Subflorescence and plaster drying dynamics

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HIGHLIGHTS

- Experimental study of water evaporation and crystal formation inside drying plaster.
- Quantification with the help of MRI and X-Ray microtomography.
- Development of a simple physical model predicting results under various conditions.

GRAPHICAL ABSTRACT
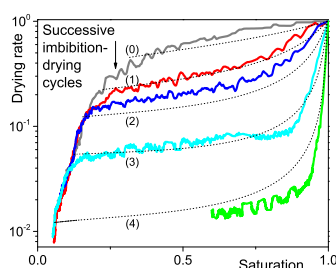
ABSTRACT

The dynamics of plaster drying and the impact of subflorescence on the process are described through Magnetic Resonance Imaging and X-Ray Microtomography measurements. It is shown that crystals deposit around the air-liquid interface the closest to the sample free surface, which induces a recession of this interface within the sample at a rate only depending on the current saturation (water to pore volume ratio). Thus the distribution of crystals deposited during evaporation essentially depends on the history of saturation. The drying dynamics then results from vapor diffusion through the less porous layers of crystal accumulation below the sample free surface. This in particular makes it possible to predict the dramatic decrease of the drying rate after successive imbibition-drying cycles.

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1. Introduction

To obtain plasterboards so useful for modern constructions, there are two important phenomena that must take place during the manufacturing process: hydration, through which plaster paste passes from a pasty state to a solid state, and drying, through which the excess of the mixing water added for workability purposes is removed. The hydration reaction can be described as the successive dissolution of hemihydrates ($CaSO_4$, ½ H_2O, initial water-to-powder ratio of 0.8) and precipitation of dihydrates ($CaSO_4$, 2 H_2O) in water (Neville, 1926; Ridge and Beretka, 1969; Hansen,

1963; Vignes and Essaddam, 1997). Detailed information on these processes may be found in (Singh and Middendorf, 2007; Lemarchand et al., 2012). After this chemical reaction which lasts about 40 min without accelerators (Jaffel and Korb, 2006), a significant excess of water must be removed from the material, an operation which requires a lot of energy. Understanding the drying processes in plaster pastes should contribute to develop more efficient drying techniques and procedures, and to consume less energy. Here we focus on one of the technics used in manufacture to remove the residual water: by a convective air flow (Frederiksen and Marchand, 2010).

Existing knowledge on drying characteristics of plasters essentially concerns materials already in solid state which are imbibed then dried and tends to suggest (Petkovic et al., 2007) that

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as long as pure water is used such materials exhibit drying properties close to usual simple homogeneous porous media. A specific aspect has been studied in more details in recent years, namely the transport of salts during drying of solid plaster samples. It has been shown that salts are transported towards the free surface and then can either crystallize inside the plaster or move outside, towards the substrate (Petkovic et al., 2007). It was also suggested that this salt crystallization leads to the formation of a structure inside the plaster, whose characteristics depend on the drying rate and in turn impact the drying rate (Vosten and Hersfeld, 1976).

The drying characteristics of plaster pastes just after their preparation has not been studied in depth so far whereas it is a critical step of the process of plasterboard production. Previous studies concerning plaster properties during its preparation focused on the structure evolution in time, in particular with the help of NMR, showing that the pore distribution evolves as a result of hydration (Song et al., 2009; Song et al., 2010). A recent work finally showed that the drying rate of plaster pastes is significantly lower than that expected for a pure liquid evaporating from a simple homogeneous porous medium (Seck et al., 2015). This effect was shown to be enhanced by the air flow velocity and the initial solid/water ratio. From further tests under various conditions it was suggested that this effect is due to the crystallization of gypsum ions below the sample free surface, which creates a dry region and decreases the drying rate by increasing the length of the path the vapor has to follow before reaching the free surface. The specificity of plaster drying is indeed that at the end of the initial setting process (due to precipitation of dihydrates) the interstitial solution is saturated with ions (Ca^{2+}, SO_4^{2-}), which can then precipitate as gypsum crystals and accumulate in some regions as soon as some water is extracted by evaporation. Further work is needed to understand the physical mechanisms and then to be able to predict the drying rate as a function of material characteristics and boundary conditions.

The understanding of this phenomenon is interesting for other reasons. Salt transport and crystallisation in building materials are responsible for major damages of modern structures (Liu et al., 2014) and cultural heritage (Sawdy et al., 2008). Similar effects in rocks can alter CO2 injectivity (Peysson et al., 2011) and are at the origin of various geomorpholocial processes (Rodriguez-Navarro and Doehne, 1999). For example ions dissolved during imbibition can then, during drying, reach the solubility limit and precipitate as crystals below (subflorescence) or above (efflorescence) the sample free surface. These crystals may clog the porous structure (Espinoza-Marzal and Scherer, 2012), lead to flaking and crumbling (Kramar et al., 2010) or reduce the compression strength of the material (Foraboschi and Vanin, 2014). The mechanisms at the origin of damages have been discussed: crystallization pressure, supersaturation, solid volume change from thenardite to mirabilite (Scherer, 2004; Flatt, 2002; Schiro et al., 2012; Flatt et al., 2014; Tsui et al., 2003); but it was also acknowledged that the remaining liquid films can play a significant role on crystallization processes (Espinosa-Marzal and Scherer, 2010). Extensive studies (Rodriguez-Navarro and Doehne, 1999; Schultz and Schlünder, 1990) showed the variety of trends observed depending on solution properties (salt type and additives), but it was finally pointed out (Rodriguez-Navarro and Doehne, 1999; Shahidzadeh-Bonn et al., 2010; Desarnaud et al., 2013) from detailed information concerning salt and damage localization, that possible damages critically depend on the localization of salt crystals which requires the description of the dynamics of salt transport, spatial distribution and crystallization and its coupling with drying mechanisms.

For efflorescence the basic theoretical concepts of salt transport resulting from water flow during drying were confirmed by following the salt distribution by MRI (Pel et al., 2004; Petkovic et al., 2010). It was then shown that crystals deposited at the sample free surface behave as a porous medium which pumps the liquid and brings ions around the most external liquid-air interface to form new crystals (Veran-Tissoires et al., 2012; Sghaier and Prat, 2009). A recent study showed in addition that the structure of the efflorescence layer can evolve with successive imbibition-drying cycles, which successively modifies the drying rate, increasing or decreasing it depending on the crystallization pathways or on the humidity of the crust (Desarnaud et al., 2015). Microtomography observations of the three phases around the sample top provided a detailed description of the process, which makes it possible to establish a model of crust formation dynamics as a function of drying rate (Norouzi Rad et al., 2015). Besides it was shown that some unexpected effects (in drying rate variations) can result from the interplay between the crust and the evaporation conditions (Gupta et al., 2014; Gupta et al., 2014).

Although it is a more damaging effect than efflorescence much less is known concerning the local mechanisms of subflorescence. It was shown from X-Ray microtomography that subtle local effects occur essentially at the scale of the pore (Shokri, 2014), and tend to induce pore clogging which reduces the drying rate, but these effects depend of the type of salt at work (Espinoza-Marzal and Scherer, 2012). From original experiments in 2D system it was also shown that a specific subflorescence pattern can grow because the crystal structure form a porous media which can drain a saturated salty solution up to the evaporating front, which eventually causes the drying rate to increase (Sghaier et al., 2014). Recently the work of Derluyn with the help of neutron radiography and X-ray microtomography provided new insights on salt transport, accumulation, and induced damage in limestone samples (Derluyn et al., 2013; Derluyn et al., 2014). However our knowledge of the relationship between subflorescence and drying dynamics in porous media is still limited, essentially because it is more difficult to get a direct view of the processes at a local scale. Yet it governs the spatial distribution of crystals which in turn determines the position of possible damages, and this knowledge would open the way to the development of relevant tools for controlling or avoiding such effects. Taking advantage of MRI (Magnetic Resonance Imaging) data such an approach was recently developed for predicting the accumulation of initially suspended colloidal particles and its impact on drying dynamics (Keita et al., 2014).

Here we aim at studying in more detail the process of subflorescence in plaster. From repeated imbibition-drying cycles on the same sample we observe that the drying rate is dramatically decreased as a result of crystal accumulation inside the sample. Through MRI and X-Ray microtomography we show that crystals are deposited around the first (i.e. most external) air-liquid interface, which induces its recession in the sample at a rate only depending on the current saturation (water to pore volume ratio) and the current total liquid volume in the sample. From this information we deduce a simple phenomenological model which predicts the drying dynamics of plaster under different conditions.

2. Materials and methods

We used a commercial α-plaster (*Saint-Gobain Recherche*, France) with a purity higher than 95% wt, a specific surface of 7500 g/m² (measured with the Blaine air permeability test), and a grain size between 10 and 20 μm. The impurities are mainly clay (colloidal) particles. Our plaster paste samples are prepared according to a well-defined mixing protocol (Seck et al., 2015; Jaffel, 2009). The initial water to powder ratio (w/p), *i.e.* the ratio of the mass of water to the mass of powder, was between 0.5 and 0.8. At the end of the hydration reaction (after about 25 min, as found from NMR measurements (Seck et al., 2015)) which consumed