GeM Institut de Recherche en Génie Civil et Mécanique

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Report on the thesis manuscript entitled

« Developments in Investigating the Durability of Porous Building Materials Under the Chemical & Physical Modes of External Sulfate Attack »

Presented by

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External sulfate attack is a major threat for construction geomaterials. Chemical sulfate attack (CSA) is due to interactions between cement hydration products and sulfate ions, from groundwater for instance, that result in the formation of ettringite and gypsum. Physical sulfate attack (PSA) is due do the precipitation of sulphated salts in the pores. Both result in the build-up of crystallization pressures affecting the physical and mechanical properties of construction materials. The transport properties, such as permeability and diffusivity, are crucial for the durability of structural materials. Although existing knowledge, the study of PSA and CSA still faces several challenges. First, the characteristic times of actual degradation mechanisms in real exposure conditions are generally not consistent with the timescale of laboratory or performance tests. It is therefore necessary to accelerate the degradation while paying attention to the representativity, and to identify relevant indicators for the assessment of the resistance of studied materials to PSA and/or CSA. It is also a challenging task to quantify the formation of new phases, to find some correlations (if any) with the evolution of macroscopic properties, and to establish models to predict their evolution from data on the microstructure. The study of CSA and PSA is often based on the microstructural characterization of porous materials at different stages of degradation. However, most of analyses can only be performed on dry specimens, and the drying process affects the stability of hydration products and pore structure. It is thus necessary to design experimental procedures to remove free water without damaging the microstructure. Laboratory experiments are often based on destructive analysis, which has to be avoided when evaluating a real structure in service, hence the need for providing non-destructive testing strategies consistent with the phenomenology of CSA and PSA.

The main focus of Iman Abbasi Nattaj Omrani's research was to describe and model the pore structure construction materials under CSA and PSA. The author studied OPC and LC3-based materials, red clay bricks and sandstones. The experiments and findings are presented around four main objectives:

- "Identifying the optimum method for extracting the pore solution of sulfated OPC paste",
- "Developing a new method for simulating and investigating the progress of PSA in cementitious mortars",
- "Developing a new non-destructive method to quantify the in-pore mirabilite content of porous building materials under PSA",

- "Estimating the PSA-induced permeability rise of cementitious mortars via the improved random hierarchical capillary bundle model".

The manuscript, written in English, includes an introduction section, three main sections, a conclusion section, and bibliography. The Introduction section (4 pages) identifies the research gaps and the four hypotheses, and then provides the content of the main sections. The section two (37 pages) presents the theoretical background about studied materials then the phenomenology of chemical and physical sulfate attacks. The section three (36 pages) describes the experimental techniques, the random hierarchical capillary bundle model, the properties and the microstructural characterization of studied materials, and the experimental programs corresponding to the four main objectives of the research. The section four (33 pages) is divided into four main subsections related to the objectives. The conclusion section (5 pages) presents first the results related to each hypothesis/objective, then some implications for future research.

General comments

The manuscript, well structured and well documented with numerous references, presents several major contributions. The removal of free water from cement-based materials without damaging the hydration products and the pore structure is a well-known challenge, however relatively few studies have provided relevant recommendations to mitigate some drawbacks of existing procedures. The terms "pore solution extraction" induce a confusion as they often refer to the extraction of pore solution under external load to assess its chemical composition. Based on experimental results, the author recommends a solvent exchange approach using isopropanol at 5°C. In order to analyse the pore structure of cement pastes exposed to CSA, "a leaching stage was proved necessary before the MIP analysis". The author also presents the design of an accelerated ageing test to assess the resistance of cement-based materials to PSA. Although the representativity of the testing conditions is not discussed enough, an effective acceleration has actually been achieved, with a significant degradation observed within less than 30 days. The influence of the water-to-cement ratio suggests that the diffusion in saturated porosity had a major influence on assessed PSA resistance. The accelerated PSA test is used to design a non-destructive testing strategy to assess the progress of PSA in building materials, here bricks and sandstone. The volume of mirabilite is deduced from DSC and correlated with ultrasonic pulse velocity (UPV) variations at different stages of PSA. Finally the last objective of the research is achieved, as the combination of the random hierarchical capillary bundle (RHCB) model and the designed sample preparation method allow estimating the gas permeability from pore size distribution (determined through mercury intrusion porosimetry).

The research strategy is thus globally sound. The novelty of testing and modeling strategies is systematically shown, which allows identifying easily the main contributions of the research. Most of statements are based on experimental evidence and/or relevant references. It is noteworthy that the author systematically came back to the basic chemical and physical phenomena when designing or improving the testing procedures and models, and discussing the results. Experimental data are analyzed quantitatively. The combination of experiments and modeling confirm that the author acquired essential skills for research.

Main sections

The **section two** presents the "theoretical background". The author first defines the porosity and the permeability of porous materials. Permeability should be more clearly distinguished from diffusivity, as some phenomena are not the same, especially at nano-scale. As the main objective of the research is to assess the permeability, the influence of pore structure on porosity and permeability is discussed. The random hierarchical capillary bundle (RHCB) model is chosen to describe this influence. This model describes the porous network as parallel pores made with capillaries of different lengths and diameters, ordered for each pore from the highest to the lowest diameter. As the capillaries are ordered randomly, there is a probability that some pores include mainly capillaries of large lengths and diameters, which would result in overestimated permeability. Thus, there is a need for additional criteria on the random assembly of segments, which are presented as a main novelty of the research. The main additional criteria suggested by the author are the adjustment of the probability density function (PDF) of the length of capillary segments and thresholds on the diameters of subsequent capillaries. As RHCB models include several parameters, could different combinations of parameters and criteria result in similar permeability values but different pore structures, and which methodology could help defining the most relevant combinations? Then the author presents the composition, the production process, and the pore structure of the four studied porous materials: Portland cement-based materials, limestone calcined clay cement (LC3)-based materials, red clay brick, and sandstone.

The second subsection presents the phenomenology of external sulfate attack on cement-based materials. As the research presented in the manuscript aims at predicting the permeability of materials from their pore structure, there is a need for a reliable assessment of the properties of pores, however most of microstructural characterization techniques require drying the materials, which is called here "pore solution extraction". The main challenge related to CSA is that cement hydration products – especially ettringite and gypsum – are very sensitive to drying, hence the need for developing a drying process with the lowest influence as possible on the structure of hydration products and pores.

The third subsection presents the existing theories describing physical sulfate attack (PSA). Changes in temperature and/or relative humidity in porous materials are likely to induce supersaturation and precipitation of hydrated sodium sulfate phases, mainly mirabilite and thenardite, and the generated crystallization pressures are likely to cause cracking and subsequent permeability increase. The authors identifies three main challenges associated to the assessment of PSA resistance, namely: the induction of PSA, the design of accelerated aging test, and the monitoring of PSA. The representativity of laboratory conditions to trigger PSA, relatively to in situ observations, is not discussed enough. The author has chosen the full immersion method, but many buildings are exposed to wetting-drying cycles and/or partial immersion. The challenges related to the monitoring of PSA are well identified, namely: How to assess the salt content and its influence on mechanical and physical properties of building materials with non-destructive methods?

The **section three** describes the studied materials, the methods, and the experimental program. The research is based on relevant techniques and properties, relatively to the studied phenomena: X-ray diffraction (XRD), thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR), mercury intrusion porosimetry (MIP), differential scanning calorimetry (DSC), mechanical testing, ultrasonic pulse velocity (UPV), and gas permeability. The heating rate of TGA tests (20°C/min) is not discussed. The loading rate of mechanical tests is not given. The author aims at predicting gas permeability from pore structure, using RHCB model and MIP as input experimental data. After describing the experimental techniques, the author gives the main equations of RHCB model and highlights the two main improvements of the model: testing different PDFs of capillary lengths, and defining a new threshold function to avoid that large capillary segments join each other in a pore.

The third subsection presents the composition and preparation of samples, as well as their macroscopic properties and the results of their microstructural characterization. It is noteworthy that high purity calcined kaolin was used. Such material is relatively scarce and thus not often used in construction. Consistently, its use in this study lead to high performances of LC3-based materials.

The fourth subsection describes the four main experimental programs associated to the four objectives and assumptions of the research. In the subsections related to the preparation of cement-based materials, it is not mentioned how the homogeneity of the samples was ensured, relatively to the risk of bleeding and segregation at high water-to-cement ratios. A 5% Na_2SO_4 solution was used to induce CSA. This is a relatively high sulfate concentration, which is not representative of most of actual exposure conditions (see the definition of XA exposure classes in EN 206 standard). This should be discussed, as high sulfate concentration is likely to modify the relative proportions of ettringite and gypsum, thus the degradation mechanisms. Were the pH and sulfate concentration monitored during the tests? The program designed for identifying the optimum "pore solution extraction method" of sulfated OPC paste is very clear and relevant. Mortar prisms were water-cured for 2 months then immersed in 20% Na_2SO_4 solution to initiate PSA. This experimental choice should be discussed as it probably had a major influence on results. As the samples remained saturated, the main mechanism of sodium and sulfate ions penetration was diffusion. Therefore, the materials with fine porosity and low diffusivity were less severely exposed to PSA, which seems consistent with the results presented in section four, as mortars with low water-to-cement ratio and LC3 were less damaged. However, lower pore radii theoretically result in higher crystallization pressures, thus a different preconditioning method could have induced different results. In some real buildings, it has been observed that low permeability mortars maintained high moisture contents in stones and this favored some pathologies. Contrarily to what is stated in page 76, a concentration gradient is also likely to induce a global expansion – this is surely what occurred during the described experiments due to diffusion – as the crystallization pressures in the outer part results in tensile stresses in the inner part (due to the mechanical equilibrium of the section). The monitoring of PSA progress in brick and sandstone is based on the determination of the volume of mirabilite through DSC and the non-destructive characterization through UPV. The main related assumptions are that UPV can be correlated to both mechanical properties and mirabilite volume. This last correlation can be used to assess the in-pore salt content. The initial cooling at - 30°C induced the formation of ice and mirabilite. Could ice formation have induced some damage, and could this be quantified?

Figures 19 and 25: a linear scale would be preferable on X-axis

P71: "10mmx10mmx2mm"

The **fourth section** includes the results and discussion. It is structured according to the four main objectives and assumptions of the research.

The first subsection discusses the influence of "pore solution extraction method" on the structure of the hydration products and the pores of cement paste. The results clearly support the use of isopropanol and low temperature of 5°C to mitigate the effects of removing pore water on pore structure. Could XRD or other technique be used to check that the actual effectiveness of leaching on sodium sulfate removal?

The second subsection discusses the use of longitudinal expansion measurement as an indicator of the progress of PSA in cement mortars. The strain data confirm the relevance of experimental procedure with respect to the objective of designing an accelerated aging test, as a significant expansion and failure of some specimens was observed within less than 30 days. The maximum value on Y-axis of Figure 47 (page 95) does not seem adapted to the strains measured on OPC 0.35 and LC3 0.5 mortars. The increase in expansion with water-to-cement ratio is attributed to "higher and wider pore volume" (page 96). This trend could be more likely due to lower diffusion of sodium and sulfate ions (see comment in section three). The concept of "internal expansion" (page 98) is not clear, as tensile forces can be generated in the internal part by crystallization pressure in the external part. It is noteworthy that the experimental program allowed distinguishing the effects of CSA and PSA.

The third subsection presents one of the main contributions of the research as it establishes an analysis method to quantify the formation of mirabilite and its correlation with UPV. The DSC data are used to determine the volume of mirabilite formed in brick and sandstone and the pore solution concentration. This allows to determine the supersaturation ratio. The "UPV rise" is shown to depend on the direction of the measurements on studied bricks; an explanatory diagram is provided. The analysis finally provided linear relations between UPV variations and "the average volume of in-pore mirabilite" (page 107). This relationship is used to assess the formation of mirabilite from the monitoring of UPV (page 108).

P107: Check the consistency of Fig. 56 and Tab. 22.

The fourth subsection discusses the capacity of the RHCB model to predict the gas permeability from MIP data. The author first presents the influence of PSA on pore structure and permeability of mortars, with an increase of several orders of magnitude. The numerical results clearly show the influence of PDF on calculated permeability. A normal distribution with an STD of 0.33 allows retrieving experimental permeability values. It is not clear if the value of 0.33 was/could be optimized. Whatever, the comments on the influence of PDF seems consistent with the phenomenology of gas permeation in studied porous materials.

Conclusion and recommendation

Iman Abbasi Nattaj Omrani has realized a significant research work with several major contributions to investigate the behavior of porous materials exposed to chemical and physical sulfate attack. The work includes both experimental studies and model improvement. The addressed challenges have been clearly identified and the main results are well analyzed and presented. The findings are useful for other researchers and practitioners to develop low-carbon materials, and to assess and protect cultural heritage buildings.

I therefore recommend the oral defense of Iman Abbasi Nattaj Omrani's thesis to obtain the degree of Doctor.

Nantes, 10 July 2025

Pr. Emmanuel ROZIERE