THE EFFECTS OF CRYSTALLIZATION OF Na_2SO_4 AND NaCl ON THE WEATHERING OF VARIOUS GRANITES

Rivas, T.; Prieto, B.; Silva, B.
Dpto. Edafología, Fac. Farmacia, Universidad de Santiago, SPAIN

Abstract

Four granites widely used in the construction and restoration of old buildings and monuments in Galicia (N.W. Spain) were subjected to sodium sulphate and sodium chloride crystallization tests in a climatic chamber under diverse sets of temperature and humidity conditions, including those of RILEM. The effects of manually working some of the faces of the test samples, and of the orientation of the granite (taking the horizontal plane of the quarry as reference plane) relative to the direction of absorption of the salt solution, were also examined. Sodium sulphate (deposited as both thenardite and mirabilite) was the most aggressive salt, causing sand disaggregation and scaling. The intensity of sand disaggregation increased with the porosity of the granite and was greatest on the worked faces. Scaling mostly affected sample faces parallel to the horizontal plane of the quarry. Sodium chloride only induced sand disaggregation, which increased in intensity with NaCl concentration, drying temperature, and granite porosity. Experiments with sodium sulphate solution alone showed that hydration of deposited thenardite to mirabilite could not be induced by increasing the humidity, but rather that mirabilite precipitated on the thenardite crystals when fresh sodium sulphate solution was supplied. Once formed, the mirabilite rapidly reverted to thenardite, even at relative humidities above 80%. Similar experiments with solutions of sodium chloride showed that it crystallized as smaller crystals at 60°C than at 20°C, which contradicts the temperature effects observed in the salt crystallization tests.

INTRODUCTION

The most severe and widespread forms of weathering affecting the granite of ancient buildings and monuments in Galicia (N.W. Spain) are sand disaggregation and plaque-shedding and scaling (the separation of plaques, plaquettes or scales of rock from the outer surfaces of ashlars). Sand disaggregation is most severe in coastal areas, while plaque-shedding and scaling typically affect urban buildings, especially the lower parts of the walls.

Previous studies [1, 2, 3] of these forms of weathering have shown them to be associated with the accumulation in the granite surface of certain salts: sodium chloride in the case of sand disaggregation, and sulphates in the case of plaque-shedding and scaling.

In the present work, insight into the mechanisms of these forms of weathering was obtained by reproducing them under controlled conditions, by subjecting four granites widely found in old buildings and monuments in Galicia, or currently used for restoration of these structures, to salt crystallization tests in a climatic chamber. These experiments also allowed determination of the relative susceptibilities of the granites to weathering, and thus of the effects of rock properties on the weathering process.

MATERIALS AND METHODS

Granites

The Galician granites studied were sound samples of *Axeitos* and *Figueiras* granites, and sound and weathered samples of *Roam* granite (RS and RW, respectively) and *Baleante* granite (BS and BW, respectively).

Figueiras is a migmatitic granitoid containing xenoliths and showing signs of flow structure. It comprises medium to coarse grains with marked orientation, in particular of biotite crystals, which tend to lie perpendicular to the horizontal plane of the quarry (taken as the reference plane at the time of sampling). *Roam* comprises fine to medium grains with no apparent mineral orientation. *Baleante* is a leucogranite rich in muscovite and comprises medium to coarse grains oriented parallel to the horizontal plane of the quarry. *Axeitos* is a pink, post-Hercynian granite comprising medium grains, and is fairly homogeneous. Table 1 lists the open porosities of the four granites, and their capillary coefficients in three directions with respect to the horizontal plane of the quarry: orthogonal (A, see Figure 1) and parallel directions (B and C, fig 1).

	Figueiras	Axeitos	RS	RW	BS	BW
OP	4.33	2.05	2.06	7.47	2.83	4.25
CC A	0.0230	0.0024	0.0089	0.0314	0.0091	0.0157
CC B	0.0231	0.0016	0.0085	0.0340	0.0112	0.0198
CC C	0.0205	0.0021	0.0085	0.0330	0.0124	0.0232

Table 1: Open porosity (OP, %) of the four granites used in this study. CC: Capillary coefficient in directions A, B and C ($kg/m^2.sg^{0.5}$); RS: Sound Roan; RW: Weathered Roan; BS: sound Baleante; BW: weathered Baleante.

Salt crystallization tests

Figure 1 summarizes the series of experiments carried out. Three orthogonal sample orientations (A, B and C) were examined in order to determine whether the direction of absorption of the salt solution relative to a reference plane (the horizontal plane of the quarry, which has been shaded in Fig. 1) influenced the durability of the granite. Five samples were tested in each orientation.

Two experiments with 14%(w/w) sodium sulphate solution were performed. In Experiment 1, 5x5x10 cm samples with their rectangular faces rendered impermeable with a plastic resin were stood upright in the salt solution and allowed to absorb it continuously while being subjected to seventy climatic cycles alternating between 20°C and 80% relative humidity (RH) and 40°C and 60% RH. At the end of this experiment, thin sections were cut perpendicular to the evaporation surface and examined by petrographic and fluorescence microscopy; small surface fragments were analysed by scanning electron microscopy with energy-dispersive X-ray detection (SEM-EDAX); and efflorescences were analysed by X-ray diffractometry (XRD).

In Experiment 2, untreated 5x5x5 cm test samples of known mass and porosity were subjected to 60 cycles consisting in 2 h partial immersion of the sample in the salt solution, 16 h at 60°C and 40% RH and 16 h at 20°C and 80% RH (RILEM, 1978). The mass of each test sample and its open porosity were redetermined after every 10 cycles. Included in this experiment were batches of *BS*, *BW* and *Figueiras* granite samples that had had several faces worked by manually chiselling them.

Four experiments were carried out with sodium chloride solution: Experiments 3 and 4 with 4% (w/w) sodium chloride solution, and Experiments 5 and 6 with 16% (w/w) sodium chloride. In each experiment, 5x5x5 cm blocks of known mass and open porosity were fully immersed in the salt solution for 2h and then dried in the climatic chamber, at 20°C and 80% RH in Experiments 4 and 6, or alternating between 60°C and 40% RH and 20°C and 80% RH in Experiments 3 and 5. The mass of each test sample and its open porosity were redetermined after every 5 cycles.

Finally, experiments with a saturated solution of sodium sulphate or 16% solution of sodium chloride were carried out in order to ascertain whether the conditions used in the salt crystallization tests had induced changes in the effloresced salts, such as transformation of sodium sulphate from the anhydrous form, thenardite, to the decahydrate mirabilite, or, in the absence of this transformation and in the case of sodium chloride, changes from one crystal size and/or habit to another.

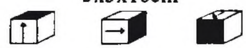
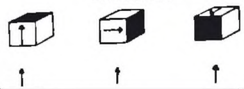
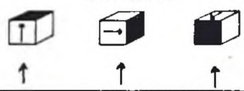
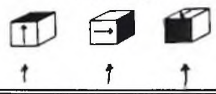
Series	Solution	Granites	Orientation			Chamber conditions			Analysis
			A	B	C	Hours	T	HR%	
1	14% Na_2SO_4	Axeitos Figueiras RS	5x5x10cm 			7 5	20 60	80 40	Study of thin sections by fluorescence microscopy, SEM-EDAX and XRD
2	14% Na_2SO_4 2h partial immersion	RS,RW Figueiras BS,BW	5x5x5cm 			16 16	60 20	40 80	Determination of mass and open porosity after every 10 cycles
3	4% NaCl 2h total immersion	RS,BS,BW Figueiras	5x5x5cm 			20	20	80	Determination of mass and open porosity after every 5 cycles
4	4% NaCl 2h total immersion	RS,BS,BW Figueiras	5x5x5cm 			10 10	60 20	40 80	Determination of mass and open porosity after every 5 cycles
5	16% NaCl 2h total immersion	RS,BS,BW Figueiras	5x5x5cm 			20	20	80	Determination of mass and open porosity after every 5 cycles
6	16% NaCl 2h total immersion	RS,BS,BW Figueiras	5x5x5cm 			10 10	60 20	40 80	Determination of mass and open porosity after every 5 cycles

Figure 1: Details of the salt crystallization tests. The shaded face of the granite blocks corresponds to the horizontal plane of the quarry.

RESULTS

Salt crystallization tests with sodium sulphate

Throughout Experiment 1, sodium sulphate was effloresced on the top surface from which the solution evaporated. On all the samples, both the anhydrous form, thenardite, and the decahydrate, mirabilite, coexisted regardless of the temperature/humidity cycle. At the end of the experiment, sand disaggregation was observed on the tops of all the samples, while the surface contacting the solution remained intact. In addition, scaling was observed on the tops of Axeitos granite samples in Orientation A (see Fig 1) and of Figueiras granite samples in Orientation C. Fluorescence microscopy of thin sections of the samples showed them to have fissures and cracks, which may have been associated with the shedding of the surface layers. In the Axeitos granite, these cracks were parallel to transgranular fissuration that was present in the unweathered rock and that lay parallel to the horizontal plane of the quarry. This pre-existing fissuration may have favoured scaling of the Axeitos granite. In the Figueiras granite, however, scaling occurred perpendicular to the mineral orientation plane.

In Experiment 2, thenardite was deposited on the tops of all the samples during the drying cycle. The test samples underwent more severe weathering than in Experiment 1. The main form of weathering was sand disaggregation, which first occurred in the sixth cycle, and which increased in intensity with the porosity of the granite. Only the BS and BW samples showed scaling, which occurred solely on the faces parallel to the horizontal plane of the quarry.

The apparently homogeneous Roan granite eroded irregularly, its faces developing grooves consistent with its containing bands of rock with different textures or compositions and thus different resistances to the action of the sodium sulphate solution.

The worked Figueiras and BS samples showed signs of sand disaggregation sooner than the unworked samples, and this disaggregation was more intense on the chiselled than the unworked faces. The worked BS sample showed scaling not only at the faces parallel to the horizontal plane of the quarry (and thus parallel to the mineral orientation plane of this granite), but also at the faces perpendicular to this plane.

The gradual deterioration of the samples during the Experiment 2 is reflected by their progressive loss of mass (Fig. 2a). Mass losses were greatest for the most porous granites, RW and Figueiras. The corresponding increases in porosity (Fig. 2b) were not proportional to the mass losses, however, presumably because deterioration (and thus loss of material) occurred mainly at the surface of the granite.

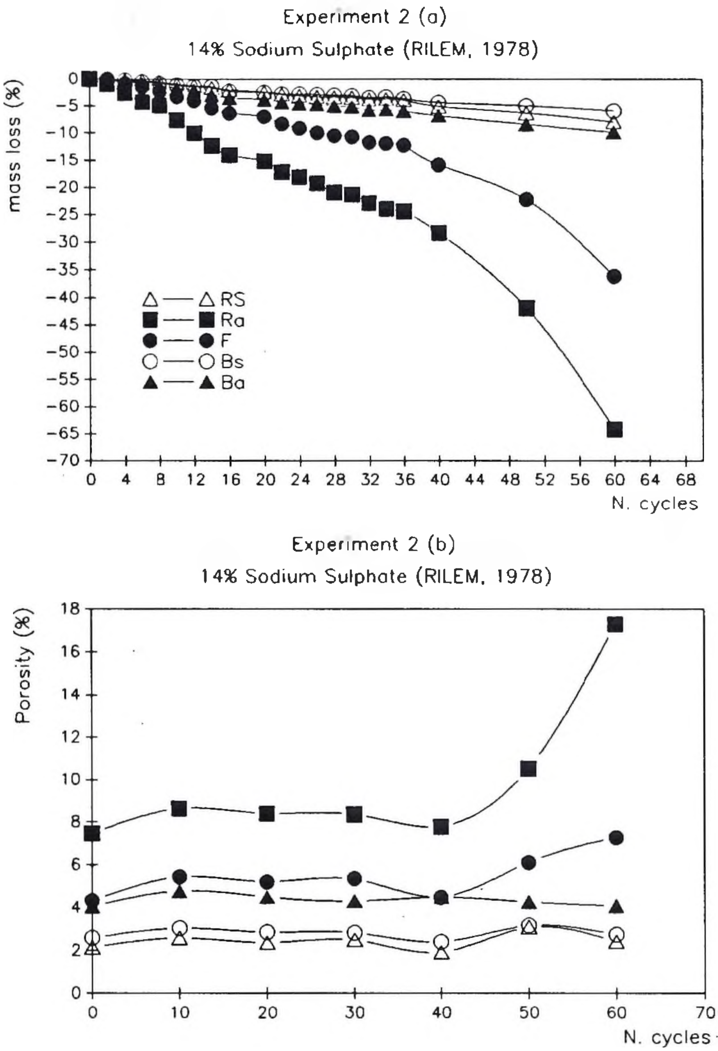


Figure 2: For Experiment 2, (a) the progressive loss of sample mass (%); and (b) the progressive increase in sample porosity (%).

Salt crystallization tests with sodium chloride

In Experiments 3, 4, 5 and 6, efflorescence of sodium chloride was slight and occurred only on the samples subjected to drying cycles at 60°C and 40% RH (Experiments 4 and 6), in which cases the salt was uniformly distributed over all the faces of the test samples.

As regards weathering of the granites, only sand disaggregation was detected, the onset of which occurred after the twentieth cycle. For a given set of temperature and humidity conditions, the mass lost by the samples was greater in the experiments with the 16% NaCl solution than in those with the 4% NaCl solution (cf. results for Experiments 3 and 5 and Experiments 4 and 6 in Fig. 3).

Likewise, for a given concentration of NaCl solution, the mass lost by the samples was greatest for the samples dried at 60°C (cf results for Experiments 3 and 4 and Experiments 5 and 6 in Fig.3). This tendency of deterioration due to sodium chloride to increase with drying temperature has been observed previously [4].

The rate of mass loss was generally greatest for the most porous granites examined, BW and Figueiras. Regardless of the temperature/humidity conditions in the chamber, sample porosity increased concurrently with mass loss (Fig. 4), these increase being greatest for the most porous granites. Once again, however, the increases in porosity were not proportional to the mass losses, which is consistent with the rock's having deteriorated mainly at its surface.

The above results concord with those of other authors [4, 5, 6] in showing that sodium chloride induces less deterioration in the laboratory than is attributed to it on buildings and monuments, and that it is much less aggressive to granite than sodium sulphate.

Tests on salt solutions

Subjecting saturated sodium sulphate solution to the range of temperature and humidity conditions in the climatic chamber did not induce formation of mirabilite from thenardite. Mirabilite crystals were only seen to form (with the characteristic increase in crystal volume) when crystallized thenardite came into contact with fresh sodium sulphate solution. Once formed, the mirabilite rapidly dehydrated to thenardite, even at relative humidities above 80%

In the tests with 16% sodium chloride solution, the salt crystallized in a well developed cubic habit, but as smaller crystals at 60°C than at 20°C. This appears to contradict the results of the salt crystallization tests, in which the deterioration of the granites was greatest for samples exposed to higher temperatures.

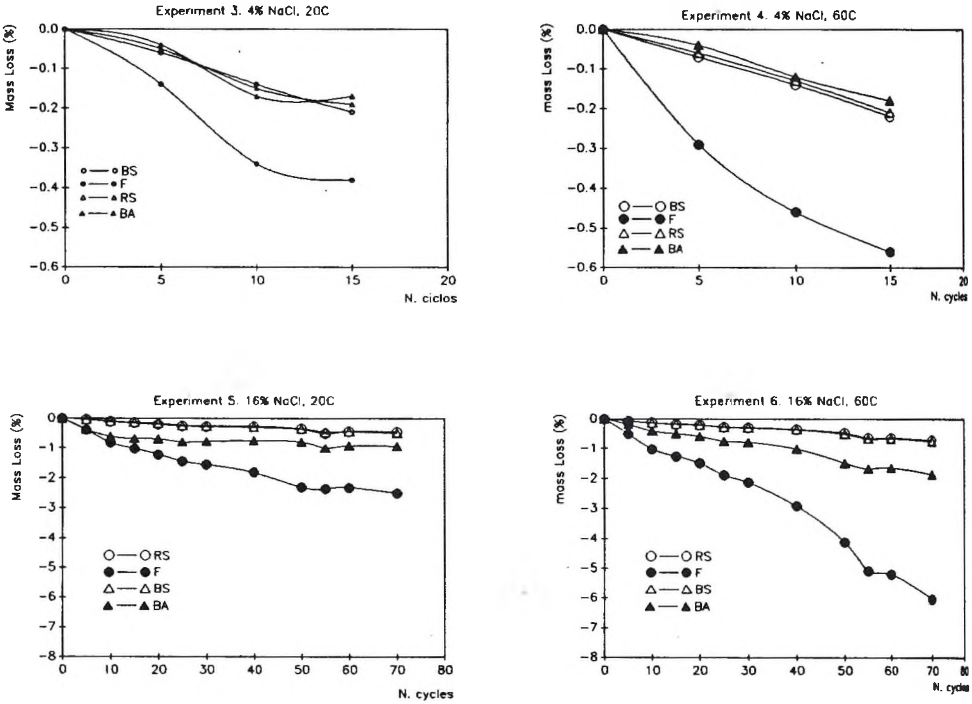


Figure 3: For Experiments 3, 4, 5 and 6, the progressive loss of sample mass (%).

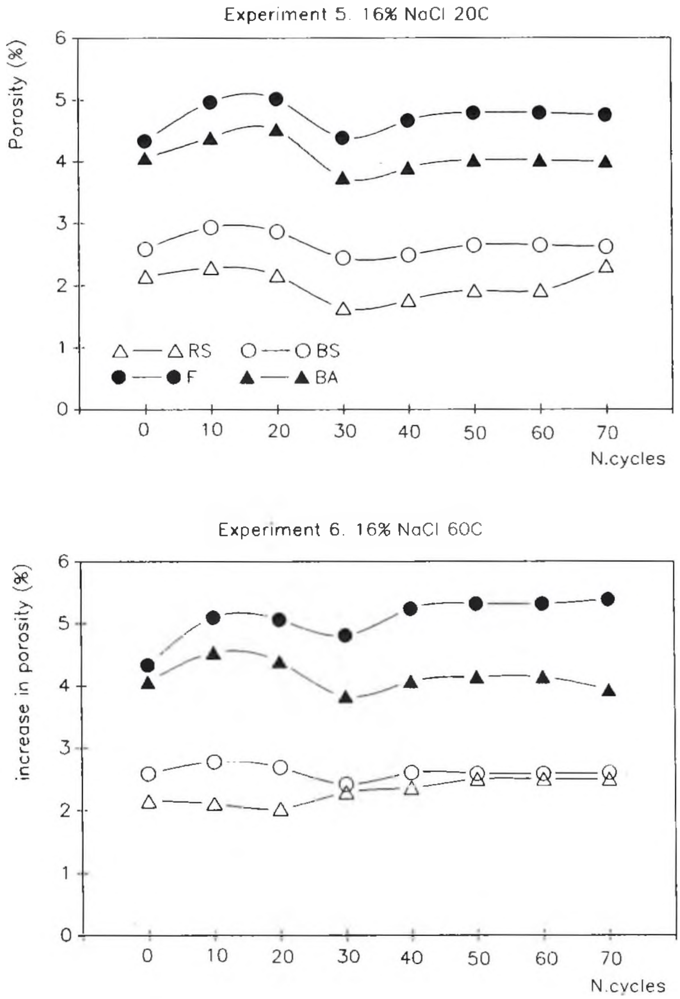


Figure 4: For experiments 5 and 6, the progressive increase in the sample porosity (%).

DISCUSSION

The results of this work confirm that sodium sulphate causes severe deterioration of granite, and is much more aggressive than sodium chloride in this regard. Thus, sodium chloride induced only sand disaggregation in laboratory tests, while sodium sulphate induced both sand disaggregation and scaling on some faces of the test samples.

These results are in keeping with the observed weathering of granitic buildings and monuments in Galicia for which sand disaggregation is associated with the presence of sodium chloride, and scaling (the shedding of small fragments of surface rock) with the presence of significant amounts of SO_4^{2-}, Ca^{2+} and Na^+, which conditions favour the precipitation of sodium sulphate [7,8]. By contrats, the shedding of rock fragments larger than scales (plaques or plaquettes) is linked to the accumulation of calcium sulphate, a much less soluble salt than Na_2SO_4 [8].

The results also show that structural characteristics of the granitic rock, such as the existence of mineral orientation or regularly distributed fissuration, can play a role in the separation of surface rock. Specifically, sodium sulphate may accumulate in existing fissuration parallel to the surface of the granite, which may thus favour deterioration through plaque-shedding parallel to that surface. In the case of the scaling of the granites studied, the existence of such fissuration does not seem to have been the determining factor, since scaling occurred both parallel and perpendicular to the plane of existing fissuration in the Figueiras and Baleante granites. Rather, our results indicate that fissuration parallel to a given surface serves only to increase the intensity of its scaling, which appears to be triggered by the presence of sodium sulphate at the surface, and the evaporation of water from it.

Irregular erosion of the surface rock, characterized by the development of grooves and hollows in a way reminiscent of alveolation, was attributed to the existence of bands of rock with different textures or compositions and thus different resistances to the action of the sodium sulphate solution.

The experiments also showed that working of the granite surface increased the rate and intensity of sand disaggregation.

Although the stability diagrams for thenardite and mirabilite suggest that these sodium sulphates can interconvert under certain temperature and humidity conditions, in the laboratory experiments carried out here the hydration of effloresced thenardite to mirabilite was induced only by the addition of fresh salt solution. Moreover, this transformation was rapidly reversible, even at relative humidities > 80%. Extension of these results for test samples to granitic structures in Galicia suggests that, under the conditions to which they are usually exposed (10-20°C and 60-90% RH), sodium sulphate in the pores of the granite will be in the form of thenardite, regardless of its origin. Absorption of water by capillary action, or through condensation at the surface of the structure, will lead to crystallization of mirabilite, leading to expansion of the salt and, thereby, deterioration of the surrounding rock.

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