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ORIGINAL ARTICLE

Investigation of NaCl deliquescence in porous substrates using RH-XRD

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Abstract We report on the use of X-ray diffractometry under controlled conditions of temperature and relative humidity (RH-XRD) for the investigation of NaCl deliquescence in the pore space of glass filter frits, which were used as model substrates. The study confirms that RH-XRD is an appropriate experimental technique for the in situ observation of phase transformation in porous materials. It is used for an investigation of both the deliquescence kinetics and the deliquescence humidity within pores of different median pore diameter. Several major influences affecting deliquescence rates in the pore space close to the surface of a porous material are discussed. It appears that quite short-term variation of ambient relative humidity, e.g., typical daily fluctuations, might induce damaging deliquescence–crystallization cycles within the pore space of building materials. In agreement with theoretical considerations it was found that confinement of NaCl crystals in pores with median diameters in the range 1.4–70 µm does not affect the deliquescence humidity of the salt.

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Introduction

The pressure generated during crystal growth in confined spaces of porous materials is generally accepted as a major cause of damage of such materials (Goudie and Viles 1997; Doehne 2002). Crystal growth damage not only affects porous building materials such as stone, brick, concrete etc., it is also an important weathering mechanism of natural rocks in hot and cold deserts (Cooke and Smalley 1968; Johnston 1973) and even on Mars (Malin 1974; Rodriguez-Navarro 1998). Crystal growth in a porous material is always the result of a phase transition reaction usually induced by a change in ambient temperature or relative humidity. Unfavorable environmental conditions may cause repeated cycles of deliquescence–crystallization or hydration–dehydration, which lead to the rapid decay of building materials or natural rocks. The identification of critical environmental conditions requires the knowledge of the thermodynamics of the relevant phase transition reactions (Steiger 2005a). In addition, the rates at which these processes take place in porous materials are extremely important in order to determine the critical levels of environmental fluctuations (Sawdy 2001). The overall kinetics of phase transition reactions in porous materials is affected by a number of different influences including the rates of chemical reactions, the moisture transport in a porous material and the rate of moisture exchange between the material and the environment.

The investigation of the deleterious processes in porous materials requires suitable experimental techniques. In previous work, we have shown that X-ray diffraction (XRD) under controlled conditions of relative humidity and temperature (RH-XRD) is an appropriate experimental technique for the investigation of phase transitions. Linnow et al. (2006) used RH-XRD for the investigation of sodium sulfate phase transitions in porous substrates. They demonstrated that hydration–dehydration and deliquescence–crystallization equilibria can be directly observed within confined spaces of a porous material. Subsequently, it was shown that dynamic RH-XRD is also a very useful experimental technique for the quantitative determination of equilibrium humidities of relevant phase transition reactions, e.g. deliquescence and hydration humidities (Linnow and Steiger 2006).

In this study we extend our previous applications of RH-XRD. The method is used in the present work for the direct observation of the deliquescence of sodium chloride (NaCl) within the pore space of glass frits with different pore diameters. One objective of the study was to test the use of RH-XRD as a potential technique for the direct observation of the kinetics of the deliquescence reaction of a salt confined in a porous substrate. The second objective was to test whether dynamic XRD measurements are also an appropriate method for the accurate and precise determination of equilibrium humidities of crystals present in small pores. The paper describes both the potential and the limitations of such applications of RH-XRD.

Materials and methods

Instrumentation

The RH-XRD measurements were carried out on a Bragg–Brentano parafocusing powder diffractometer (D 5000, Siemens, Germany) with a θ:2θ configuration, using Cu Kα-radiation (generated at 25 kV and 20 mA) and a position sensitive detector recording data from a 12° 2θ band at one time. The diffractometer is equipped with an environmental cell (Linnow et al. 2006) consisting of an air-tight cylindrical stainless steel chamber which is fixed to the goniometer. In order to avoid temperature gradients in the chamber, not only the air flow from the humidity generator but also the chamber walls and the sample stage are thermostated. A Pt-100 sensor and a capacitive humidity sensor (HMP 233, Vaisala, Finland) are used for temperature and humidity control in the chamber. They are placed close to the surface of the samples. The window for the passage of X-rays is sealed with a 6 μm Mylar film.

The humidity sensor is connected to the humid air generator. In the temperature range 10–50°C the humidity control system allows the variation of the relative humidity (RH) in the chamber within a range of 3–97% RH. Humidity control is accomplished by mixing of dry and water-saturated air using automated mass-flow controllers. Appropriate mixing ratios of the wet and dry air flows are controlled by a computer program. A more detailed description of the humidity control system is provided by Linnow et al. (2006).

A Hitachi S 4004 scanning electron microscope (SEM) was used to determine crystal size and shape and the distribution of NaCl in the glass frits that were used for the XRD measurements.

Sample preparation

Analytical grade NaCl (Merck, Germany) was directly used throughout the study. The size distribution of the crystals was determined by mechanical sieving and yielded the following weight percentage distribution in the respective crystal size ranges: 94% (>125 μm), 5% (63–125 μm), 0.2% (40–63 μm), and 0.03% (<40 μm). The deliquescence of a bulk sample of NaCl (146 mg) was investigated at 78% RH and 25°C.

Disks of glass frits (VitraPOR, ROBU Glasfilter-Geräte GmbH, Germany) of four different porosity classes (P2–P5) with a diameter of 20 mm and varying heights between 2.4–3.2 mm were used as porous substrates. Porosity classes P4 and P5 of the same glass frits were already successfully applied in a previous study with sodium sulfate (Linnow et al. 2006). The amorphous material did not significantly interfere with the X-ray pattern of crystalline NaCl. Median pore diameters d_m of 70 μm (P2), 28 μm (P3), 11.1 μm (P4), and 1.44 μm (P5) are provided by the manufacturer and are based on mercury intrusion porosimetry. These median pore sizes are typical for many building materials such as natural stone and brick. In contrast to such materials however, the pore size distribution of the glass filters is very narrow, thus, the filter frits are well suited for an investigation of pore size influences.

Glass frits of each porosity class were washed, dried and immersed in a NaCl solution at room temperature. Preliminary tests showed that evaporative drying of the glass frits in dry air lead to the formation of a salt crust on the surface of the frits. However, since XRD patterns of efflorescences and NaCl crystals within the pore space of the glass frits are nearly indistinguishable, it is absolutely essential that the formation of efflorescences during the drying procedure is avoided.

Otherwise, an unambiguous determination of the deliquescence humidity of NaCl crystals within the pores is impossible. In order to avoid efflorescences during the sample preparation, freeze-drying was used. The impregnated glass frits were subjected to rapid cooling rates by placing the impregnated sample into melting nitrogen (slush nitrogen) such that the NaCl solution forms a glassy solid matrix. Subsequent sublimation of water and crystallization of NaCl were carried out under applied vacuum until the whole nitrogen is evaporated.

Two glass frits of each porosity class were impregnated with a 10% (w/w) solution. After cryo-preparation the glass frits did neither show visible efflorescences nor any discoloration of the surfaces that would indicate the presence of crystalline surface deposits. One specimen of each porosity class was selected to determine the crystal sizes and distributions of crystalline NaCl by using SEM. The frits were broken in the center and their cross sections were examined. The SEM observations confirmed that there were practically no efflorescences present on the surfaces. The remaining specimens were used to observe the deliquescence reaction at constant humidity of 78% RH and at 25°C. The total weights of NaCl in these glass frits after the impregnation and drying procedure were 222.3 mg (d_m = 1.44 μm), 70.3 mg (d_m = 11.1 μm), 21.8 mg (d_m = 28 μm), and 55.2 mg (d_m = 70 μm), respectively.

The X-ray intensities in the initial experiments with glass frits that were impregnated with a 10% (w/w) NaCl solution were relatively low. In order to improve the sensitivity for the subsequent determination of the deliquescence humidities of NaCl in the porous substrates, several glass frits of each porosity class were immersed in a saturated NaCl solution. After freeze-drying these specimens appeared slightly brighter on their surfaces, thus, indicating the presence of NaCl crystals. To remove these efflorescences the surfaces were carefully brushed. Thereby, glass particles flaked off, such that the weight fraction of NaCl in each specimen could not be determined. The deliquescence of NaCl in these specimens was observed at different relative humidities in order to determine the equilibrium deliquescence humidity as discussed below.

Measurement procedure

An improved dynamic method for the quantitative determination of equilibrium humidities of phase transition reactions was recently proposed by Linnow and Steiger (2006). The method is based on kinetic measurements, namely on the evaluation of total reaction times required until the reaction is complete. If a phase transition reaction induced by a sudden change in relative humidity, e.g., a deliquescence reaction, is carried out at different humidities, the total reaction time t_c increases as one approaches the equilibrium value of the relative humidity, i.e. the deliquescence humidity. At equilibrium, according to the phase rule, the crystalline solid and the saturated solution coexist indefinitely, thus, the reaction rate vanishes. As shown recently (Linnow and Steiger 2006), an exponential function of the form

$$\mathrm{RH} = \mathrm{RH}_{\mathrm{eq}} \exp\left(Bt_c^{-1}\right) \tag{1}$$

provides an accurate representation of the RH dependence of the total reaction times of phase transition reactions such as hydration or deliquescence of a solid. In Eq. 1 $\mathrm{RH}_{\mathrm{eq}}$ is the equilibrium relative humidity of the respective reaction. In the case of a deliquescence reaction, the equilibrium humidity corresponds to the deliquescence humidity $\mathrm{RH}_{\mathrm{del}}$. Both $\mathrm{RH}_{\mathrm{del}}$ and B are treated as adjustable parameters. For a deliquescence reaction, linearization of Eq. 1 yields:

$$\ln \mathrm{RH} = \ln \mathrm{RH}_{\mathrm{del}} + Bt_c^{-1} \tag{2}$$

Values of $\mathrm{RH}_{\mathrm{del}}$ and B can be determined by linear least squares analysis from experimental measurements of t_c at different relative humidities. It was shown in our previous work (Linnow and Steiger 2006) that the extrapolation to $t_c^{-1} = 0$ allows for the accurate determination of $\mathrm{RH}_{\mathrm{del}}$ from Eq. 2. This method was also adopted in the present work.

All experiments were carried out at 25°C in the environmental chamber of the diffractometer. Samples were equilibrated in the chamber at 40% RH until the reaction was induced by a sudden increase in the relative humidity to the desired value. Subsequently, the humidity was kept constant until the absence of sodium chloride peaks in the diffraction pattern indicated that the reaction was complete. Progress of the deliquescence reaction was observed by successively recorded diffraction patterns. For the determination of the deliquescence humidities, diffraction patterns were recorded in the range 25°–70° 2θ. The time required for the collection of the patterns was 19 min. Relative humidity and temperature in the chamber were continuously monitored during all experiments. Typical fluctuations were less than 0.4% RH. The accuracy of the RH determinations with the calibrated Vaisala sensor was tested by repeated measurements on different days of the equilibrium humidity of saturated solutions of various salts (Linnow and Steiger 2006).

No systematic deviations from tabulated reference values (Greenspan 1977) could be observed and the standard deviation of these measurements did not exceed 0.6% RH.

All kinetic experiments were carried out at 78% RH. These experiments included a bulk sample and the glass frits impregnated with 10% (w/w) NaCl solution in order to compare the kinetics of the deliquescence reaction and to assess the influence of confinement on the rate of the deliquescence reaction. The XRD patterns of the bulk sample and the P3 specimen were recorded in the range 10°–70° 2θ , which required 24 min. A new measurement was started every 30 min. In order to improve the time resolution, XRD patterns in the subsequent measurements with the P2, P4 and P5 specimens were recorded in the range 25°–55° 2θ such that a new measurement could be started every 15 min.

Results and discussion

SEM observations

SEM images of the cross sections of the glass frits are shown in Fig. 1. Salt crystals appear brighter than the glass matrix in the backscattered electron image due to the higher average atomic number of NaCl compared to the borosilicate material. An even distribution of crystalline NaCl over the whole cross section was found in the P2 (d_m = 70 μm) and P4 (d_m = 11.1 μm) glass frits. In contrast, there is an accumulation of NaCl close to the surface into a depth of about 300–500 μm in the P3 glass frit (d_m = 28 μm). Only minor amounts of NaCl are obviously present in the interior of this specimen. Though it appears that the salt is also evenly distributed in the P5 glass frit (d_m = 1.4 μm), there are two narrow zones of high salt enrichment in depths of about 150 μm on the upper side and about 300–450 μm on the opposite side of the specimen. These enrichment zones indicate the presence of cracks in the fabric of the P5 frit.

Figure 2 shows crystal sizes and morphologies in the freeze-dried glass frits. In the pore space of the P2 glass frit (d_m = 70 μm) agglomerates of euhedral NaCl crystals of about 1–3 μm edge length are found. Similar crystal sizes are observed in the P3 (d_m = 28 μm) and P4 (d_m = 11.1 μm) frits. However, in these specimens the crystals are less well-formed and show rounded edges. The SEM image of the enrichment zone in the P5 frit (d_m = 1.4 μm) confirms that the pore space is nearly entirely filled with a compact aggregate of NaCl crystals of different sizes. The size of the largest crystals (6 μm, see arrow in Fig. 2) exceeds the median pore size by far and, thus, confirms the presence of a crack in the P5 frit. Though evenly distributed (see Fig. 1) only small amounts of NaCl were found in the interior pore space of the P5 specimen. This result is in contradiction with the substantial weight increase of 222 mg determined for another P5 specimen which was treated in the same way and was used for the determination of the

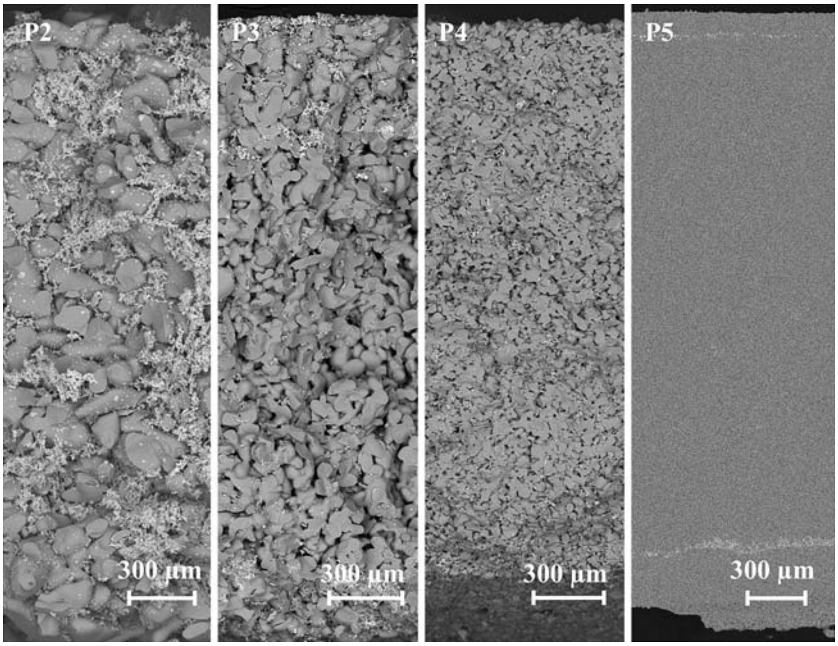

Fig. 1 SEM micrographs of NaCl distribution in the glass frits P2 (d_m = 70 μm), P3 (d_m = 28 μm), P4 (d_m = 11.1 μm), and P5 (d_m = 1.44 μm) (BSE-images, 20 kV)

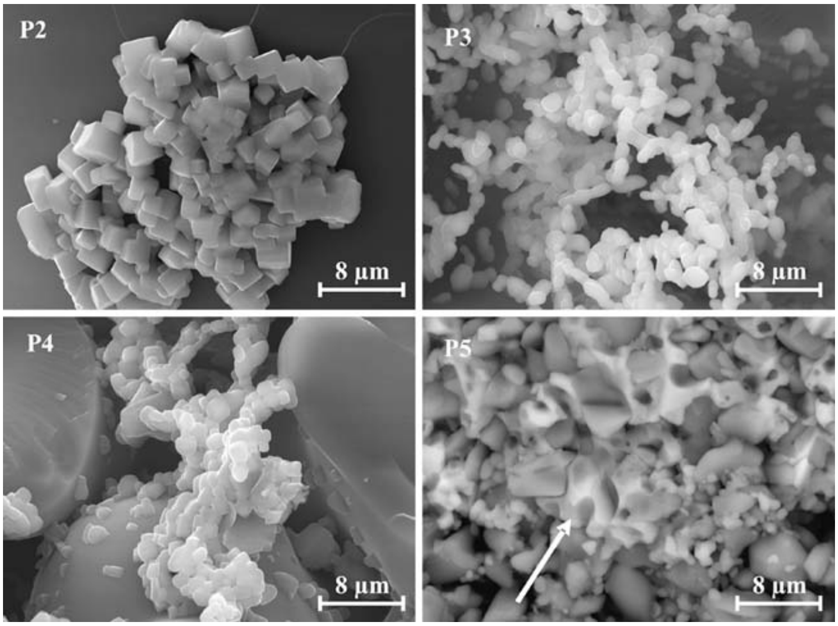

Fig. 2 SEM micrographs of NaCl crystals in the glass frits P2 (d_m = 70 µm), P3 (d_m = 28 µm), P4 (d_m = 11.1 µm), and P5 (d_m = 1.44 µm) (SE-images, 20 kV)

deliquescence rate at 78% RH. It is concluded that the cracks parallel to the surface in the P5 specimen shown in Fig. 1 did also affect the sample preparation procedure. Therefore, it is likely that the cracks already existed prior to the imbibition and freeze-drying procedure. Though it could be suspected that the cracks were also caused by the rapid freezing of the samples, it should be noted that we have never observed damage to glass filter frits upon freeze-drying including previous work on Na_2SO_4 (Linnow et al. 2006) and in experiments with the freeze-drying of $MgSO_4$ solutions in filter frits (Juling et al. 2004).

The morphologies of the NaCl crystals observed after the freeze-drying of the porous substrates show more or less significant deviations from the cubic equilibrium shape of halite crystals (Fig. 2). Nonetheless, the morphologies of salt crystals growing from evaporating solutions in porous substrates are known to show a whole variety of different morphologies including isometric shapes and forms far from the equilibrium shape of the respective salt (Zehnder and Arnold 1989, Rodriguez-Navarro and Doehne 1999). For instance, depending on the conditions during crystal growth, Zehnder and Arnold (1989) observed both isometric forms, sometimes with rounded edges, and acicular forms like columnar crystals, whiskers or fibrous aggregates. They also report on aggregates of euhedral crystals with rounded edges comparable with those shown in Fig. 2. It is concluded therefore, that freeze-drying does not yield unrealistic crystal morphologies, which would restrict the interpretation of the results.

Kinetics of deliquescence

Diffraction patterns, recorded successively during one of the experiments, are shown in Fig. 3 together with the JCPDS (Joint Committee on Diffraction Pattern) standard 5-0628 for NaCl. Apart from an obvious increase in background intensities in the range of 18°–30° 2θ which is caused by the amorphous glass matrix, the diffraction patterns of NaCl in the glass frit compare nicely to the JCPDS standard and the identification did not pose any problems. The peak area intensities of the peaks at 31.7°, 45.4°, 53.8°, 56.5° and 66.3° 2θ, respectively, were used for the evaluation of the diffraction patterns during the course of the deliquescence reactions. The highest peak intensities were observed at the beginning of the experiment during the equilibration of the glass frit at 40% RH (cf. Fig. 3). At $t = 0$ the deliquescence reaction was induced by a sudden increase in relative humidity to the desired value, i.e., 78% RH in the case of the experiment shown in Fig. 3. In the subsequent XRD patterns, the peak intensities continuously decrease during the course of the deliquescence reaction.

The experiment with the bulk NaCl sample was evaluated in the same way, though of course, there were no increased background intensities caused by the glass matrix such that the peak at 27.3° 2θ could be used for the evaluation of the peak intensities as well. The change in peak intensities during the experiment at 78% RH is shown in Fig. 4. The values plotted are averaged relative intensities I/I_0 of the different NaCl peaks where I is the peak intensity at time t and I_0 is

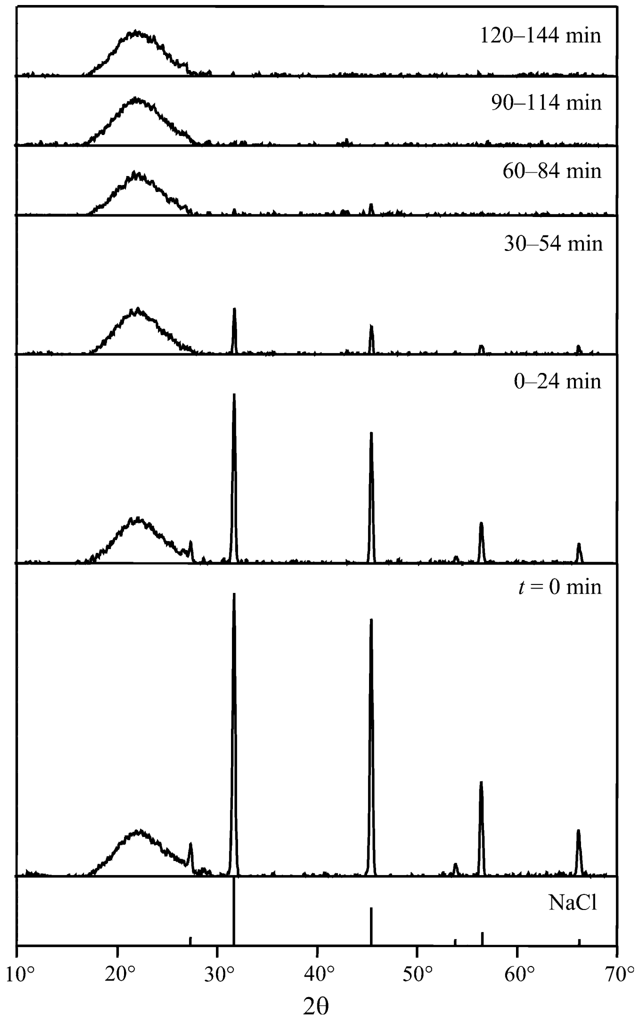

Fig. 3 Successively recorded diffraction patterns during deliquescence of NaCl in the pore space of glass frit P3 (d_m = 28 μm) at 78% RH and 25 °C and comparison with JCPDS standard 5-0628 of NaCl

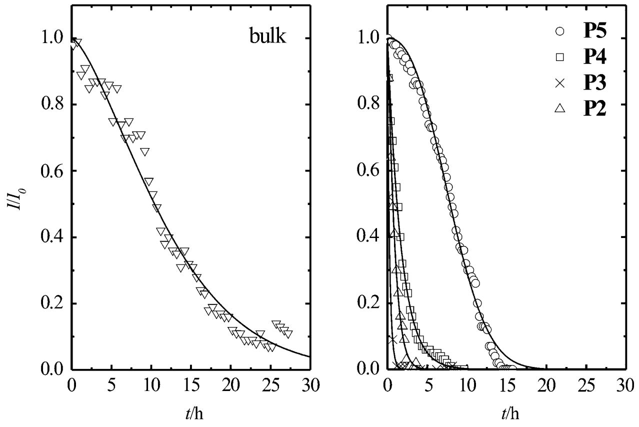

Fig. 4 Course of the deliquescence of NaCl at 78% RH (25 °C) in bulk samples and in the glass frits P2 (d_m = 70 μm), P3 (d_m = 28 μm), P4 (d_m = 11.1 μm), and P5 (d_m = 1.44 μm)

the intensity of the respective peak at the very beginning of the experiment (t = 0). During the course of the reaction the relative intensities continuously decrease approaching the final value I/I_0 = 0. In the case of the bulk sample however, the deliquescence reaction was still not complete, even after 25 h when the measurements were terminated. The measured intensities were fitted to an exponential function of the form

$$I/I_0 = \exp\left(-kt^n\right) \tag{3}$$

in order to represent the experimental data in intensity vs. time curves (Fig. 4). In Eq. 3 k and n are treated as empirical adjustable parameters that are not meant to be related to a particular reaction mechanism.

The peak intensities during the deliquescence of NaCl in the glass frits at the same relative humidity (i.e. 78% RH) are also shown in Fig. 4. It is obvious that the reaction times are smaller in the case of the porous substrates compared to the bulk sample. However, in the case of the porous substrates, the relative intensities have to be interpreted in a different way. Due to the limited penetration depth of the X-rays in the glass frits, the total loss of intensity does not indicate that the deliquescence reaction in the whole specimen is complete. It rather means that no more crystalline NaCl can be detected in a layer close to the surface of the substrate. The thickness of this layer depends on the penetration depth of the X-rays. For Cu Kα radiation and the substrate used in this work, it can be estimated from the absorption law that the penetration of the X-rays for different angles θ would hardly exceed about 100–200 μm.

Due to the limited penetration depth of X-rays in the salt loaded glass frits, only a fraction of the total amount of NaCl present in the specimens is observable by XRD. In principle it should be possible to assess this fraction, if the total mass load of the specimens and the penetration depth are known. However, the heterogeneous distribution of crystalline NaCl at least in some of the glass frits does not permit an accurate assessment of the NaCl fraction in the outer pore space. Transport processes across the layer penetrated by the X-rays may further affect the measured intensities. In the case of a deliquescence reaction, the solution that is initially formed might be transported by capillary action into greater depth. This results in a reduced attenuation of the X-ray intensities in the outermost layer and, eventually, increases the penetration depth slightly. In effect, the intensity vs. time plots shown in Fig. 4 may also be affected by solution transport.

For the reasons given, the intensity curves obtained during the deliquescence of the bulk samples and the glass substrates are not directly comparable. Nonetheless, despite of the difficulties in the interpretation of the reaction curves, the measurements of the deliquescence kinetics in the porous substrates clearly indicate that in the pore space close to the surface the reaction proceeds on a time-scale of a few hours. It is concluded that quite short-time variations of relative humidity, e.g., the typical daily variation of ambient relative humidity, may be sufficient to cause dissolution of crystalline salts in the pore space close to the surface of building materials. A subsequent decrease in relative humidity may then cause crystallization and the generation of stress in the material. However, much longer reaction times may be required for the deliquescence of salt crystals in greater depth of a porous material.

In general, the rate of deliquescence of a crystalline solid is affected by (1) the rate of dissolution of the crystalline core in the solution film that is initially formed on the particle surface and (2) the transfer of water vapor from the surrounding gas phase into the solution. The rate of water vapor transfer depends on the available surface area of the gas–liquid interface. Considering the deliquescence of a confined crystal, e.g. a crystal in a pore, the available surface area of the gas–liquid interface is limited as a large part of the total surface area of the liquid phase is in direct contact with the pore wall. Similar arguments apply to the deliquescence of powders or crystal agglomerates. In this case, the solution formed during the initial phase of the deliquescence reaction fills the free space in the aggregate but is not necessarily accessible to water vapor transfer from the surrounding atmosphere.

This implies that the rate of deliquescence of crystal aggregates or crystals confined in a pore should be lower than for single crystals that form free droplets upon deliquescence. In fact, this was confirmed by Linnow et al. (2006) for the deliquescence of small crystals of mirabilite ($Na_2SO_4 \cdot 10H_2O$) adhered to the surface of a fiber filter. In the present work however, the experiments with bulk NaCl were carried out with a powder of rather coarse grained material with a median crystal size of >125 μm. Furthermore, the total sample weights were considerably larger than in our previous experiments with mirabilite. Therefore, the significantly lower reaction rate observed in the present study for the bulk NaCl sample appears to be plausible.

The deliquescence of a bulk sample may correspond to the situation of a salt efflorescence on a building. The time required for the complete deliquescence of a salt efflorescence strongly depends on its morphology. The deliquescence of the bulk NaCl sample may correspond to the situation of a fluffy or powdery efflorescence on a building. However, efflorescences may also form compact crusts as sometimes found on heavily contaminated building materials. The more compact a crust is, the longer will the deliquescence reaction take. It is well known that dense salt crusts on buildings in some instances require quite a long time, i.e. days or even weeks, until their deliquescence is complete. For example, Arnold and Zehnder (1991) reported that sodium nitrate efflorescences in the crypt of Grossmünster Zurich disappeared about one or two months after the ambient RH exceeded the deliquescence humidity of the salt. Diaz Gonçalves et al. (2006) obtained similar reaction times in laboratory experiments with different salts.

The relative intensity curves for the deliquescence in the glass frits shown in Fig. 4 reveal considerable differences between the specimens. In particular, the deliquescence rate in the P5 glass frit (d_m = 1.44 μm) is significantly lower than in the glass frits P2–P4. As shown in Fig. 2 the NaCl in the pore space of these latter specimens forms small agglomerates of individual crystals about 2 μm in size. The agglomerates do not entirely fill the pore space of the specimens, thus, leaving sufficient space for the transfer of water vapor from the surrounding gas phase. This is also in agreement with the moderate load of these specimens with NaCl, i.e. 55.2 mg (P2), 21.8 mg (P3) and 70.3 mg (P4), respectively. In contrast, the mass load of the P5 glass frit used for the deliquescence measurements was much higher (222 mg). Unfortunately, the P5 glass frit used for the microscopic examinations does not appear to be representative due to the presence of cracks as discussed before. Hence, we do not have representative SEM micrographs of the NaCl distribution in the pore space of the P5 specimen. However, NaCl agglomerates with similar morphology to those found in the other specimens should be also present in the P5 specimen. Considering the much higher concentration of NaCl together with the smaller pore size, it is then very likely that a much larger fraction of the pores in the P5 frit was filled with NaCl resulting in the considerably slower deliquescence rate observed.

The discussion so far indicates that the kinetics of the deliquescence in porous building materials is strongly affected by a number of different influences including pore size and geometry, crystal morphology and the volume fraction of the available pore space that is filled with the crystalline salt. Finally, the relative humidity itself strongly influences the deliquescence rate. As mentioned before and discussed in more detail below, this influence of the ambient humidity on the deliquescence kinetics can be utilized for the determination of the equilibrium deliquescence humidity of a salt in a porous material.

Deliquescence humidities

The method proposed by Linnow and Steiger (2006) was used for the determination of the equilibrium deliquescence humidities ($\mathrm{RH}_{\mathrm{del}}$) of NaCl in the pore space of the glass frits. This method is based on the use of Eq. 2 for the determination of $\mathrm{RH}_{\mathrm{del}}$ and requires the measurement of total reaction times t_c at different relative humidities. For maximum accuracy, it is important to measure t_c close to the equilibrium humidity. While measurements at high relative humidity are helpful to fix the parameter B in Eq. 2, such measurements are less important for the accurate determination of $\mathrm{RH}_{\mathrm{del}}$. For that reason, most of the measurements were carried out at relative humidities close to the expected $\mathrm{RH}_{\mathrm{del}}$ (Table 1).

In contrast to the previous study, total reaction times t_c were not determined by visual inspection of the diffraction patterns in the present work. The fits of the experimental intensities to Eq. 3 were used instead by taking t_c as the time corresponding to a decrease in the intensity to 0.1% of its initial value, i.e., $I/I_0 = 0.001$. The resulting values of t_c are listed in Table 1. As discussed before, approaching the deliquescence humidity, the reaction rate decreases. Hence, the total reaction times in Table 1 increase with decreasing RH.

Table 1 Relative humidities and total reaction times t_c of the NaCl deliquescence in glass frits P2–P5 with different median pore diameters d_m at 25°C

d_m/μm	RH/%	t_c/h
70	75.8	23.4
	76.0	15.7
	76.3	11.2
	76.7	13.3
	77.0	10.2
28	75.9	26.3
	76.0	18.7
	76.5	19.2
	76.2	4.9
	77.9	1.2
11.1	75.8	25.2
	76.0	22.8
	76.2	33.6
	76.5	9.2
	76.8	20.0
	77.0	11.7
1.44	76.5	33.7
	77.0	26.3
	77.7	19.7
	78.5	12.5
	78.8	15.0

Table 2 Coefficients ln $\mathrm{RH}_{\mathrm{del}}$ and B of Eq. (2) and coefficient of determination R^2 in the glass frits with different median pore sizes d_m

d_m/μm	ln $\mathrm{RH}_{\mathrm{del}}$	B/s	R^2
70	4.317 ± 0.007	897 ± 327	0.715
28	4.330 ± 0.002	99 ± 18	0.911
11.1	4.329 ± 0.005	416 ± 291	0.337
1.44	4.322 ± 0.006	2,043 ± 361	0.911

The experimental data were used together with Eq. 2 to determine ln $\mathrm{RH}_{\mathrm{del}}$ and the coefficient B by linear least squares analysis. The results are summarized in Table 2. As an example, the results for the glass frit P4 are depicted in Fig. 5. The error bars represent both the uncertainty in the control of the relative humidity in the XRD chamber and the uncertainty in the determination of t_c. In comparison to our previous study with bulk samples, the present measurements are more scattered resulting in increased standard errors of ln $\mathrm{RH}_{\mathrm{del}}$ and B, and less satisfactory coefficients of determination R^2. In part, the increased experimental error is caused by the loss of intensity in the measurements with the glass frits and the resulting difficulties in the determination of t_c. Other important sources of error include material inhomogeneities of the glass frits and the limited reproducibility of the sample preparation resulting in an inhomogeneous distribution of the NaCl in the pore space of the specimens.

Despite of the increased experimental error, Eq. 2 provides a satisfactory representation of the experimental data to within their stated uncertainty (Fig. 5) while the standard error of the $\mathrm{RH}_{\mathrm{del}}$ is still acceptable. This is illustrated in Fig. 6 where the deliquescence humidities of NaCl in the glass frits and their standard errors are plotted as a function of the median pore diameter. The deliquescence humidities in the glass frits compare nicely with the value of 75.4 ± 0.5% determined in our previous work for bulk NaCl (Linnow and Steiger 2006), which was in excellent agreement with the commonly accepted reference value of 75.3% (Stokes and Robinson 1949; Greenspan 1977). To within the combined experimental uncertainties there are no significant deviations of the deliquescence humidities in the porous substrates and the bulk sample. This is in agreement with theoretical considerations according to which a significant increase in the chemical potentials of small crystals is not expected at crystal sizes above about 0.1 μm (Steiger 2005b). According to Fig. 2 the crystal sizes in the porous specimens that were investigated in the present work

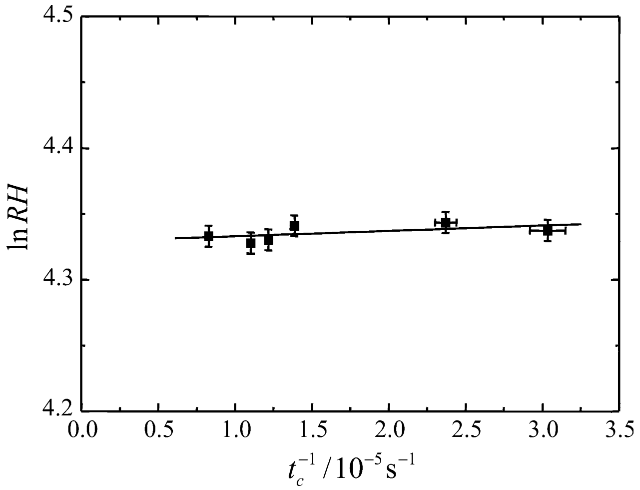

Fig. 5 Plot of ln RH versus t_c^{-1} for the deliquescence of NaCl in the pore pace of the glass frit P4 (d_m = 11.1 μm) at 25°C; *vertical error bars* represent uncertainties in the measurement and control of RH in the XRD-chamber, *horizontal error bars* represent uncertainties in the determination of t_c from the XRD patterns

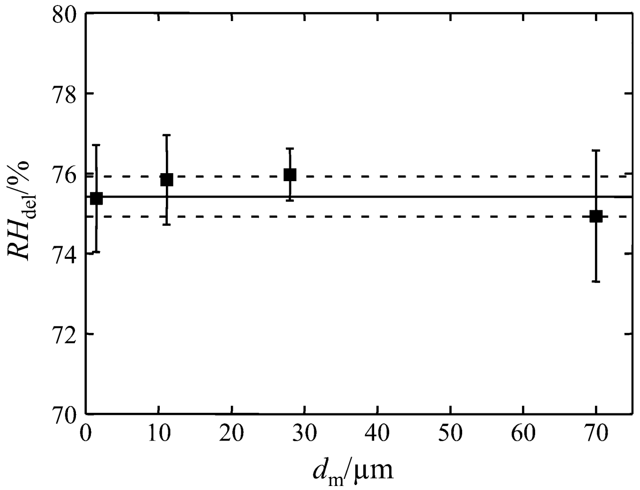

Fig. 6 Deliquescence humiditiy RH_{del} of NaCl in porous glass frits at 25°C as a function of median pore diameter d_m. *Error bars* represent the uncertainties in the determination of RH_{del} from experimental data by least squares analysis. *Solid* and *dashed lines* are the RH_{del} and the range of experimental uncertainty for bulk NaCl as reported by Linnow and Steiger (2006)

are hardly smaller than about 1 μm. The results of the present measurements confirm that there is no crystal size influence on the deliquescence humidity of such large NaCl crystals that are deposited in the pore space of glass frits.

The results listed in Table 1 also confirm that the deliquescence rates are lower in the P5 glass frit. As discussed before, this is most likely the result of a higher load of the P5 frit with NaCl. Considering the scatter in the experimental data, the differences in the deliquescence rates in the P2–P4 specimens are less obvious and not significant. Finally, it is important to note that there is a strong influence of the relative humidity on the deliquescence rate. Most measurements in the present work were carried out at <80% RH, i.e. only slightly above the deliquescence humidity of NaCl. However, according to Eq. 1 and as shown by Linnow and Steiger (2006), there is a substantial increase in the reaction rates at high humidity. The present work largely focused on the low to intermediate RH range, which is most important for the accurate determination of the deliquescence humidity. In future studies, it might be useful to carry out measurements at high RH in order to evaluate the effects of short-term RH maxima. This however, will require an optimization of the measurement conditions to improve the limited time resolution of the RH-XRD method.

Conclusions

The present study confirms that RH-XRD is an appropriate experimental technique for the in situ investigation of phase transformations in confined spaces of porous materials. By using an X-ray amorphous substrate such as glass frits problems with interfering XRD patterns are avoided, however, the technique might also be successfully applied in future studies with materials of simple mineralogical composition, e.g. limestones or quartzitic sandstones.

Due to the limited penetration depth of X-rays the diffraction measurements are limited to a narrow zone close to the surface of the porous material under investigation. Moreover, the penetration depth is not defined sharply but follows the exponential absorption law and, in addition, depends on the Bragg angle. It follows that the distribution of the salt under investigation within the porous substrate is critical in direct XRD studies with porous substrates. The sample preparation procedure used in the present work including impregnation with salt solution and subsequent freeze-drying did not always yield a homogeneous salt distribution in the porous substrates. Therefore, additional characterization of the samples using scanning electron microscopy is recommended in RH-XRD studies with porous substrates. Also, future studies should aim at an optimization of the sample preparation.

The kinetic measurements that were carried out in the present work show that the deliquescence of NaCl in the pore space close to the surface of a porous substrate proceeds on a time scale of a few hours. Since our measurements were all carried out at comparably low relative humidity (<80%) even shorter reaction times are to be expected at high RH as predicted by Eq. 1. This implies that the dynamics of deliquescence–crystallization cycles in building materials is strongly affected by both frequency and amplitude of the ambient humidity variation. There appears to be no doubt however, that quite short-term variation of ambient relative humidity, e.g. typical daily fluctuations, might induce damaging deliquescence–crystallization cycles within the pore space of building materials.

RH-XRD measurements do not provide information on the deliquescence in greater depth, i.e. beyond the X-ray penetration depth. With increasing depth, the overall rate of the deliquescence process is not only affected by the reaction kinetics and the supply with water vapor, but is increasingly limited by transport processes, i.e. water vapor diffusion and capillary transport of the solution initially formed by the dissolution of the salt crystals in the pore space near the surface. At a given depth, the deliquescence kinetics in the porous building material is expected to follow a considerably more complex rate law and a number of different parameters need to be taken into consideration, including porosity and pore size distribution, the nature of the salt, crystal morphology and the ambient RH. In order to investigate the kinetics of deliquescence in building materials, it will be useful in future studies to combine different experimental techniques. For instance, RH-XRD appears to be very useful to study the deliquescence in the pores close to the surface, while bulk measurement techniques such as gravimetric sorption measurements reveal additional information on the rates in greater depth. For example, Sawdy (2001) carefully measured the rates of moisture uptake and loss in salt-contaminated samples and identified the major rate controlling influences. NMR measurements could provide further insight as this technique allows for the simultaneous determination of moisture and ion transport (Pel et al. 2002).

The limited penetration depth of X-rays in porous materials does not pose any particular problems in the determination of equilibrium humidities of confined crystals. The present work shows that the dynamic approach for the determination of equilibrium humidities that was successfully used with bulk samples (Linnow and Steiger 2006) can also be applied for the determination of the deliquescence humidity of NaCl in glass frits without significant loss of accuracy. In agreement with theoretical considerations, the present measurements confirm that the deliquescence humidity of NaCl crystals of about 1–3 μm in size is not affected by the confinement in the pore space of glass frits with median pore diameters in the range of 1.4–70 μm. The ability of RH-XRD for the direct determination of equilibrium humidities within pores offers the possibility in future studies to apply the technique to mesoporous materials in order to determine the influence of confinement of very small (<0.1 μm) crystals on the deliquescence humidity.

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