

## MEASURING CRYSTALLIZATION PRESSURE: CAN CORRENS' EXPERIMENT BE REPEATED?

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### Abstract

A novel set up for the measurement of crystallization pressure of potassium alum (potassium and aluminium sulfate dodecahydrate,  $KAl(SO_4)_2 \cdot 12H_2O$ ) in its supersaturated solutions under a constant load is here proposed, along the lines of the early Correns and Steinborn's experiment, in 1939. Some preliminary data on the characterisation (stability, pH, density) of supersaturated solutions in the  $c/c_s$  range between 1.0 and 1.5, which would eventually be useful to shed some more light on the complex chemistry of aluminium solutions, are also presented.

**Keywords:** crystallization pressure, salt, Correns, thermodynamics

### 1. Introduction

Salt crystallization is considered to be the most relevant degradation mechanism affecting the natural stone as well as most of mineral building materials. Herodotus seemed to have a clue of it when writing his Histories, nearly two and a half millennia ago. However, salt by itself is not damaging. It requires the presence of water for its aggressiveness to become evident (Charola and Herodotus 2000).

The wet or humid growth of salts in the porosity and the consequent induced stresses can thus overcome the tensile strength of a building material, turning it into a powder (Doehne and Price 2010; Scherer 1999, 2004; Espinosa-Marzal and Scherer 2010). Such stresses are directly related to crystallization pressure. This is defined as the pressure necessary for the stability of a crystal in its supersaturated solution.

One of the first authors treating the thermodynamics of such a phenomenon is C.W. Correns in an attempt to explain the schistosity developed in schists under the influence of linear pressure (Correns and Steinborn 1939; Correns 1949; Flatt *et al.* 2007). He derived the first equation for quantifying the pressure of a crystal immersed in its aqueous supersaturated solution and subjected to a constant load:  $P = RT \ln(c/c_s)/v$ , where  $P$  is the crystallization pressure,  $R$  is the gas constant,  $T$  is the temperature,  $c_s$  is the concentration of the substance when saturated,  $c$  is the actual concentration and  $v$  is the molar volume of the substance. However, this equation neglects some aspects of real highly concentrated solutions, being only valid for systems with monomolecular solutes (Flatt *et al.* 2007).

Besides, Correns' equation is oddly in agreement with the results of an ingenious experiment. In fact, Correns designed a sensitive pressure balance (*Druckwaage*) in which a crystal was submerged in its stirred supersaturated solution. The crystal was loaded by an arm featuring an aluminium pushrod covered with a glass socket at the end in contact with the solution and the crystal. On the other side, such a pushrod was

connected to a bar that moved a mirror device that reflected a light beam on a scale. In this apparatus (and in a slightly modified version), a 1  $\mu\text{m}$  growth of the crystal corresponded to an approximate 20 mm reading on the scale (Correns 1949). It is still an open question how Correns obtained such a good agreement between the measured crystallization pressure and the one calculated with a partially inadequate equation (Flatt *et al.* 2007).

At the same time, Correns observed that the occurrence of the growth and its extent depend on the material used for the coverage of the pushrod. Therefore, the following condition of interfacial tensions (which he called “phase-boundary forces”) must be satisfied:  $\sigma_{ac} > \sigma_{bc} + \sigma_{ab}$ , where a is the crystal, b is the solution and c is the support.

The aim of the research described in this paper is to re-examine this experiment, with a more modern experimental way, nevertheless following the main lines of the one Correns conducted. In contrast to other recent attempts to measure crystallization pressure (Desarnaud 2009), we stick to potassium alum (potassium and aluminium sulfate dodecahydrate,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) as Correns did (probably because he acknowledged alum’s ability to produce very good monocrystals). The reason for this is that this salt appears to have a much-reduced risk of nucleation, which is a key feature for these experiments.

Commercial crystals of pure potassium alum (with orientation accuracy of the (111) plane of less than  $1^\circ$  and less than  $0.1^\circ$ ) were characterized by optical profilometry to ensure the absence of asperities on the surface that can give rise to experimental artifacts (Flatt *et al.* 2007). Density and pH measurements of supersaturated alum solutions were also carried out.

With these pre-requisites for conducting proper experiments being filled, we are proceeding to setting up the experimental devices for measuring crystallization pressure.

## 2. Experimental

### 2.1 Crystals of potassium alum and product used

Five 5 (l)  $\times$  5 (w)  $\times$  1 (d) mm<sup>3</sup> crystals of pure (grade: 99+%) potassium alum were purchased from MaTecK GmbH (Jülich, Germany). Their declared polishing roughness is  $< 0.03 \mu\text{m}$ . Three of them are with  $1^\circ$  orientation accuracy of the (111) plane whereas two of them are with  $0.1^\circ$  orientation accuracy of the same plane.

Pure (ACS Reag. Ph. Eur, Assay 99.0% – 100.5%) potassium alum was purchased from Merck KGaA (Damstadt, Germany) and used (with demineralised water) for the preparation of the supersaturated solutions.

### 2.2 pH measurements

A SevenMulti pH meter by Mettler-Toledo GmbH (Greifensee, Switzerland) equipped with a Mettler-Toledo InLab Experto Pro pH combination polymer electrode was used for the measurements of pH of solutions with supersaturation in the range of  $c/c_s$  between 1.0 and 1.4. The electrode mounts a temperature sensor, too. The pH meter was linearly calibrated with three buffer solutions purchased from Fluka (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) at pH values of 1.0, 2.00, 3.00 (the three of them at  $20^\circ\text{C}$ ).

### 2.3 Density

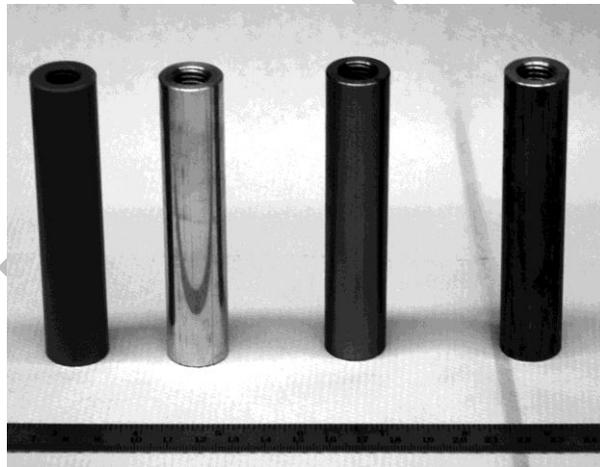
Density measurements of solution with supersaturation in the range of  $c/c_s$  between 1.0 and 1.3 were obtained at 23.0(5) °C by weighing precise volumes of solution with an analytical balance. For this purpose, a MS204S analytical balance by Mettler-Toledo and an Acura 835 automatic pipette by Socorex Isba SA (Ecublens, Switzerland) with a precision of 0.01 mL were employed.

#### 2.4 Optical profilometry

A Sensofar P Lu Neox (Sensofar-Tech, S.L., Terrassa, Spain) 3D optical profilometer was used for the topographic characterisation of the purchased potassium alum crystals. Data acquisition was carried out with SensoSCAN (Sensofar-Tech, S.L.) software. The data processing and profile extraction were carried out with SensoMAP (Digital Surf, Besancon, France) software. All the measurements were performed using the confocal configuration with 5× and 20× objectives.

#### 2.5 Proposed setup for a new crystallization pressure experiment

Cylindrical pushrods of four different materials (stainless steel, PVC, brass and aluminium) were produced with a screw thread for the connection to a 10 kN load cell (see Figure 1). Likewise Correns' experiment, these pushrods will be used to maintain an alum crystal under load in its supersaturated solution.



**Figure 1.** The four pushrods in different materials (from left to right: PVC, aluminium, stainless steel, brass) that will be employed for the new setup of a crystallization pressure experiment. It is well visible the thread for the connection of the upper part to a load cell for a universal testing machine.

The next steps for the setup of the final experiment on the five commercial potassium alum crystals will be the following ones:

- 1) Laboratory made crystals of potassium alum will be weighed and characterized before and after the immersion in supersaturated solutions to provide further information about the stability of such systems;

- 2) The bottom side of some of the pushrods will be finely polished with abrasive papers up to 4000 mesh/in and such a side will be coated with a thin but homogenous layer of glass (or silica). The possibility of using a sol-gel synthesis (De Sanctis *et al.* 1990) for such a purpose is under investigation. The same coating would also be characterized by optical profilometry;
- 3) A possible alternative to a glass (or silica) coating would be the use of other polymeric materials that do not nucleate potassium alum;
- 4) A stirring and constant temperature apparatus for the supersaturated solutions will be developed;
- 5) Tests of nucleation of laboratory made crystals of potassium alum in their supersaturated solutions and under the load applied by coated and uncoated pushrod will be carried out. A small load cell connected to a universal testing machine will ensure the constant load and monitor the displacement from crystallization pressure.

It is quite evident that the laboratory design of the pushrod represents the main challenge of the experimental setup.

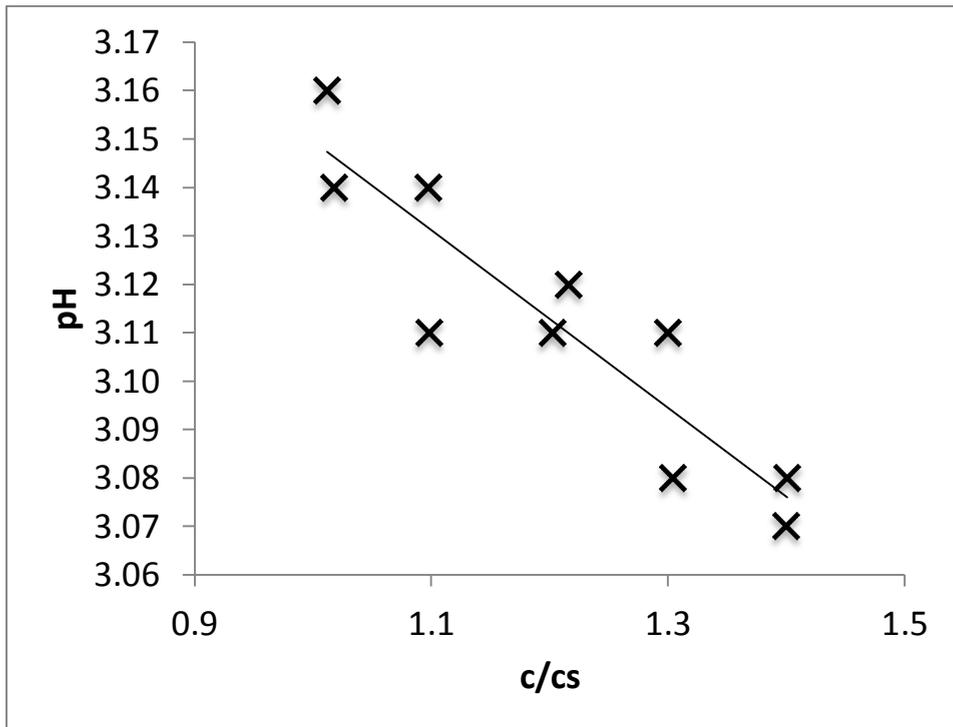
### 3. Results and Discussion

#### 3.1 Stability of the solutions

We observed that supersaturated potassium alum solutions (in the range of  $c/c_s$  between 1.0 and 1.5) can easily remain on the table of the laboratory for long periods of time (from 12 hours to several days), even with minor perturbations. This is an important condition that other systems that have been considered for crystallization pressure measurements do not fulfil. Indeed, spontaneous nucleation of additional crystals would consume supersaturation. This prevents from sustaining high supersaturation needed to generate meaningful pressures. Therefore, on this front at least, the experiment by Correns and Steinborn remains reliable.

#### 3.2 pH measurements

The pH of solutions of potassium alum with supersaturation ranging from 1.0 to 1.4 was measured at a temperature of 22.0(3) °C. This ranged from 3.14 to 3.08, showing a quite clear (although small) decrease, according to the following empirical linear equation:  $\text{pH} = -0.1837(c/c_s) + 3.3333$  ( $R^2 = 0.82938$ ). The results are also shown in the graph in Figure 2. This pH shift could constitute one way of testing the reliability of thermodynamic models intended to describe alum solutions. Indeed, the chemistry of low pH aluminium solutions is complex and proper description of it is crucial to properly quantify supersaturation.

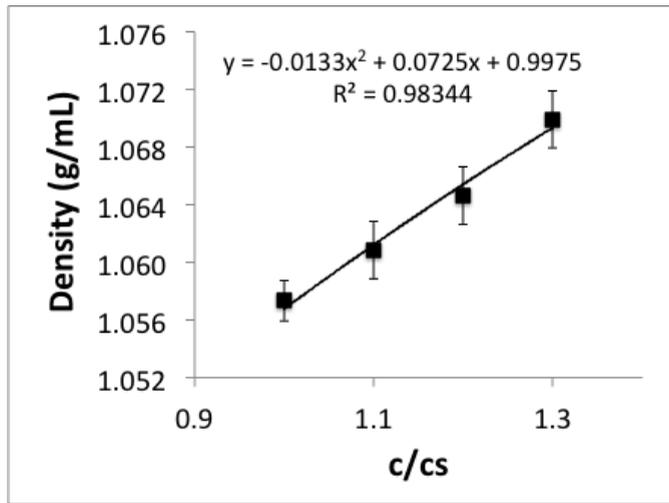


**Figure 2.** pH values of potassium alum supersaturated solutions measured at 22.0(3) °C. A small but meaningful linear decrease of this is visible.

### 3.3 Density measurements

The density of solutions of potassium alum with supersaturation ranging from 1.0 to 1.3 was measured at a temperature of 23.0(5) °C. This ranged from 3.14 to 3.08, showing an increase that can be best fitted by a quadratic equation. The ordinate at the origin of this regression is forced to the density of pure water at 23°C, 0.9975412 g/mL (from Lide 2011). The results are shown in the graph in Figure 3.

This also constitutes useful data to confront predictions of models for the thermodynamics of potassium alum solutions. Indeed, this pH decrease points to the ionic speciation and formation of alumina-hydroxy complexes. These impact the activity of alum in solution and change the thermodynamic supersaturation at a given solution concentration. As Correns expressed supersaturation in terms of concentration, understanding ion speciation would allow recovering the thermodynamic supersaturation needed in the equation of crystallization pressure.



**Figure 3.** Density values of potassium alum supersaturated solutions, measured at 23.0(5) °C. The data are best fitted by the shown empirical equation and forced at the ordinate of the origin of the regression line to the standard density of water at 23 °C (Lide 2011).

### 3.4 Topographic characterisation

The topographic characterisation by optical profilometry on the commercial potassium alum crystals showed an average profile roughness parameter (according to the definitions reported in the ISO 4287 standard),  $R_a$ , between 0.03 and 0.06  $\mu\text{m}$  (the uncertainty of these values is on the last figure) and a root mean square profile roughness parameter (also according to what defined in the ISO 4287 standard),  $R_q$ , between 0.04 and 0.08  $\mu\text{m}$  (the uncertainty of these values is on the last figure). This is in the same order of magnitude of what declared by the manufacturer.

No big differences between the crystals with 1° orientation accuracy of the (111) plane and the ones with 0.1° orientation accuracy were recorded.

## 4. Conclusions

We presented some preliminary data on supersaturated potassium alum solutions for the set up of a new crystallization pressure experiment. This will be probably based on the use of a pushrod connected to the loading cell of a universal testing machine and commercial potassium alum crystals.

Finally, the results of this work will help to understand the original experiment by Correns and Steinborn. A very important observation was the long-term stability of supersaturation potassium alum solutions, including when subject to stimuli (as stirring). This together with crystal topology and solution characterization should provide a reliable way for the direct measurement of crystallization pressure of crystals under load in their supersaturated solutions.

## Acknowledgements

The help of Clément Cremmel from the Laboratory for Surface Science and Technology, D-MATL, ETH Zürich is kindly acknowledged for the profilometry characterisation.

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