

Appendix I Adsorption of water to salt in a humid atmosphere

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1 Motivation

In case of brine inflow into the backfill of a repository in rock salt there will be evaporation at the interface between the solution and the pore atmosphere. The water vapour will subsequently spread rather quickly in the pore space by means of vapour diffusion because of the quite high vapour diffusion coefficient. Crushed salt as backfill material will be assumed further on.

Generally, water vapour can be sorbed on the surface of the salt grains. Depending on the capacity of this process two different consequences follow from evaporation. In case of little interdependency between water vapour and salt, evaporation leads essentially to a high local humidity in the pore atmosphere. Driven by the gradient of the vapour partial density the vapour can quickly spread out within the pore space of the backfill until it eventually reaches the waste canisters and initiates corrosion. If, however, vapour is sorbed in sufficient quantities at the surface of the crushed salt, this may prevent the vapour from reaching the canisters but could lead to a softening of the backfill and local acceleration of compaction. The experiment described in the following was therefore intended to quantify the sorption of water on crushed salt.

2 Experiment

2.1 Description

The crushed salt used in the experiment was prepared from the z2HSSP facies (table salt) from the Asse mine. It contained more than 99 % halite and was mixed according to the grain size distribution described in Appendix G of the main report.

Six samples with a weight between 85 to 139 g were dried at 105 °C over 24 hours. Another batch of six samples was prepared but left at the moisture content of 0.02 % that represents the equilibrium content at storage conditions. The samples were allocated to two desiccators in such a way that each desiccator contained three moist and three dried samples. The set-up is shown in Fig. 2.1.



Fig. 2.1 Test set-up

The desiccators were located in a climate controlled room with nearly constant temperature. The humidity in the desiccators was controlled by salt solutions at the bottom. The first solution used at the beginning of the test had an equilibrium humidity of 12 % above the surface. The mass of the samples was measured frequently. After periods of 2 to 4 weeks, depending on the data, the salt solution was exchanged, thereby increasing the relative humidity. The final test period was performed under 75 % humidity which is the equilibrium humidity over a fully NaCl-saturated solution. The target humidity and the period of time over which each humidity level prevailed are listed in Tab. 2.1.

Tab. 2.1 Humidity levels and related test durations

Humidity level [%]	Test duration [d]	Time [d]
12	27	0 - 26
22	16	27 - 43
31	31	44 - 75
43	14	76 - 90
62	37	91 - 128
75	288	129 - 417

Initially, also a test period at 50 % humidity had been planned. It was dropped later on when it became clear that the related weight difference would have been too small.

After 220 days the measurements were done less often and not always checked immediately for plausibility. Some of the phenomena in the data can therefore not be satisfyingly explained.

2.2 Results

The evolution of humidity and temperature in the desiccators is depicted in Fig. 2.2. It shows that the temperature had been kept indeed nicely between 22 °C and 24 °C for most of the time. A temporary increase to about 27 °C between day 85 and day 100 had apparently rather little influence on the humidity anyway (cp. Fig. 2.3).

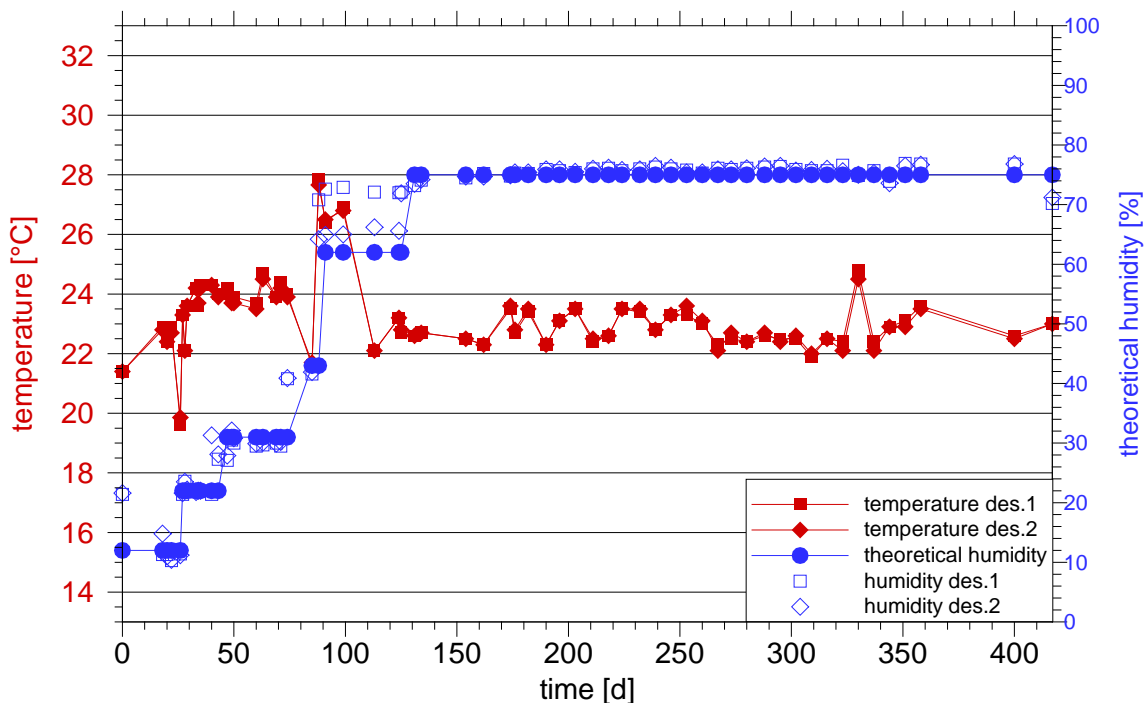


Fig. 2.2 Evolution of humidity and temperature in the desiccators

The measured relative humidity corresponded well to the theoretical values for the respective salt solution which are also indicated in Fig. 2.2. An exception is the 62 %-level, though, where the measured humidity exceeded the theoretical value in both desiccators considerably. No explanation for this behaviour could be found.

The evolution of the total weight of the samples is shown in Fig. 2.3. It appears that very little happens until full humidity is reached. There are, however, several jumps in the otherwise exceptionally smooth course of the curves in this range. These jumps can

partly be related to irregularities such as mass losses during the weighing procedure. In case of the moist sample 5 the jar containing the sample was broken and had to be re-placed.

The development of only minimal weight changes continues for the first 40 – 50 days at 75 % humidity. But then a significant increase in weight could be observed that exceeded all previously water uptake and did not seem to come to an end over time. In hindsight it was suspected that this was not an effect of sorption but rather an effect of condensation (see section 2.3). The data for the period after 120 days are therefore considered to be spoiled.

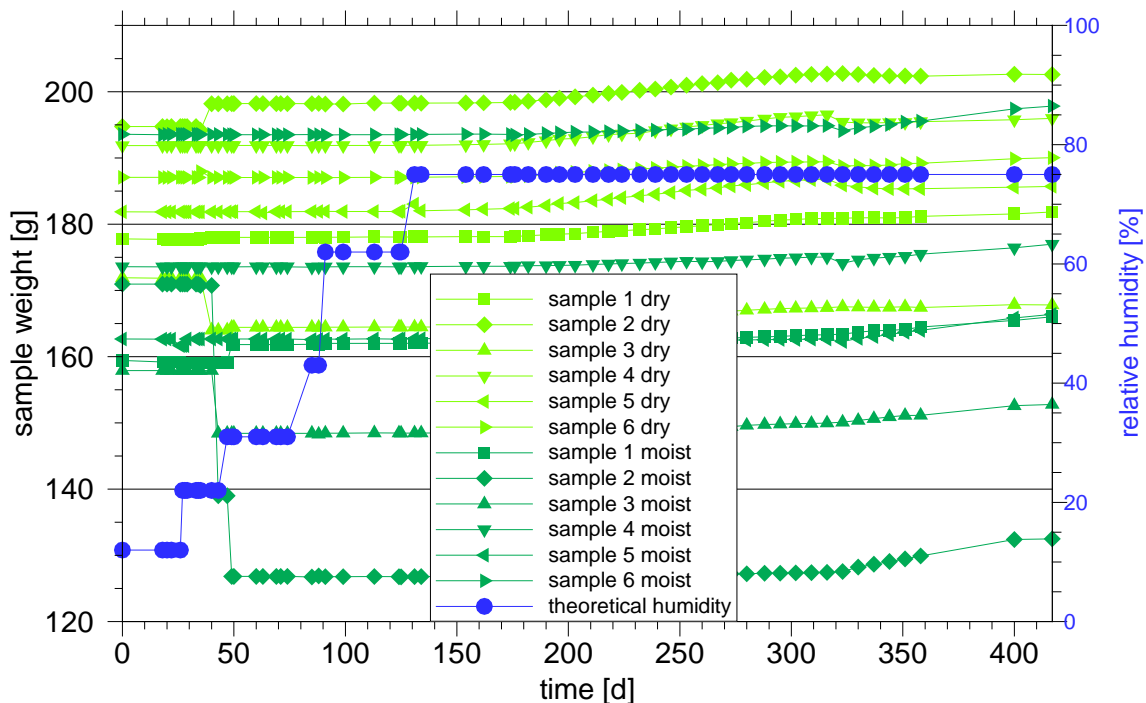


Fig. 2.3 Evolution of the total mass of the samples

2.3 Interpretation

Weight changes of the samples during the experiment and in particular before reaching maximum humidity were apparently minimal. The irregularities mentioned above had a much bigger impact on the sample weight than the sorption process itself thus making it difficult to recognise the effect of sorption in the weight data. To gain a clearer picture of the evolution of the moisture content the weight data was therefore corrected to show no

higher difference in weight from measurement to measurement than 0.1 g. The resulting curves are depicted in Fig. 2.4.

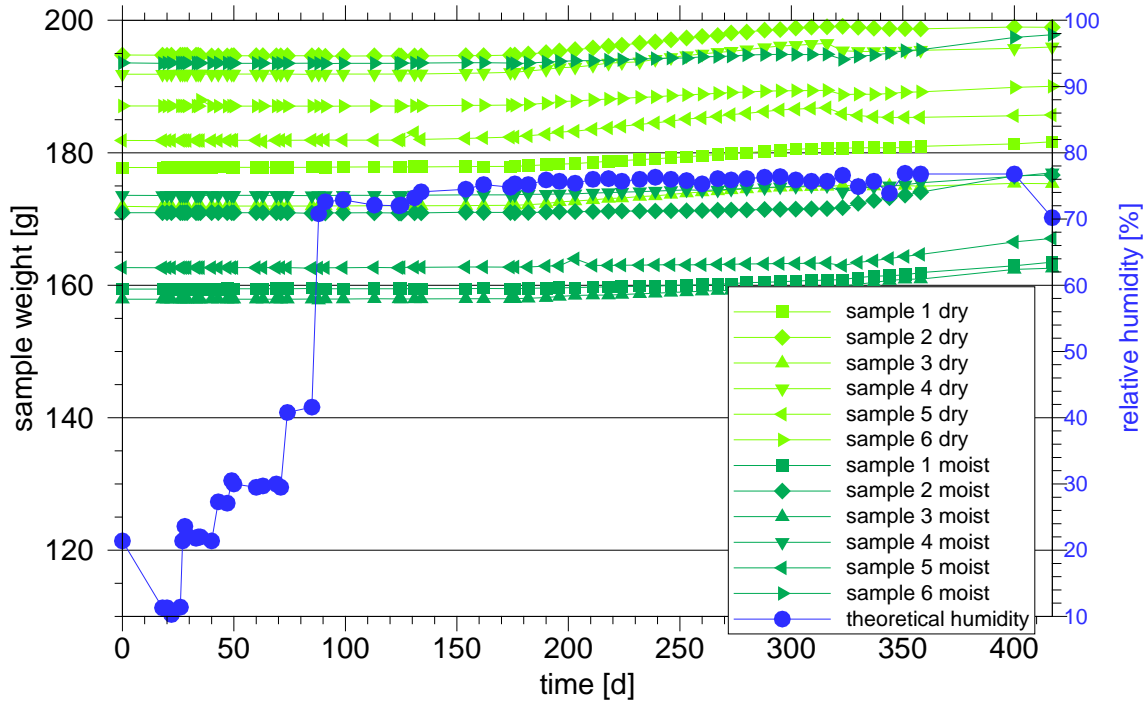


Fig. 2.4 Evolution of the total mass of the samples – corrected data

From the weight data the amount of the water sorbed during the experiment could be derived by calculating the difference of the moist salt mass and the dry mass. The result for the whole experiment is shown in Fig. 2.5. The plot confirms the observation that much more water was gained by the samples during maximum humidity than at the previous humidity levels. While the initially dry samples seem to take up water more readily at first than the initially moist samples these trends go into reverse for the last 100 days.

The somewhat delayed begin of the comparatively strong water uptake after raising the humidity to 75 % is not easily explained. It might be that the vapour saturation pressure in the samples could have been temporarily exceeded because of temperature variations. This would have caused condensation of water which would have retreated to the contact zones of the salt grains due to capillary forces. Lowering of the vapour saturation pressure at the meniscus of the water air interface leads then to further condensation. This effect, known as “capillary condensation”, would thus be self-sustaining even if loosening strength over time as the amount of accumulated water would increase thereby decreasing the curvature of the menisci. However, this effect has nothing to do with sorp-

tion so that the period after 120 days can be considered to be spoiled rendering further discussions concerning this phase pointless.

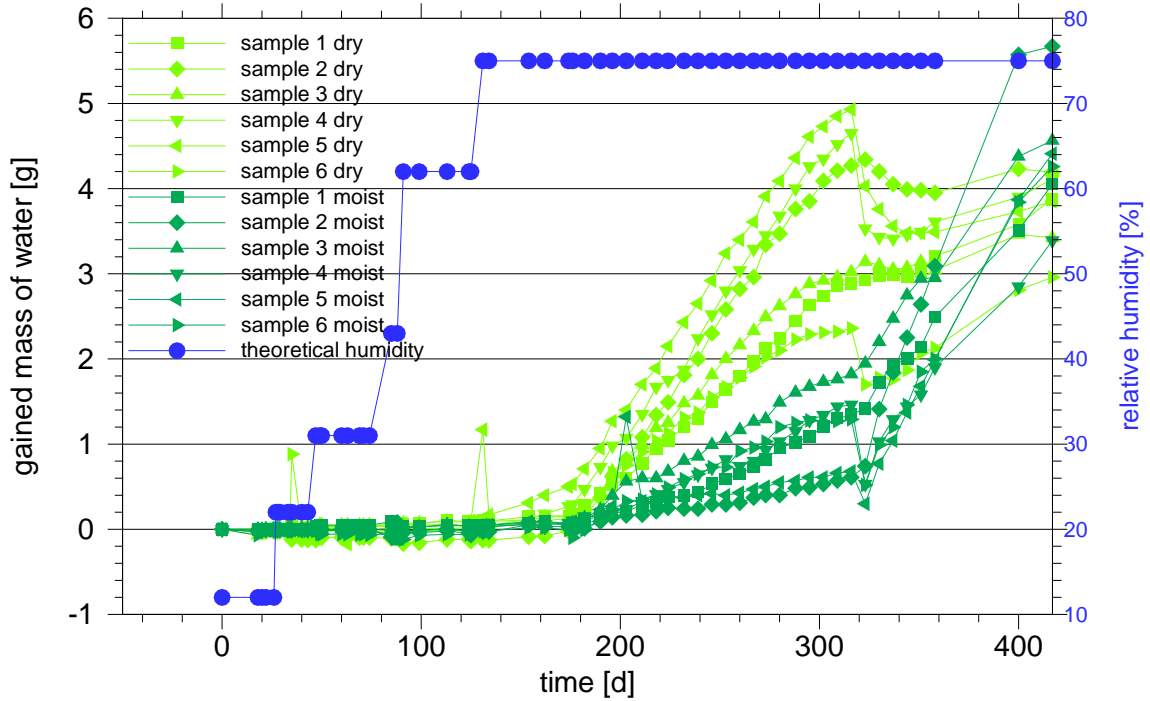


Fig. 2.5 Mass of water gained by the samples during the experiment

The following discussion thus concentrates on the first 120 days. Fig. 2.6 shows the mass of gained water for the initially dry samples. The cluster of individual curves seems to indicate a certain increase of adsorbed water which is confirmed by the curve for the mean values. The curve for the mean values even allows quantifying the gain to amount to roughly 0.04 g before maximum humidity was reached. At a mean sample mass of 112 g of dry salt this translates into a moisture content of roughly 0.04 %.

A still open question is if an equilibrium between relative humidity and moisture content has actually been reached at each humidity level. This cannot conclusively deduced from the data. What can be stated, though, is that if adsorption was still ongoing at the times of humidity increase, the kinetics involved must very slow.

In contrast to the initially dry samples, the mean for the initially moist samples – depicted in Fig. 2.7 – indicates an increase of adsorbed water only after increasing the humidity to the maximum. Again, it cannot entirely be excluded that the sorption process is just extremely slow.

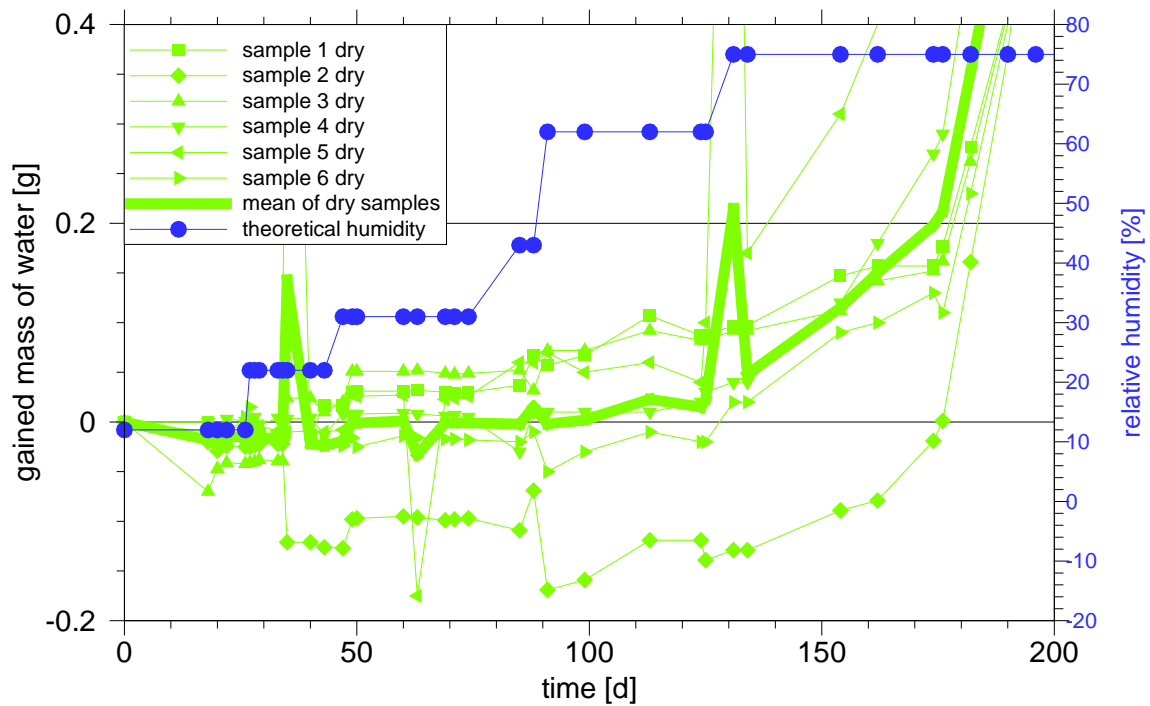


Fig. 2.6 Mass of water gained by the initially dry samples; close-up

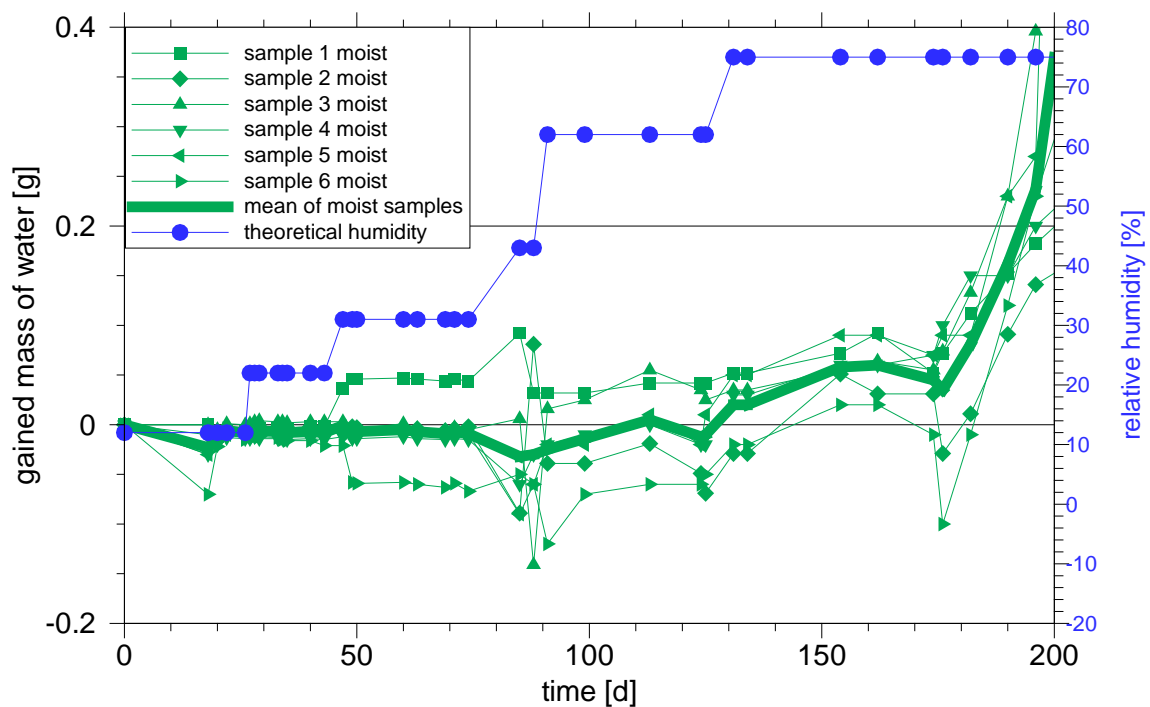


Fig. 2.7 Mass of water gained by the initially moist samples; close-up

From the mass of gained water the evolution of the moisture content can be calculated. The resulting plots are shown in Fig. 2.8 and Fig. 2.9.

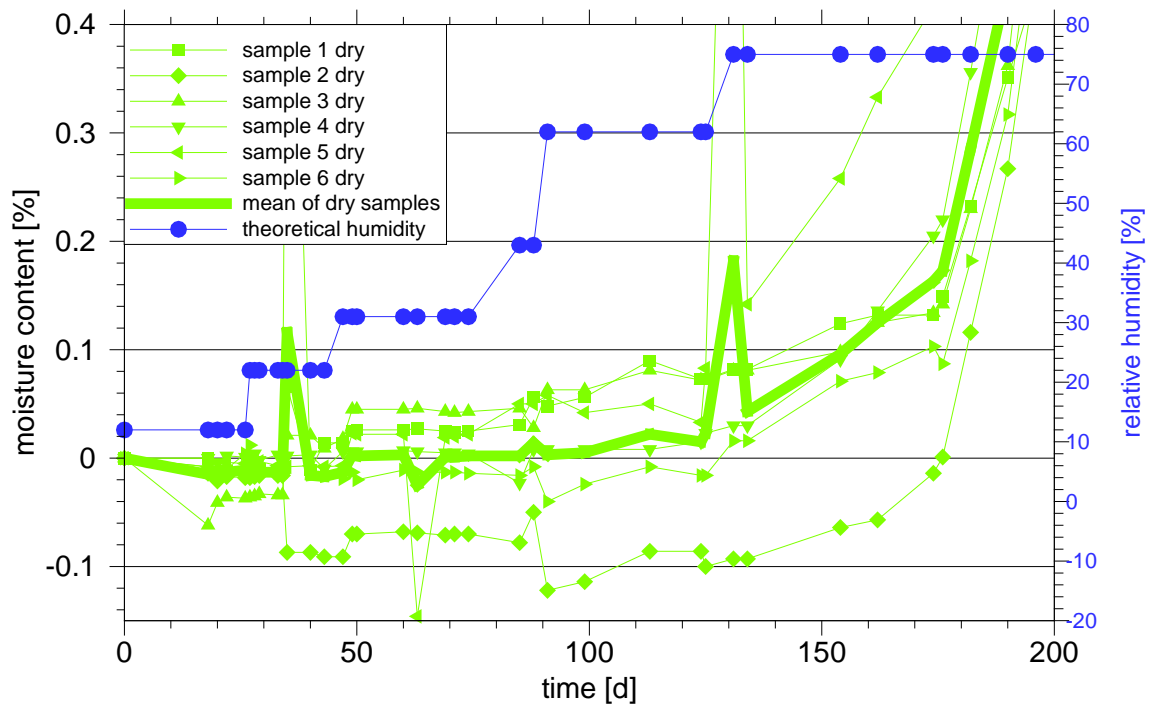


Fig. 2.8 Evolution of the moisture content of the initially dry samples

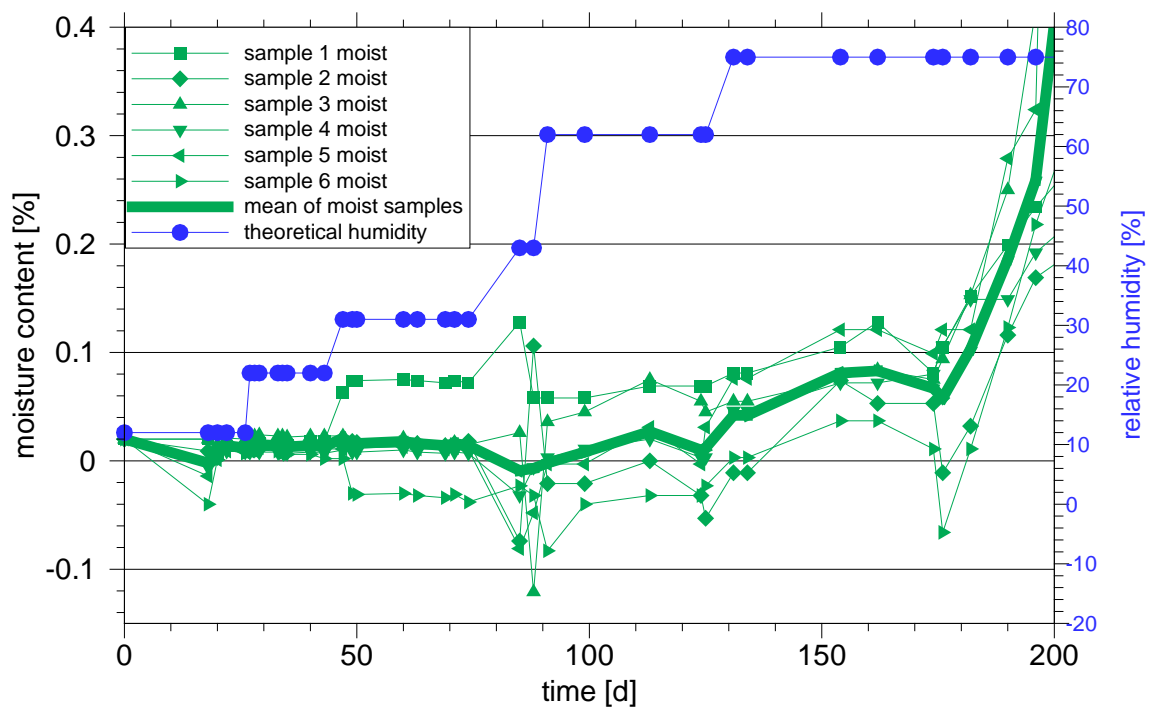


Fig. 2.9 Evolution of the moisture content of the initially moist samples

3 Error estimations

Since the dry mass of salt as well as the mass of the respective jar was obviously constant during the experiment¹, the amount of water sorbed between two weight measurements could be determined by the difference of the total mass. This means that the error of the first weighing has to be added to the error of the second weighing in order to get the error for the mass of water gained between the two measurements.

Different weighing scales were used during the experiment to determine the sample weight. Between day 22 and 71 a scale with a reading accuracy of 1/1000 g was used. During the remaining time a scale with a reading accuracy of only 1/100 g was available. The uncertainty in the data introduced by the reading accuracy of the less accurate scale thus should be in the range of plus minus the symbol size for the humidity in Fig. 2.6 and Fig. 2.7. This appears to be tolerable in comparison of the other test inherent uncertainties that cannot be quantified.

4 Comparison to an earlier experiment

4.1 Description

In an earlier experiment the isotherms for crushed salt from different salts of the Asse mine – among them the Staßfurt rock salt z2 with an anhydrite content of almost 5 % – had been determined [FRÖ 95]. The samples were dried and then exposed to a stream of moistened air for several days. The moisture content was determined by weighing. After terminating a test for a humidity level the samples were dried again and then exposed to air of a different humidity. Maximum grain size of the samples did not exceed 1 mm to assure a certain accuracy of the weight data. The results are shown in Fig. 4.1 in terms of a moisture content by mass over the relative humidity in percent. The data for z2-salt relates to curve marked with triangles.

¹ except in case of the broken jar

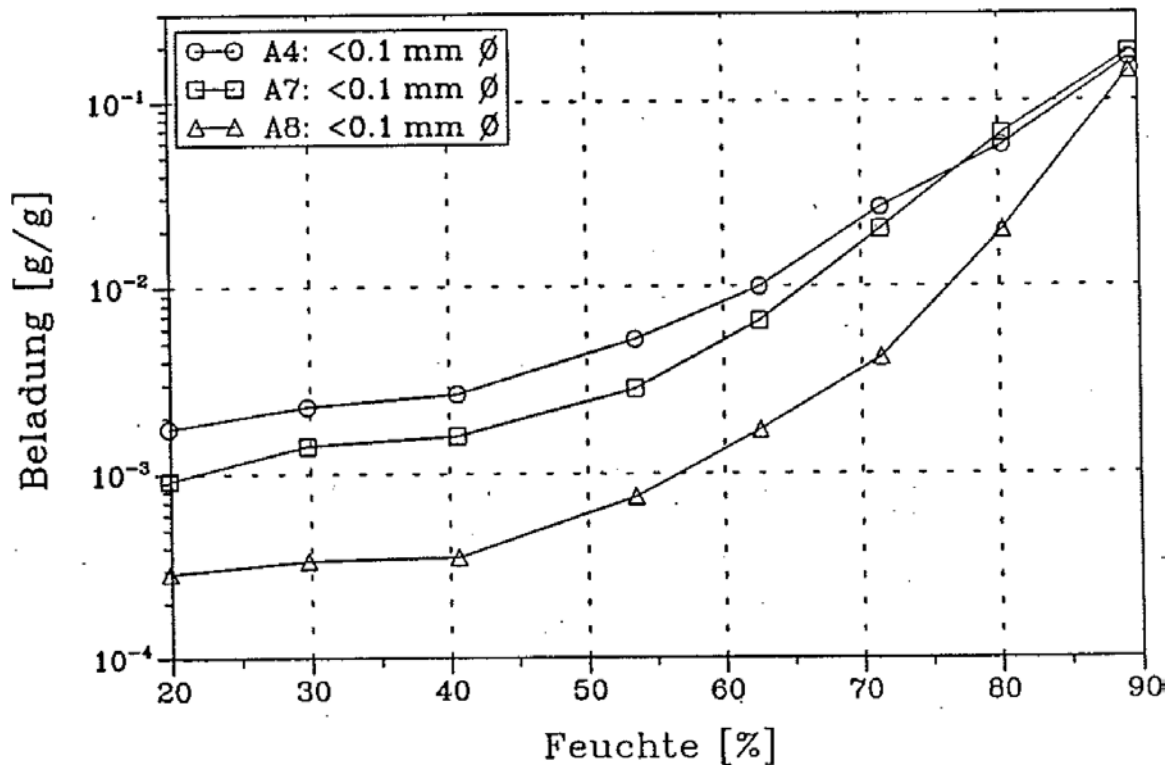


Fig. 4.1 Isotherms after /FRÖ 95/ for crushed salt from the Asse mine

The isotherm for z2-salt in Fig. 4.1 shows for humidity values up to 40 % an almost constant moisture content of 0.03 %. Above 50 % humidity the moisture content increases exceeding 0.1 % between 54 % and 63 % humidity. Close to the saturation vapour pressure for NaCl-brine relating to 75 % humidity the moisture content reaches about 0.4 %.

For air with more than 75 % humidity the samples are prone to condensation as described above. The seemingly consistent extension of the isotherm above 75 % could therefore just be a consequence of the fact that each test period lasted only a few days.

4.2 Comparison

Assuming that the method by which the crushed salt samples are exposed to humid air is of secondary relevance the main difference of the two experiments lies in the grain size distribution of the samples. Even if the sieve line for the material used in /FRÖ 95/ is not known the assumption appears to be reasonable that the inner surface of the samples of /FRÖ 95/ was bigger than in the GRS-experiment presented here leading consequently to higher moisture contents. While the scatter of the data in the GRS-experiment does not allow for a direct comparison of values indirect evidence is given by the initial

moisture content of 0.02 % for the crushed salt in the GRS-experiment. This value relates to the conditions at storage where an ambient humidity of about 40 % appears to be reasonable which is indeed lower than the value of 0.03 % at comparable conditions in the experiment of /FRÖ 95/.

However, comparability of the two experiments is compromised by the mineralogical composition of the crushed salt materials investigated. While the anhydrite content in the samples of the GRS-experiments is probably negligible it adds up to almost 5 % in the experiment of /FRÖ 95/. Together with the different inner surface it might explain why the moisture content at a humidity of about 70 % differs substantially between both experiments: about 0.3 % (/FRÖ 95/) and about 0.04 % (GRS). Further comparison thus appears to be pointless.

5 Summary and conclusions

The deficiencies in the presented experiment to determine isotherms for the sorption of water vapour on crushed salt from the z2HSSP facies of the Asse mine (table salt) prevent a quantitative evaluation of the data. Some conclusions can nevertheless be drawn, though.

In the investigated crushed salt the amount of water drawn from a moist atmosphere is either rather low or it takes time in the order of years to reach a significant mass of adsorbed water. Low sorption capability in combination with a high diffusivity of water vapour in air thus strongly suggests that vaporous water can reach deeply into a crushed salt backfill. It might even reach the waste canister and be doing harm to them by corrosion.

The little amount of sorbed water indicates furthermore that a reduction of the resistance of the backfill to compaction will remain minimal. This deduction is consistent with the results of the compaction tests in a humid atmosphere of different relative humidities (see section 2.4.4 of the main report).

It has to be pointed out, though, that these results refer to an almost pure halite. Different observations and conclusions cannot be excluded for other types of salt with a different mineralogical composition.

In general, the experiment shows the extreme difficulties arising from test conditions with relatively high air humidity. It had been expected that the relative humidity of 75 % created over the surface of a salt solution would not interact with the crushed salt sample beyond water adsorption on the surface of the salt grains as in the previous test step at 62 % humidity. A considerable uptake of water in the samples has been observed, though, that continued over the remaining almost 300 days until termination of the experiment. While it is suspected that little temperature variations might have led to condensation triggering further capillary condensation this assumption needs confirmation yet.

References

- /FRÖ 95/ Fröhlich, H., Förster, S., Hohenthanner, C.R.: Bestimmung des Diffusions- und Permeabilitätsverhaltens von Wasserstoff in Steinsalz und kompaktiertem Salzgruz. Abschlußbericht. Batelle Ingenieurtechnik, Eschborn, 1995.
- /ROT 99/ Rothfuchs, T.; Feddersen, H.-K.; Kröhn, K.-P.; Miehe, R.; Wieczorek, K.: The DEBORA-Project: Development of Borehole Seals for High-Level Radioactive Waste - Phase II. Final report, FZK02E8715, Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Bericht GRS-161, GRS Köln, 1999.