

Thermal analysis of the chemical weathering of chalk stone materials

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Crystallization of soluble salts in the building materials, is considered today one of the most important decay process. The soluble salts are responsible for the crystallization process within the pores causing the stone damage. By DSC techniques is possible to detect the soluble salts arising from the chalk stone degradation, because the soluble salts are usually hydrated, so they undergo changes at low temperatures, less than 100 °C. Also, the sulphates, as the most aggressive salts undergo phase transition under 600 °C. Taking into account the degradation temperature of soluble salts, in this paper it has been identified by DSC techniques: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, Na_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Can be observed that the Mg and Na sulphates are present in the chalk material, both in salt efflorescences and scarcely in patinas and crusts.

(Received March 25, 2013; accepted July 11, 2013)

Keywords: Thermal analysis, Chalk stone, Weathering

1. Introduction

Salt attack is the main cause for decay of masonry materials such as stone, brick and mortar due to the soluble salts forming crystals within the pores of the masonry, patinas and crusts of building stones [1-3].

Sodium chloride (NaCl), sodium sulphate (Na_2SO_4), calcium chloride (CaCl_2) and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and calcium sulphate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are commonly found causing salt attack problems in different walls [4].

Some salts have water in the crystal structure and from this cause they may exist in several different hydration states. These include sodium sulphate, which can exist as Na_2SO_4 or as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and is a particularly damaging salt [5].

Sodium chloride and sodium sulfate are two of the most damaging salts for porous materials. The former is characterized by a single crystal phase, halite (NaCl), while the latter has different crystal phases: thenardite (Na_2SO_4), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) [6,7].

On the other hand, the only naturally occurring members of the $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ series are epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 51 wt% water), hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, 47 wt% water) and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$, 13 wt% water) [8-11].

Epsomite transforms readily to hexahydrate by loss of extra-polyhedral water; this transition is reversible and occurs at 50-55% relative humidity (RH) at 298 K and at lower temperatures as the activity of water diminishes [12]. Both magnesium and sodium sulfates are used for

stone accelerated decay testing because their crystallization is highly damaging [13,14].

In this paper, we have studied differences in crystallization behavior of sodium and magnesium sulfates. These two salts are extensively found in porous building stones, as chalk stone from Basarabi Churches.

Both salts are extremely damaging and show completely different crystallization patterns, in order to identify possible solutions to reduce damage caused by such sulfates [15].

2. Experimental

2.1. Methods

Thermal analysis have been performed on a Mettler Toledo Thermo-gravimetric Analyzer TGA / SDTA 823°, in the range of temperature 25 °C to 1000 °C, in dynamic air, with 60 ml/min, at a heating rate of 10 °C/min, in alumina crucible, for all the samples, of 10mg to 12mg. DSC was performed on a Mettler-Toledo Instrument DSC 823°. Samples (10-16 mg) were loaded into sealed aluminum pans with lids and heated to 600°C at a heating rate of 10 °C/min in oxygen flux (100 ml/min). The empty aluminum pan was used as reference and the heat flow between the sample and reference pans was recorded. Measurements were repeated at least three times. The peak temperature of melting of each sample and the heat of fusion were determined from the DSC traces by thermal analysis program.

The samples prelevated from Basarabi Church (samples collected from the exterior of the monument)

without any value for this church. Samples were obtained by taking a minimum part of the archaeological object, with the aid of a scalpel with diamond tip, to minimize any damage and contamination. These samples were ground in an agate mortar and pestle before analyses, in order to reduce the particle size and to secure homogeneity.

3. Results

In this paper we studied some samples prelevated from Basarabi chalk churches, now in an advanced state of degradation. Discovered in 1957, the Basarabi - Murfatlar Ensemble is one of the most impressive archaeological sites of Europe, consisting of churches dated from 9th - 11th century. Situated in the cliff of a chalk stone hill, this ensemble is built from amorphous calcium carbonate and very sensitive to humidity, frost, salts etc. Usually, calcium carbonate is occurring as limestone, chalk and biomaterials. It is known that calcite dissolution is affected by the presence of Mg^{2+} and Na^+ sulphates. Processes as crystallization and dissolution of salts take place, new pores being generated in a self-acceleratory process through some stone micro-cracks. These salts have a significant danger to cultural heritage, generally.

In building materials, the salts can enter porous wall in general only when dissolved in water. Water can enter either as a liquid or vapour. In the liquid state, three mechanisms can be applied:

1. Anhydrites salt action in pores, transported by capillary rise, strongly related of the amount of crystalline water they contain, can get easily deep into mortar.

2. Into second group belong salts which crystals contain crystalline water ($CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 2H_2O$ etc.). These salts may lose crystalline water with the decrease of relative humidity in the air, forming anhydrite form, and with the increasing humidity they recrystallize. Recrystallization is accompanied with the development of hydration pressures.

3. Another group is formed by the salts which seldom crystallize. These salts are hygroscopic; they can easily absorb water from the air, thus causing long-term wetness of the material.

Depending on the balance between the evaporation rate and the supply of salts into the structure, few cases can be observed:

- if the evaporation is slower than the salt solution supply, salts precipitate on building surface, forming so-called efflorescence.

- if the evaporation rate predominates the supply of the salt solution from the material, crystallization take place inside the matter causing damage to the material.

- the most harmful is subflorescence, which takes place when the evaporation rate and the supply of the salt solution are in an approximate equilibrium and salts crystallize beneath the surface, which may lead to bulging, scaling and spalling of the whole outer layer, causing serious damage to the material.

By DSC techniques is important to detect the soluble salts arising from the degradation, because the soluble salts are usually hydrated, so they undergo changes at low temperatures, less than 100 °C. Also, the sulphates, nitrates and phosphates undergo phase transition under 600 °C. The DSC technique gives additional information about the sample features since the type of salt or salts present can be identified in samples with a good peak separation as a function of the temperature of the processes.

Cooke [17] concluded that sodium sulphate is so damaging because:

- (a) sodium sulphate undergoes a high degree of volume change when hydrated;

- (b) sodium sulphate suffers a decrease of solubility at temperatures above (slow decrease) and below (rapid decrease) 32 - 48 °C;

- (c) sodium sulphate is very soluble, thus a substantial quantity of solid salt is available for crystals to grow when evaporation takes place;

- (d) the needle-shaped nature of sodium sulphate crystals might tend to increase their destructive force due to the crystallization pressure being concentrated over a smaller surface area.

4. Discussion

Analyzed as pure compounds, the sulphates offered the number water molecules, and the main polymorphic forms of them.

Na_2SO_4 , known as thenardite has an endotherm peak at 275 °C, and undergoes a polymorphic transformation; at 897 °C it has another endotherm peak, attributed to thenardite melting (Fig. 1).

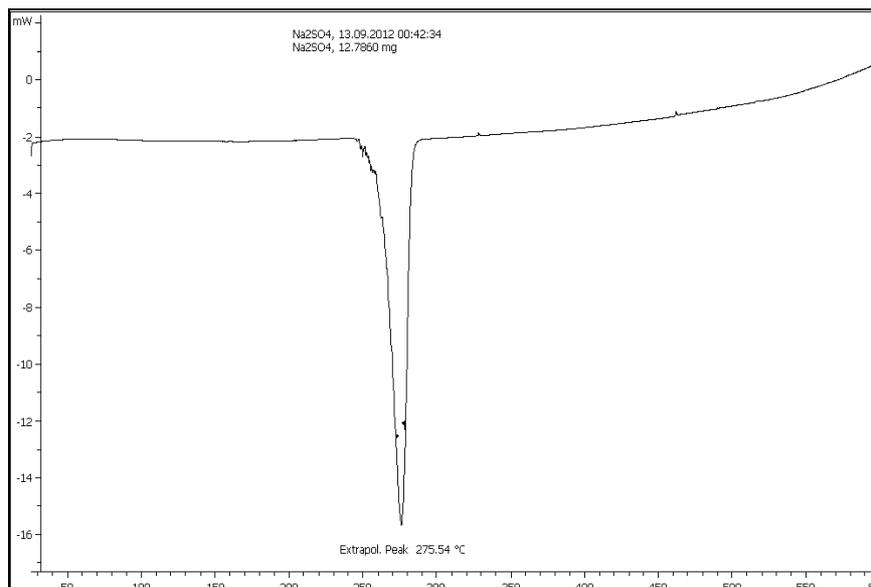


Fig. 1 DSC curve of Na_2SO_4

$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ – known as mirabilite shows endotherm peaks at 40 °C, 91 °C where releases water of

crystallization; and 271 °C another endothermic peak corresponding to anhydrous sodium sulphate (Fig.2).

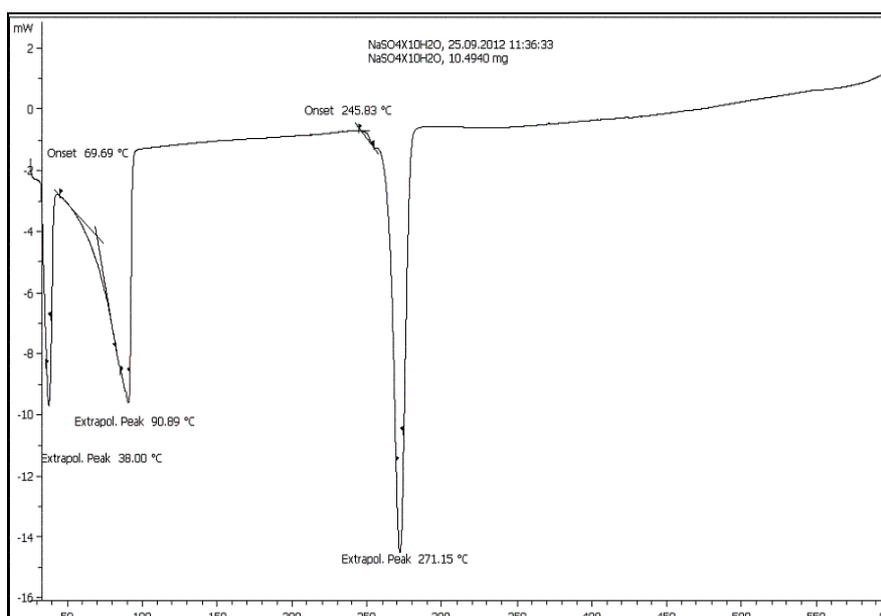


Fig. 2. DSC curve of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

Using this method, we determined that the first phase to form within our porous system was the metastable heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), followed by thenardite (Na_2SO_4).

Anhydrous sodium sulphates (i.e. Na_2SO_4) occur in several five polymorphic forms [18]. Phases I, II and IV are high temperature polymorphs (I > 270 °C and II > 225 °C).

Sodium sulphates can also occur as hydrates: the decahydrate (Mirabilite: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) which is stable below 32.4 °C and the heptahydrate (named, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) which is metastable below 24 °C. Anhydrous

Na_2SO_4 (III and V) can form directly upon evaporation of a sodium sulfate solution above 32.4 °C [18] but also by dehydration of mirabilite [13]. Hydrated Na_2SO_4 can form upon evaporation of a sodium sulfate solution below 32.4 °C, as well as upon cooling of the same solution. The relationship between the heptahydrate and the decahydrate is not straightforward.

The result of a TGA-DSC experiment performed in air atmosphere with a heating rate of 10 °C/min is typical for all dehydration measurements. The shape of the TGA curve (Fig. 3 and Fig. 4) shows that the mass loss occurs in three steps, each accompanied by a change in DSC signal.

1. The first step occurs at a low temperature 25–55 °C which corresponds to the loss of one water molecule. The negative DSC peak shows that the first dehydration step is an endothermic process. However, the fact that this transition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ already starts at 25 °C and it will slowly convert to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. Between the first and the second step, a melting process occurs at 52.5 °C.

2. The second dehydration step occurs between 60 °C and 265 °C. From the shape of the TGA curve, it can be seen that the second dehydration step consists of at least two dehydration steps:

a. An initial steep decrease in weight loss signal is followed by a more gradual decrease, corresponding to a loss of approximately four water molecules. This suggests that the dehydration of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ proceeds through a $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ intermediate. Under all conditions the TGA curve for dehydration always showed a third mass loss at high temperatures near 275 °C, which indicates that there is still some water present in the material after the second dehydration step.

b. The second dehydration step is accompanied by a negative DSC peak indicating that this transition is also endothermic, as a result of a recrystallization from an amorphous precursor to crystalline MgSO_4 [13].

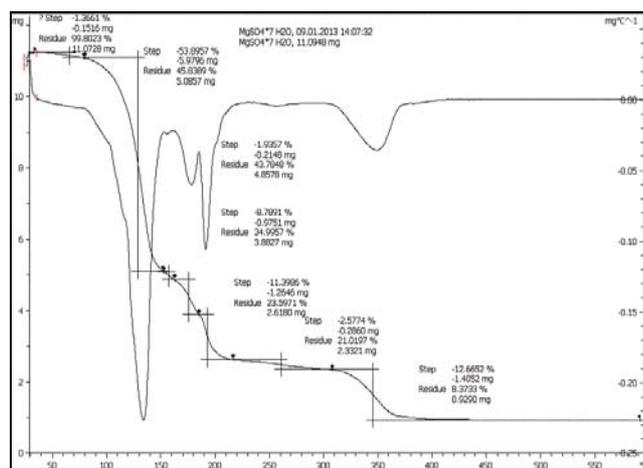


Fig. 3. TGA and DTG curves of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

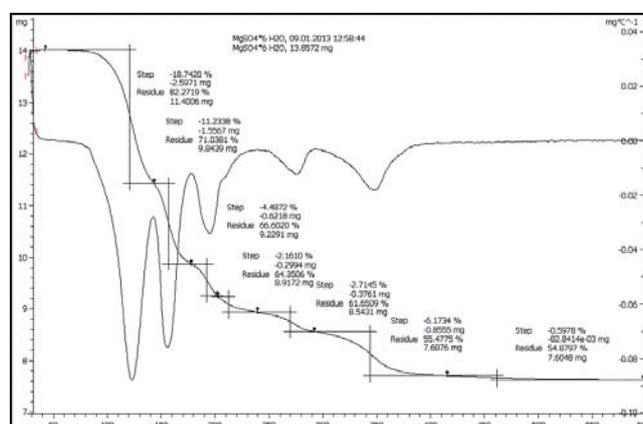


Fig. 4. TGA and DTG curves of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, named Epsomite, have few endothermic peaks at 112, 162 and 177 °C, 1 mol epsomite releases 6 mol H_2O in these stages; 342 °C endotherm, epsomite releases 1 mol H_2O to give MgSO_4 (Fig. 5); 910 °C endotherm, MgSO_4 melts; 1120 °C endotherm MgSO_4 decomposes to MgO and releases SO_3 .

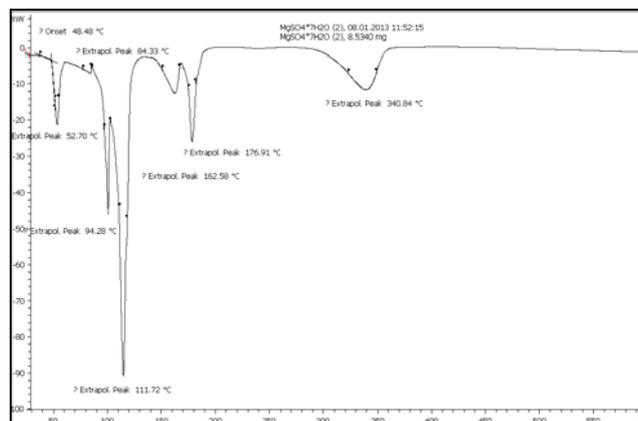


Fig. 5. DSC curve of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ – Hexahydrate, behave analogously to epsomite only in the first phase releases 5 molecules of water of crystallization in several stages 114, 140, 184, 258 and 343 °C endotherm to give MgSO_4 (Fig. 6).

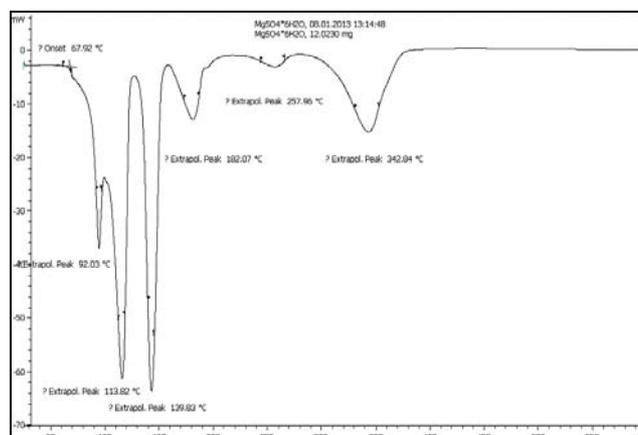


Fig. 6. DSC curve of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$

In Basarabi chalk sample, such magnesium sulphate could be identified in the region 25 - 300 °C, and another peak at 885 °C, assigned to sodium sulphate. Both results could conclude the salts damaging of these monument, due to crystallization, recrystallization repeated processes.

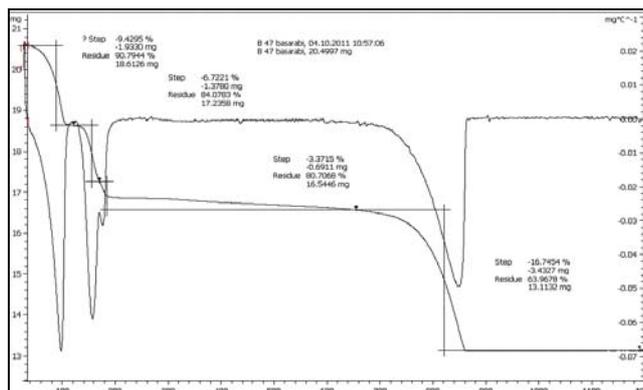


Fig. 7. TGA and DTG curves of Basarabi chalk

5. Conclusions

In this paper, we have studied differences in thermal behavior of sodium and magnesium sulfates. These two salts are extensively found in porous building stones, as chalk stone from Basarabi Churches. Analyzed as pure compounds, the sulphates offered the number of water molecules, and the main polymorphic forms of them.

Acknowledgments

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDS-UEFISCDI, project number 222/2012.

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