

Code VIPER

Theory and Current Status



Gesellschaft für Anlagenund Reaktorsicherheit (GRS) mbH

Code Viper

Theory and Current Status

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# Abstract

Compacted air-dry bentonite is foreseen in many repository designs to be utilised as a geotechnical barrier since its hydrophilic and thereby swelling properties let it appear to be a material ideally suited for this purpose. The work reported here concentrates on the re-saturation of a partially saturated (air-dry) bentonite.

Numerical simulation of this process is presently based on a thermo-hydromechanically (THM) coupled approach. The underlying conceptual model, however, is not entirely consistent with the processes on a micro-scale. Thus an alternative approach was developed at GRS that is more closely related to microstructural phenomena and fits the requirements of a bentonite buffer in a repository as realistically as possible. Based on balance equations that were especially derived for this purpose a numerical code was developed for testing the theory. The code – now called VIPER – was stepwise advanced from physically simple to the expected complex conditions in a repository.

This report summarises the theory behind VIPER including the conceptual model, the properties of bentonite relevant for the model, and the development of the related balance equations. Also described are the transfer of the mathematical model into a numerical model and the steps taken to qualify the model for repository relevant conditions including the latest effort to extend the applicability of the model to bentonite-sand mixtures. However, since the development of VIPER is not yet finished some questions still remain to be answered.

# Table of contents

1	Introduction	1
2	Conceptual model underlying VIPER	5
2.1	Microstructure of bentonite	5
2.2	Water uptake process	7
2.2.1	Swelling, water density, and mobility	8
2.2.2	Process velocity	9
2.2.3	Re-saturation stages	. 16
2.3	Condensation	. 19
3	Re-saturation stage 1: quantitative description	. 23
4	Re-saturation stage 2: balance equation for vapour flow	. 25
4.1	General balance equation	. 25
4.2	Double-continuum approach	. 25
4.3	Balance equation for vapour in the pore space	. 26
4.4	Balance equation for the water in the interlamellar space	. 28
4.5	Combining balance equations	. 30
4.5.1	Coupling	. 30
4.5.2	Simplification of the term for binary gas diffusion	. 31
4.5.3	Simplification of the term for interlamellar water diffusion	. 32
4.5.4	Substituting of the water content in the balance equation	. 33
4.5.5	General approach for a temperature-dependent isotherm	. 36
4.5.6	Simplification of the storage term	. 37
4.5.7	Isothermal balance equation	. 39
4.6	Coupling of the parameters in the balance equation	. 40
4.7	Numerical solution	. 42
4.7.1	Introductory remarks	. 42
4.7.2	1-D geometry	. 42
4.7.3	2-D axisymmetric geometry	. 45
4.7.4	Time step limiting criteria	. 49
5	Re-saturation stage 3: balance equation for unsaturated flow	. 51
5.1	Introductory remark	. 51

5.2	Condensation	51
5.3	Balance equation for water based on two-phase flow theory	52
5.4	Equations of state	55
5.4.1	Capillary pressure-saturation relation	55
5.4.2	Relative permeability-saturation relation	57
5.4.3	Viscosity	57
5.5	Numerical solution	57
6	Confidence building for the vapour diffusion model	59
6.1	Qualification of the vapour flow concept	59
6.2	Application to an isothermal in-situ experiment with a bentonite-sand	
6.2.1	Description of the ITT-experiment	
6.2.2	Measured data	
6.2.3	Model description	71
6.2.4	Modelling results	
6.3	Application to a non-isothermal in-situ experiment	
6.3.1	Description of the CRT-experiment	
6.3.2	Data relevant for the model	
6.3.3	Model description	79
6.3.4	Modelling results	
7	Summary and Outlook	89
	References	91
	Table of figures	99
	List of tables	103
Α	Appendix: Comparison of different isotherms for MX-80	105
A.1	Published data	105
A.1.2	Description of the sources	105
A.1.2	Adsorption	106
A.1.3	Desorption	107
A.2	Consistency of the data	108
A.2.1	Content of montmorillonite	108

A.2.2	Initial water content1	09
A.3	Comparison of scaled data 1	111
A.3.1	Adsorption 1	111
A.3.2	Desorption 1	14
A.4	Conclusions 1	115
В	Appendix: Hydrate layers and related water content1	17
с	Appendix: Saturation with liquid water during stage 1	23
C.1	Two-phase flow effects on the microscopic level1	23
C.2	Adding hydration dynamics1	24
C.3	Expanding to a channel network 1	27
D	Appendix: Derivatives of the water content1	29
E	Appendix: Balance equation for heat transport1	133
<b>E</b> E.1	Appendix: Balance equation for heat transport	<b>133</b> 133
<b>E</b> E.1 E.2	Appendix: Balance equation for heat transport	I <b>33</b> I33 I36
E E.1 E.2 F	Appendix: Balance equation for heat transport       1         Balance equation for heat transport       1         Numerical solution       1         Appendix: Compilation of model assumptions       1	<b>133</b> 133 136 1 <b>37</b>
E E.1 E.2 F F.1	Appendix: Balance equation for heat transport       1         Balance equation for heat transport       1         Numerical solution       1         Appendix: Compilation of model assumptions       1         Re-saturation stage 1       1	I <b>33</b> I33 I36 I <b>37</b> I37
E E.1 E.2 F F.1 F.2	Appendix: Balance equation for heat transport       1         Balance equation for heat transport       1         Numerical solution       1         Appendix: Compilation of model assumptions       1         Re-saturation stage 1       1         Re-saturation stage 2       1	<b>133</b> 133 136 <b>137</b> 137
E E.1 E.2 F F.1 F.2 F.3	Appendix: Balance equation for heat transport       1         Balance equation for heat transport       1         Numerical solution       1         Appendix: Compilation of model assumptions       1         Re-saturation stage 1       1         Re-saturation stage 2       1         Re-saturation stage 3       1	<b>133</b> 133 136 <b>137</b> 137 137
E E.1 E.2 F F.1 F.2 F.3 F.4	Appendix: Balance equation for heat transport       1         Balance equation for heat transport       1         Numerical solution       1         Appendix: Compilation of model assumptions       1         Re-saturation stage 1       1         Re-saturation stage 2       1         Re-saturation stage 3       1         Balance equation for heat transport       1	133 133 136 137 137 137 138 138
E E.1 E.2 F F.1 F.2 F.3 F.4 G	Appendix: Balance equation for heat transport       1         Balance equation for heat transport       1         Numerical solution       1         Appendix: Compilation of model assumptions       1         Re-saturation stage 1       1         Re-saturation stage 2       1         Re-saturation stage 3       1         Balance equation for heat transport       1         Appendix: Local effect of heating on relative humidity       1	<ul> <li><b>133</b></li> <li>136</li> <li><b>137</b></li> <li>137</li> <li>138</li> <li>138</li> <li>141</li> </ul>

### 1 Introduction

Multiple barriers are envisaged to prevent radionuclide escape from underground radioactive waste repositories. If the geological barrier is a water bearing host rock like granite the geotechnical barriers are of particular importance in order to protect the waste canisters and the waste matrix against a corrosive attack of the water. Actually in some countries compacted air-dry bentonite is foreseen in a number of repository designs to be utilised as a geotechnical barrier since its hydrophilic and thereby swelling properties let it appear to be a material ideally suited for this purpose. However, the behaviour of bentonite during re-saturation is very complex and may be controlled by hydraulic, mechanical and thermal processes.

As soon as water reaches the bentonite barrier the process of re-saturation begins. The clay minerals take up water, swell and reduce the pore space and thereby the permeability of the bentonite. Thus, water entering the bentonite is buffered to a certain extent, and concurrently, further inflow is impeded effectively. In a fully saturated bentonite the mobile water moves (a) very slowly due to the low permeability and (b) in little quantities due to the small pore volume.

The work described in the present report was restricted to the re-saturation of a partially saturated (air-dry) bentonite. This period is rather short in comparison to the time span for which the buffer is expected to be fully operational but understanding the involved processes is nevertheless important for setting up initial conditions for the longterm evolution of the buffer.

The first re-saturation experiments with regard to radioactive waste disposal were performed in the early 1980's and were focused on the time-dependent water uptake of bentonite. It was found that water uptake under laboratory conditions, meaning room temperature and atmospheric pressure, can be well described by a Fickian approach ("diffusion law") with a constant "diffusion coefficient". The bandwidth of values found for the empirical "diffusion coefficient" in laboratory tests with compacted MX-80 bentonite is remarkably narrow and amounts to a little more than one order of magnitude /KRÖ04a/.

But the empirical "diffusion" law could not be confirmed for experimental conditions differing from laboratory conditions, especially from room temperature /BÖR01/. New approaches lead in the early 1990's to the development of thermo-hydro-mechanically

1

(THM) coupled models. Initially developed to investigate the interdependencies of heat transport, groundwater flow and mechanical effects in fractured rock, the necessity to include a bentonite buffer for a complete description of the near-field turned out soon. These models were therefore also used to describe the re-saturation of the bentonite buffer as for instance in the DECOVALEX II exercise /STE01/. Based on the assumption that liquid water migrates within the pore space of the bentonite, these approaches made use of the similarities between the hydraulic phenomena during re-saturation and the classical two-phase flow theory.

With the turn of the millennium an intensive theoretical review of the existing THMcodes was performed at GRS. Comparing the conceptual model of the codes with the microstructural phenomena in the re-saturating bentonite revealed that the THMapproach to bentonite re-saturation was not entirely consistent with the processes on a micro-scale /KRÖ03/, /KRÖ04c/.

Motivated by these findings as well as some supporting experimental evidence /KRÖ04a/ it was decided to develop an alternative approach that is more closely related to microstructural processes /KRÖ04b/. Here, the dominant water transport process was not considered to be advection of liquid water as in the THM-models but diffusion of water vapour where the lower density of vapour is compensated by a high migration velocity.

A corresponding water balance equation was derived and it could be shown that this balance equation could actually be transformed into the empirical "diffusion law" /KRÖ05/ allowing for the first time to explain the "diffusion coefficient" as a product of physically meaningful parameters.

Based on this balance equation the numerical code VAPMOD was developed that initially could only simulate re-saturation at room temperature and atmospheric pressure. Later, the code was stepwise adapted to increasingly complex physical conditions. Especially the extension to non-isothermal re-saturation required much theoretical work and many changes in the balance equation so that rewriting of the code lead eventually to the code VIPER, which is presently used.

From the beginning on the purpose of the alternative model was to simulate the resaturation of a bentonite buffer in a repository as realistically as possible. Therefore it made use of the fact that the volume into which the buffer material is emplaced is more

2

or less confined. This lead to a decoupling of the mechanical and the thermo-hydraulic processes. In that respect the range of possible applications is certainly much more restricted than that of a full THM-model. On the other hand, this restriction reduces the computational effort significantly.

The present report summarises the theory behind VIPER including the conceptual model, the properties of bentonite relevant for the model, and the development of the related balance equations. Also described are the transfer of the mathematical model into a numerical model and the steps taken to qualify the model for repository relevant conditions with emphasis on the latest effort to extend the applicability of the model to bentonite-sand mixtures. However, since the development of VIPER is not yet finished some questions remain to be answered in the future.

### 2 Conceptual model underlying VIPER

#### 2.1 Microstructure of bentonite

Bentonite consists mainly of montmorillonite, a clay mineral of the smectite group. The typical composition of an MX-80 bentonite is: 65 - 75 % montmorillonite, 10 - 14 % quartz, 5 - 9 % feldspar, 3 - 5 % carbonate, 2 - 4 % mica and chlorite as well as 1 - 3 % heavy minerals (e.g. /PUS99/)<sup>1</sup>. Only the montmorillonite is participating in the water uptake and swelling processes of the bentonite. In order to understand the phenomenon of re-saturation it is therefore necessary to have a closer look at the montmorillonite.

The clay minerals as indicated in Fig. 2.1 consist of stacks of negatively charged crystal aluminosilicate layers, the so-called lamellae who have a lateral size of about 200 nm but a thickness of only 1 nm (e.g. /DRU05/). They are bonded by cations e.g. Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> or K<sup>+</sup> which are located in the space between the lamellae. This space is called the "interlayer" or the "interlamellar space". Depending on the respective interlayer cation between three and twenty lamellae can be stacked on top of each other to form a particle. Fig. 2.2 shows TEM pictures of these particles. Re-saturation is closely related to hydration of the interlayer cations and will be described in detail in the next section.

Natural bentonite is ground up by the production process, with an ensuing grain formation. The grain size of industrially processed bentonite powder is between 0.1 and 2 mm e.g. /LIU02/, /PUS99/. Compacted bentonite can therefore be considered to be a porous medium. Thus, in principle two types of volumes are to be distinguished: the pore space between the clay grains and the intragranular space. Those two spaces are often addressed as "macro- and micro-porosity". Mercury intrusion porosimeter tests with FEBEX bentonite by /LLO03/ showed two pronounced peaks in the pore size distributions as shown in Fig. 2.3. The maximum at 10 nm represents micro-porosity which appears to be independent of the degree of compaction while the maximum representing macro-porosity shifted from 40 µm at a dry density of 1500 kg/m<sup>3</sup> down to 10 µm at a dry density of 1800 kg/m<sup>3</sup>.

<sup>&</sup>lt;sup>1</sup> In case of bentonite-sand mixtures the percentages change according to the additional amount of quartz.

		symbolic representation
ions and molecules	octahedral element octahedral sheet (O) tetrahedral sheet (T)	<ul> <li>O<sup>2-</sup></li> <li>OH<sup>-</sup></li> <li>Ai<sup>3+</sup></li> <li>Si<sup>4+</sup></li> <li>cations</li> <li>(T)</li> </ul>
elementary layer or lamella	(T) Si <sup>4+</sup> partly replaced by Al <sup>3+</sup> (O) Al <sup>3+</sup> partly replaced by Fe <sup>2+</sup> , Mg <sup>2+</sup> (T)	~ 1 nm¢
particle or stack of lamellae	interlayer or interlamellar space thickness: up to 1 nm depending on the amount of hydrated water 3 – 20 lamellae depending on the interlayer cation	~ 3 to 40 nm ~ 300 nm
grain	3D-view 2D-representation particle	~0.1 mm
macro- structure	bentonite in natural bedding grains in the bentonite powder grains grains grains grains in the bentonite powder grains pores	

Fig. 2.1 The structure of montmorillonite on different scales; compiled in /KRÖ04a/ after /JAS93/, /KRN98/, /PUS03/, and /KRÖ03/



Fig. 2.2 TEM/HRTEM pictures of montmorillonite/smectite particles; from a) /LEE05/, b) /JIN04/, and c) /BAN99/



Fig. 2.3 Incremental pore volume for two compacted bentonite samples; from /SAN06/ (after /LLO03/)

### 2.2 Water uptake process

### 2.2.1 Swelling, water density, and mobility

After penetration of water into the interlamellar space the water molecules become attached to the interlayer cations which means that the interlayer cations become hydrated. This widens the interlamellar space. Consequently, the particles either swell under unconfined conditions or they exert a "swelling pressure" if swelling of the bentonite body is impeded (e.g. /HEI90/). Under confined conditions swelling of the particles means that the increase of volume taken by the expanding clay particles reduces the pore space accordingly. A basic concept for the volume changes during water uptake is illustrated in Fig. 2.4.

The density of interlayer water can be determined by considerations on the microscopic scale involving charge density and interlayer spacing or on the macroscopic scale using water content and grain density of a fully saturated specimen. Several measurements for deriving the density of the hydrated water in the interlayer have been reported. A compilation of density values in /KRÖ04a/ based on microscale data shows that the density of interlayer water can be expected to be in the same order as that of fresh water. However, a significant uncertainty about this value can be seen from the calculated densities. Data cited from literature even extends the range to values between 700 kg/m<sup>3</sup> and 1400 kg/m<sup>3</sup>.



#### Fig. 2.4 Volume changes in bentonite during water uptake on a macroscopic scale

In case of using macroscopic quantities to determine interlayer water density there also exists an uncertainty concerning the correct value of the grain density. It could be shown in /KRN06/ that the related measurements yield lower values using unpolar flu-

ids like kerosene or benzene than those evaluated from measurements with water or water solutions. Using the lower grain density value to determine interlayer water density results consequently in a misleading high value. Presently this question is still under debate. However, recent molecular dynamics simulations suggest also adopting fresh water density for the interlayer water /HED09/.

Movement of water in the interlamellar space appears to be negligible. E.g. /PUS06/ ascribe a "very limited mobility" to hydrated water. However, there is experimental evidence that diffusion of cations in the interlamellar space as well as self-diffusion of interlamellar water can amount to significant proportions. According to /SKI06/ both effects depend on the degree of saturation. Based on data from /POI87/, /POI89/, and /CHA97/ the diffusion coefficient of Na-ions is given there as  $1 \cdot 10^{-11}$  m²/s for one hydrate layer,  $1 \cdot 10^{-10}$  m²/s for two layers and  $2 \cdot 10^{-10}$  m²/s for three hydrate layers. In case of self-diffusion it is suggested that the corresponding coefficient is close to the value for free water self-diffusion at two or more hydrate layers. At one hydrate layer this value is supposed to decrease "by around one order of magnitude". As discussed in detail in Appendix B the water content representing the boundary between one and two hydrate layers in MX-80 bentonite can roughly be expected around 7.5 % and between two and three layers around 18 %.

While diffusion of interlayer water is therefore taken into account in the later discussed balance equations it was not yet considered in the older calculations presented in section 6.1. (Most models presented there were also based on a simplified adsorption isotherm.)

### 2.2.2 Process velocity

#### **Equilibrium conditions**

The amount of water that is hydrated in the interlamellar space under equilibrium conditions depends on the chemical potential of the pore water (e.g. /KAR86/). This relation is empirical and can easily be determined since the potential depends mainly on the relative humidity in the pore space. It can be either expressed by an isotherm in terms of water content w vs. relative humidity  $r_h$  or as a retention curve in terms of suction svs. degree of saturation S. For conversion between suction and relative humidity the Kelvin equation

$$s = \frac{RT\rho_{w}}{M_{w}} \ln(r_{h})$$
(2.1)  

$$s - \text{suction [Pa]}$$
  

$$T - \text{temperature [K]}$$
  

$$R - \text{universal gas constant; } R = 8.31 [J/(\text{mol K})]$$
  

$$\rho_{w} - \text{density of liquid water; } \rho_{w} = 1000 [\text{kg/m}^{3}]$$
  

$$M_{w} - \text{molecular mass of water; } M_{w} = 0.018 [\text{kg/mol}]$$
  

$$r_{h} - \text{relative humidity [-]}$$
  
can be used. Conversion between water content and degree of saturation is given by

$$S = \frac{w}{w_{tot}}$$
(2.2)  

$$S - \text{degree of saturation [-]}$$

$$w - \text{water content [-]}$$

*w<sub>tot</sub>* - maximum water content [-]

The maximum water content can be calculated from bentonite dry density and grain density assuming that the pore space is completely water-filled.

Such isotherms or retention curves depend primarily on the type of interlayer cations but also on temperature. An extensive discussion of isotherms for MX-80 bentonite is given in Appendix A. An example for a retention curve and the equivalent isotherm for a 50/50 mixture of Saskatchewan bentonite and sand is given in Fig. 2.5.

From the existence of these adsorption isotherms it can be concluded that water is taken up by the clay particles regardless of the phase state of the water. Not only liquid water but also water vapour can provide the means for hydration. The case of liquid water in the pore space is covered by a value of 100 % relative humidity in the isotherm.

Furthermore, the isotherms show that water is not only present in the pore space in vaporous form but also in hydrated form in the interlamellar space. Hydrated water has a very high density in comparison to water vapour. An increase of the relative humidity means therefore that a major amount of water has moved from the pore space into the interlamellar space of the clay particles. The particles thus act as sinks for the vapor-

ous pore water, they immobilise it in the interlamellar space and swell at the same time, thereby reducing the available pore space.



**Fig. 2.5** Analytical retention curve (after /GUO06/) and the equivalent isotherm from applying equation (2.1) for Saskatchewan bentonite

Note that the term "water" shall be used here as synonym for "liquid water". If water vapour is meant, this shall be stated explicitly.

### The effect of swelling constraints on the isotherm

Generally and most easily measured is the relation of relative humidity and water content in the bentonite using free swelling samples. The resulting isotherms for MX-80 bentonite are discussed in Appendix A.

However, application to the re-saturation of buffers in a repository implies that only a confined space is available for the bentonite. If this space is completely filled with buffer material virtually no volumetric expansion of the buffer is possible. Instead, an increasing swelling pressure develops after contact with water. Geometrical considerations based on grain and interlayer water density show that the water content of a bentonite with a given dry density cannot exceed a certain end value (e.g. /KRÖ04a/). For example, in case of MX-80 with a dry density of 1600 kg/m<sup>3</sup> this saturation water content  $w_{sat}$ 

amounts to 26.5 % by mass. This poses a certain problem since the isotherm exceeds this value by far at high relative humidities (q.v. Fig. A.4).

As an ad hoc solution to reconcile the isotherm data for free swelling bentonite with confined conditions the isotherm is modified in VIPER by a third order polynomial. This polynomial replaces the original isotherm data above the water content  $w_{80}$  of 80 % of the saturation water content. It is constructed to match the water contents  $w_{80}$  and  $w_{sat}$  with the slope of the original isotherm at  $w_{80}$  and a horizontal tangent at  $w_{sat}$  as depicted in Fig. 2.6.

A physically better justified solution for such a modification can be adapted from a proposal of /DUE07/ that refers to the retention curve. The suction  $s_{free \ sat}$  corresponding to the water content at full saturation  $w_{sat}$  can be read off the retention curve for free swelling conditions. This suction value equals the swelling pressure  $p_{s \ sat}$  at saturation. Since suction  $s_{free \ sat}$  and swelling pressure  $p_{s \ sat}$  are functions of  $w_{sat}$  they depend ultimately on a parameter such as bentonite dry density that characterises the initial state of bentonite compaction.



Fig. 2.6 Ad hoc correction in VIPER of an isotherm for confined conditions

The authors assume that the swelling pressure increases linearly with the water content from the initial value  $w_{ini}$  up to the saturation value  $w_{sat}$ :

$$p_{s} = \frac{w - w_{ini}}{w_{sat} - w_{ini}} \cdot p_{s \ sat}$$
(2.3)

 $p_s$  - swelling pressure [Pa]

- $p_{ssat}$  swelling pressure at saturation [Pa]
- w water content [-]
- *w*<sub>ini</sub> initial water content [-]
- $w_{sat}$  water content at saturation [-]

The difference  $\Delta s$  in suction between the retention curves for free swelling and for confined swelling corresponds to the swelling pressure  $p_s$  developing with the water content in the range between  $w_{ini}$  and  $w_{sat}$  as indicated in Fig. 2.7:

$$\Delta s = p_s \tag{2.4}$$

$$\Delta s$$
 - correction of suction for confined conditions [Pa]



Fig. 2.7 Modification of the retention curve for confined conditions after /DUE07/

From equation (2.4) finally follows

$$s^{free}(w) - s^{conf}(w) = \frac{w - w_{ini}}{w_{sat} - w_{ini}} \cdot p_{s \, sat}$$

$$s^{free} - \text{ suction according to free swelling conditions [Pa]}$$

$$conf - w_{ini} = 0 \text{ suction according to free swelling conditions [Pa]}$$

*s<sup>conf</sup>* - suction according to confined conditions [Pa]

This modification can also be applied to isotherms using Kelvin's law (2.1) to transform equation (2.5) into

$$\ln(r_h^{free}) - \ln(r_h^{conf}) = \frac{w - w_{ini}}{w_{sat} - w_{ini}} \cdot \ln(r_h^{free})$$
(2.6)

- $r_h^{free}$  relative humidity according to free swelling conditions [-]
- $r_h^{conf}$  relative humidity according to confined conditions [-]

$$r_{h\,sat}^{free}$$
 - relative humidity at saturation according to free swelling conditions [-]

which finally reads

$$r_{h}^{conf} = r_{h}^{free} \left[ r_{h\,sat}^{free} \right]^{\left( -\frac{w - w_{ini}}{w_{sat} - w_{ini}} \right)}$$
(2.7)

Equation (2.7) means that an isotherm for free swelling conditions can be adapted to confined conditions by modifying the relative humidity values. An example for MX-80 with a dry density of 1480 kg/m<sup>3</sup> and an initial water content of 8 % is shown in Fig. 2.8. Based on the MX-80 isotherm data presented in /KAH86/ these parameters result in a water content of 23 % at saturation which relates to a relative humidity of 96 % under free swelling conditions. The isotherm for free swelling conditions is depicted by black squares connected by straight lines. The modified data is represented by red diamonds that are connected by cubic splines as used in VIPER for smoothing the tabulated data. The modification becomes significant only for high relative humidities values.

Note that the modification after /DUE07/ has been implemented in VIPER at a late development stage so that modelling results presented in this report are mainly based on preliminary methods of corrections.



Fig. 2.8 Example of an isotherm for MX-80 at confined conditions

### **Kinetics**

Hydration and dehydration are time-dependent processes because they are related to the migration of water molecules between pore space and interlamellar space. This migration process occurring if the system is not in equilibrium involves therefore certain kinetics.

An early conceptual model addressing this problem by considering hydration as a sink for the pore water has been proposed by /GEN93/. It was developed and incorporated in CODE\_BRIGHT in order to explain the temporal swelling behaviour of argillaceous rock. In this model liquid water is drawn from the pore space into the interlayer space by the difference between capillary pressure in the pores and a "microstructural" suction of the clay minerals which depends on the water content. However, vapour is not considered with regard to hydration.

Another approach for this effect has been proposed by /KRÖ04a/. Here, the flow rate of water between the pore space and the interlamellar space, called "hydration rate" further on, is assumed to depend on the differences of the chemical potential of pore water and hydrated water. The case of liquid water in the pore space is here included as a special case of water vapour at a relative humidity of 100 %.

The question about the ratio of the process velocities of vapour transport and hydration was first raised in /BUH04/. A parameter variation based on data from /KRÖ04a/ showed only little sensitivity of the results to the hydration velocity. Further systematic investigations by /KRÖ06/ confirmed these observations by defining a realistic range of admissible hydration parameters and comparing the results of the model with kinetics to the results of a model with instantaneous hydration. It was thus concluded that hydration is a much faster process than vapour diffusion. Locally, an equilibrium of humidity and hydrated water develops very quickly so that the simplifying assumption of instantaneous hydration with respect to vaporous pore water appears to be justified.

Remark: In case of liquid pore water with a density that is several thousand times higher than that of water vapour the supply of water molecules at the particle surfaces is accordingly higher. This fact indicates an even higher hydration rate for liquid water than that for vaporous water. It thus has to be concluded further that liquid water cannot remain in the pore space for significant periods of time unless interlamellar swelling is at least locally completed.

### 2.2.3 Re-saturation stages

The conceptual model for isothermal re-saturation of pre-compacted confined bentonite underlying VIPER was firstly formulated in /KRÖ04b/. It divides the process into three stages that are described in the following in more detail. The illustrating figures for the three stages are exemplarily based on a characteristic experiment in which bentonite was compacted in a steel cylinder (providing confined conditions) and brought into contact with water at the open face side of the cylinder as shown in Fig. 2.9.



# **Initial conditions**

- air-dry bentonite
- homogeneous density
- confined conditions

Fig. 2.9 Initial conditions of an exemplary re-saturation situation

The first stage or pre-stage begins with the first contact of water with the bentonite. In a rather short period of time water is sucked into the pore space rather fast, mainly by capillary forces. With the liquid water present in the pore space hydration kicks in. The reduction of pore space caused by the swelling of the minerals is accompanied by a dramatic reduction of permeability. Since uptake of liquid water by clay minerals is a fast process, too (e.g. /PUS03/), only very little water penetrates into the bentonite before any further water inflow is hindered very effectively due to the low permeability. This view is supported by the experimental evidence of /KRÖ04a/ which shows exclusively for the immediate vicinity of the inlet an unproportionally high water content and a particularly low dry density indicating a local and comparatively high swelling. The end of stage 1 is illustrated in Fig. 2.10.



# Stage 1 (pre-stage)

- two-phase water flow
- water uptake by clay particles
- swelling in the contact area
- narrow water-filled low permeability zone

### Fig. 2.10 End of stage 1 in an exemplary re-saturation situation

Parallel to the uptake of liquid water evaporation takes place in the pore space at the interface of the fluid and the gas phase. This becomes significant when the influx of liquid water is low after the end of stage 1 because progress of the water/air-interface in the pore space is slowed down even further by this process. A rough estimation of the flux densities at the end of the stage 1 shows that the supply of liquid water through the narrow, already saturated zone equals the following vapour flow further into the bentonite /KRÖ04a/. Thus the saturation with liquid water is temporarily limited to the wetted bentonite surface. The measurements of /PUS02/ indicate that the pre-stage of capillary water uptake takes times in the order of minutes rather than hours or even days.

**The second stage or main stage** is a stage in which no two-phase flow occurs at all. All the water entering during stage 2 evaporates at the established interface between liquid water and air. Water transport further into the bentonite takes places only by means of vapour diffusion in the gas phase and of interlayer water diffusion. The low density of the vapour is here compensated by the high process velocity of the gas diffusion. The varying vapour density during stage 2 is indicated by different shades of light blue in Fig. 2.11.

During the main stage the vapour flux at the water/air-interface decreases as the gradient of the relative humidity decreases. Concurrently the water vapour increases the amount of hydrated water next to the interface. This reduces the suction and thus the liquid water flow through the thin saturated zone at the inlet. It is therefore quite probable that the water/air-interface moves very little for quite some time.



# Stage 2 (main stage)

- water flow and evaporation rate are more or less equal, so
- no movement of the water front
- vapour diffusion and interlayer water diffusion are main water transport processes

Fig. 2.11 Stage 2 in an exemplary re-saturation situation

In the **third stage or final stage** two-phase flow commences again when the vapour flux eventually drops below the likewise decreasing liquid water flux because of the decreasing vapour density gradient. But by then the suction forces are also reduced considerably due to re-saturation via water vapour. Additionally, the permeability would be very low in the third stage of re-saturation. The significance of this stage is not quite clear at the moment. It is illustrated by Fig. 2.12.



# Stage 3 (final stage)

- no further swelling possible
- remaining suction draws water in

Fig. 2.12 Stage 3 in an exemplary re-saturation situation

Note that this model is consistent with a statement in /JNC99/ where it is indicated that water movement in the pore space at low water contents is dominated by vapour transport while transport of liquid water is predominant at high water content. Unfortunately, the primary literature is in Japanese so the background of this remark could not be checked.

As mentioned at the outset of this subsection this conceptual model covers resaturation at isothermal conditions. The processes described basically also hold for non-isothermal conditions but several properties of water and clay particles are temperature-dependent as discussed in detail in section 4.6. The effect of varied temperature on the water content distribution may be rather complex. Especially the effect of temporary local increase of relative humidity as a consequence of a temperature increase (q.v. Appendix G) can change the re-saturation dynamics significantly.

#### 2.3 Condensation

Condensation of water denotes the transition from gaseous water vapour to liquid water. This process depends on temperature and pressure. It occurs if the vapour becomes supersaturated meaning that the partial pressure of the vapour  $p_v$  exceeds the vapour saturation pressure  $p_{v,sat}$ :

$$p_{v} > p_{v\,sat} \tag{2.8}$$

 $p_v$  - vapour partial pressure [Pa]

 $p_{vsat}$  - vapour saturation pressure [Pa]

Partial pressure relates to partial density by the ideal gas law:

$$\rho_v = \frac{p_v}{RT} \tag{2.9}$$

 $\rho_v$  - vapour partial density [kg/m<sup>3</sup>]

The saturation vapour pressure depends on temperature but not on pressure. This relation was mathematically formulated in /IAP97/ and is depicted in Fig. 2.13. At constant pressure partial vapour pressure can exceed saturation pressure either by increasing the vapour mass locally or by decreasing temperature.



Fig. 2.13 Vapour saturation pressure of pure water; after /IAP97/

Re-saturation of a bentonite buffer being located between a heat-generating waste canister and the host rock generally means that heat and water enter the buffer at opposite sides. In this situation water transport is not necessarily directed towards the heater /KRÖ08a/. As a consequence of heating hydrated water in the clay is set free causing vapour flow in the direction of the temperature gradient as illustrated in Fig. 2.14.



**Fig. 2.14** Flow and transport processes in a re-saturating buffer located at a heatgenerating canister

Since the saturation vapour pressure is directly proportional to temperature the situation could occur that vapour migrating to the cool side of the buffer exceeds saturation pressure and condensates there. During swelling, though, the fast local equilibrium between vapour and hydrated water prevents the pore atmosphere from reaching vapour saturation.

In the theoretical framework described above a relative humidity of 100 % is related to a state where bentonite under confined conditions cannot swell anymore (stage 3 of the re-saturation; see section 2.2.3). In this stage the clay particles cannot adsorb additional water. However, vapour diffusion can still continue as long as a gas-filled pore space remains.

Prerequisite condition for vapour diffusion is of course a density gradient. Over a free water surface vapour in the pore atmosphere is saturated. In case of constant temperature vapour saturation pressure is also constant and thus the density gradient equals zero. In case of spatially varying temperature, though, the temperature-dependent vapour saturation pressure provides a density gradient. Consequently, vapour transport as well as condensation along this gradient occur until the whole pore space is filled with water.

## 3 Re-saturation stage 1: quantitative description

The first stage in which the liquid water penetrates effectively into the bentonite is rather short as mentioned above. The considerations given in Appendix C lead to

 assumption 3.1: During the first stage a thin, homogeneously water-saturated zone develops until equilibrium is reached between water flow through the swollen bentonite and evaporation into the free pore space (see Fig. 3.1).



Fig. 3.1 Conditions and processes around the bentonite-water contact zone

Water-uptake experiments have been performed at atmospheric pressure and with a solution as found at the Swedish island Äspö. Those indicate that the interface between water and air reached a depth of approx. 4 mm under these conditions /KRÖ04a/. Recent anion diffusion experiments with different electrolyte solutions suggest the same effect with a depth of approx. 2 mm /GLA11/.

For the end of the pre-stage

 assumption 3.2: Water transport in the thin saturated zone between the bentonite-water contact and the water-air interface is dominated by advective flow. is adopted. In this case a constant pressure gradient prevails in the pore water. This gradient maintains an advective flux that corresponds to the evaporation rate at the water-air interface. The gradient is not influenced by the hydraulic pressure at the ben-tonite-water contact since the evaporation rate is independent of this hydraulic pressure.

From this it follows that the penetration depth of the water-filled zone increases with increasing hydraulic pressure at the bentonite-water contact. Darcy's law allows to quantify this relation:

$$\frac{\Delta p}{\Delta x} = \frac{\Phi \ \mu}{k} v = const. \tag{3.1}$$

- *p* hydraulic pressure [Pa]
- $\Delta x$  penetration depth [m]
- $\Phi$  porosity [-]
- $\mu$  viscosity [Pa s]
- *k* permeability [m<sup>2</sup>]
- v velocity [m/s]

Equation (3.1) yields a linear relationship between applied hydraulic pressure and penetration depth. Using the value of 4 mm at atmospheric pressure as a reference proved to be successful as shown in /KRÖ06/ and /KRÖ08a/.

Note that all assumptions are compiled in Appendix F.

### 4 Re-saturation stage 2: balance equation for vapour flow

#### 4.1 General balance equation

The most general starting point for the derivation of a balance equation is the definition of a time-dependent state variable Z(t) in a moving domain B(t):

$$Z(t) = \int_{B(t)} z(\mathbf{x}, t) \, dV \tag{4.1}$$

- Z(t) extensive state variable in B(t) with the dimension <dim> [<dim>]
- B(t) time-dependent 3D-domain [m<sup>3</sup>]
- z(t) density of Z [<dim>/m<sup>3</sup>]

Allowing for a flux *J* of quantity *Z* across the moving surface of *B* and including a source *r* of quantity *Z* within *B* Reynolds' transport theorem yields for a fixed domain *G* (e.g. / $G\ddot{A}R87$ /):

$$\int_{G} \left[ \frac{\partial z}{\partial t} + \nabla (\mathbf{v}z + \mathbf{J}) - r \right] dV = 0$$
(4.2)

- G fixed domain [m<sup>3</sup>]
- v flow velocity [m/s]

*J* - non-advective across the surface of *G* [<dim>/(m<sup>2</sup> s)]

r - sink/source of Z in G [<dim>/(m<sup>3</sup> s)]

#### 4.2 Double-continuum approach

The general balance equation (4.2) can apparently be used to describe mass conservation of water in the bentonite. In doing so, discrimination between vapour in the pore space and hydrated water in the interlamellar space appears to be advantageous. It allows to distinguish clearly between relative humidity in the pore space and water content, which are both easily measured as indicators of the actual status of re-saturation. The price to pay for this separation is that the two resulting continua have to be coupled. This method of coupling two continua was already suggested in 1963 to describe flow in a fracture system and in the porous matrix simultaneously /WAR63/. Fig. 4.1 illustrates the principle for a typical two-dimensional re-saturation situation. One continuum represents the pore space in which vapour diffusion takes place; the other continuum comprises the interlamellar space accommodating interlayer water. The coupling process is hydration which provides exchange of water between the two continua.



Fig. 4.1 Double-continuum approach for re-saturating bentonite

### 4.3 Balance equation for vapour in the pore space

In the domain describing the pore space of the bentonite *Z* represents the mass  $m_v$  of water vapour in the pore space. Also adopting

- assumption 4.1: Diffusion of water vapour in air can be described as a binary diffusion process.
- assumption 4.2: Advection of water vapour does not occur.
- assumption 4.3: Fick's second law is valid.
- assumption 4.4: Diffusion is isotropic.
- assumption 4.5: Apparent diffusion is impeded due to tortuosity of the pore space.
- assumption 4.6: The local amount of water vapour can change due to hydration or condensation.
enables to specify the quantities in equation (4.2):

$$z = \Phi \rho_{v}$$

$$\mathbf{v} = \mathbf{0}$$

$$\mathbf{J} = -\Phi \tau D_{m} \cdot \nabla \rho_{v}$$

$$r = r_{hyd} + r_{cond}$$
(4.3)

$\Phi$	-	porosity [-]
$ ho_v$	-	vapour partial density [kg/m³]
τ	-	tortuosity [-]
$D_m$	-	coefficient of the binary gas diffusion [m²/s]
$r_{hyd}$	-	sink/source for vapour mass due to hydration [kg/(m <sup>3</sup> s)]
r <sub>cond</sub>	-	sink/source for vapour mass due to condensation [kg/(m³ s)]

Thus equation (4.2) is transformed into:

$$\int_{G} \left[ \frac{\partial (\Phi \rho_{v})}{\partial t} - \nabla (\Phi \tau D_{m} \cdot \nabla \rho_{v}) - r_{hyd} - r_{cond} \right] dV = 0$$
(4.4)

Based on assumption 4.1 the diffusion coefficient  $D_m$  can be written after /VAR96/ as:

$$D_{m} = D_{m0} \frac{p_{g0}}{p_{g}} \left(\frac{T}{T_{0}}\right)^{\theta}$$
(4.5)

*p* - pressure [Pa]

$$D_{m0}$$
 - reference value for the binary diffusion coefficient [m<sup>2</sup>/s]

 $p_{g\,0} \quad$  - reference gas pressure [Pa]

 $T_0$  - reference temperature [K]

Certain continuity conditions assured – for details see e.g. /GÄR87/ – the integral form (4.4) of the balance equation can also be written as a partial differential equation:

$$\frac{\partial(\Phi\rho_v)}{\partial t} - \nabla(\Phi\tau D_m \cdot \nabla\rho_v) - r_{hyd} - r_{cond} = 0$$
(4.6)

#### 4.4 Balance equation for the water in the interlamellar space

Analogously to the procedure in the previous section state variable *Z* can be chosen to represent the mass of water  $m_w$  in the interlamellar space of the clay minerals. Additionally applying

– assumption 4.7: Interlayer water can only migrate by a Fickian diffusive process.

yields the balance equation

$$\int_{G} \left[ \frac{\partial \left( \Phi_{hyd} \,\rho_{w} \right)}{\partial t} - \nabla \left( \tau_{hyd} \,D_{hyd} \cdot \nabla \left( \Phi_{hyd} \,\rho_{w} \right) \right) - \overline{r}_{hyd} \right] dV = 0 \tag{4.7}$$

 $\rho_{\rm w}$  - density of the interlayer water [kg/m<sup>3</sup>]

 $\Phi_{\scriptscriptstyle h\!v\!d}$   $\,$  -  $\,$  fraction of volume taken by interlamellar water [-]

 $au_{hyd}$  - tortuosity of the interlamellar space [m<sup>2</sup>/s]

 $D_{hvd}$  - diffusion coefficient of the interlamellar water [m<sup>2</sup>/s]

 $\overline{r}_{hvd}$  - sink/source for interlamellar water due to hydration [kg/(m<sup>3</sup> s)]

#### Introducing

 assumption 4.8: Density of interlayer water is independent of the state of hydration.

simplifies equation (4.7) to

$$\rho_{w} \frac{\partial \Phi_{hyd}}{\partial t} - \nabla \left( \tau_{hyd} \ \rho_{w} \ D_{hyd} \cdot \nabla \Phi_{hyd} \right) - \overline{r}_{hyd} = 0$$
(4.8)

Based on

- assumption 4.9: Constant-volume conditions apply.
- assumption 4.10: The sum of the volumes of pore space and interlayer water is constant.

the fraction of volume taken by interlamellar water  $\Phi_{\it hyd}$  can be related to the porosity  $\Phi$  by

$$\Phi_{hyd} = \Phi_d - \Phi \tag{4.9}$$

$$\Phi_d$$
 - porosity of the dry bentonite [-]

The porosity of the dry bentonite can easily be determined using the grain density of the bentonite  $\rho_s$  (e.g. /KRÖ04a/):

$$\Phi_d = 1 - \frac{\rho_d}{\rho_s} \tag{4.10}$$

 $ho_d$  - dry density of the bentonite [kg/m<sup>3</sup>]

## $\rho_s$ - density of the solid matter in the bentonite [kg/m<sup>3</sup>]

Additionally, defining the water content as

$$w = \frac{m_w}{m_s} \tag{4.11}$$

*w* - water content of the bentonite [-]

 $m_{_{\!W}}$  - mass of the interlayer water [kg]

$$m_s$$
 - dry mass of the bentonite [kg]

allows to relate porosity  $\Phi$  to the water content *w*:

$$\Phi = \Phi_d - \frac{\rho_d}{\rho_w} W \tag{4.12}$$

Combining equations (4.9) and (4.12) yields

$$\Phi_{hyd} = \frac{\rho_d}{\rho_w} w \tag{4.13}$$

Thus, equation (4.8) can be transformed into:

$$\rho_d \frac{\partial w}{\partial t} - \rho_d \nabla (\tau_{hyd} \ D_{hyd} \cdot \nabla w) - \overline{r}_{hyd} = 0$$
(4.14)

Note that the density of the interlayer water is at least as high as the density of fresh water and thus several orders of magnitude higher than the partial density of the water vapour in the pore space. This allows safely for

 assumption 4.11: The local mass of water vapour is negligible compared with the local mass of hydrated water.

This assumption leads to the conclusion that a water content measured during stage 2 of re-saturation reflects the entire mass of interlamellar water for all practical purposes.

## 4.5 Combining balance equations

## 4.5.1 Coupling

The two balance equations (4.6) and (4.14) describe water transport in two different continua that are coupled by exchange terms, formally the source terms  $r_{hyd}$  or  $\overline{r}_{hyd}$ , respectively. In /KRÖ04a/ an exchange term was suggested that introduced the kinetics of hydration into the resulting balance equations<sup>2</sup>. Following this approach two independent variables – the partial vapour density in the pore space and the water content in the interlamellar space – remained to be calculated. As mentioned earlier, however, the hydration kinetics appear to play a minor role in the re-saturation process which leads to

 assumption 4.12: Hydration occurs instantaneously. Thus, water content is always in equilibrium with the relative humidity in the pore space.

Since water is either present in the pore space as vapour or in the interlamellar space as hydrated water the process of hydration/dehydration decreases water in one continuum and adds the same amount of water in the other continuum:

$$r_{hyd} = -\overline{r}_{hyd} \tag{4.15}$$

<sup>&</sup>lt;sup>2</sup> This approach led eventually to the code VAPMOD, the isothermal predecessor of VIPER.

Equations (4.6) and (4.14) can thus be added in such a way that the sink/source terms  $r_{hvd}$  and  $\overline{r}_{hvd}$  cancel out:

$$\frac{\partial(\Phi\rho_{v})}{\partial t} - \nabla(\Phi\tau D_{m}\cdot\nabla\rho_{v}) + \rho_{d}\frac{\partial w}{\partial t} - \rho_{d}\nabla(\tau_{hyd} \ D_{hyd}\cdot\nabla w) - r_{cond} = 0$$
(4.16)

Applying the product rule to the first time derivative in equation (4.16) and inserting equation (4.12) in the time derivative of the porosity  $\Phi$  yields:

$$\Phi \frac{\partial \rho_{v}}{\partial t} + \rho_{d} \left( 1 - \frac{\rho_{v}}{\rho_{w}} \right) \frac{\partial w}{\partial t} - \nabla \left( \Phi \tau D_{m} \cdot \nabla \rho_{v} \right) - \rho_{d} \nabla \left( \tau_{hyd} \quad D_{hyd} \cdot \nabla w \right) - r_{cond} = 0 \quad (4.17)$$

#### 4.5.2 Simplification of the term for binary gas diffusion

The first diffusion term in equation (4.17) contains not only the coefficient of molecular diffusion acccording to FICK's law but also porosity and tortuosity. During re-saturation porosity as well as tortuosity decrease and are thus functions of the water content. However, concurrently decreasing are the pore channel diameters. Since they are already quite small in the compacted air-dry state molecular diffusion may change to Knudsen diffusion during the re-saturation.

Molecular diffusion changes to Knudsen diffusion if the mean free pathway of the diffusing molecules reaches the order of the pore diameter. The mean free pathway of water molecules in air amounts to approximately 100 nm at room temperature and atmospheric pressure, e.g. /KRÖ04a/. Only at pore diameters greater than 1  $\mu$ m the influence of Knudsen diffusion disappears (/MAS89/, cited in /HEL97/). The major part of the pore channels in compacted MX-80 bentonite has a diameter of less than 1  $\mu$ m (/JOH99/; /PUS99/; /PUS03/). In the light of these considerations the incidence of Knudsen diffusion appears to be quite probable. This compensates the decreasing of tortuosity and porosity and leads to

- assumption 4.13: The product of porosity, tortuosity and molecular diffusion coefficient is called the apparent diffusion coefficient  $D_a$ . Under isothermal conditions is  $D_a$  constant. According to assumption 4.13 the macroscopic diffusion coefficient reads

$$D_a = \Phi_0 \tau_0 D_m \tag{4.18}$$

*D<sub>a</sub>* - macroscopic diffusion coefficient [m<sup>2</sup>/s]

 $\tau_0$  - initial tortuosity [-]

## where

- assumption 4.14: The apparent diffusion coefficient  $D_a$  changes with temperature and pressure proportionately to the molecular diffusion coefficient.

also applies.

## 4.5.3 Simplification of the term for interlamellar water diffusion

The variable  $D_{hyd}$  in (4.14) can be specified to be the self-diffusion coefficient D' following

 assumption 4.15: Interlamellar water migrates diffusively at rates corresponding to the process of self-diffusion.

According to the Einstein relation for diffusion due to Brownian motion the diffusion coefficient is directly proportional to the absolute temperature:

$$D = \mu_p k_B T \tag{4.19}$$

*D* - diffusion coefficient [m²/s]

 $\mu_p$  - particle mobility [m/(N·s)]

 $k_{\scriptscriptstyle B}$  - Boltzmann constant [J/K]

The pathway of migrating interlamellar water is established by a series of clay particles in the direction of migration. The orientation of each of these particles usually differs from the orientation of the respective neighbours thus constituting a tortuosity of the interlamellar pathway. Based on

assumption 4.16: Change of particle orientation during re-saturation has negligible influence on the pathway tortuosity for the interlamellar water.

tortuosity of the interlamellar space can be treated as a constant. The apparent diffusion coefficient for the interlamellar water, defined here as

$$D'_a = \tau_{hyd} D' \tag{4.20}$$

 $D'_a$  - makroscopic diffusion coefficient of the interlamellar water [m<sup>2</sup>/s]

is therefore only dependent on temperature (because of D'(T)).

Thus equation (4.17) can be written as

$$\Phi \frac{\partial \rho_{v}}{\partial t} + \rho_{d} \left( 1 - \frac{\rho_{v}}{\rho_{w}} \right) \frac{\partial w}{\partial t} - \nabla \left( D_{a} \cdot \nabla \rho_{v} \right) - \rho_{d} \nabla \left( D_{a}' \cdot \nabla w \right) - r_{cond} = 0$$
(4.21)

#### 4.5.4 Substituting of the water content in the balance equation

The two variables in balance equation (4.21) – the vapour partial density  $\rho_v$  and the water content w – are not independent. Because of assumption 4.12 isotherms for the bentonite can be used to eliminate one of the two variables in equation (4.21).

As mentioned earlier, isotherms relate water content to relative humidity under equilibrium conditions and – as the term tells – at constant temperature. Isotherms for MX-80 bentonite are discussed in detail in Appendix A. However, isotherms change shapes depending on the temperature thus leading to the relation

$$w = f(r_h, T)$$
 (4.22)  
 $r_h$  - relative humidity [-]

This relation will still be called "isotherm" in the following even if it includes a temperature dependency. Furthermore, it is presumed that the following assumption holds:

assumption 4.17: The adsorption isotherm depends only on temperature. Influence of pressure, adsorption-/desorption-hysteresis<sup>3</sup>, and temperature-induced mineral alterations are negligible.

Relative humidity can be expressed by the ratio of the vapour partial density  $\rho_v$  and the vapour saturation partial density  $\rho_{v sat}$ :

$$r_{h}(\rho_{v},T) = \frac{\rho_{v}}{\rho_{v\,sat}(T)}$$
(4.23)
$$\rho_{v\,sat} - \text{vapour saturation partial density [kg/m³]}$$

So relative humidity is basically a function of the vapour partial density and temperature:

$$r_h = g(\rho_v, T) \tag{4.24}$$

With the help of equation (D.1) in Appendix D the storage term in equation (4.21) can be written as

$$\Phi \frac{\partial \rho_{v}}{\partial t} + \rho_{d} \left(1 - \frac{\rho_{v}}{\rho_{w}}\right) \frac{\partial w}{\partial t} = \left(\Phi + \rho_{d} \left(1 - \frac{\rho_{v}}{\rho_{w}}\right) \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{v \, sat}}\right) \frac{\partial \rho_{v}}{\partial t}$$

$$+ \rho_{d} \left(1 - \frac{\rho_{v}}{\rho_{w}}\right) \frac{\partial w}{\partial T} \frac{\partial T}{\partial t} - \rho_{d} \left(1 - \frac{\rho_{v}}{\rho_{w}}\right) \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \frac{\partial T}{\partial t} \rho_{v}$$

$$(4.25)$$

The diffusion coefficients in equation (4.21) are subject to a spatial differential operator. This requires some more attention since these coefficients are dependent on temperature and can therefore vary in space. For the sake of simplicity and since no sound approach for a possible anisotropy of the diffusion coefficients exists

<sup>&</sup>lt;sup>3</sup> This is of course a working hypothesis. /MOO52/ and /KAR86/ show clearly a certain hysteresis in the adsorption/desorption data that is neglected here for the sake of simplicity.

– assumption 4.18: Only homogeneous diffusion is considered.

is taken to be valid. According to assumption 4.2 (pressure gradients are negligible), the dependency of the binary gas diffusion coefficient on pressure can also be neglected. Product rule applied to the referring diffusion term leads to two terms in which the gradient of the diffusion coefficient can be further transformed into a gradient of temperature:

$$\nabla (D_a \cdot \nabla \rho_v) = D_a \Delta \rho_v + \nabla D_a \cdot \nabla \rho_v = D_a \Delta \rho_v + \frac{\partial D_a}{\partial T} \nabla T \cdot \nabla \rho_v$$
(4.26)

The same consideration applied to the term for interlamellar diffusion yields

$$\nabla (D'_a \cdot \nabla w) = D'_a \Delta w + \nabla D'_a \cdot \nabla w = D'_a \Delta w + \frac{\partial D'_a}{\partial T} \nabla T \cdot \nabla w$$
(4.27)

Substituting the derivatives of the water content in equation ( 4.27 ) according to equations ( D.5 ) and ( D.8 ) leads to

$$\nabla (D'_{a} \cdot \nabla w) = \left\{ \begin{bmatrix} \nabla \left(\frac{\partial w}{\partial r_{h}}\right) \end{bmatrix} \cdot \left[ \frac{1}{\rho_{v \, sat}} \nabla \rho_{v} - \frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \nabla T \right] \\ + \frac{\partial w}{\partial r_{h}} \begin{cases} \begin{bmatrix} \nabla \left(\frac{1}{\rho_{v \, sat}}\right) \end{bmatrix} \cdot \nabla \rho_{v} + \frac{1}{\rho_{v \, sat}} \Delta \rho_{v} \\ - \left[ \nabla \cdot \left(\frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \right) \right] \cdot \nabla T - \frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \Delta T \\ + \left[ \nabla \left(\frac{\partial w}{\partial T}\right) \right] \cdot \nabla T + \frac{\partial w}{\partial T} \Delta T \\ + \frac{\partial D'_{a}}{\partial T} \nabla T \cdot \left\{ \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{v \, sat}} \nabla \rho_{v} + \left( \frac{\partial w}{\partial T} - \frac{\partial w}{\partial r_{h}} \frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \right) \nabla T \right\}$$

$$(4.28)$$

Thus (4.21) can be written as

$$\left\{ \Phi + \rho_d \left( 1 - \frac{\rho_v}{\rho_w} \right) \frac{\partial w}{\partial r_h} \frac{1}{\rho_{v\,sat}} \right) \frac{\partial \rho_v}{\partial t}$$

$$+ \rho_d \left( 1 - \frac{\rho_v}{\rho_w} \right) \frac{\partial w}{\partial T} \frac{\partial T}{\partial t} - \rho_d \left( 1 - \frac{\rho_v}{\rho_w} \right) \frac{\partial w}{\partial r_h} \frac{1}{(\rho_{v\,sat})^2} \frac{\partial \rho_{v\,sat}}{\partial T} \frac{\partial T}{\partial t} \rho_v$$

$$- D_a \Delta \rho_v - \frac{\partial D_a}{\partial T} \nabla T \cdot \nabla \rho_v$$

$$\left\{ \begin{bmatrix} \nabla \left( \frac{\partial w}{\partial r_h} \right) \end{bmatrix} \cdot \left[ \frac{1}{\rho_{v\,sat}} \nabla \rho_v - \frac{\rho_v}{(\rho_{v\,sat})^2} \frac{\partial \rho_{v\,sat}}{\partial T} \nabla T \right]$$

$$+ \frac{\partial w}{\partial r_h} \left\{ \nabla \left( \frac{1}{\rho_{v\,sat}} \right) \right] \cdot \nabla \rho_v + \frac{1}{\rho_{v\,sat}} \Delta \rho_v$$

$$- \left[ \nabla \left( \frac{\rho_v}{(\rho_{v\,sat})^2} \frac{\partial \rho_{v\,sat}}{\partial T} \right) \right] \cdot \nabla T - \frac{\rho_v}{(\rho_{v\,sat})^2} \frac{\partial \rho_{v\,sat}}{\partial T} \Delta T \right]$$

$$+ \left[ \nabla \left( \frac{\partial w}{\partial T} \right) \right] \cdot \nabla T + \frac{\partial w}{\partial T} \Delta T$$

$$- \rho_d \frac{\partial D'_a}{\partial T} \nabla T \cdot \left\{ \frac{\partial w}{\partial r_h} \frac{1}{\rho_{v\,sat}} \nabla \rho_v + \left( \frac{\partial w}{\partial T} - \frac{\partial w}{\partial r_h} \frac{\rho_v}{(\rho_{v\,sat})^2} \frac{\partial \rho_{v\,sat}}{\partial T} \right) \nabla T \right\} - r_{cond} = 0$$

By eliminating the water content as a primary variable in the balance equation the temperature has been introduced instead.

Note: While assumption 4.2 allows to dispense with all possible pressure derivatives in the present approach there are nevertheless secondary variables like the binary gas diffusion coefficient that depend directly on the pressure. A complete compilation of all parameters required for the balance equation (4.29) including their dependencies – on primary as well as on secondary variables – can be found in section 4.6.

#### 4.5.5 General approach for a temperature-dependent isotherm

In the non-isothermal balance equation (4.29) for water residing in the pore space as well as in the interlamellar space the information of the temperature-dependent isotherm is condensed in the various expressions containing derivatives of the water content. The only approach for the temperature-dependent isotherm found in the literature

has been suggested in /KRÖ08/. Laboratory measurements indicate that water content at equilibrium decreases with increasing temperature especially in the range of 70 % relative humidity /GAI05/. The mathematical description of the temperature-dependent isotherm is therefore split into a product of a reference isotherm  $w_{iso}(r_h, T_0)$  (referring to the reference temperature  $T_0$ ) and a material-specific deviation factor  $g(r_h, T, T_0)$  to introduce the temperature dependency:

$$w(r_h, T) = w_{iso}(r_h, T_0) \cdot g(r_h, T, T_0)$$
(4.30)

- w equilibrium water content at variable temperature [-]
- *w*<sub>iso</sub> equilibrium water content at reference temperature [-]
- *g* material-specific deviation factor [-]

Both terms,  $w_{iso}$  as well as g, are dependent on relative humidity.

#### 4.5.6 Simplification of the storage term

The first possible simplification becomes apparent by looking at the bracket in the first term of equation (4.29). Apparently valid is<sup>4</sup>

$$\frac{\rho_v}{\rho_w} \ll 1 \tag{4.31}$$

A second simplification becomes evident after rewriting the storage term as

$$\left(\Phi + \frac{\rho_d}{\rho_{v\,sat}} \left[g \frac{\partial w_{iso}}{\partial r_h} + w_{iso} \frac{\partial g}{\partial r_h}\right]\right) \frac{\partial \rho_v}{\partial t}$$
(4.32)

Laboratory data from /GAI05/ indicates that the water content changes less than 20 % in the temperature range between 25 °C and 98 °C. The deviation factor is thus rather close to 1. The partial derivative of water content with respect to relative humidity amounts approximately to 0.05 up to 0.35 depending on the shape of the reference isotherm.

<sup>&</sup>lt;sup>4</sup> In /KRÖ05/ it was just assumed that the time derivative of the porosity times vapour partial density can be neglected in comparison to the other terms. This is now justified by the fact that the ratio  $\rho_V / \rho_W$  is much less than 1.

Thus porosity can be neglected in the storage term:

$$\Phi \ll \frac{\rho_d}{\rho_{v\,sat}} g(r_h, T) \frac{\partial w_{iso}}{\partial r_h}$$
(4.33)

Simplifying and rearranging balance equation (4.29) finally yields

$$\begin{split} \rho_{d} \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \frac{\partial \rho_{v}}{\partial t} \\ &+ \left\{ \rho_{d} \frac{\partial w}{\partial T} \right\} \frac{\partial T}{\partial t} \\ &+ \left\{ -D_{a} - \rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \right\} \Delta \rho_{v} \\ &+ \left\{ -D_{a} - \rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \right\} \Delta \rho_{v} \\ &+ \left\{ -\frac{\partial D_{a}}{\partial T} \nabla T \\ &- \rho_{d} D_{a}^{\prime} \left[ \nabla \left( \frac{\partial w}{\partial r_{h}} \right) \right] \frac{1}{\rho_{vsat}} - \rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial r_{h}} \left[ \nabla \left( \frac{1}{\rho_{vsat}} \right) \right] - \rho_{d} \frac{\partial D_{a}^{\prime}}{\partial T} \nabla T \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \right\} \cdot \nabla \rho_{v} \\ &+ \left\{ -\rho_{d} \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \frac{\partial T}{\partial t} + \rho_{d} D_{a}^{\prime} \left[ \nabla \left( \frac{\partial w}{\partial r_{h}} \right) \right] \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \cdot \nabla T \\ &+ \left\{ -\rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial r_{h}} \nabla \left( \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \right) \cdot \nabla T + \rho_{d} \frac{\partial D_{a}^{\prime}}{\partial T} \nabla T \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \cdot \nabla T \\ &+ \left\{ -\rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial r_{h}} \left( \frac{1}{\rho_{vsat}} \right)^{2} \frac{\partial \rho_{vsat}}{\partial T} \Delta T \\ &+ \left\{ -\rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial T} \right\} \Delta T \\ &+ \left\{ -\rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial T} \right\} \Delta T \\ &- r_{cond} = 0 \end{split}$$

Note: In the course of deducing the balance equation (4.34) the storage term of the balance equation (4.4) for vapour transport in the pore space vanished as a consequence of several simplifying assumptions. Apparently, the steady-state solution for the momentary diffusion problem (including sinks and sources accounting for moisture redistribution) suffices to describe the re-saturation via water vapour.

#### 4.5.7 Isothermal balance equation

In case of isothermal conditions temperature gradients vanish and the saturation vapour partial density  $\rho_{vsat}$  is constant. Condensation cannot occur. The related isothermal balance equation reduces then to:

$$\rho_{d} \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{v \, sat}} \frac{\partial \rho_{v}}{\partial t} - \left( D_{a} + \rho_{d} D_{a}^{\prime} \frac{\partial w}{\partial r_{h}} \frac{\partial r_{h}}{\partial \rho_{v}} \right) \Delta \rho_{v} - \rho_{d} D_{a}^{\prime} \frac{1}{\rho_{v \, sat}} \nabla \left( \frac{\partial w}{\partial r_{h}} \right) \cdot \nabla \rho_{v}$$

$$= 0$$

$$(4.35)$$

Equation (4.35) is equivalent to the much simpler formulation presented in /KRÖ05/ where

 assumption 4.19: The isotherm of MX-80 bentonite at 25 °C can be approximated by a linear function up to a relative humidity of 95 %.

was introduced based on the work of /MOO52/. This assumption lead to the relation

$$w_{iso} = w_e r_h \tag{4.36}$$

*w<sub>e</sub>* - fictitious water content at 100 % relative humidity [-]

For the isothermal problem formulated in /KRÖ05/ which did not consider interlayer water diffusion thus follows

$$\frac{\partial w}{\partial r_h} = w_e \text{ and } D'_a = 0 \tag{4.37}$$

where  $w_e$  is a constant. Inserting into the balance equation (4.35) yields

$$\frac{\rho_d}{\rho_{v\,sat}} w_e \frac{\partial \rho_v}{\partial t} - D_a \Delta \rho_v = 0 \tag{4.38}$$

which is consistent with the result of the much less complex deduction presented in /KRÖ05/.

## 4.6 Coupling of the parameters in the balance equation

Solving balance equation (4.34) requires the calculation of several secondary variables. Fig. 4.2 illustrates the dependency of these secondary variables on the three primary variables vapour density, temperature, and pressure. Where possible the related conditional equations are listed in Tab. 4.1.



Fig. 4.2 Dependency of secondary variables (white boxes) from the primary variables (coloured boxes); based on /KRÖ08a/

## Tab. 4.1 Compilation of conditional equations

quantity	unit	equation
saturation vapour pressure $n(T)$	[Pa]	calculated after /IAP97/
saturation vapour density	FI ( 27	
$\rho_{v sat}(p_s)$	[kg/m³]	calculated after /IAP97/
partial derivative $\partial \rho_{v  sat} / \partial T(T)$	[-]	calculated numerically
relative humidity $r_h(\rho_v, \rho_{v \text{ sat}})$	[-]	$r_h = \frac{\rho_v}{\rho_{v  sat}} \tag{4.39}$
	[-]	first approximation:
isotherm at reference tempera- ture $w_{iso}(r_h T_0)$		$w_{iso} = w_e r_h \tag{4.40}$
		alternatively data given in tabulated form as an analytical function using splines
	[-]	product of temperature term and humidity
deviation factor $g(r_{h},T)$		refin, present proposal. $\alpha(n,T) = \begin{bmatrix} 1 & n & (1 - n) \end{bmatrix}^{0,8}$
8(m-)		$g(r_h, I) = [I - r_h(I - r_h)] $ (4.41)
		(1-25)/(98-25)0,6
water content $w(w_{iso}, g)$	[-]	$w = w_{iso} g(r_h, T)$ (4.42)
partial derivative $\partial w / \partial r_h(r_h, T)$	[-] <sup>5</sup>	calculated numerically
partial derivative $\partial w/\partial T(r_h, T)$	[-]	calculated numerically
porosity $\Phi(w)$	[-]	$\Phi = 1 - \frac{\rho_d}{\rho_s} - \frac{\rho_d}{\rho_w} w \qquad (4.43)$
molecular diffusion coefficient $D_m(p,T)$	[m²/s]	$D_{m} = D_{m0} \frac{p_{g0}}{p_{g}} \left(\frac{T}{T_{0}}\right)^{\theta} $ (4.44)
macroscopic diffusion coefficient $D_a(D_m)$	[m²/s]	$D_a = \Phi_0 \tau_0 D_m \tag{4.45}$
partial derivative $\partial D_a / \partial T(p,T)$	[-]	calculated numerically
coefficient of interlayer water diffusion $D'(p,T)$	[m²/s]	$D' = \begin{cases} 0.5 - 4 \cdot 10^{-10} \text{ m}^2/\text{s 1 hydrate layer} \\ 10 \cdot 10^{-10} \text{ m}^2/\text{s} & 2 \text{ hydrate layers} \end{cases}$ (4.46)
macroscopic coefficient of in- terlayer water diffusion $D'_a(D')$	[m²/s]	$D'_{a} = \tau_{hyd} D' \tag{4.47}$
partial derivative $\partial D'_a / \partial T(p,T)$	[-]	calculated numerically

 $<sup>^5</sup>$  This derivative is easily transformed into  $\left.\partial w \! \middle/ \partial 
ho_v$  using equation ( D.4 ).

#### 4.7 Numerical solution

## 4.7.1 Introductory remarks

Balance equation (4.34) which is formulated in 3D will be restricted to one dimension in the following and then be solved approximately by the Finite Element Method. The primary variables are represented by piecewise linear functions in space and time. An explicit solution scheme with the collocation point on the old time level is developed in the following sections in terms of algebraic equations for each node of a discretised solution domain.

The effect of condensation is presently realised in a heuristic way. The calculated vapour partial density  $\rho_v$  is compared to the saturation density  $\rho_{v sat}$ . If  $\rho_v$  is greater than  $\rho_{v sat}$  the referring excess mass of vaporous water is assumed to accumulate in the remaining pore space until this space is completely filled with water. This procedure substitutes a direct treatment of the sink/source term for condensation in balance equation (4.34). The sink/source term is therefor not considered in the following anymore.

### 4.7.2 1-D geometry

#### Approximation

In order to ascribe a discrete value of a variable to a node location and a time level the following conventions are introduced: subscript refers to location, superscript to time level. Subscript "0" means the node itself, subscripts "-" and "+" the neighbouring nodes to the left and to the right. If the subscript refers to elements "-" means the left and "+" the right element. Superscript "+" stands for the next time level where the values of the variables are unknown, superscript "-" for the present level with known values. For simplification the subscript "v" in the symbol  $\rho_v$  for the vapour partial density is omitted.

In order to bring equation (4.34) into a manageable form it is rewritten as

$$f_1 \frac{\partial \rho}{\partial t} + f_2 \frac{\partial T}{\partial t} + f_3 \Delta \rho + f_4 \cdot \nabla \rho + f_5 \rho + f_6 \nabla T + f_7 \Delta T = 0$$
(4.48)

with the abbreviations

$$\begin{split} f_{1} &= \rho_{d} \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \\ f_{2} &= \rho_{d} \frac{\partial w}{\partial T} \\ f_{3} &= -D_{a} - \rho_{d} D_{a}' \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \\ f_{4} &= -\frac{\partial D_{a}}{\partial T} \nabla T - \rho_{d} D_{a}' \left[ \nabla \left( \frac{\partial w}{\partial r_{h}} \right) \right] \frac{1}{\rho_{vsat}} \\ &- \rho_{d} D_{a}' \frac{\partial w}{\partial r_{h}} \left[ \nabla \left( \frac{1}{\rho_{vsat}} \right) \right] - \rho_{d} \frac{\partial D_{a}'}{\partial T} \nabla T \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \\ f_{5} &= -\rho_{d} \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \frac{\partial T}{\partial t} + \rho_{d} D' \left[ \nabla \left( \frac{\partial w}{\partial r_{h}} \right) \right] \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \cdot \nabla T \\ &+ \rho_{d} D' \frac{\partial w}{\partial r_{h}} \nabla \left( \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \right) \cdot \nabla T \\ &+ \rho_{d} \frac{\partial D_{a}'}{\partial T} \nabla T \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \cdot \nabla T \\ &+ \rho_{d} D' \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \Delta T \\ f_{6} &= -\rho_{d} D_{a}' \left[ \nabla \left( \frac{\partial w}{\partial T} \right) \right] - \rho_{d} \frac{\partial D_{a}'}{\partial T} \nabla T \frac{\partial w}{\partial T} \\ f_{7} &= -\rho_{d} D_{a}' \frac{\partial w}{\partial T} \end{split}$$

Note that temperature T is an independent variable in equation (4.34). In case that vapour transport and heat transport are assumed to be decoupled the transient temperature field has to be calculated first and used as input in vapour transport simulations.

The factors  $f_1$  to  $f_7$  are calculated at node 0. The differential operators in equation (4.34) are approximated by:

$$\frac{\partial u}{\partial t} \approx \frac{u_0^+ - u_0^-}{\Delta t} \tag{4.50}$$

$$\nabla u \approx \frac{u_+^- - u_-^-}{2\Delta x}$$
$$\Delta u \approx \frac{u_+^- - 2u_0^- + u_-^-}{\Delta x^2}$$

The approximating algebraic equation at node *i* is thus written as

$$\rho_{0}^{+} = \rho_{0}^{-} - \frac{\Delta t}{f_{1}} \left( f_{2} \frac{T_{0}^{+} - T_{0}^{-}}{\Delta t} + f_{3} \frac{1}{\Delta x^{2}} \left( \rho_{+}^{-} - 2\rho_{0}^{-} + \rho_{-}^{-} \right) + f_{4} \frac{1}{4\Delta x^{2}} \left( T_{+}^{-} - T_{-}^{-} \right) \left( \rho_{+}^{-} - \rho_{-}^{-} \right) \right) + f_{5} \rho_{0}^{-} + f_{6} \frac{1}{2\Delta x} \left( T_{+}^{-} - T_{-}^{-} \right) + f_{7} \frac{1}{\Delta x^{2}} \left( T_{+}^{-} - 2T_{0}^{-} + T_{-}^{-} \right) \right)$$
(4.51)

This equation could also be derived from approximating the original partial differential equation by a standard Galerkin-procedure. A deviation is allowed for the time derivate, though, because this term would introduce the necessity to include values from neighbour nodes on the new time level /KRÖ91/. As a result all equations would have to be solved simultaneously which would have increased the programming effort considerably. Instead, the time derivative is "concentrated" at one node which involves certain numerical disadvantages e.g. /DAU85/, but which also leads to an explicit solution scheme.

#### **Boundary conditions**

In case of a Dirichlet boundary condition a specific value is assigned to a node. The equation referring to that node is not to be solved.

In case of a Neumann boundary condition, however, the referring equation must be solved. Here however, only the special case of a no-flow boundary is discussed. At the left boundary – where numbering starts – boundary node i has no left neighbour i-1. The central differences  $\nabla u$  are therefore replaced by forward differences:

$$\nabla u \approx \frac{u_+^- - u_0^-}{\Delta x} \tag{4.52}$$

The divergence  $\Delta u$  on a no-flow boundary must be zero. For that purpose the node next to the boundary is mirrored to provide an additional fictitious node outside the solution domain as shown in Fig. 4.3.



Fig. 4.3 Numerical treatment of a closed boundary

If this fictitious node has the same value as the first inner node the resulting tangent slope on the boundary can be assumed to be zero. From these considerations follows:

$$\Delta u \approx \frac{2\left(u_{+}^{-} - u_{0}^{-}\right)}{\Delta x^{2}} \tag{4.53}$$

The approximating algebraic equation for the node at the left boundary is thus written as

$$\rho_{0}^{+} = \rho_{0}^{-} - \frac{\Delta t}{f_{1}} \left( f_{2} \frac{T_{0}^{+} - T_{0}^{-}}{\Delta t} - f_{3} \frac{1}{\Delta x^{2}} 2(\rho_{+}^{-} - \rho_{0}^{-}) - f_{4} \frac{1}{\Delta x^{2}} (T_{+}^{-} - T_{0}^{-})(\rho_{+}^{-} - \rho_{0}^{-}) \right) + f_{5} \rho_{0}^{-} + f_{6} \frac{1}{\Delta x} (T_{+}^{-} - T_{0}^{-}) + f_{7} \frac{1}{\Delta x^{2}} 2(T_{+}^{-} - T_{0}^{-}) \right)$$
(4.54)

The referring formulations for the right boundary ensue analogously.

#### 4.7.3 2-D axisymmetric geometry

#### Approximation

Flow and transport processes in a plane of axisymmetric geometry can be approximated by a one-dimensional model in cylindrical coordinates. However, it is much easier to retain Cartesian coordinates and increase the cross-section area A with increasing distance from the symmetry axis. In this case the cross-section A of each element is chosen to be equal to the fictitious surface of a cylinder with height "1" and radius r if r

is the distance between cylinder axis and centre of the element (see Fig. 4.4). In a torus with the inner radius  $r_0$  the cross-section  $A_m$  of an arbitrary element m can be calculated from the element length  $\Delta r$  using

$$A_{m} = 2r_{0}\pi + (2(m+1)-1)\Delta r\pi$$
(4.55)  

$$A_{m} - \text{cross-section of an arbitrary element } m \text{ [m}^{2}\text{]}$$

$$r - \text{radius [m]}$$

$$r_{0} - \text{inner radius (} r_{0} = 0 \text{ for a cylinder) [m]}$$

$$\Delta r - \text{element length [m]}$$

$$m - \text{element number (numbering beginning with 0) [-]}$$

For setting up an appropriate balance equation, the option to use element-wise constant cross-sections that vary from element to element requires to start over again with equation (4.2) before the transition from integral equation to differential equation has been carried out. At this point it has to be considered that

$$dV = A(r)dr \tag{4.56}$$

applies in the integral equation. A value of  $A(r_m)$  is then assigned to each element m.





The resulting Finite Element equations are somewhat more complicated because the element equations are now multiplied by  $A(r_m)$  and thus weighed differently when it is assembled to the stiffness matrix for the whole domain. Therefore the process of deriving the algebraic node equations from the assembled element equations was repeated. Any term *F* that is just evaluated at the local node  $\theta$  is simply multiplied by the cross-section which is assumed to be the mean value of the cross-section areas of the neighbouring elements:

$$A(r)F \approx \frac{A_{+} + A_{-}}{2}F_{0}$$
(4.57)

Note the different meaning of subscripts "-" and "+" if used in combination with the cross-section area A. Here, the subscripts refer to the neighbouring elements rather than the neighbouring nodes.

A little bit more complicated are the expressions for terms including first and second order spatial derivatives of the vapour partial density because they require data from the neighbouring nodes:

$$A(r) \nabla \rho \approx_{i} \frac{A_{+} \rho_{+}^{-} - (A_{+} - A_{-}) \rho_{0}^{-} - A_{-} \rho_{-}^{-}}{2\Delta r}$$

$$A(r) \Delta \rho \approx \frac{A_{+} \rho_{+}^{-} - (A_{+} + A_{-}) \rho_{0}^{-} + A_{-} \rho_{-}^{-}}{\Delta r^{2}}$$
(4.58)

The factors  $f_l$  to  $f_4$  read then as

$$\begin{split} f_{1} &= \rho_{d} \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \frac{A_{+} + A_{-}}{2} \\ f_{2} &= \rho_{d} \frac{\partial w}{\partial T} \frac{A_{+} + A_{-}}{2} \\ f_{3} &= -D_{a} - \rho_{d} D_{a}' \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \\ f_{4} &= -\frac{\partial D_{a}}{\partial T} \nabla T - \rho_{d} D_{a}' \left[ \nabla \left( \frac{\partial w}{\partial r_{h}} \right) \right] \frac{1}{\rho_{vsat}} \\ &- \rho_{d} D_{a}' \frac{\partial w}{\partial r_{h}} \left[ \nabla \left( \frac{1}{\rho_{vsat}} \right) \right] - \rho_{d} \frac{\partial D_{a}'}{\partial T} \nabla T \frac{\partial w}{\partial r_{h}} \frac{1}{\rho_{vsat}} \\ \\ f_{5} &= \rho_{d} \begin{cases} -\frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \frac{\partial T}{\partial t} + D' \left[ \nabla \left( \frac{\partial w}{\partial r_{h}} \right) \right] \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \cdot \nabla T \\ &+ D' \frac{\partial w}{\partial r_{h}} \nabla \left( \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \right) \cdot \nabla T \\ &+ \frac{\partial D_{a}'}{\partial T} \nabla T \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \cdot \nabla T \\ &+ D' \frac{\partial w}{\partial r_{h}} \frac{1}{(\rho_{vsat})^{2}} \frac{\partial \rho_{vsat}}{\partial T} \Delta T \end{cases} \\ f_{6} &= \left\{ -\rho_{d} D_{a}' \left[ \nabla \left( \frac{\partial w}{\partial T} \right) \right] - \rho_{d} \frac{\partial D_{a}'}{\partial T} \nabla T \frac{\partial w}{\partial T} \right\} \frac{A_{+} + A_{-}}{2} \end{cases}$$

Using approximations (4.57) and (4.58) as well as the conventions (4.59) the approximating algebraic equation at node i is written as

$$\rho_{0}^{+} = \rho_{0}^{-} - \frac{\Delta t}{f_{1}} \begin{pmatrix} f_{2} \frac{T_{0}^{+} - T_{0}^{-}}{\Delta t} + f_{3} \frac{1}{\Delta r^{2}} (A_{+}\rho_{+}^{-} - (A_{+} + A_{-})\rho_{0}^{-} + A_{-}\rho_{-}^{-}) \\ + f_{4} \frac{1}{4\Delta r^{2}} (T_{+}^{-} - T_{-}^{-}) (A_{+}\rho_{+}^{-} - (A_{+} - A_{-})\rho_{0}^{-} - A_{-}\rho_{-}^{-}) \\ + f_{5}\rho_{0}^{-} + f_{6} \frac{1}{2\Delta r} (T_{+}^{-} - T_{-}^{-}) + f_{7} \frac{1}{\Delta r^{2}} (T_{+}^{-} - 2T_{0}^{-} + T_{-}^{-}) \end{pmatrix}$$
(4.60)

#### **Boundary conditions**

As discussed in the previous section special formulations have to be used for the boundary node equations. Considering different cross-section areas in different elements the equations (4.58) read:

$$\nabla \rho \approx \frac{\rho_{+}^{-} - \rho_{0}^{-}}{\Delta r} A_{+}$$

$$\Delta \rho \approx \frac{2(\rho_{+}^{-} - \rho_{0}^{-})}{\Delta r^{2}} A_{+}$$
(4.61)

The approximating algebraic equation for the node at the left boundary is thus written as

$$\rho_{0}^{+} = \rho_{0}^{-} - \frac{\Delta t}{f_{1}} \begin{pmatrix} f_{2} \frac{T_{0}^{+} - T_{0}^{-}}{\Delta t} + f_{3} \frac{1}{\Delta r^{2}} (A_{+}\rho_{+}^{-} - (A_{+} + A_{-})\rho_{0}^{-} + A_{-}\rho_{-}^{-}) \\ + f_{4} \frac{1}{\Delta r^{2}} A_{+} (T_{+}^{-} - T_{0}^{-}) (\rho_{+}^{-} - \rho_{0}^{-}) \\ + f_{5}\rho_{0}^{-} + f_{6} \frac{1}{2\Delta r} (T_{+}^{-} - T_{-}^{-}) + f_{7} \frac{1}{\Delta r^{2}} (T_{+}^{-} - 2T_{0}^{-} + T_{-}^{-}) \end{pmatrix}$$
(4.62)

The referring formulation for the right boundary ensues analogously.

#### 4.7.4 Time step limiting criteria

Equation (4.60) can be rearranged to

$$\frac{\partial \rho}{\partial t} + \frac{f_4}{f_1} \nabla T \cdot \nabla \rho + \frac{f_3}{f_1} \Delta \rho + \frac{f_5}{f_1} \rho = -\frac{f_2}{f_1} \frac{\partial T}{\partial t} - \frac{f_6}{f_1} \nabla T - \frac{f_7}{f_1} \Delta T$$
(4.63)

in order to correspond to a standard advection-diffusion transport equation

$$\frac{\partial \overline{c}}{\partial t} + \overline{v} \cdot \nabla \overline{c} - \overline{D} \Delta \overline{c} + \overline{q} c = \overline{q} c'$$
(4.64)

where

$$\begin{array}{ll} \rho & \mbox{corresponds to concentration } \overline{c} \ , \\ \hline \frac{f_4}{f_1} \nabla T & \mbox{corresponds to velocity } \overline{v} \ , \\ \hline -\frac{f_3}{f_1} & \mbox{corresponds to the diffusion coefficient } \overline{D} \ , \\ \hline \frac{f_5}{f_1} & \mbox{corresponds to the source term for the fluid } \overline{q} \ , \mbox{ and } \\ \hline -\frac{f_2}{f_1} \frac{\partial T}{\partial t} - \frac{f_6}{f_1} \nabla T - \frac{f_7}{f_1} \Delta T \\ & \mbox{corresponds to the source term for the solute } \overline{q} \ c' \end{array}$$

For the standard advection-diffusion equation there exist two stability conditions that provide upper boundaries for the time step (e.g. /KIN87/), namely

the Courant-number 
$$Cr = \overline{v} \frac{\Delta t}{\Delta x} \le 1$$
, and  
the Neumann-criterion  $Ne = \overline{D} \frac{\Delta t}{\Delta x^2} \le \frac{1}{2}$ , (4.66)

The maximum allowable time step thus is the minor of the minima for both criteria which in turn result from the maximum of  $\overline{v}$  and  $\overline{D}$ , respectively. According to equation (4.65) the Courant criterion is only applicable in situations with a transient temperature field. Experience with some non-isothermal simulations indicates that the Courant criterion provides excessively high values for the time step even for high temperature changes. It thus appears that it is sufficient to use the Neumann-criterion only. However, experience has also shown that the increase of the time step should nevertheless be limited in order to avoid numerical problems. In VIPER a new time step length is limited to a value of 1.5 times the length of the previous time step.

# 5 Re-saturation stage 3: balance equation for unsaturated flow

#### 5.1 Introductory remark

Stage 3 of re-saturation is presently only partially considered in the model. While the possible effect of condensation is implemented in the latest VIPER version water migration due to two-phase flow theory is not yet realised. But the underlying theory will nevertheless also be described below.

#### 5.2 Condensation

As explained in subsection 2.3 condensation can only occur during stage 3. The amount of water accrued from condensation can be expressed by means of the water content. For this purpose the water content  $w_e$  at the end of stage 2 (end of swelling) and the water content for an additionally completely water-filled pore space  $w_{tot}$  are required (for derivation of the formulae see e.g. /KRÖ04a/):

$$w_{e} = \rho_{w} \left( \frac{1}{\rho_{d}} - \frac{1}{\rho_{s}} - \frac{\Phi_{min}}{\rho_{d}} \right)$$

$$w_{tot} = \rho_{w} \left( \frac{1}{\rho_{d}} - \frac{1}{\rho_{s}} \right)$$
(5.1)

*w<sub>e</sub>* - water content at the end of stage 2 (end of swelling) [-]

 $\Phi_{min}$  - porosity at the end of stage 2 (end of swelling) [-]

*w*<sub>tot</sub> - water content with a completely water-filled pore space [-]

The amount of condensated water can then be expressed as an excess water content  $w_p$  over the water content  $w_e$ :

$$w_e < w_e + w_p < w_{tot} \tag{5.2}$$

 $w_p$  - water content related to liquid water in the pore space [-]

The increase of water content in the bentonite can be calculated evaluating the storage term in equation (4.34):

$$f_1 \frac{\partial \rho_v}{\partial t} = \rho_d \frac{\partial w}{\partial r_h} \frac{1}{\rho_{v \, sat}} \frac{\partial \rho_v}{\partial t} = \rho_d \frac{\partial w}{\partial t}$$
(5.3)

For sufficiently small time steps the increase of water content can be approximated by

$$\Delta w = \frac{\partial w}{\partial t} \Delta t \tag{5.4}$$

In the numerical model this can be done after solving the algebraic equation system. The criterion for condensation is then simply given by

$$\left(\rho_{v}^{+}-\rho_{v\,sat}\right)>0\tag{5.5}$$

and the amount of condensated water is expressed by

$$\Delta w_p = w^- + \Delta w - w_e \tag{5.6}$$

In the numerical model the excess mass of vapour in a finite volume V after a time step of the length  $\Delta t$  is calculated according to

$$m_{wc} = \left(\rho_v - \rho_{v\,sat}\right) \Phi V_f \qquad \text{if} \quad \left(\rho_v - \rho_{v\,sat}\right) > 0 \tag{5.7}$$

 $m_{wc}$  - mass of condensated vapour [kg]

 $V_f$  - local finite Volume; e.g. a Finite Element patch [m<sup>3</sup>]

#### 5.3 Balance equation for water based on two-phase flow theory

The conditions of the final stage – characterised by a state without further swelling – may evolve locally first. Thus porosity is already rather low and vapour transport does not significantly contribute to further water uptake anymore. Instead

– assumption 5.1: Re-saturation in the third stage is dominated by two-phase flow.

is taken to be valid. The general form of the balance equations for multi-phase flow is given by /HEL97/ as

$$\int_{G} \left[ \frac{\partial (\Phi S_{\alpha} \rho_{\alpha})}{\partial t} + \Delta (\rho_{\alpha} \mathbf{v}_{\alpha}) - \rho_{\alpha} q_{\alpha} \right] dG = 0$$
(5.8)

In differential form and introducing compressibility (5.8) becomes

$$\Phi \rho_{\alpha} \frac{\partial S_{\alpha}}{\partial t} + \rho_{\alpha} S_{\alpha} \frac{\partial \Phi}{\partial t} + \Phi S_{\alpha} \frac{\partial \rho_{\alpha}}{\partial p_{\alpha}} \frac{\partial p_{\alpha}}{\partial t} + \Delta \{\rho_{\alpha} \mathbf{v}_{\alpha}\} - \rho_{\alpha} q_{\alpha} = 0$$
(5.9)

- $\rho_{\alpha}$  density of the  $\alpha$ -phase [kg/m<sup>3</sup>]
- $S_{\alpha}$  saturation of the  $\alpha$ -phase [-]
- $p_{\alpha}$  pressure of the  $\alpha$ -phase [Pa]

$$\mathbf{v}_a$$
 - velocity vector for the  $\alpha$ -phase [m/s]

 $q_{\alpha}$  - sink/source of the  $\alpha$ -phase [kg/(kg s)]

From here on the general balance equation (5.9) will be used to describe only movement of the water:

- assumption 5.2: Gas flow is neglected.

The index *w* is used instead of the general index  $\alpha$ , and the specific properties of water will be considered in order to simplify (5.9) referring to the following points:

- assumption 5.3: Compressibility of water can be neglected.
- assumption 5.4: Thermal strain of water can be neglected.
- assumption 5.5: Porosity is constant.
- assumption 5.6: Sources are not to be taken into account.

These assumptions are mathematically expressed by

$$\rho_{w} = const.,$$

$$\frac{\partial \rho_{w}}{\partial p_{w}} = 0, \ \frac{\partial \rho_{w}}{\partial T} = 0, \text{ and}$$

$$\Phi = const.$$

$$q_{w} = 0$$
(5.10)

which leads to

$$\Phi \frac{\partial S_w}{\partial t} + \Delta \mathbf{v}_w = 0 \tag{5.11}$$

Inserting the generalised Darcy's law

$$\mathbf{v}_{a} = -\frac{k_{ra}}{\mu_{\alpha}} \mathbf{K} \cdot \left(\nabla p_{\alpha} - \rho_{\alpha} \mathbf{g}\right)$$
(5.12)

 $k_{r\alpha}$  - relative permeability of the  $\alpha$ -phase [-]

 $\mu_{\alpha}$  - viscosity of the  $\alpha$ -phase [Pa s]

K - tensor of the absolute permeability [m<sup>2</sup>]

g - vector of the gravitational acceleration [m/s<sup>2</sup>]

in equation (5.11) respecting

- assumption 5.7: The influence of gravity can be neglected.

yields

$$\Phi \frac{\partial S_{w}}{\partial t} - \Delta \left( \frac{k_{rw}}{\mu_{w}} \mathbf{K} \cdot \nabla p_{w} \right) = 0$$
(5.13)

Water pressure can be expressed by air pressure and capillary pressure as

 $p_w = p_a - p_c \tag{5.14}$ 

 $p_a$  - air pressure [Pa]

Considering assumption 4.2 of constant air pressure leads to

$$\nabla p_w = -\nabla p_c \tag{5.15}$$

Additionally introducing a capillary pressure-saturation relation yields

$$\Phi \frac{\partial S_{w}}{\partial t} + \Delta \left( \frac{k_{rw}}{\mu_{w}} \mathbf{K} \cdot \frac{\partial p_{c}}{\partial S_{w}} \nabla S_{w} \right) = 0$$
(5.16)

In this form balance equation (5.16) represents a diffusion equation with a variable coefficient:

$$\frac{\partial S_w}{\partial t} + \Delta \left( \hat{\mathbf{D}} \cdot \nabla S_w \right) = 0 \quad \text{with} \quad \hat{\mathbf{D}} \left( S_w, T \right) = \frac{k_{rw}(S_w)}{\mu_w(T)} \frac{\mathbf{K}}{\Phi} \cdot \frac{\partial p_c(T)}{\partial S_w} (S_w)$$
(5.17)

## 5.4 Equations of state

## 5.4.1 Capillary pressure-saturation relation

The isothermal capillary pressure-saturation relation - also called "retention curve" – and its derivative with respect to saturation are often following the approach of Brooks and Corey /BRO64/

$$p_{c} = p_{d} (S_{w})^{-\frac{1}{\lambda}}$$
 and  $\frac{dp_{c}}{dS_{w}} = -p_{d} \frac{1}{\lambda} (S_{w})^{-(1+\frac{1}{\lambda})}$  (5.18)

 $p_d$  - entry pressure [Pa]

 $\lambda$  - pore size distribution index [-]

The parameter  $\lambda$  characterises the variability of pore sizes. For a material with uniform pore size  $\lambda = 0$  is valid. For classic two-phase flow applications in porous media  $\lambda$  is in the range of  $0.2 \le \lambda \le 3$  /HEL97/.

Also often used is the approach of van Genuchten /VGN80/

$$p_{c} = p_{c0} \left[ \left( S_{w} \right)^{-\frac{1}{m}} - 1 \right]^{\frac{1}{m}} \quad \text{and} \quad \frac{dp_{c}}{dS_{w}} = -\frac{p_{c0}}{m n} \left[ \left( S_{w} \right)^{-\frac{1}{m}} - 1 \right]^{\frac{1}{m}} \left( S_{w} \right)^{-\left(1+\frac{1}{m}\right)} \quad (5.19)$$

 $p_{c0}$  - scaling parameter [Pa]

*m*,*n* - parameters [-]

where *m* is usually set to

$$m = 1 - \frac{1}{n}$$
 (5.20)

Temperature dependency of the capillary pressure is introduced via the surface tension at the water-air interface. The relation between capillary pressure in a cylindrical tube with the radius r and the surface tension reads

$$p_c = \frac{2\sigma}{r}$$
 (5.21)  
 $\sigma$  - surface tension [N/m]  
 $r$  - radius of the capillary [m]

and after /IAP94/ surface tension at the water-air interface can be calculated as

$$\sigma(T) = 0.2358 \ \tau^{1.256} (1 - 0.625 \ \tau)$$
 with  $\tau = 1 - \frac{T}{647.096}$  (5.22)

*T* - temperature [K]

In the non-isothermal case capillary pressure has thus to be corrected by:

$$p_c(T) = p_c(T_0) \frac{\sigma(T)}{\sigma(T_0)}$$
(5.23)

 $T_0$  - reference temperature [K]

#### 5.4.2 Relative permeability-saturation relation

For the relative permeability-saturation relation of /BRO64/

$$k_{rw} = \left(S_{w}\right)^{\frac{2+3\lambda}{\lambda}}$$
(5.24)

and of /VGN80/

$$k_{rw} = \sqrt{S_w} \left[ 1 - \left( 1 - S_w^{\frac{1}{m}} \right)^m \right]^2$$
 (5.25)

the same parameter values are to be used as for the referring capillary pressuresaturation relation.

#### 5.4.3 Viscosity

Water viscosity can be calculated from the formulations of /IAP03/ as a function of temperature and pressure. Note that the influence of pressure on water viscosity is negligible according to /ADA02/ or /KRÖ08b/.

#### 5.5 Numerical solution

Due to extensive formal similarity of equation (5.17) with the corresponding terms in equation (4.34) here the process of deriving the approximating algebraic node equations is described more shortly. A comparison with equation (4.60) using the same index conventions as in section 4 yields

$$S_{w0}^{+} = S_{w0}^{-} + \frac{\Delta t}{\Delta x^2} \hat{D}_0^{-} \left( A_+ S_{w+}^{-} - \left( A_+ + A_- \right) S_{w0}^{-} + A_- S_{w-}^{-} \right)$$
(5.26)

for an inner node and a comparison with equation ( 4.62 ) for the node at the left hand side

$$S_{w0}^{+} = S_{w0}^{-} + 2\frac{\Delta t}{\Delta x^{2}}\hat{D}_{0}^{-}A_{+}\left(S_{w+}^{-} - S_{w0}^{-}\right)$$
(5.27)

The Neumann stability criterion is the only applicable criterion here and it applies analogously to ( 4.66 ):

$$Ne = \hat{D} \frac{\Delta t}{\Delta x^2} \le \frac{1}{2} \tag{5.28}$$

## 6 Confidence building for the vapour diffusion model

#### 6.1 Qualification of the vapour flow concept

Right from the start it was planned to test the alternative conceptual model step by step against uptake tests with physically increasing complexity, beginning with the most simple conditions, until the model was shown to be viable even for the expected repository conditions. This procedure was foreseen to ensure that important effects previously not considered could clearly be identified and incorporated into the model. In this section only the qualification of the vapour flow concept (stage 2) is described.

In the early stage of the vapour diffusion model development – with hydration dynamics still included – just one parameter describing the hydration dynamics had to be derived from experiments. All others were already provided by standard textbooks. However, after supplying the numerical model with realistic values for this parameter first generic calculations lead to surprising conclusions. It became clear that hydration is a very fast process in comparison to vapour diffusion in the pore space. Thus, when hydration dynamics were dropped in favour of instantaneous hydration the previously derived balance equation of the new conceptual model could be transformed into the well-known empirical "diffusion law" as discussed in detail in /KRÖ05/. This transformation allows to quantify the empirical "diffusion coefficient" using exclusively physically meaningful parameters. In an example that is given in /KRÖ05/, too, a "diffusion coefficient" is calculated by these means which differs from the calibrated value only by a factor less than 3. Therefore, the validation procedure was continued on the basis of this simplified balance equation.

Having demonstrated a good correspondence between the vapour diffusion model and experimental results for laboratory conditions as shown exemplarily in Fig. 6.1, water uptake under an increased hydraulic pressure was tackled in the next step. Here, the new model produced results that agreed sufficiently with the referring laboratory experiment – as shown in Fig. 6.2 /KRÖ06/ – after correcting the thickness of the water saturated zone according to the hydraulic pressure at the water contact.



**Fig. 6.1** Measured and calculated water content distributions in an isothermal uptake experiment with atmospheric water pressure; after /KRÖ05/



Fig. 6.2 Measured and calculated breakthrough curves of relative humidity in an isothermal uptake experiment with increased water pressure; from /KRÖ06/

When modelling the isothermal tests proved to be successful, temperature dependencies were incorporated in this equation. The development of a new code called VIPER (Vapour transport In Partially saturated bentonite as Engineered barrier for Repositories) based on the theory described in section 4 was begun to model non-isothermal resaturation. A laboratory test with a heat up-phase in a closed system and a second phase with an additional liquid water uptake /VIL05/ provided the basis for this exercise. In the first phase only moisture redistribution due to temperature changes took place in the air-dry bentonite. This phase of the test was used to check the validity of the non-isothermal vapour flow approach. The measurements of the second phase were used to investigate the non-isothermal water uptake. The results are shown in Fig. 6.3. Even the complex curve for relative humidity at the heated side of the specimen – drawn in red – was reproduced. In the framework of the vapour diffusion model the shape of this curve can be explained by a local and temporary increase of vapour in the pore space due to the heating as explained in detail in Appendix G and subsequent vapour transport proportional to the developing density gradient. In the end the alternative conceptual model in the non-isothermal form proved to be valid even under repository conditions /KRÖ08/.



**Fig. 6.3** Measured and calculated relative humidity at three different locations in a non-isothermal experiment with a) no water inflow and b) with water inflow at increased pressure; from /KRÖ08/

# 6.2 Application to an isothermal in-situ experiment with a bentonite-sand mixture

## 6.2.1 Description of the ITT-experiment

A 50:50 mixture of Saskatchewan bentonite and sand was emplaced and compacted to a dry density of 1730 kg/m<sup>3</sup> in a vertical cylindrical borehole in the Canadian underground rock laboratory (URL) /GUO06/. The resulting bentonite-sand body was confined by a massive concrete plug on top as indicated in Fig. 6.4 a). The compacted buffer material had a height of 2 m, a radius of 0.62 m, and an initial water content of ~17.5 % by weight. After emplacement and instrumentation, the so-called "isothermal test" (ITT) was left undisturbed and monitored for six and half years during which pore water was taken up from the adjoining granite host rock.



## Fig. 6.4 Location of the psychrometric sensors IBX<number>; a) from /GUO06/, b) from /ÅKE08/

Twenty-four thermocouple psychrometers – labeled IBX<number> – were installed in the bentonite-sand buffer to measure the suction (moisture content) during the course
of the experiment. The locations of 16 psychrometers are shown in graph a) of Fig. 6.4 and additional 8 psychrometers in a different cross-section are shown in graph b). The sensors were arranged in four levels. The vertical distance of each of these levels to the concrete plug is given in Tab. 6.1. Radial distances of the sensors from the cylinder axis were 20 cm, 40 cm and 55 cm, respectively.

	horizontal distance	vertical distance
sensor	from the axis [cm]	to the plug [m]
IBX1	55	0.11
IBX 2	40	0.11
IBX 3	55	0.47
IBX 4	40	0.47
IBX 5	55	0.47
IBX 6	40	0.47
IBX 7	20	0.47
IBX 8	40	0.47
IBX 9	55	0.47
IBX 10	55	0.47
IBX 11	40	0.47
IBX 12	20	0.47
<b>IBX 13</b>	55	1.45
IBX 14	40	1.45
IBX 15	55	1.45
IBX 16	40	1.45
IBX 17	20	1.45
IBX 18	40	1.45
IBX 19	55	1.45
IBX 20	55	1.45
IBX 21	40	1.45
IBX 22	20	1.45
IBX 23	55	1.85
IBX 24	40	1.85

 Tab. 6.1
 Position of the psychrometric sensors; the different shades of blue depict different height levels; from /GUO06/

The transient data acquired by the installed instrumentation was supplemented by an extensive post-test investigation of the buffer material. A thorough sampling to determine water content and density of the bentonite-sand buffer was conducted by /DIX00/. Up to 107 moisture content samples and 33 density samples were taken at each of eight elevations (layers A through H). Locations of the samples in each layer are shown in Fig. 6.5. The distance between each sampling layer averaged about 0.25 m as shown in Tab. 6.2.



Fig. 6.5 Location of the numbered samples at each layer; from /GUO06/

|--|

Layer designation	Depth of moisture content samples below the top of the bentonite-sand buffer [m]
А	0.05
В	0.31
С	0.61
D	0.81
E	1.07
F	1.31
G	1.62
Н	1.81

### 6.2.2 Measured data

### Transient sensor data

In Fig. 6.6 the results of the transient measurements are shown. In order to allow a clear interpretation of the measurements the sensors are divided into three groups according to their distance from the borehole axis (20 cm, 40 cm and 55 cm, respective-ly). The height of the sensors is indicated analogously to Tab. 6.1 by the degree of saturation of the colour blue in the lines. The darker the blue the higher the location, so

there are 4 shades of blue altogether. Obviously curious curves are dashed. The results are given in terms of water content over time using the analytical retention curve given in  $/GUO06/^{6}$ 

$$\log s = 1.983 - 0.074w \tag{6.1}$$

to convert the published suction data to water content data. Assuming a homogeneous bentonite-sand mixture, and an evenly distributed water supply all over the buffer-rock contact planes, a monotonously increasing water content can be expected. Axial symmetry of the re-saturation process over the whole buffer follows from the cylindrical geometry. Water movement would be approximately horizontal in the direction of the borehole axis in the upper part of the buffer but would have also a significant vertical component in the lower part. However, what can be observed in Fig. 6.6 a) and b) is a significant decrease of water content at the lowest sensors (IBX23/24) and at some of the sensors above the lowest ones (IBX13/15/19/20) beginning at times between 400 and 1500 days.

For no apparent reason the data from IBX08 at 40 cm distance from the axis shows the same characteristic sharp increase after approximately 300 days as IBX01 and IBX10 at 55 cm distance. Data from sensor IBX09, though, which is located next to IBX08 and at 55 cm distance does not yield this behavior.

Also curious is an apparent correlation between IBX3 and IBX19 during the period between 1000 and 1100 days as shown in Fig. 6.6 a). Water content at IBX3 decreases in the same way and by the same amount as the water content at IBX19 increases. However, the significance of this observation is unclear since IBX3 and IBX19 lie on different sides of the axis and on different levels according to Fig. 6.4.

A rather quick initial response to the water supply at the buffer-rock contact can be observed in Fig. 6.6 a). The subsequent steady increase over the whole test period is remarkable. The significance of this increase is unclear.

<sup>&</sup>lt;sup>6</sup> see w > 11 % in Fig. 2.5



**Fig. 6.6** All transient data concerning the water content during the test at a) r = 55 cm, b) r = 40 cm, and c) r = 20 cm

At 40 cm distance from the borehole axis there is very little variation in the water content for about one year as shown in Fig. 6.6 b). Afterwards, an increase can clearly be seen. This increase is apparently slower in the upper region of the buffer than in the lower region. Fig. 6.6 c) shows a similar development but with a steady period of about 1200 days until the water content increases.

A reason for the annual disturbances recorded by the majority of the sensors at 1000 days and later is not known.

## Conclusions referring to transient data from End-of-test (EOT) data

The extensive sampling after the test provides a three-dimensional impression of the water distribution in the buffer at the end of re-saturation. In Fig. 6.7 a sketch of a cross-section through the compacted buffer material indicates the height of the 8 post-test sample layers as well as the referring water content distributions for each layer. For reference, the positions of the sensors are given as well. Cross-section, sample layers and sensor positions are drawn to scale. A small ring-shaped area between the outermost sensors and the buffer-rock interface is left white due to the lack of information in that region.

According to Fig. 6.7 layer F is the lowest layer that is in trend with the layers above indicating a more or less horizontal water movement during re-saturation. Layer G is clearly influenced by upward water flow.

The psychrometric sensors at the second lowest level are located between layers F and G. It is therefore not clear if these sensors can be assigned to the zone with horizontal water flow or to the zone with three-dimensional water flow. In other words, the influence of the upward flow component on the measured water content at this level is not clear. However, the water content data provided by those sensors as shown in Fig. 6.6 b) and c) show consistently higher values than those of the upper levels. The corresponding data in Fig. 6.6. a) even shows a long decrease period as mentioned above.



**Fig. 6.7** Horizontal cross-sections showing the water content at EOT at all tested elevations; included is a principle sketch (on scale) of the buffer including heights of the samples and the position of the sensors

Moreover, the data from post-test buffer density measurements as plotted in Fig. 6.8 show that even level F may have been influenced by upward flow. The comparatively low density as in layers F to H indicates swelling and consequently higher water contents than in the layers above. The measurements of IBX13 through IBX24 appear therefore not relevant for a two-dimensional axisymmetric analysis of the re-saturation process. For reasons given above also data from IBX08 is not included. The remaining water content curves which form the basis for the comparison between experimental and model results are given in Fig. 6.9 a) to c).



Fig. 6.8 End-of-test distribution of buffer density in the ITT; from /DIX06/

The water content distributions for layers A to F at the end of the test are shown in Fig. 6.9 d). The colour coding is analogous to the previous graphs. The height of the samples relates directly to the colour saturation and thereby suggests that up to a distance of approximately 40 cm from the axis, the data from the upper levels tends to be lower than the data from the lower levels.



**Fig. 6.9** Transient water content data representing 2D-flow at a) r = 55 cm, b) r = 40 cm, and c) r = 20 cm; water content distribution in layers A to F at end-of-test d)

70

# 6.2.3 Model description

## Geometry, initial and boundary conditions

The model of the ITT-Test was based on a 2D-axisymmetric disc with a diameter of 1.26 m representing a horizontal cross-section through the bentonite in the borehole. The initial water content was set to 17.9 %, final water content as assigned to the right boundary to 21.2 % (c.f. Fig. 6.10). Temperature was assumed to be 25 °C corresponding to a depth of 800 m.



### Fig. 6.10 Initial water content distribution in the model

### Interlayer water diffusion

As mentioned above, the value of the interlayer water diffusion coefficient depends on the amount of hydration layers that are adsorbed at the interlamellar cations. At least one threshold level exists at the number of 2 hydrate layers above which a considerably greater diffusion coefficient can be assumed than for lower ones.

For MX-80, that resembles the Saskatchewan bentonite which was used in the ITT, this threshold is related to a water content of about 17.5 % with respect to the dry bentonite mass (see Appendix B). However, in a bentonite-sand mixture the clay content is obviously lower than in pure bentonite so that less water is sufficient to reach the same degree of hydration in the individual clay particles. This means that the threshold value of 17.5 % valid for the bentonite was already exceeded by far by the initial water content of the bentonite-sand mixture in the ITT. A constant high value was thus assigned to the coefficient of interlayer water diffusion in the model. Note: This is the first application of VIPER using the option of interlayer water diffusion.

# Parameters

Most parameters of the model are defined as in Tab. 4.1. Supplemental data is given in Tab. 6.3. An adsorption isotherm/retention curve according to Fig. 2.5 was also used.

quantity	value
initial buffer density [kg/m³]	2017
mean grain density [kg/m³]	2710
tortuosity of the pore space [-]	0.5
coeff. of interlamellar water diffusion [m²/s]	10 <sup>-9</sup>
tortuosity of the interlamellar space [-]	0.2
temperature [°C]	25

**Tab. 6.3**Material parameters required by the model

## 6.2.4 Modelling results

The results of the model are compared to the measurements in terms of the transient water content at distances from the cylinder axis of 55 cm, 40 cm, and 20 cm, respectively, as well as the end-of-test distribution of the water content. Fig. 6.11 a) shows the comparison with the sensors closest to the host rock. The calculated water content curve compares well to the data of the sensor IBX01 and at least qualitatively well with the sensors at lower levels considering the spreading of the data curves.

The agreement is particularly good in case of the comparison at 40 cm distance as shown in Fig. 6.11 b). The calculated water contents are everywhere close to the measured data. Moreover, the model not only reproduces a turning point in the course of the curve but also the time at which it occurs.

At 20 cm distance the calculated water content curve begins to rise too early in comparison to the measurements and then the rise is slower in the model (see Fig. 6.11 c)). As can be deduced from the end-of-test distributions in Fig. 6.11 d), the model yields a water transport to the axis of the cylindrical bentonite body which is to low. Apart from that observation, the agreement between measurements and model appears to be very well.







#### 6.3 Application to a non-isothermal in-situ experiment

### 6.3.1 Description of the CRT-experiment

In the Swedish Äspö Hard Rock Laboratory (HRL) a vertical deposition hole was bored with a depth of 8.55 metres and a diameter of 1.76 metres for the Canister Retrieval Test (CRT). At the perimeter of the hole 16 filter mats with a width of 10 cm were installed with uniform spacing, 0.15 m from the bottom of the hole up to 6.25 m height. Ring-shaped as well as cylindrical bentonite blocks were placed in the hole to encase a heater with the dimensions of a KBS-3 canister. As buffer material MX-80 was chosen. The outside diameter of the canister was 1,050 mm. An inner gap of 1 cm remained between heater and the bentonite rings. The volume between the bentonite blocks and the borehole wall was filled with bentonite pellets. The complete test set-up is shown in Fig. 6.12.



Fig. 6.12 Sketch of the Canister Retrieval Test; from /KRI07/

At the beginning of the test water was pumped into the pellet-filled gap by means of four water supply tubes that were installed before pellet filling and were withdrawn with the raising of the water table. There were indications that the water had not only been filled voids between the pellets but also the inner gap between heater and the bentonite rings. After direct filling-up water was supplied artificially via the filter mats to ensure saturation conditions at the outside of the compacted bentonite.

Then heating was started. Initially the temperature amounted to 17 °C. A maximum temperature of 100 °C on the surface of the canister was aimed at for the Canister Retrieval Test. During the test the power for the heater was stepwise changed several times according to Tab. 6.4. After 679 days also hydraulic pressure was increased.

Day	Heater power [kW]
0	0
1	0.7
18	1.7
110	2.6
375	0
376	2.6
494	0
501	2.6
684	2.1
1134	1.6
1596	1.15
1811	0

 Tab. 6.4
 Heater power protocol; from /KRI07/

# 6.3.2 Data relevant for the model

The modelling exercise concentrates on the water uptake in the horizontal mid height of the experiment (see Fig. 6.13 a)). A disc of the buffer was modeled assuming rotational symmetry. It encompasses

- (A) the inner gap (0.01 m width)
- (B) the ring shaped bentonite block (0.285 m width)
- (C) the outer gap filled with bentonite pellets (0.055 m width)

as indicated in Fig. 6.13 b).



Fig. 6.13 Location of the model domain (a) and dimensions (b); from /KRI07/

The highly compacted bentonite ring had an initial dry density of 1782 kg/m<sup>3</sup> and an initial water content of 17.1 %. While the bulk density of an individual pellet was approx.  $1970 - 2110 \text{ kg/m}^3$  the bulk dry density amounted only to 1001 kg/m<sup>3</sup> accounting also for the void space between the pellets. Initial water content of the pellets was 10 %. Grain density of the buffer material was assumed to be 2780 kg/m<sup>3</sup>.

Several sensors were installed at mid height to measure the temperature development. The location of the sensors is given graphically in Fig. 6.14 and numerically in Tab. 6.5. The resulting time-dependent temperature distributions for the first 43 days are shown in Fig. 6.15. For modelling purposes an analytical function was derived to describe the temperature development in time and space. This function is also shown in Fig. 6.15. A comparison with the measurements of the sensors W119T, W120T and W121T that were in very good agreement with the other temperature sensors are depicted in Fig. 6.16. Colours indicate the radial distance: red – 585 mm, green – 685 mm, and blue – 785 mm.



Fig. 6.14 Location of the temperature sensors at mid height

sensor	height/ring	direction	radial distance
P12	mid height	a = 200°	525
T111	R5	А	635
T112	R5	А	735
T121	R5	D	685
W119T	R5	D	585
W120T	R5	D	685
W121T	R5	D	785
TR121	R5	a = 80°	875
TR125	R5	a = 170°	875

 Tab. 6.5
 Location of temperature sensors



Fig. 6.15 Spatial distributions of temperature; data and analytical approximation



Fig. 6.16 Temporal development of temperature; data and analytical approximation

Two different types of sensors based on different principles for measuring relative humidity were used. Depending on the underlying method they showed reasonable accuracy either below 95 % humidity or above 96 % humidity. Fig. 6.17 shows the measured humidity data where the two different sensor types are differentiated by open and closed symbols. Both were used for the comparison with the simulation data and both were located at a radial distance of 585 mm (orange symbols), 685 mm (green symbols), and of 785 mm (blue symbols).



Fig. 6.17 Temporal development of relative humidity; colour coding (see text)

## 6.3.3 Model description

### Geometry

The planar model domain at mid height is assumed to be axisymmetric so that a onedimensional model with a varying cross-section could be used.

### Initial and boundary conditions

While the initial conditions for earlier models could be explained in a rather straightforward manner according to the considerations in section 3 (stage 1 of re-saturation) the experimental set-up for the CRT is a more complex since at the inner as well as at the outer side of the compacted bentonite was a gap.

The inner gap next to the heater became water filled rather quickly. It is assumed here that clay particles at the surface of the bentonite ring also swelled quickly when in contact with the water. They used up water from the gap and increased their volume. Eventually, the outer layer of clay particles broke off, thus widened the gap and formed a suspension with the water. This process repeated layer after layer until all mobile water was used up and hydrated in the clay particles. In the end the gap had vanished

and next to the heater was a zone of highly saturated bentonite with a comparatively low dry density. This development is illustrated in Fig. 6.18.

The length *x* representing the depth of the bentonite affected by the gap water as indicated in Fig. 6.18 can be estimated assuming a mean dry density  $\rho_d$  in this zone. From  $\rho_d = 1200 \text{ kg/m}^3$  follows x = 2.0 cm. However, for the actual model calculations a modification was used: the initially water saturated zone in the model had a depth of only 7 mm but it was supplemented by an adjacent transition zone over 2.0 cm with a linear decrease of the water content from 24.7 % down to the initial value of 17.1 %.

Obviously, a no-flow boundary condition was appropriate here.





In case of the pellet-filled annulus at the outer side of the bentonite ring it is assumed that water began to enter the bentonite ring while the pellets swelled and formed a more or less homogeneous water-saturated bentonite. The former pellets then impeded water inflow from the filter mats. Due to a hydrostatic pressure of 1.5 bars in the filter mats a zone of completely water saturated bentonite of approx. 1 cm thickness is assumed. Pore water beyond that zone migrated further into the ring.

The affected part of the ring swelled into the pellet-filled space until the mobile water was used up. As at the inner gap a zone of high water content but dry pores and a rather low bentonite density is expected. A first estimation of the depth of this zone provided a value of 2.0 cm. Best results of the model calculations, however, were achieved with a value of 6.5 cm with an adjacent transition of linearly decreasing water content over 2.0 cm.

The initial development at the outer gap is illustrated in Fig. 6.19. The initial water content distribution used in the model is depicted in Fig. 6.20. The inflow boundary was accordingly set at a radial distance of 0.865 m.



Fig. 6.19 Conceptual model for initial and boundary conditions at the cool side

One result of the extensive post-test investigations was that the dry density of the bentonite rings was fairly equally distributed as shown in Fig. 6.21. For modelling purposes a constant dry density of 1617 kg/m<sup>3</sup> was assumed.



Fig. 6.20 Initial conditions

### Adsorption isotherm

From the discussion of adsorption isotherms in Appendix A a natural choice would be to use the highly resolved curve provided by /KAH86/. However, the relative humidity at the initial water content of 17.1 % in the curve from /KAH86/ amounts to approx. 86 % while the measured data indicates a value of approx. 72 %. Much better fitting in this respect is the adsorption path measured by /DUE04/ with an initial water content of 17.5 %. For water contents below 17.5 % the desorption path beginning at 17.5 % also reported by /DUE04/ was supplemented. The isotherm used in the model is depicted in Fig. 6.22. It is based on the data from /DUE04/, modified according to /DUE07/ (see section 2.2.1), and the data points are connected with cubic splines. For reference the data from /KAH86/ and /DUE04/ is also plotted. Note that this was the first model in which the modification after /DUE07/ was applied.



Fig. 6.21 Radial dry density distribution in two bentonite rings; from /KRI07/



Fig. 6.22 Isotherm used in the model as well as data from /KAH86/ and /DUE04/

#### 6.3.4 Modelling results

The two types of sensors used in the CRT to monitor the transient water content provided data either in terms of relative humidity or in terms of suction. Hydraulic model results can therefore be checked against both quantities. Fig. 6.23 shows a comparison of measured and calculated hydraulic data in both respects.

The results of the model are compared to the measurements at radial distances of 585 mm, 685 mm, and 785 mm. The calculated relative humidity curves (as well as the suction curves) compare well to the data of the sensors at the cool side (r = 785 mm) and the sensors in the middle of the bentonite ring (r = 685 mm). Absolute values as well as curvature and inflection points are also well met. A little bit farther off are the results for the sensors at the heated side (r = 585 mm) due to a certain phase shift. However, all curves reproduce the trend of the development quite good.



Fig. 6.23 Measured and calculated relative humidity/suction

The quality of the results is remarkable considering that the vapour density distribution in combination with temperature controls not only vapour diffusion but also the diffusion of interlayer water. The gradient of the water content which is assumed to be the driving force for the interlayer water diffusion relates in a complex manner to the vapour density distribution. This complexity is illustrated by Fig. 6.24 showing plots of the key quantities as spatial distributions at four points in time (t = 0, t = 10 d, t = 110 d, t = 650 d):

- independent variables
  - vapour density  $\rho_v$
  - temperature T
- secondary variables
  - vapour saturation pressure  $\rho_{v sat}$  ( $\rho_{v}$ , T)
  - relative humidity  $r_h (\rho_{v sat})$
  - water content  $w(r_h)$

Not explicitly shown here are the adsorption isotherm (Fig. 6.22) and the relation of vapour pressure and temperature (Fig. 2.13).

The development of the water content in Fig. 6.24 shows that the initially highly saturated zone at the heater dries. The water content next to the heater drops even below the initial value of the non-wetted part of the bentonite rings. Concurrently, vapour density rises here leading to vapour diffusion away from the heater. The effect of condensation can be seen in Fig. 2.13 as an increase of the water content above the value represented by the dashed line. This line depicts the state of maximum content of interlayer water without any water in the pore space. Note: This is the first application of VIPER using the option of condensation.

At the cool side of the buffer more and more water is taken up. The related increase of water content reaches the heated zone eventually but not the boundary at the heater. At the same time the vapour density does not only rise at the heater but also remains to be elevated. A vapour flux away from the heater is thus maintained without changing the water content accordingly.

After starting the experiment the initially high water content at the boundaries begins to level out at both sides of the buffer (heated and cool side). While the water content drops down at the heater a high water content spreads out from the cool side due to the continuous water supply until a dynamic equilibrium is reached. Apparently, a counter-flow system is then established in which



Fig. 6.24 Physical interaction in the CRT-model

- interlayer water migrates in the direction of the gradient of the water content i. e. towards the heater,
- interlayer water dehydrates at the heater providing a source for vapour in the pore space, and
- vapour is then transported in the direction of the gradient of the vapour density i. e. away from the heater.

These dynamics of the model explain the characteristic initial peak of relative humidity close to the heater at approx. 30 days along with the second increase after approx. 80 days (see Fig. 6.23). Spreading of water from the inner gap is responsible for the peak and the second increase of water content is caused by the uptake from the cool side.

However, these dynamics also explain the high sensitivity of the system to parameter variations as observed during modelling. Considering additionally the simplifying adhoc assumptions concerning the development after water filling at the inner gap and in the pellet-filled outer gap the match of model and measurements is satisfying.

# 7 Summary and Outlook

An approach has been developed for the re-saturation of compacted bentonite under confined and non-isothermal conditions. These conditions meet the situation of a resaturating bentonite buffer in a repository for radioactive waste. Theoretical considerations at a microscopic scale of observation have lead to a straight-forward conceptual model in which the processes in a microscopic scale are entirely consistent with an averaged macroscopic description. Only basic physical data and relations are required which leaves very little room for calibration of uncertain parameters. The sound background of the model in combination with the fact that the model apparently works even for bentonite re-saturation under repository conditions strongly indicates the validity of the model.

For the specific applications considered here a further advantage over the usual THMmodel is the fact that the assumption of negligible deformations in the buffer allows to discard mechanical considerations. In combination with the computationally less demanding mathematical description of water transport in the buffer very little computational power is required in comparison.

Of course some open questions remain and thus several possible directions for further developments. To begin with, the complexity of the underlying conceptual model as well as the accuracy of the material data was increased during the development of VIPER. Interlayer water diffusion and condensation was introduced, the linear approximation for the adsorption isotherm was replaced by better resolved laboratory data, and the corrections of the isotherm for confined conditions were refined. While earlier qualification exercises still provide a certain evidence for the validity of the model they should now be repeated using the latest model version to ensure that former conclusions still hold true for the approach.

The water content in bentonite-sand mixtures with reference to the montmorillonite content is generally very high in comparison to pure bentonite. Therefore the relevance of processes in an advanced state of re-saturation is much higher for bentonite-sand mixtures than for pure compacted bentonite. In the light of the latest findings about diffusion of interlayer water the significance of two-phase flow in a state when the influence of vapour diffusion becomes insignificant is not quite clear. As a matter of fact even the conditions at the end of a re-saturation propagating against a temperature gradient

89

could not be shown unambiguously by the related experiments. This question is subject of presently ongoing experimental investigations at GRS.

In the past only little attention has been paid to the hysteretic property of the water retention curve or the adsorption isotherm, respectively. As step in this direction the work of /DUE04/ can be seen where adsorption isotherms were introduced as a function of the initial water content. Seeing also the results of /MOO52/ it could concluded that the adsorption isotherm has indeed to be modified according to the wetting and drying history of the investigated bentonite. Hysteresis may also have a significant influence on the re-saturation dynamics in situations where the water content is not monotonously increasing as is typically the case under non-isothermal conditions.

Up to now the main reason for developing the code VIPER was testing the vapour diffusion theory. In that respect a one-dimensional numerical model simulating only the hydraulic processes is sufficient. This applies also for the non-isothermal models because up to now temperature data for the non-isothermal models could be taken from measurements. But for predictions under non-isothermal conditions the means of simulating heat transport must be provided since hydraulic processes are obviously influenced by temperature. A tentative balance equation for heat is derived in Appendix E. The question whether a full coupling between hydraulic and thermal processes is required is still open and thus has to be further investigated.

Since the focus of the investigations with VIPER lay on hydraulic processes it has also not been the intention to calculate swelling pressures. However, if displacements under confined conditions are little it should be possible to compute swelling pressures from a correctly calculated local water content. Investigations along these lines could prove to be worthwhile.

The approximation of an axial symmetric model domain using elements with constant cross-sections that vary from element to element is possible but not entirely satisfying. A 2D- and ultimately even 3D-version of VIPER will be required in the long run.

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# Table of figures

Fig. 2.1	The structure of montmorillonite on different scales
Fig. 2.2	TEM/HRTEM pictures of montmorillonite/smectite particles7
Fig. 2.3	Incremental pore volume for two compacted bentonite samples
Fig. 2.4	Volume changes in bentonite during water uptake on a macroscopic scale. 8
Fig. 2.5	Analytical retention curve and the equivalent isotherm
Fig. 2.6	Ad hoc correction in VIPER of an isotherm for confined conditions
Fig. 2.7	Modification of the retention curve for confined conditions after /DUE07/ 13
Fig. 2.8	Example of an isotherm for MX-80 at confined conditions
Fig. 2.9	Initial conditions of an exemplary re-saturation situation
Fig. 2.10	End of stage 1 in an exemplary re-saturation situation 17
Fig. 2.11	Stage 2 in an exemplary re-saturation situation
Fig. 2.12	Stage 3 in an exemplary re-saturation situation
Fig. 2.13	Vapour saturation pressure of pure water; after /IAP97/ 20
Fig. 2.14	Flow and transport processes in a re-saturating buffer
Fig. 3.1	Conditions and processes around the bentonite-water contact zone 23
Fig. 4.1	Double-continuum approach for re-saturating bentonite
Fig. 4.2	Dependency of secondary variables 40
Fig. 4.3	Numerical treatment of a closed boundary 45
Fig. 4.4	Simplification of a 2D-axisymmetric problem to a 1D-element grid
Fig. 6.1	Measured and calculated water content distributions in an isothermal uptake experiment with atmospheric water pressure
Fig. 6.2	Measured and calculated breakthrough curves of relative humidity in an isothermal uptake experiment with increased water pressure
Fig. 6.3	Measured and calculated relative humidity at three different locations in a non-isothermal experiment61

Fig. 6.4	Location of the psychrometric sensors IBX <number></number>
Fig. 6.5	Location of the numbered samples at each layer; from /GUO06/ 64
Fig. 6.6	All transient data concerning the water content during the test
Fig. 6.7	Horizontal cross-sections showing the water content at EOT
Fig. 6.8	End-of-test distribution of buffer density in the ITT; from /DIX06/ 69
Fig. 6.9	Transient water content data representing 2D-flow
Fig. 6.10	Initial water content distribution in the model71
Fig. 6.11	Measured and calculated water content73
Fig. 6.12	Sketch of the Canister Retrieval Test; from /KRI07/
Fig. 6.13	Location of the model domain (a) and dimensions (b) ; from /KRI07/
Fig. 6.14	Location of the temperature sensors at mid height77
Fig. 6.15	Spatial distributions of temperature78
Fig. 6.16	Temporal development of temperature78
Fig. 6.17	Temporal development of relative humidity79
Fig. 6.18	Conceptual model for initial and boundary conditions at the heated side 80
Fig. 6.19	Conceptual model for initial and boundary conditions at the cool side 81
Fig. 6.20	Initial conditions
Fig. 6.21	Radial dry density distribution in two bentonite rings; from /KRI07/
Fig. 6.22	Isotherm used in the model as well as data from /KAH86/ and /DUE04/ 84
Fig. 6.23	Measured and calculated relative humidity/suction
Fig. 6.24	Physical interaction in the CRT-model
Fig. A.1	Data for the first adsorption path for sodium bentonite/montmorillonite 106
Fig. A.2	First and second adsorption path 107
Fig. A.3	Desorption path 108
Fig. A.4	First adsorption path scaled to a clay content of 75 % 112
Fig. A.5	First adsorption path scaled to a clay content of 75 %

Fig. A.6	First adsorption path scaled to a clay content of 75 % 113
Fig. A.7	First adsorption path scaled to a clay content of 75 % 114
Fig. A.8	Desorption path scaled to a clay content of 75 % 115
Fig. B.1	Adsorption isotherms for MX-80 with high resolution 117
Fig. B.2	Isotherm data in different scaling for deriving adsorption energy 118
Fig. B.3	Isotherm data for deriving adsorption energy showing linear sections 118
Fig. B.4	Isotherm data highlighting the 2 <sup>nd</sup> energy level
Fig. B.5	Isotherm data highlighting the 3 <sup>rd</sup> energy level
Fig. B.5	Isotherm data highlighting the 4 <sup>th</sup> energy level
Fig. B.6	Water contents at the transition between different energy levels
Fig. B.7	Transition of energy levels related to the adsorption isotherm 121
Fig. C.1	Evolution of water uptake in a single flow channel during stage 1 126
Fig. C.2	Re-saturation of the flow channel network in a bentonite 127
Fig. G.1	Local equilibria at different temperatures in a closed system

## List of tables

Tab. 4.1	Compilation of conditional equations	. 40
Tab. 6.1	Position of the psychrometric sensors	. 63
Tab. 6.2	Vertical layer distance to the top surface of the bentonite-sand buffer	. 64
Tab. 6.3	Material parameters required by the model	. 72
Tab. 6.4	Heater power protocol	. 75
Tab. 6.5	Location of temperature sensors	. 77

## A Appendix: Comparison of different isotherms for MX-80

#### A.1 Published data

## A.1.2 Description of the sources

Isotherms for clay or MX-80 bentonite, respectively, under unconfined conditions were measured by /MOO52/, /KAH86/, /WAD04/, /DUE04/ and /GAI05/. These authors were interested in different aspects of the sorption isotherms of the bentonite:

- /MOO52/: comparison of different types of montmorillonite; hysteresis of several adsorption-desorption cycles.
- /KAH86/: comparison of two types of bentonite (Na- and Ca-bentonite); high resolution for adsorption and desorption isotherm.
- /WAD04/: testing of a new measuring method for isotherms using cellulose fibres and bentonite.
- /DUE04/: dependence of the isotherms for MX-80 on constraining test conditions.
- /GAI05/: dependence of the adsorption isotherm on temperature.

The following discussion concentrates on the isotherms for sodium bentonite. In case of the data from /MOO52/ it has to be acknowledged that pure montmorillonite was investigated instead of bentonite which requires an appropriate adjustment (see section A.2.1). Two saturation-desaturation cycles were applied to sodium montmorillonite. Some additional conclusions about the nature of hysteresis in the isotherms can be drawn from the test with three cycles on natural montmorillonite (see section A.1.3). /KAH86/ made measurements during just one such cycle but with a remarkably high resolution of the curves. These data were confirmed by the measurements of /WAD04/ who became aware of a delay of equilibrium at high relative humidities. A more detailed investigation including additional effects like the influence of the initial water content (0 % <  $w_{ini}$  < 27 %) was performed by /DUE04/. /GAI05/ addressed the dependency of the adsorption isotherm on temperature covering a temperature range between 25 °C and 99 °C, again with high resolution. Hysteresis, however, was not investigated.

## A.1.2 Adsorption

In Fig. A.1 the data referring to adsorption is compiled. In case of the data from /MOO52/ only the data for the first adsorption path is shown. The data points measured by /DUE04/ for isotherms starting at a point between adsorption and desorption isotherm are given as open symbols to avoid confusion.



Fig. A.1 Data for the first adsorption path for sodium bentonite/montmorillonite

First observations from the data in Fig. A.1 are:

- The data points of /KAH86/, /WAD04/, /DUE04/ and /GAI05/ lie closely together. A characteristic piecewise curvature can be seen in the highly resolved data of /KAH86/ (red squares) and of /GAI05/ (blue squares) (see also Fig. A.7). However, the sections of constant curvature in these two tests are not congruent.
- The data of natural and processed montmorillonite /MOO52/ lie close to each other, too. Both isotherms appear to be parallel over a wide range of relative humidities.
- Generally, the increase of water content is disproportionately high at high relative humidities, especially in the range of relative humidities above 90 %.
- The data point representing the initial water content appears to be missing for the test with w<sub>ini</sub> = 27 % in /DUE04/.

The effect of hysteresis on the adsorption isotherm can be seen in Fig. A.2. First and second adsorption path of the natural montmorillonite show a significant difference. In the range between 20 % and 90 % relative humidity the isotherm for the second adsorption path seems to be shifted upwards. For the sodium montmorillonite this appears not to be the case. Moreover, the data for the second and third adsorption path and the data for both adsorption paths of the sodium montmorillonite form a consistent pattern. A certain scatter in the lower humidity range is attributed to the third adsorption path of the natural montmorillonite and the second adsorption path of the sodium montmorillonite where the preceding desorption was stopped at a humidity of 10 % and not at complete desiccation.



Fig. A.2 First and second adsorption path

### A.1.3 Desorption

The data from /MOO52/ for desorption comprises up to three adsorption-desorption cycles for natural as well as for sodium montmorillonite. The data points from any desorption path appear to be very closely related as shown in Fig. A.3. All other sources provide data from only one cycle.



Fig. A.3 Desorption path

A close matching can be observed, too, in the data from /KAR86/ and /WAD04/ for bentonite. The data from /MOO52/, /KAR86/ and /WAD04/ show a characteristic piecewise curvature of the desorption isotherms similar to that which has been seen for the adsorption isotherms. The data points from /DUE04/ are too scarce to confirm this trend. They match the data from /KAR86/ and /WAD04/ for the measurements with an initial water content below 20 %. In case of higher initial water content the desorption isotherably in the range above 50 % relative humidity.

### A.2 Consistency of the data

#### A.2.1 Content of montmorillonite

The definition of the water content w as the ratio between the mass of interlamellar water  $m_w$  and the mass of solids in the bentonite  $m_s$ 

$$w = \frac{m_w}{m_s} \tag{A.1}$$

shows that isotherms  $w_c(r_h)$  for pure montmorillonite are easily converted into isotherms for bentonites  $w_b(r_h)$  provided that the clay in both cases is of the same type and that there is no impact of the residual material. In case of pure clay the mass of water is related to the clay mass  $m_c$  while in case of bentonite the mass of the accessory minerals  $m_m$  also contributes to the solid mass. For a specific clay content  $x_s^c$  – expressed here as a mass fraction

$$x_s^c = \frac{m_c}{m_s} \tag{A.2}$$

follows conversion between the water content  $w_c$  and the water content  $w_c$  as

$$w_b = x_s^c w_c \tag{A.3}$$

The water content in the isotherm for pure clay  $w_c(r_h)$  can thus simply be scaled accordingly in order to derive the appropriate isotherm  $w_b(r_h)$  for any bentonite based on the same type of clay

$$w_b(r_h) = x_s^c w_c(r_h) \tag{A.4}$$

Apparently, this scaling method applies also to the case of bentonite-sand mixtures which differ from pure bentonite only in terms of the specific clay content.

#### A.2.2 Initial water content

The definition of the dry state of a bentonite is somewhat arbitrary since the bonding forces between the water molecules and the cations are rather strong at low water contents. Thus a certain amount of water which is very difficult to assess always remains in a specimen after any drying procedure.

This phenomenon becomes a particular problem here because test results are compared that are based on different drying methods. According to the authors the specimen of /MOO52/ were dried in a vacuum equivalent to drying in air at 140 °C. A similar method was applied by /GAI05/ where the author specifies the vacuum to a pressure of 10<sup>-5</sup> millimetres of mercury while /DUE04/ dried the samples for 24 hours at 105 °C. The drying procedures applied in the other experiments cited here are not reported.

From these uncertainties and differences in the drying methods it follows apparently that a common origin of the isotherms in a comparative plot cannot exactly be determined. The consequences of the uncertainty in the definition of the dry state are discussed in the following.

An isotherm consists of data points reflecting the water content of a sample in equilibrium with the ambient relative humidity. The water content is usually derived from the mass difference between the sample in equilibrium and the same sample after drying. Weighing the dried sample provides the solid mass  $m_s$ , weighing the partially saturated sample provides the sum of solid and water mass  $m_b$ :

$$m_b = m_w + m_s \tag{A.5}$$

The mass of water  $m_{_{W}}$  taken up can be then calculated from

$$m_w = m_b - m_s \tag{A.6}$$

The same test under the same conditions but using different methods of drying would yield the same mass  $m_b$  but different values for  $m_s$ . The differing values between two tests will be identified as  $m_s^I$  and  $m_s^{II}$  further on. To quantify the difference

$$m_s^{II} = (1+a) \cdot m_s^I \tag{A.7}$$

with constant *a* is assumed. The ratio of the resulting two water contents  $w^{I}$  and  $w^{II}$  reads then

$$\frac{w^{II}}{w^{I}} = \frac{\frac{m_{w}^{II}}{m_{s}^{II}}}{\frac{m_{w}^{I}}{m_{s}^{I}}} = \frac{\frac{m_{b} - (1+a) \cdot m_{s}^{I}}{(1+a) \cdot m_{s}^{I}}}{\frac{m_{b} - m_{s}^{I}}{m_{s}^{I}}} = \frac{1}{(1+a)} \left(\frac{m_{b} - (1+a) \cdot m_{s}^{I}}{m_{b} - m_{s}^{I}}\right) = \frac{1}{(1+a)} \left(1 - \frac{a}{w^{I}}\right)$$
(A.8)

and finally

$$w^{II} = \frac{w^{I}}{1+a} - \frac{a}{1+a}$$
(A.9)

The effective difference of two drying methods expressed by the constant a is reflected by a scaling of the initial isotherm (Index I) in w-direction by a factor of 1/(1+a) and by translating it by a value of -a/(1+a), also in w-direction. Scaling, however, has a negligible effect in the range of a considered here.

#### A.3 Comparison of scaled data

#### A.3.1 Adsorption

In the following the curves from /MOO52/ are scaled down to a clay content of 75 % – a value reported for MX-80 in /KAH86/ – in order to make the data comparable. Fig. A.4 shows the compilation analogous to Fig. A.1 after scaling.

Up to a relative humidity of 80 % the curves agree quite well with each other with the following exceptions:

- The data for sodium montmorillonite provided by /MOO52/ is less curved in comparison to the more curvilinear sections of the other isotherms (q.v. Fig. A.2). It matches the other curves for humidities up to 10 % and above 90 % rather well but exceeds the trend line of the other curves by up to 3 % water content in the medium range (q.v. Fig. A.5).
- The same applies to a lesser extend to the data for natural montmorillonite from /MOO52/ (q.v. Fig. A.5).
- Data from /DUE04/ deviates generally in cases where the initial water content was above zero. The starting points of these curves lie between the bounding curves for adsorption and desorption and thus show too high water contents (q.v. Fig. A.6).
- Even the adsorption isotherm from /DUE04/ that starts with a completely dry sample deviates from the rest of the curves for humidities above 90 %. This is explained by the author with the extremely long test duration in this humidity range which appeared necessary to reach equilibrium (q.v. Fig. A.6).



Fig. A.4 First adsorption path scaled to a clay content of 75 %



Fig. A.5 First adsorption path scaled to a clay content of 75 %; some data points of /MOO52/ connected for better recognition



Fig. A.6 First adsorption path scaled to a clay content of 75 %; data points of /DUE04/ connected for better recognition

Discarding the data from /MOO52/ and taking only those isotherms from /DUE04/ that cover the total range of relative humidity leads to Fig. A.7. To facilitate drawing of some conclusions from the detailed isotherms from /KAH86/ and /GAI05/ the data points are connected to a line in this figure.

Fig. A.7 shows clearly that the characteristic course of the curve from /KAH86/ can also be seen in the data from /GAI05/. But in the range between 20 % and 80 % relative humidity they appear to be shifted against each other by a value of 0.1 in  $r_h$ -direction. An explanation for this phenomenon could not be found. Nevertheless, the data from both sources do not differ very much from each other. And they are confirmed nicely by the measurements of /DUE04/ and /WAD04/ which are just too scarce to confirm also the characteristic curvature of the two other isotherms.

The absolute uncertainty of all measured data in the range below 60 % relative humidity is never in excess of 1 % water content. In the range between 60 % and 80 % the data appears to be somewhat more scattered. Above 80 % relative humidity the data converges again except for the data from /DUE04/ which is systematically higher for reasons given above. Thus the highest uncertainties are found in the range above approx. 80 % water content which is unfortunately the relevant range for bentonite resaturation under in-situ conditions.



Fig. A.7 First adsorption path scaled to a clay content of 75 %; different view without data from /MOO52/ and only selected isotherms from /DUE04/ (see text)

#### A.3.2 Desorption

Using the same scaling as for the adsorption isotherms all desorption isotherms are congruent below 50 % relative humidity. Above that value all data is still in excellent agreement with each other except for the data from /DUE04/ which deviates considerably from the other data. All isotherms with sufficient resolution – meaning all except those from /DUE04/ – show a particular piecewise curvature of the desorption isotherm: the first section covering the humidity range up to 45 %, the second one between 45 % and 93 % and a third section above 93 % relative humidity. This result is in agreement with the conclusion of /MOO52/ that the desorption path can be much better reproduced than the adsorption path.



Fig. A.8 Desorption path scaled to a clay content of 75 %

#### A.4 Conclusions

The data for the adsorption isotherm for MX-80 bentonite is consistently showing an exponential-shape increase of water content with the relative humidity up to 90 % humidity followed by a disproportionately high further increase. A systematic substructure in the run of this curve as indicated by the rather detailed measurements from /KAH86/ could not be confirmed either due to scarcity of the data or due to a substantially different distribution of such substructures as in the data from /GAI05/.

The investigations of /DUE04/ indicate that the water contents measured by the other authors could be too low due to the apparently long time required to reach equilibrium, especially in the humidity range above 85 %. The required time can easily lie in the order of 1 - 2 months. This means the data from /DUE04/ are a better representation of the isotherm. However, it also questions the assumption of instantaneous equilibrium between water content and relative humidity (or suction) that is usually implicitly applied for modelling bentonite re-saturation. This assumption is apparently only justified in cases where a calculated change of the water content takes considerably more time than equilibration of water content and relative humidity. Otherwise the water uptake kinetics have to be taken into account as has been pointed out by /HAS05/ with respect

to the capillary pressure-saturation relation in the framework of conventional two-phase flow.

In contrast the data for the desorption isotherm agree very well with each other with the exception of the data from /DUE04/ which exceed the data of all other authors. A reason for these deviations could not be found. Otherwise three sections in the desorption isotherm could be identified with a characteristic curvature confirming the existence of substructures in the course of the desorption isotherm. Note that the measurements of /DUE04/ indicate that a period of time of less than 10 hours is required for equilibration along the desorption path. All in all there is much less uncertainty in the data for the desorption path than for the adsorption path.

## B Appendix: Hydrate layers and related water content

A method ascribed to Dubinin and Radushkevich to identify the water contents correlating with the completion of hydrate layers of the interlamellar cations is described in /KAR86/. It is based on adsorption isotherms and requires a rather high resolution in terms of data points. Data for MX-80 that appears to comply with this requirement are taken from Appendix A and is plotted in Fig. B.1.



Fig. B.1 Adsorption isotherms for MX-80 with high resolution in terms of data points

Using isotherm data plotted as log (*w*) over  $(\log r_h)^2$  – see Fig. B.2 – the adsorption energy which is characteristic for each level of adsorption can be calculated from the slope of the resulting curve. From the fact that this curve is roughly composed of several linear sections – see Fig. B.3 to B.5 with comparatively small connecting transition sections it can be concluded that

- a hydration layer has to be completed at almost all cations before the next layer is formed and that
- a value of the water content characteristic for the transition to the next hydration layer can be identified.



Fig. B.2 Isotherm data in different scaling for deriving adsorption energy



Fig. B.3 Isotherm data for deriving adsorption energy showing linear sections



**Fig. B.4** Isotherm data highlighting the 2<sup>nd</sup> energy level



**Fig. B.5** Isotherm data highlighting the 3<sup>rd</sup> energy level



**Fig. B.5** Isotherm data highlighting the 4<sup>th</sup> energy level

The locations of the intersections are depicted in Fig. B.6. According to the interpretation given in /KAR86/ the filling of the hexagonal openings is completed at 1 % to 2 %, the first hydrate layer is completed at 6 % to 9.5 % and the second layer at 16 % to 18 %. As shown in Fig. B.7 these values correspond nicely with the changes in the trend of the adsorption isotherm from /KAR86/ except for some data from /GAI05/. A reason for these deviations could not be found.



Fig. B.6 Water contents at the transition between different energy levels



Fig. B.7 Transition of energy levels related to the adsorption isotherm from /KAR86/

## C Appendix: Saturation with liquid water during stage 1

#### C.1 Two-phase flow effects on the microscopic level

Water distribution at the end of stage 1 of the re-saturation is the result of several processes that interact in a rather complex manner. However, during the first seconds the migration of water inside the bentonite is assumed to resemble a two-phase flow before hydration and accompanying swelling changes pore space and flow patterns significantly /PUS03/. These first moments are looked at more closely in the following.

In the classical two-phase flow theory water is assumed to move in a bundle of pipelike capillaries with different radii. The uptake velocity in such a capillary depends on the product of permeability and the pressure gradient as shown in equation (5.12). The influence of gravity can be neglected here:

$$\mathbf{v} \approx \frac{\mathbf{k}}{\mu} \cdot \nabla p \tag{C.1}$$

In the absence of an applied hydraulic pressure the pressure gradient depends only on the capillary pressure. Regarding capillary flow as a one-dimensional process without sinks and sources equation (C.1) can be simplified to

$$v \approx \frac{k}{\mu} \frac{p_c - p_0}{\Delta x} \tag{C.2}$$

and if only excess pressure  $\overline{p}$  over atmospheric pressure is considered even simplified to

$$v \approx \frac{k}{\mu} \frac{\overline{p}_c}{\Delta x}$$
 (C.3)

However, while permeability is directly proportional to the capillary radius, capillary pressure is inversely proportional. It is therefore not obvious if water is moving faster in wide or in thin capillaries.

In order to decide this question Hagen-Poiseuille's law for pipe flow

$$Q = \frac{\pi r^4}{8 \mu} \nabla p \tag{C.4}$$

is transformed to get an expression for the permeability in terms of Darcy's law using

$$Q = A v$$
 and  $A = \pi r^2$  (C.5)

which leads to

$$v = \frac{r^2}{8\,\mu} \,\nabla p \tag{C.6}$$

so that the relation

$$k = \frac{r^2}{8}$$
 (C.7)

is derived for the problem at hand. Capillary pressure on the other hand is a function of the surface tension as described in equation (5.21)

$$p_c = \frac{2\sigma}{r} \tag{C.8}$$

Inserting equations (B.7) and (B.8) into (B.3) yields

$$v \approx \frac{1}{4\mu} \frac{\sigma}{\Delta x} r$$
 (C.9)

and finally reveals that instant velocity of a water column of the length  $\Delta x$  is higher in large capillaries than in thin ones. Water is thus taken up faster in the large capillaries.

## C.2 Adding hydration dynamics

After the first few seconds water uptake is not only controlled by two-phase flow in the pore space but also by hydration of pore water in the interlamellar space of the particles. Parallel to migrating in the flow channels between the grains water is also attract-

ed to the surface of the clay particles and is ultimately drawn into the clay particles where it hydrates at the interlamellar cations. This additional process takes a short time and the hydration rate – an expression that is used here synonymously for the mass flux between pore space and interlamellar space – is proportional to the difference of the chemical potential of pore water and hydrated water. This difference decreases with the locally increasing amount of hydrated water meaning that the uptake rate and the concurrent swelling rate decrease with time.

Two effects impede the uptake of water increasingly. First, the confinement of the swelling bentonite constricts the pore channels and thus reduces the permeability. Second, while the driving capillary forces at the front end of the water column in a flow channel persist to be constant, the flow resistance increases with the length of this water column leading to a decrease of flow velocity with time.

If the progress of water has been slowed down sufficiently a third effect becomes noticeable. Water evaporates all the time at the interface between water and air and is subsequently transported further into the pore atmosphere by vapour diffusion. This effect causes a little but steady mass flux of water leaving the water column. Migration of the water-air interface comes therefore to an end when liquid water flow in the flow channel equals the diffusive vapour flux at the interface. For a single flow channel the combined effects of two-phase flow and beginning hydration are illustrated in Fig. C.1.





## C.3 Expanding to a channel network

As explained in the previous section, if an air-dry bentonite comes into contact with water the water in wider channels moves faster than that in narrower channels. This process is illustrated by Fig.s C.2 a) and b). Wetting of the clay grains, hydration and subsequent swelling begins in the large channels. The swelling not only reduces the channel diameter by taking up water but also affects the neighbouring dry channels by applying swelling pressure locally. It can be expected that this effect acts locally and proportional to the diameter of the channels still filled with air. Wider channels are more easily squeezed than smaller ones due to a higher resistance to compaction in more densely packed regions. The highest variations can thus be expected in the widest channels.

Wherever wide water bearing flow channels intersect narrower air-filled channels the latter start to take up water from there on, too. The bulk volume containing the narrow water-filled channels thus more or less coincides with the bulk volume containing large water-filled channels. At the end of stage 1 it can therefore be expected

- that channel sizes in the water-filled region of the channel network are equalised to a certain extent, and
- that a completely water saturated, narrow zone at the bentonite-water contact is followed by air-dry bentonite without much of a transition in between.

This situation is illustrated by Fig. C.2 c).





bentonite at initial water content free pore space water-filled reduced pore space additional bentonite volume due to swelling.

Fig. C.2 Re-saturation of the flow channel network in a bentonite; a) air-dry condition, b) intermediate water distribution, c) water distribution at the end of stage 1

## D Appendix: Derivatives of the water content

During the development of the balance equation (4.34) several derivatives of the water content and the relative humidity with respect to time as well as to space are required. An unspecified independent variable u, representing either time or space, is introduced here to acquire a generally valid formulation for the different derivatives. Note that the simple partial derivative with respect to u can be replaced by the gradient operator in case of more than one spatial coordinate.

#### First order derivative of *w* with respect to *u*

In the light of relation (4.22) applies

$$\frac{\partial w}{\partial u} = \left(\frac{\partial w}{\partial r_h}\frac{\partial r_h}{\partial u} + \frac{\partial w}{\partial T}\frac{\partial T}{\partial u}\right)$$
(D.1)

According to equation (4.23) the first order derivative of  $r_h$  with respect to u can be written as

$$\frac{\partial r_h}{\partial u} = \frac{\partial r_h}{\partial \rho_v} \frac{\partial \rho_v}{\partial u} + \frac{\partial r_h}{\partial T} \frac{\partial T}{\partial u}$$
(D.2)

which leads to

$$\frac{\partial w}{\partial u} = \frac{\partial w}{\partial r_h} \left[ \frac{\partial r_h}{\partial \rho_v} \frac{\partial \rho_v}{\partial u} + \frac{\partial r_h}{\partial T} \frac{\partial T}{\partial u} \right] + \frac{\partial w}{\partial T} \frac{\partial T}{\partial u}$$
(D.3)

From equation (4.23) follows directly

$$\frac{\partial r_h}{\partial \rho_v} = \frac{1}{\rho_{v\,sat}} \text{ and } \frac{\partial r_h}{\partial T} = -\frac{\rho_v}{(\rho_{v\,sat})^2} \frac{\partial \rho_{v\,sat}}{\partial T}$$
(D.4)

This allows a formulation alternative to equation (D.3):

$$\frac{\partial w}{\partial u} = \frac{\partial w}{\partial r_h} \frac{1}{\rho_{v \, sat}} \frac{\partial \rho_v}{\partial u} + \left( \frac{\partial w}{\partial T} - \frac{\partial w}{\partial r_h} \frac{\rho_v}{(\rho_{v \, sat})^2} \frac{\partial \rho_{v \, sat}}{\partial T} \right) \frac{\partial T}{\partial u}$$
(D.5)

Note: Inserting equation ( D.4 ) introduces a term that depends directly on the vapour partial density  $\rho_{\rm v}$ .

## Second order derivative of *w* with respect to *u*

The second order derivative of w with respect to u can be derived from applying the first order derivative to w twice:

$$\frac{\partial^2 w}{\partial u^2} = \frac{\partial}{\partial u} \left( \frac{\partial w}{\partial r_h} \frac{\partial r_h}{\partial u} + \frac{\partial w}{\partial T} \frac{\partial T}{\partial u} \right)$$
$$= \left[ \frac{\partial}{\partial u} \left( \frac{\partial w}{\partial r_h} \right) \right] \frac{\partial r_h}{\partial u} + \frac{\partial w}{\partial r_h} \frac{\partial^2 r_h}{\partial u^2} + \left[ \frac{\partial}{\partial u} \left( \frac{\partial w}{\partial T} \right) \right] \frac{\partial T}{\partial u} + \frac{\partial w}{\partial T} \frac{\partial^2 T}{\partial u^2}$$
(D.6)

The second order derivative of  $r_h$  is apparently also required:

$$\frac{\partial^{2} r_{h}}{\partial u^{2}} = \frac{\partial}{\partial u} \left( \frac{\partial r_{h}}{\partial \rho_{v}} \frac{\partial \rho_{v}}{\partial u} + \frac{\partial r_{h}}{\partial T} \frac{\partial T}{\partial u} \right)$$

$$= \left[ \frac{\partial}{\partial u} \left( \frac{\partial r_{h}}{\partial \rho_{v}} \right) \right] \frac{\partial \rho_{v}}{\partial u} + \frac{\partial r_{h}}{\partial \rho_{v}} \frac{\partial^{2} \rho_{v}}{\partial u^{2}} + \left[ \frac{\partial}{\partial u} \left( \frac{\partial r_{h}}{\partial T} \right) \right] \frac{\partial T}{\partial u} + \frac{\partial r_{h}}{\partial T} \frac{\partial^{2} T}{\partial u^{2}}$$

$$= \left[ \frac{\partial}{\partial u} \left( \frac{1}{\rho_{v \, sat}} \right) \right] \frac{\partial \rho_{v}}{\partial u} + \frac{1}{\rho_{v \, sat}} \frac{\partial^{2} \rho_{v}}{\partial u^{2}}$$

$$- \left[ \frac{\partial}{\partial u} \left( \frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \right) \right] \frac{\partial T}{\partial u} - \frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \frac{\partial^{2} T}{\partial u^{2}}$$
(D.7)

Inserting of equation ( D.7 ) into equation ( D.6 ) finally yields

$$\frac{\partial^{2} w}{\partial u^{2}} = \frac{\partial}{\partial u} \left( \frac{\partial w}{\partial r_{h}} \left[ \frac{\partial r_{h}}{\partial \rho_{v}} \frac{\partial \rho_{v}}{\partial u} + \frac{\partial r_{h}}{\partial T} \frac{\partial T}{\partial u} \right] + \frac{\partial w}{\partial T} \frac{\partial T}{\partial u} \right)$$

$$= \left[ \frac{\partial}{\partial u} \left( \frac{\partial w}{\partial r_{h}} \right) \right] \left[ \frac{1}{\rho_{v \, sat}} \frac{\partial \rho_{v}}{\partial u} - \frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \frac{\partial T}{\partial u} \right]$$

$$+ \frac{\partial w}{\partial r_{h}} \left\{ \frac{\partial}{\partial u} \left( \frac{1}{\rho_{v \, sat}} \right) \right] \frac{\partial \rho_{v}}{\partial u} + \frac{1}{\rho_{v \, sat}} \frac{\partial^{2} \rho_{v}}{\partial u^{2}} - \frac{\rho_{v}}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \frac{\partial^{2} T}{\partial u^{2}} + \frac{\partial}{\partial u} \left[ \frac{\partial T}{(\rho_{v \, sat})^{2}} \frac{\partial \rho_{v \, sat}}{\partial T} \frac{\partial^{2} T}{\partial u^{2}} \right]$$

$$+ \left[ \frac{\partial}{\partial u} \left( \frac{\partial w}{\partial T} \right) \right] \frac{\partial T}{\partial u} + \frac{\partial w}{\partial T} \frac{\partial^{2} T}{\partial u^{2}}$$
(D.8)

## E Appendix: Balance equation for heat transport

### E.1 Balance equation for heat transport

In principle, there are three mechanisms for the transport of thermal energy:

- heat conduction,
- convection, and
- thermal radiation.

However, thermal radiation does not play a role in the context of fluid flow in porous media. On a microscopic level of observation heat flow occurs in the solid particles as well as in the interlayer water according to the referring thermal properties.

assumption E.1: Heat flow in gaseous phases can be neglected.

Separate balance equations for heat in the water as well as in the solid material can therefore be written as

$$\int_{G} \left[ \frac{\partial \left( \Phi_{\alpha} \hat{Q}_{\alpha} \right)}{\partial t} + \Delta \left( \Phi_{\alpha} \hat{Q}_{\alpha} \mathbf{v}_{\alpha} + \Phi_{\alpha} J_{Q_{\alpha}} \right) - r_{Q_{\alpha}} \right] dG = 0$$
 (E.1)

 $\hat{Q}_{\alpha}$  - heat density of  $\alpha$  [J/m<sup>3</sup>]

 $\Phi_{\alpha}$  - volumetric fraction of  $\alpha$  of the bulk volume [-]

 $J_{O_a}$  - heat flow density [J/(m<sup>2</sup> s)]

 $r_{Q_{\alpha}}$  - heat source in  $\alpha$  [J/(m<sup>3</sup>s)]

$$\alpha$$
 - index for interlayer water  $(\alpha = hyd)$  or solid  $(\alpha = s)$ 

assumption E.2: Neither interlayer water nor solids are transported by advection.

Assumption E.2 allows to drop the advective term in equation ( E.1 ). Adding equations ( E.1 ) gives

$$\int_{G} \left[ \frac{\partial \left( \Phi_{hyd} \hat{Q}_{hyd} + \Phi_{s} \hat{Q}_{s} \right)}{\partial t} + \Delta \left( \Phi_{hyd} J_{Q_{hyd}} + \Phi_{s} J_{Q_{s}} \right) - r_{Q_{hyd}} - r_{Q_{s}} = 0 \right] dG = 0$$
 (E.2)

It is much more convenient to express heat density  $\hat{Q}_{\alpha}$  and heat flow density  $J_{Q_{\alpha}}$  by the directly measurable temperature T. Equation (E.2) contains heat density only as a subject to derivatives and differences of the heat density can be related to differences of temperature (e.g. /FLÜ61/) by

$$\delta \hat{Q} = c_p \rho \delta T \tag{E.3}$$

*c*<sub>p</sub> - specific heat capacity [J/(kg K)]

ho - material density [kg/m<sup>3</sup>]

*T* - temperature [K]

For heat conduction in solid matter and immobile fluids Fourier's law applies which is formally identical with Fick's law of diffusion:

 assumption E.3: In the case of heat conduction heat flow density – defined as heat per area and second – can be computed by Fourier's law:

$$J_{Q} = -\lambda \, \nabla T \tag{E.4}$$

 $\lambda$  - thermal conductivity [J/(m K s)]

Inserting (E.3) and (E.4) in the general balance equation (E.2) results in

$$\int_{G} \left[ \frac{\partial (\Phi_{hyd} c_{phyd} \rho_{hyd} T_{hyd} + \Phi_{s} c_{ps} \rho_{s} T_{s})}{\partial t} - \Delta (\Phi_{hyd} \lambda_{hyd} \nabla T_{hyd} + \Phi_{s} \lambda_{s} \nabla T_{s}) \right] dG \quad (E.5)$$
$$= 0$$

 assumption E.4: Hydrated water and solid particles are always in local thermal equilibrium:

$$T_{hyd} = T_s = T \tag{E.6}$$
From assumption E.4 follows that it is not necessary to distinguish between heat sources in solids and in interlayer water:

$$r_{Q} = r_{Q_{hyd}} + r_{Q_s} \tag{E.7}$$

While the volume fraction taken by the solid particles is related to dry and grain density (q.v. equation (4.10)) and thus is a constant the volume fraction of the interlayer water is a function of the water content (q.v. equation (4.13)). However, provided that

 assumption E.5: Thermal conduction is a much faster process than water transport in clay.

holds, it follows that the initial water content in the clay persists until the heat front has crossed the clay. In other words, before significant changes in the water content can happen the temperature profile in the clay is already more or less at steady-state. This reduces the influence of the time-dependent water content on the storage term compared to the diffusion term during this period.

If changes in the temperature distribution are very slow the shape of the distribution can be influenced by the distribution of thermal diffusivity. A maximum ratio of 2 between thermal conductivity of dry and saturated clay does not distort the temperature results intolerably, though, leading to

 assumption E.6: volumetric fraction of the interlayer water and thermal conductivity are assumed to adopt a typical but constant value.

Balance equation ( E.5 ) is therefore further transformed by equations ( 4.13 ), ( E.6 ), and ( E.7 ) into

$$\int_{G} \left[ \left( \Phi_{hyd} c_{p hyd} \rho_{hyd} + \Phi_{s} c_{p s} \rho_{s} \right) \frac{\partial T}{\partial t} - \Delta \left\{ \left( \Phi_{hyd} \lambda_{hyd} + \Phi_{s} \lambda_{s} \right) \nabla T \right\} - r_{Q} \right] dG$$

$$= 0$$
(E.8)

Without the source term equation (E.8) represents another diffusion equation:

$$\frac{\partial T}{\partial t} + \Delta (\kappa \cdot \nabla T) = 0 \qquad \text{with} \qquad \kappa = \frac{\Phi_{hyd} \lambda_{hyd} + \Phi_s \lambda_s}{\Phi_{hyd} c_{phyd} \rho_{hyd} + \Phi_s c_{ps} \rho_s} \tag{E.9}$$

 $\kappa$  - thermal diffusivity [m<sup>2</sup>/s]

#### E.2 Numerical solution

Balance equation (E.9) is formally identical with equation (5.17) which has already been discussed in section 5. The resulting approximating equations for the inner nodes and the left node as well as the Neumann stability criterion are therefore analogue to equations (5.26) to (5.28):

$$T_0^+ = T_0^- + \frac{\Delta t}{\Delta x^2} \kappa_0^- \left( A_+ T_+^- - \left( A_+ + A_- \right) T_0^- + A_- T_-^- \right)$$
 (E.10)

for an inner node and a comparison with equation (4.62) for the node at the left

$$T_0^+ = T_0^- + 2\frac{\Delta t}{\Delta x^2}\kappa_0^- A_+ \left(T_+^- - T_0^-\right)$$
(E.11)

The Neumann stability criterion is the only applicable criterion here and it applies analogously to equation (4.66):

$$Ne = \kappa \frac{\Delta t}{\Delta x^2} \le \frac{1}{2} \tag{E.12}$$

### F Appendix: Compilation of model assumptions

#### F.1 Re-saturation stage 1

- assumption 3.1: During the first stage a thin, homogeneously water-saturated zone develops until equilibrium is reached between water flow through the swollen bentonite and evaporation into the free pore space (see Fig. 3.1).
- assumption 3.2: Water transport in the thin saturated zone between the bentonite-water contact and the water-air interface is dominated by advective flow.

#### F.2 Re-saturation stage 2

- assumption 4.1: Diffusion of water vapour in air can be described as a binary diffusion process.
- assumption 4.2: Advection of water vapour does not occur.
- assumption 4.3: Fick's second law is valid.
- assumption 4.4: Diffusion is isotropic.
- assumption 4.5: Apparent diffusion is impeded due to tortuosity of the pore space.
- assumption 4.6: The local amount of water vapour can change due to hydration or condensation.
- assumption 4.7: Interlayer water can only migrate by a Fickian diffusive process.
- assumption 4.8: Density of interlayer water is independent of the state of hydration.
- assumption 4.9: Constant-volume conditions apply.
- assumption 4.10: The sum of the volumes of pore space and interlayer water is constant.
- assumption 4.11: The local mass of water vapour is negligible compared with the local mass of hydrated water.
- assumption 4.12: Hydration occurs instantaneously. Thus, water content is always in equilibrium with the relative humidity in the pore space.

- assumption 4.13: The product of porosity, tortuosity and molecular diffusion coefficient is called the apparent diffusion coefficient  $D_a$ . Under isothermal conditions is  $D_a$  constant.
- assumption 4.14: The apparent diffusion coefficient  $D_a$  changes with temperature and pressure proportionately to the molecular diffusion coefficient.
- assumption 4.15: Interlamellar water migrates diffusively at rates corresponding to self-diffusion.
- assumption 4.16: Change of particle orientation during re-saturation has negligible influence on the pathway tortuosity for the interlamellar water.
- assumption 4.17: The adsorption isotherm depends only on temperature. Influence of pressure, adsorption-/desorption-hysteresis, and temperature-induced mineral alterations are negligible.
- assumption 4.18: Only homogeneous diffusion is considered.

 assumption 4.19: The isotherm of MX-80 bentonite at 25 °C can be approximated by a linear function up to a relative humidity of 95 %.

#### F.3 Re-saturation stage 3

- assumption 5.1: Re-saturation in the third stage is dominated by two-phase flow.
- assumption 5.2: Gas flow is neglected.
- assumption 5.3: Compressibility of water can be neglected.
- assumption 5.4: Thermal strain of water can be neglected.
- assumption 5.5: Porosity is constant.
- assumption 5.6: Sources are not to be taken into account.
- assumption 5.7: The influence of gravity can be neglected.

#### F.4 Balance equation for heat transport

- assumption E.1: Heat flow in gaseous phases can be neglected.
- assumption E.2: Neither interlayer water nor solids are transported by advection.
- assumption E.3: In the case of heat conduction heat flow density defined as heat per area and second – can be computed by Fourier's law:

- assumption E.4: Hydrated water and solid particles are always in local thermal equilibrium:
- assumption E.5: Thermal conduction is a much faster process than water transport in clay.
- assumption E.6: volumetric fraction of the interlayer water and thermal conductivity are assumed to adopt a typical but constant value.

#### G Appendix: Local effect of heating on relative humidity

The effect of heating on the relative humidity in the pore atmosphere can most clearly be derived from the behavior of partially saturated bentonite in a closed system. This behavior can in principle be transferred to the problem of the local response to heating in a bentonite buffer especially since instantaneous hydration is already assumed anyway.

The following considerations are based on isotherms for bentonite which basically represent the equilibrium between the relative humidity in the pore space and the water content. Note that relative humidity represents a measure for the amount of water in the pore space while the water content represents a measure for the amount of inter-lamellar water.

From /GAI05/ it is known that heating causes a certain lowering of the isotherms. In Fig. G.1 a principle sketch is given for two isotherms, the one in blue for a temperature  $T_0$  and the one in red for a temperature  $T_1$  which is assumed to be higher than  $T_0$ . Equilibrium at  $T_0$  is characterized by the relative humidity  $r_{h,0}$  and the related water content  $w_0$  (blue circle in Fig. G.1). Heating the bentonite up to temperature  $T_1$  shifts the blue isotherm to the position of the red isotherm.



Fig. G.1 Local equilibria at different temperatures in a closed system

If the interlamellar water were unaffected by the heating it would remain at  $w_0$  so that the new equilibrium would be represented by the orange circle in Fig. G.1. However, this would not be consistent with the corresponding increase of relative humidity. An increase of relative humidity can only be achieved by an increase of water vapour in the pore atmosphere even more so since the temperature is also increased. In a closed system this additional water vapour can only come from the interlamellar water by dehydration. The increase of relative humidity therefore reduces the water content to a certain extent and means that the new equilibrium is reached a little left from the position of the orange circle. The orange circle thus provides an upper boundary for the relative humidity at  $T_1$ .

If on the other hand relative humidity were unaffected by the heating water content would be decreased as indicated by the purple circle which again is not possible. Lowering the water content sets interlamellar water free thereby increasing the vapour density and thus relative humidity. The new equilibrium is therefore reached right from the position of the purple circle. The purple circle thus provides a lower boundary for the relative humidity at  $T_I$ . It thus follows generally that changing from one state of equilibrium to another state of equilibrium at a higher temperature causes the water content to decrease and the relative humidity to increase.

From the fact that the density of interlamellar water is several orders of magnitude higher than that of water vapour it follows that little changes in water content are sufficient to change relative humidity considerably. This in turn means that during heating the water content changes only little in comparison to the relative humidity. The equilibrium at  $T_I$  represented by the red circle is therefore much closer located to the orange than to the purple circle.

# Symbols and notations

## Symbols

A	cross-section area [m <sup>2</sup> ]
B(t)	time-dependent volume [m <sup>3</sup> ]
D	diffusion coefficient [m²/s]
$D_{m \ 0}$	reference value for the binary gas diffusion coefficient [m²/s]
$D_m$	coefficient of binary gas diffusion [m²/s]
$D_{\mathrm{a}}$	macroscopic diffusion coefficient [m²/s]
$D'_a$	macroscopic diffusion coefficient of the interlamellar water [m²/s]
$D_{hyd}$	diffusion coefficient of the interlamellar water [m²/s]
G	fixed domain volume [m <sup>3</sup> ]
J	non-advective across the surface of <i>G</i> [ <dim>/(m<sup>2</sup> s)]</dim>
K	tensor of the absolute permeability [m <sup>2</sup> ]
$M_w$	molecular mass of water; $M_w$ = 0.018 [kg/mol]
R	universal gas constant; $R = 8.31 [J/(mol K)]$
S	degree of saturation [-]
Т	temperature [K]
$T_0$	reference temperature [K]
$V_{f}$	local finite Volume [m³]
Z(t)	extensive state variable in $B(t)$ with the dimension <dim> [<dim>]</dim></dim>
$c_p$	specific heat capacity [J/(kg K)]
g	material-specific deviation factor [-]
g	vector of the gravitational acceleration [m/s <sup>2</sup> ]
k	permeability [m²]
$k_{r\alpha}$	relative permeability of the $lpha$ -phase [-]
$k_{\scriptscriptstyle B}$	Boltzmann constant [J/K]
т	element number [-]
$m_w$	mass of the interlayer water [kg]
$m_{wc}$	mass of condensated vapour [kg]
$m_s$	dry mass of the bentonite [kg]
р	pressure [Pa]
$p_s$	swelling pressure [Pa]
$p_a$	air pressure [Pa]
$p_c$	capillary pressure [Pa]

$p_d$	entry pressure [Pa]
$p_{c0}$	scaling_parameter [Pa]
$p_v$	vapour partial pressure [Pa]
$p_{v  sat}$	vapour saturation pressure [Pa]
$q_{\alpha}$	sink/source of the $lpha$ -phase [kg/(kg s)]
r	sink/source of Z in G [ <dim>/(<math>m^3</math> s)]</dim>
$r_{cond}$	sink/source for vapour mass due to condensation [kg/(m <sup>3</sup> s)]
r <sub>hyd</sub>	sink/source for vapour mass due to hydration [kg/(m³ s)]
$\overline{r}_{hyd}$	sink/source for interlamellar water due to hydration [kg/(m³ s)]
$r_h$	relative humidity [-]
$r_h^{free}$	relative humidity according to free swelling conditions [-]
$r_{hsat}^{free}$	relative humidity at saturation according to free swelling conditions [-]
$r_h^{conf}$	relative humidity according to confined conditions [-]
S	suction [Pa]
S <sup>free</sup>	suction according to free swelling conditions [Pa]
s <sup>conf</sup>	suction according to confined conditions [Pa]
v	velocity [m/s]
W	water content of the bentonite [-]
W <sub>iso</sub>	equilibrium water content at reference temperature [-]
W <sub>e</sub>	water content at the end of stage 2 (end of swelling) [-]
$W_{tot}$	water content with a completely water-filled pore space [-]
$W_p$	water content related to liquid water in the pore space [-]
z(t)	density of Z [ <dim>/m<sup>3</sup>]</dim>
$\theta$	empirical exponent [-]
К	thermal diffusivity [m²/s]
λ	pore size distribution index [-]
λ	thermal conductivity [J/(m K s)] (Appendix E only)
μ	viscosity [Pa s]
$\mu_{p}$	particle mobility [m/(N·s)]
ρ	material density [kg/m³]
$ ho_{\scriptscriptstyle w}$	density of liquid water; $ ho_{_{\scriptscriptstyle W}}$ = 1000 [kg/m³]
$ ho_v$	vapour partial density [kg/m³]
$ ho_{vsat}$	vapour saturation partial density [kg/m³]
$ ho_{\scriptscriptstyle w}$	density of the interlayer water [kg/m³]
$ ho_{d}$	dry density of the bentonite [kg/m³]
$ ho_{s}$	density of the solid matter in the bentonite [kg/m <sup>3</sup> ]

[N/m]

- $\tau$  tortuosity [-]
- $\tau_{\rm hyd}$  tortuosity of the interlamellar space [m²/s]
- $\tau_0$  initial tortuosity [-]
- $\Phi$  porosity [-]
- $\Phi_{_{hyd}}$  fraction of volume taken by interlamellar water [-]
- $\Phi_d$  porosity of the dry bentonite [-]
- $\Phi_{\rm min}$  porosity at the end of stage 2 (end of swelling) [-]

#### Indices

- $\alpha$  denoting the  $\alpha$ -phase
- $x_{+}/x_{0}/x_{-}$  variable x left of/at/right of the node
- $x^+/x^-$  variable x on the new/old time level

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