ for $C > C_{SRA}$

Figure 7: Surface tension as function of concentration for a) deicing salt solutions and b) SRA solution

TEMPERATURE

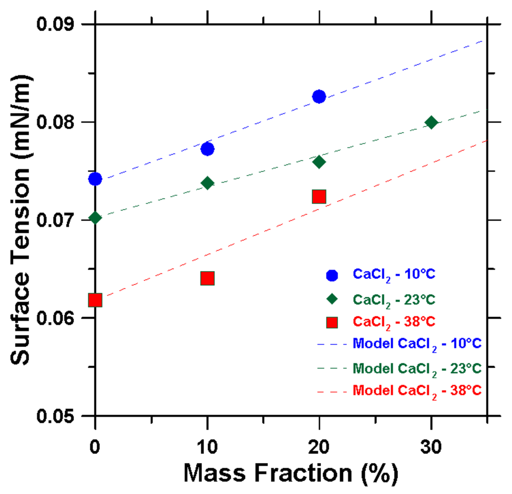


Figure 8: Surface Tension of deicing salts as function of temperature

Surface tension of **deicing salt solutions** increases linearly with mass concentrations. **SRAs** show a decrease in surface tension following two distinct trends for concentration lower or higher than a critical value C_{crit}. C_{crit} depends on the SRA type and on temperature.

NON-LINEAR MOISTURE DIFFUSION COEFFICIENT 4

The process of drying in cementitious materials is often described by means of the non-linear differential equation developed by Bazant and Najjar:

$$\frac{\partial RH}{\partial t} = \frac{\partial}{\partial x}\left[D_h(RH)\frac{\partial RH}{\partial x}\right]$$

In presence of **deicing salts** the diffusion coefficient (D_h) significantly decreases. The system does not start to dry until the relative humidity goes below RH_{eq} (*Figure 12*).

NON-LINEAR MOISTURE DIFFUSION COEFFICIENT

$$RH < RH_{eq} \quad D_h(RH) = \alpha_h + \beta_h\left[1 - 2^{10^{\gamma_h (RH - RH_{eq})}}\right]$$

$$RH \ge RH_{eq} \quad D_h(RH) = 0$$

Xi et al.

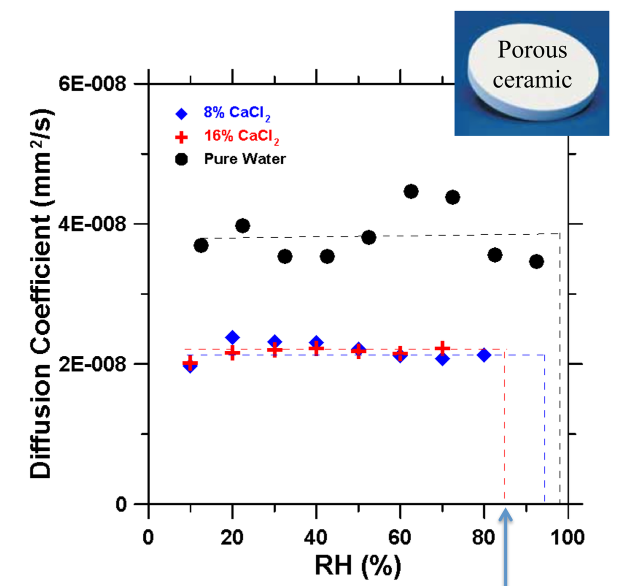


Figure 9: Diffusion coefficient for $CaCl_2$ solutions and pure water measured on porous ceramic

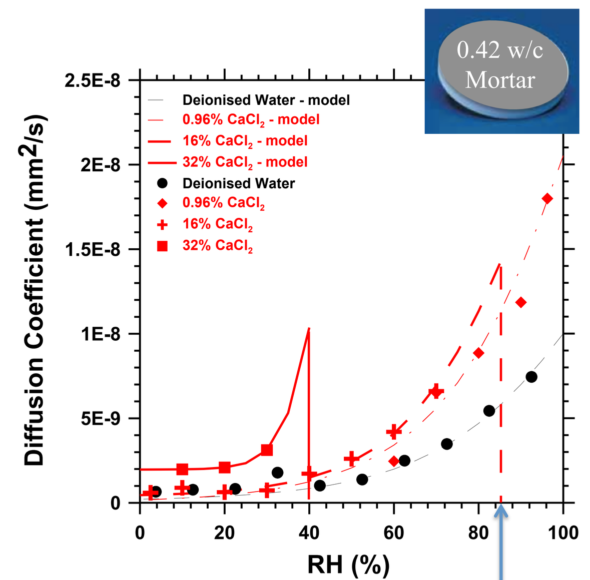
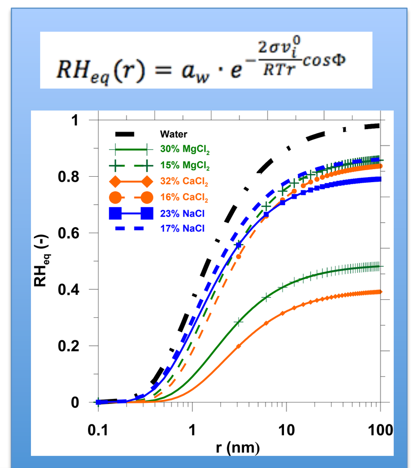


Figure 10: Diffusion coefficient for $CaCl_2$ solutions and pure water measured on mortar sample

RH_{eq} = f (fluid properties, r)

$$RH_{eq}(r) = a_w \cdot e^{-\frac{2\gamma v^0}{rRT}\cos\Phi}$$



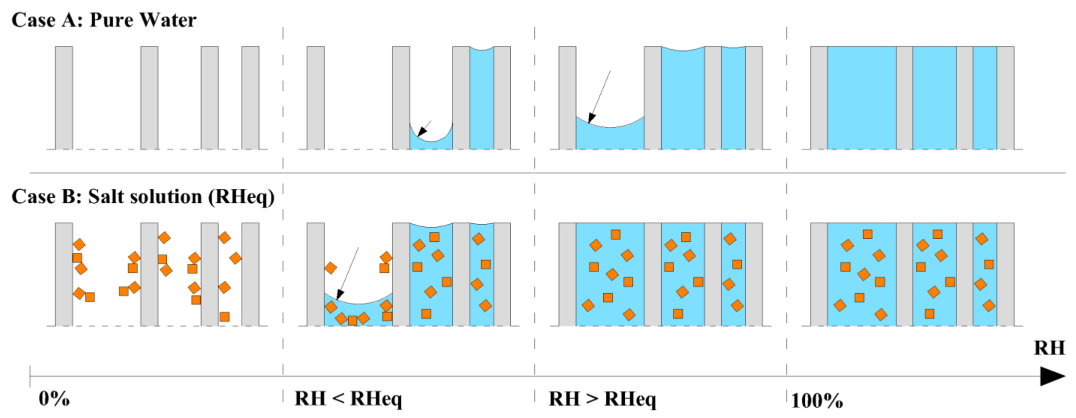


Figure 11: Schematic of the mechanism of drying in the case of pure water and salt solutions

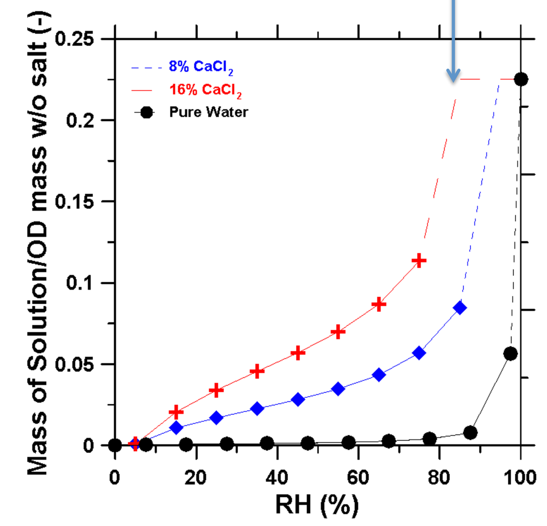


Figure 12: Desorption curves for ceramic samples saturated in $CaCl_2$ solutions and pure water

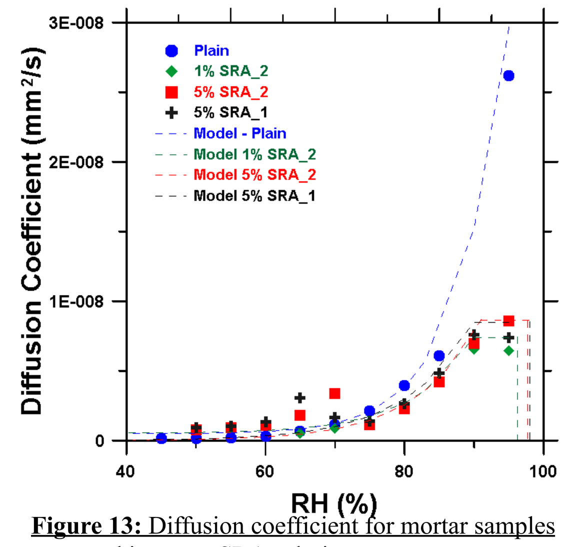


Figure 13: Diffusion coefficient for mortar samples saturated in water-SRA solutions

In presence of **SRA** the diffusion coefficient at high relative humidity is lower than the case of pure water. The diffusion-RH curves show a shift towards higher values of relative humidity in presence of SRA.

In practice, both systems containing SRAs and deicing salts will likely have an higher DOS that those saturated with pure water.

Conclusions

- The presence of deicing salts and of SRAs alters fluid properties. When adding deicing salts, viscosity and surface tension of the fluid increases. In presence of SRAs instead, the viscosity of the fluid increases while the surface tension decreases.
- Several models were successfully fit to experimental data, proving the possibility to predict the variation of fluid properties if the characteristics of the additions (deicing salts or SRAs) are known;
- Fluid properties are strongly related to the drying mechanism. The presence of deicing salts lead to a decrease of Rh_{eq} and consequently to a lower diffusion coefficient. Similarly, it is the case of SRAs. Both systems will likely have an higher DOS in practice than systems saturated with pure water.