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Influence of capillary properties and evaporation on salt weathering of sedimentary rocks

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ABSTRACT: The importance of capillary imbibition and evaporation processes in the decay of stone through salt crystallization is estimated by different experiments adapted from the European standard EN 12370. The various tests consist in slightly modifying the salt (sodium sulphate) supply in the porous network of stones as well as the amount of evaporation and in checking the weathering evolution of the stone. The results show that ionic diffusion and dissolution of pre-existent salts are not efficient enough to imply supersaturation, hence to visually alter the stone. An exterior supply of salt is required. The influence of evaporation is clearly shown when evaporation process could not occur through a side of the sample. In this case, isolated sides are never subjected to weathering, even to simple salt efflorescences.

1 INTRODUCTION

Salts are one of the main destructive agents governing the decay of natural building stones and historic masonry. Salt crystallization is identified in many cases of building stones weathering, from simple harmless efflorescence to alveolar erosion and sometimes contour scaling. Salts and sources of salts from the atmosphere (halite from the seashore; carbonates, nitrates and sulphates from urban pollution), external agents (de-icing salts) or cement repointing mortars may be carried by water, penetrate by capillary imbibition or ionic diffusion into the stone porous network. It is well known that the pore network characteristics, as tortuosity, constrictivity or mean pore radius, can interact in the process of decay of porous media by crystallization of salt as well as the salt chemical nature.

Recent researches on salt crystallization in porous networks, using thermodynamic approach based on Correns (1949) or Pitzer (1991) equations have shown that stone decay due to crystal growth is related to the mechanical stress induced by salt crystallization pressure. This stress is transmitted to the stone by a thin film (2 or 3 nm thick) of supersaturated solution which lays between the growing crystal and the pore walls. This stress is inversely proportional to the mean pore radius, which means that stress is higher in smaller pores (La Iglesia et al. 1997, Scherer 1999, 2004, Nicholson 2001, Flatt, 2002, Benavente et al. 2004, Steiger 2005a,b).

In our study, capillary imbibition is considered as the source of salt penetration into the porous net-

work of sedimentary rocks. We evaluate the influence of evaporation in the crystallization process by running various tests with various evaporation configurations, by isolating 0, 3 or 4 faces of the samples. Five natural building stones were studied regarding to the penetration of mirabilite saturated solution (14%).

2 MATERIALS AND METHODS

2.1 *Materials*

Five different stones were used, three Lutetian limestones and two Fontainebleau sandstones from the Parisian basin (Table 1). The Lutetian limestone has been widely used in the construction of the oldest monuments in Paris and its surroundings (e. g. Notre-Dame-de-Paris). The Fontainebleau sandstone is the main stone used in the Parisian basin for the paved streets, but also for some monuments around Fontainebleau (castle of Fontainebleau, tower of Montlhéry...)

The three lutetian limestones come from Saint-Maximin-sur-Oise (France). The “roche fine” (FL) is a detritic micritic limestone with more than 90% calcite, few grains of quartz and oxides. Its porosity is interparticle and around 36%. It has a very low tensile strength around 1.5 MPa. The “roche franche” (RL) is a limestone with many microfossils (mainly milioles), a few macrofossils (bivalves) and traces of oxides. Its porosity is mainly interparticle but also intraparticle (macrofossils) and ranges from 19 to 21%. Its tensile strength is 3.0 MPa. The

“liais” (LL) is very similar to RL. The fossils are the same, but the intraparticle porosity has been partly filled with calcite precipitation. The porosity is between 13 and 15%. Its tensile strength reaches 4.2 MPa.

The two sandstones come from Moigny-sur-Ecole near Fontainebleau (France) and are called the “grès dur” (HF) and the “grès tendre” (SF). They are both very pure sandstones with porosity around 6% for HF, while it varies for SF from 7 to 13%. The other striking feature is their contrast in tensile strength: 5.2 MPa for HF and 2.5 MPa for SF.

Table 1. Physical parameters of the stones used in the experiments.

| | FL | RL | LL | SF | HF |
|---|------|------|------|------|------|
| Porosity in % | 36.1 | 20.3 | 14.0 | 10.7 | 5.9 |
| Absorption in % | 28.2 | 10.4 | 8.4 | 1.9 | 0.8 |
| Apparent density in g.cm ⁻³ | 1.72 | 2.13 | 2.30 | 2.36 | 2.49 |
| Bulk density in g.cm ⁻³ | 2.69 | 2.67 | 2.67 | 2.64 | 2.64 |
| Capillary coef. in g.m ⁻² .s ^{-1/2} | 1250 | 101 | 34 | 95 | 3 |
| Tensile strength in MPa | 1.5 | 3.0 | 4.2 | 2.5 | 5.2 |

2.2 Methods

The EN 12370 standard test concerning salt crystallization of stone has been widely used and provides us with a large amount of data on the resistance of stone to salt weathering, data which are reviewed by Goudie & Viles (1997). In order to take into account the effect of capillary imbibition and evaporation on salt crystallization process, four different tests adapted from EN 12370 standard were performed on our samples. Using 7x7x7 cm³ samples, four experimental configurations for salt supply and evaporation are chosen for 24 hours crystallization cycles. The different conditions of salt supply are respectively immersion as in standard test, capillary imbibition, remobilisation, and for the last test, both capillary imbibition and remobilisation of the salts in the sample (explained below). For each experimental configuration, the cycle consists in two hours of salt supply, sixteen hours of drying at 105±5°C, and six hours of drying in laboratory conditions (20-25°C, 40-55% RH). All the samples are weighed after each cycle with a precision balance (±0.01 g).

In the immersion test (IMM) the stone samples are immersed in a 16% saturated mirabilite solution as indicated in the EN 12370 standard. For capillary imbibition test (CAPI), the samples are partially immersed (8±3 mm) in a mirabilite saturated solution. In the remobilisation test (REMOB), the samples are immersed before the test during two days in a mirabilite saturated solution, dried until constant weight, and partially immersed (8±3 mm) in demineralised water, i.e. there is no additional salt supply. Finally, the capillary imbibition and remobilisation

test (CAPI&REMOB) is a combination of the last two: the samples are immersed two days in a mirabilite saturated solution before the test, dried until constant weight, and partially immersed (8±3 mm) in a mirabilite saturated solution.

In order to be as close as possible to stone conditions in buildings and monuments (i.e. taking into account the fact that evaporation is not possible through every side of the stone), the same experiments were performed with only one side exposed (or two in case of corner stones) to evaporation, and the others isolated by an aluminium film.

After 7 cycles, one sample in each experiment has been dried at 105±5°C until constant weight. Then new salt supply cycles were performed on these samples. The interest of this experiment is to evaluate the fraction of water in the isolated samples weight evolution. Once the water has entirely evaporated, the only weight variation is due to presence of salt alteration.

3 RESULTS AND DISCUSSION

3.1 Quantification of alteration

Decay of stone is evaluated by the number of the cycle during which the first observable feature of alteration appears. AI as alteration index is used, after each experiment (Table 2), for the quantification of the samples alteration. AI index was defined on three samples for each experiment after 10 cycles for the immersion test and 15 cycles for the other tests. If the sample does not show alteration at the end of an experiment, the value of AI is 10 for the immersion test, and 15 for the other tests.

Table 2. Values of alteration index (AI) for each test: immersion (IMM), capillary imbibition (CAPI), remobilisation (REMOB) and capillary imbibition & remobilisation (CAPI&REMOB).

| | IMM | CAPI | REMOB | CAPI&REMOB |
|---------------------------------|---------|------|---------|------------|
| Non-isolated | | | | |
| LL | 6 | 10 | 15 | 8 |
| RL | 4 | 8 | 15 | 5 |
| FL | 2 | 3 | 15 | 2 |
| SF | 3 | 5 | 15 | 3 |
| HF | 10 | 15 | 15 | 15 |
| 4 faces isolated | | | | |
| LL | 10 | 15 | 15 | 15 |
| RL | 6 | 10 | 15 | 8 |
| FL | 2 | 3 | 15 | 2 |
| SF | 4 | 6 | 15 | 4 |
| HF | 10 | 15 | 15 | 15 |
| 3 faces isolated (corner stone) | | | | |
| FL | No data | 2 | No data | 1 |
| SF | No data | 5 | No data | 3 |

3.2 Brief overview of the stones resistance by the immersion test (IMM)

This test was performed to evaluate the general behaviour of our stones with salt crystallization. HF is the least altered stone by mirabilite crystallization (AI=10). Its weak capillary coefficient as well as its low porosity is certainly responsible for its resistance to salt decay. LL (AI=6) and RL (AI=4) suffer from slight decay, but after several cycles of salt uptake without apparent alteration. In contrast, SF (AI=3) and FL (AI=2) are strongly altered with a high weight loss, mainly due to high capillary coefficient (hence high and rapid salt uptake) as well as low tensile strength.

3.3 Capillary imbibition (CAPI)

The first step to evaluate stone resistance is to consider the importance of salt supply in the samples. Figures 1a, b, c show the relationships between alteration index and three water-supply related properties (porosity, absorption and capillary coefficient) for each stone and three tests (immersion, capillary imbibition and capillary imbibition & remobilisation).

The correlation is better with the log of the capillary coefficient, which confirms that this parameter, and thus this process, is more representative of the salt supply governing salt decay (Benavente et al. 2001, Scherer 2004). During this test, the zones which undergo the more damage from salt are those which are immersed during the salt supply, specially the four lower corners of the samples (Fig. 2).

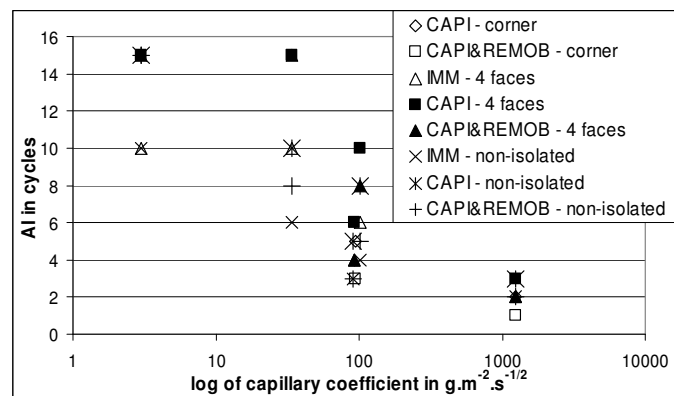


Figure 1a. Correlation between alteration indicator and the log of the capillary coefficient.

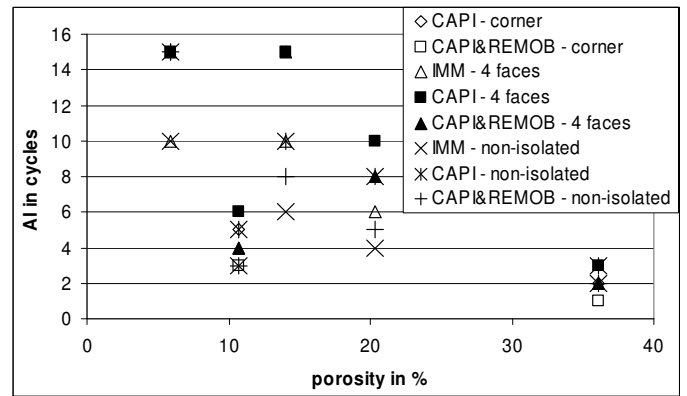


Figure 1b. Correlation between alteration indicator and porosity.

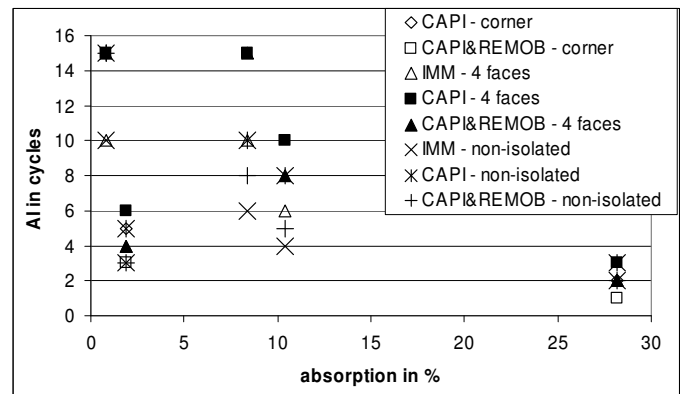


Figure 1c. Correlation between alteration indicator and absorption at atmospheric pressure.



Figure 2. Picture of a 7x7x7 cm³ sample with the four lower corners damaged (SF, capillary imbibition & remobilisation after 7 cycles).

3.4 Capillary imbibition and remobilisation (CAPI&REMOB)

The aim of this experiment is to illustrate the fact that supersaturation is a major process in the stress from crystallization of salt. The damages occur faster in this case than with only capillary imbibition (Figs. 3, 4a, b), which means that higher stresses are induced earlier.

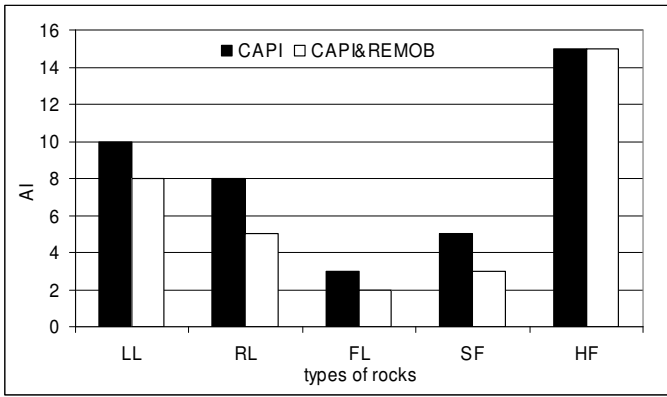


Figure 3. Capillary imbibition experiment vs capillary imbibition and remobilisation for the five types of stones.



Figure 4a. Picture of a $7 \times 7 \times 7 \text{ cm}^3$ sample of FL after 6 cycles of capillary imbibition.



Figure 4b. Picture of a $7 \times 7 \times 7 \text{ cm}^3$ sample of FL after 6 cycles of capillary imbibition & remobilisation.

Comparing both tests, we can notice that the first signs of decay appear approximately for the same proportional weight increase, i.e. with the same proportion of salt in the sample (Figs. 5a, b). This suggests, for a given stone, that the amount of salt supplied by capillary imbibition necessary to imply

decay is roughly constant in the conditions of our experiments.

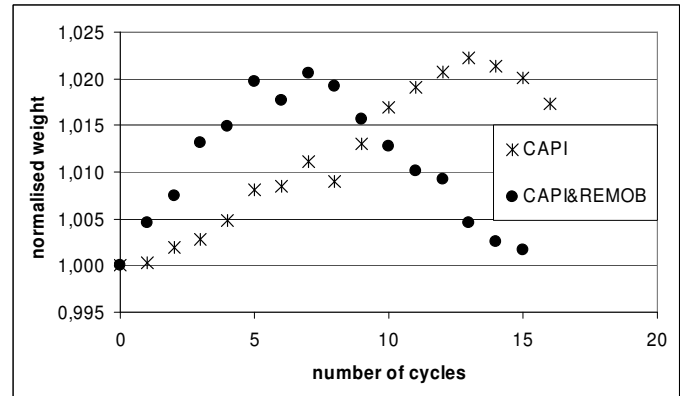


Figure 5a. Evolution of samples weight during capillary imbibition and capillary imbibition & remobilisation for RL (non-isolated samples).

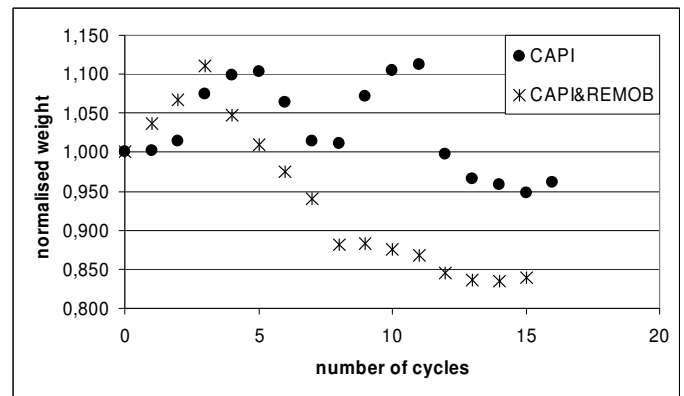


Figure 5b. Evolution of samples weight during capillary imbibition and capillary imbibition & remobilisation for FL (non-isolated samples).

3.5 Consistency of the remobilisation test (REMOB)

In the remobilisation experiment with non-isolated samples, the weight is roughly constant and no damage is visible during the entire experiment (Fig. 6). The weight only decreases for stones with massive efflorescences: this decrease is due to sample manipulations during the cycles. Assuming that the salt quantity is constant in the samples during the cycles, and that the samples are totally dried before weighing, this constant weight means that there is no loss of material during this test.

This means that the water has remobilized the salt in the porous network without involving high enough stresses to damage the sample. It suggests that no damage has been induced by the only presence of salts at the beginning. This is the illustration of the fact that the simple dissolution of thenardite in the solution cannot imply supersaturation with respect to mirabilite, according to the commonly admitted models (Benavente et al. 1999, Rodriguez-Navarro et al. 2000, Flatt 2002).

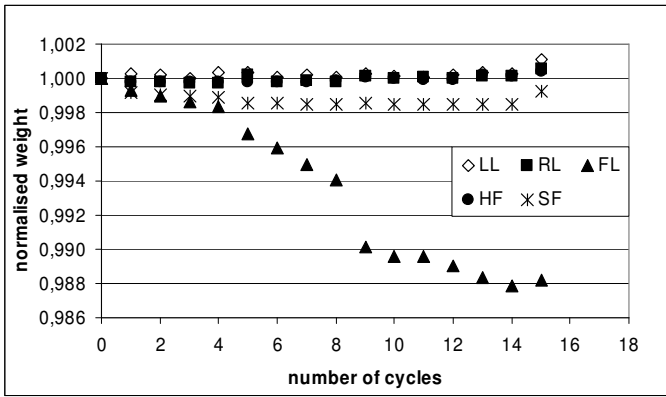


Figure 6. Percentage of initial weight vs number of cycles of remobilisation test on isolated samples for the 5 stones.

3.6 Consistency of evaporation tests: the drying after seven cycles

Let us focus on the remobilisation test with 4 faces isolated. With the new results from the experiment above, we can assume that the weight increase is only due to the water trapped in the porous network which cannot evaporate. This raise stops as soon as the zones of the porous network where water cannot evaporate (in the conditions of the experiment) are totally filled. Drying the samples after seven cycles tends to prove it: when the sample is totally dry, its weight becomes approximately the same as at the start of the experiment (Fig. 7).

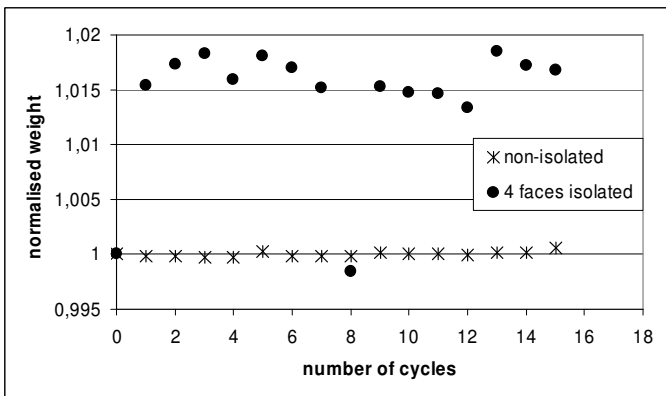


Figure 7. Percentage of weight variation vs number of cycle - remobilisation experiment for RL.

The same behaviour is observed when the sample is totally dried until constant weight in the case of the capillary imbibition test (Figs. 8a, b). Just after the drying, at the 8th cycle, the isolated and non-isolated samples show the same relative weight increase. This means that the difference between the two weight curves comes from the water which cannot evaporate inside the isolated samples during the 16 hours at $105 \pm 5^\circ\text{C}$, and that this difference of evaporation has no influence on the samples salt uptake. Hence, the variation in the decay comes from the difference in evaporation pathways of the solution

trapped in the pores, since salt supply and mechanical strength are the same for both samples.

3.7 Influence of the isolation of some faces on the weight loss

In order to quantify the importance of the evaporation process as suggested above, tests were performed using samples with three or four of their faces isolated by an aluminium film. We notice that for each test, the more faces are subjected to evaporation, the greater the decay of the sample (Table 2, Figs. 9a, b, c). But there is a contradiction with our observations in the capillary tests. We noticed that the samples were more damaged in the zones that were immersed during the capillary imbibition. If we consider that this statement is true in every situation, the zones of the samples which are always filled with mirabilite-saturated solution due to lack of evaporation should be also damaged. But on the opposite, these zones, which are located close to the isolated faces, are totally intact. It shows that total immersion is not always destructive, only in the cases where evaporation is possible.

This confirms that in addition to capillary imbibition, evaporation is another important process governing salt decay as suggested in the literature (Goudie & Viles 1997, Rodriguez-Navarro & Doehne 1999, Rodriguez-Navarro et al. 2000).

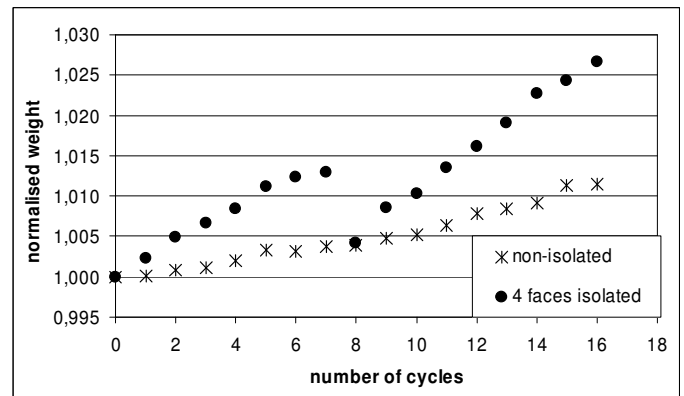


Figure 8a. Capillary imbibition with non-isolated and 4 faces isolated samples for LL.

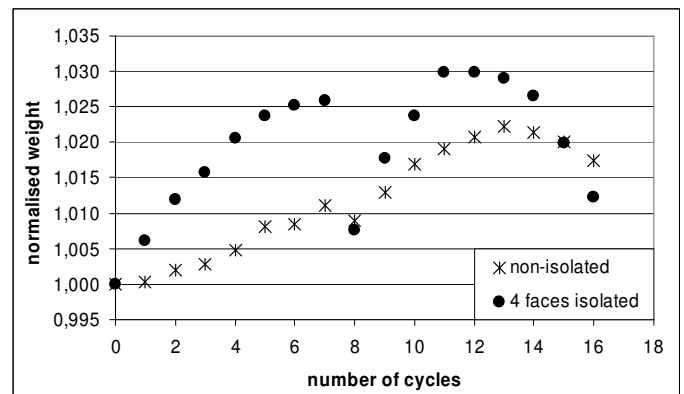


Figure 8b. Capillary imbibition with non-isolated and 4 faces isolated samples for RL.

4 CONCLUSION

The capillary coefficient as measured in the EN 1925 is the experimental parameter which is the most relevant to estimate stone decay by crystallization of salts regarding the characteristics of the porous network. It quantifies the possibility of the water to flow into the stone and to enable the mechanism of crystallization-dissolution which is harmful for the porous stones.

The remobilisation test suggests that no stress related to salt crystallization can be transmitted to the samples if no salt is provided by the solution, even if the sample is already loaded with salt.

All the tests concerning the possibility of evaporation show that the easier the evaporation, the faster and the larger the decay. They also show a contradiction with phenomenon occurring on old masonries in the fact that the main damages happen in the immersed zones of the sample.

Even if the experiments presented in this study try to be as close as possible to the situation in buildings, their results are still representative of what happens in a laboratory. We can only assume that the difference in duration, temperature, RH and evaporation mechanisms does not imply drastic changes in the processes.

This study, which characterizes the important fluid properties which participate to the mechanism of salt decay, can be continued in several natural directions. One would be to quantify more precisely salt decay by using the dry weight loss indicator instead of AI. It would be also interesting to take into account the stone strength in order to fully understand what makes a stone sensitive to salt alteration, and eventually use these processes as a basis for a simple numerical model of experimental ageing of natural stone through crystallization of salt.

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Figure 9a. Picture of a $7 \times 7 \times 7 \text{ cm}^3$ non-isolated sample of FL after cycle 12.



Figure 9b. Picture of a $7 \times 7 \times 7 \text{ cm}^3$ sample of FL with 3 faces isolated after cycle 12.



Figure 9c. Picture of a $7 \times 7 \times 7 \text{ cm}^3$ sample of FL with 4 faces isolated after cycle 12.

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