Doctoral Thesis

On the dissolution, precipitation and transport processes in sulphatic swelling rocks

Author(s):
Serafeimidis, Konstantinos

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On the dissolution, precipitation and transport processes in sulphatic swelling rocks

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presented by

Konstantinos Serafeimidis

Dipl. Civil Engineer
Aristotle University of Thessaloniki
School of Engineering
Department of Civil Engineering

born on 8 June 1981
citizen of the Hellenic Republic

Accepted on the recommendation of

Prof. Dr. Georg Anagnostou, examiner
Prof. Dr. Jan Carmeliet, co-examiner
Prof. Dr. Peter Huggenberger, co-examiner

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Abstract

Swelling rocks experience a volume increase when interacting with water. In tunnelling, the swelling causes a heave of the tunnel floor, which may impair the serviceability of the structure. If attempts are made to prevent floor heave by means of an invert arch, the so-called swelling pressure develops, which may damage the tunnel lining. Swelling rocks are widely distributed in Switzerland in particular and have caused serious damage to many tunnels. Anhydritic claystones, i.e. rocks consisting of a clay matrix with finely distributed anhydrite, are an especially problematic rock type. The swelling of anhydritic claystones is mainly attributed to the chemical transformation of anhydrite into gypsum.

Considerable knowledge gaps persist with respect to important aspects of the behaviour observed macroscopically (e.g. the effect of counterpressure on heave) and to the microscopic mechanisms underlying swelling behaviour. The knowledge deficit is due to the complexity of the physicochemical processes involved (dissolution of anhydrite and growth of gypsum crystals, seepage flow, ionic diffusion), to the large heterogeneity of natural rock and to the duration of the swelling process, which is very long even under optimum laboratory conditions, making systematic experimental investigation very difficult. Almost all theoretical and experimental investigations reported in the literature focus on the mechanical behaviour of the material. In view of the underlying chemical processes and the potential effects of ionic transport, this is unsatisfactory.

The present dissertation aims to improve our understanding of the mechanisms behind the macroscopic behaviour of swelling in anhydritic claystones. More specifically, the following aspects are investigated: (i) the thermodynamic fundamentals of the anhydrite–water equilibrium and gypsum–water equilibrium; (ii) the kinetics of the chemical reactions involved, i.e. anhydrite dissolution and gypsum precipitation; and (iii) the significance of the transport processes (advection and diffusion). Besides serving as a basis for further research (e.g. through the formulation of comprehensive continuum-mechanical models), the dissertation investigates quantitatively a series of scientifically relevant and interesting questions such as: why is anhydrite rather than gypsum present at shallow depths? why is the swelling pressure in situ and in laboratory tests lower by one order of magnitude than the crystallisation pressure of gypsum? what is the effect on the rate of swelling when anhydrite is sealed by gypsum? is ionic transport really relevant or is it sufficient to consider anhydrite transformation as a relatively simple topochemical process? These topics are explained in the following in more detail.

The dissertation starts by setting out the thermodynamic fundamentals (prerequisites for any continuum-mechanics model explicitly incorporating chemical reactions) of the mechanisms underlying the swelling of anhydritic claystones. In contrast to earlier studies, the equilibrium state in the anhydrite–gypsum–water system is approached by starting from the underlying dissolution and
precipitation equations. A thermodynamic model is therefore developed first for estimating the individual anhydrite and gypsum solubilities. Although the model is based on well-known thermodynamic principles, it makes the innovative step of considering a range of influencing factors coherently. In addition to the factors commonly considered (temperature, pore water pressure, solid pressure, presence of foreign ions) the model also takes the effect of clay minerals into account, along with solid-liquid interfacial effects. The clay minerals decrease water activity, thus shifting the thermodynamic equilibrium in favour of gypsum. Surface energy effects are significant particularly for the extremely small pores of claystones and they shift the thermodynamic equilibrium in the same direction. The predictions of the model agree well with existing data from the literature.

In tunnels crossing the Gypsum Keuper formation, anhydrite, rather than gypsum, is found at relatively shallow depths of cover. This cannot be explained in simplified thermodynamic terms with reference to the temperature and pressure conditions of the rock at these depths. The fact that anhydrite occurs at shallow depths in Gypsum Keuper has been discussed in the literature, but without finding a quantitatively supported explanation. Understanding why anhydrite, rather than gypsum, occurs at shallow depths is not only interesting from a scientific point of view, but is also indispensable for the formulation of adequate initial conditions in continuum-mechanical models for the swelling of anhydritic claystones. The present dissertation investigates three possible explanatory hypotheses: (i) the rock pores are so small and the solid-liquid interface effects consequently so large that the chemical potential of gypsum is significantly increased; (ii) gypsum growth increases stresses locally to values which are much higher than the overburden pressure and which prevent further growth; and (iii) the pore water has such low activity, due to its interaction with the clay minerals, that anhydrite rather than gypsum represents the thermodynamically stable phase.

In order to investigate the first hypothesis, results are taken from porosimetry experiments (MIP) on samples of Gypsum Keuper. The results show that the rock also contains larger pores where it is thermodynamically possible for gypsum to grow. This means that the entire anhydrite would transform into gypsum as a result of diffusive ionic transport from the smaller pores to the larger pores. This hypothesis therefore has to be abandoned. The validity of the second hypothesis was checked by means of a simplified cavity expansion model and finite element analyses of rock models with randomly distributed pores. The numerical results show that there are always a smaller or larger number of pores around which the developing stresses are lower than the pressure thermodynamically required for anhydrite to be stable. As with the first hypothesis, this would lead to the entire transformation of anhydrite into gypsum, which means that the second hypothesis must also be abandoned. In contrast to these, the low water activity hypothesis is theoretically consistent and does not involve any doubtful assumptions. The third hypothesis therefore seems to be the most convincing one. Although there are theoretical grounds explaining why the activity of the pore water in sulphatic claystones must be low, activity measurements from natural samples are required before a definite statement can be made.
The present dissertation also investigates why the swelling pressures observed in oedometer tests or in situ are lower by one order of magnitude than the crystallisation pressure of gypsum. In this respect it is essential to draw a clear distinction between three scales: (i) the scale of a gypsum crystal that exerts pressure on the surrounding matrix when its growth is completely constrained (microscale); (ii) the scale of a rock specimen in an oedometer swelling pressure test under volume constraint (macroscale); and (iii) the scale of the rock mass in which swelling is at least partially prevented by a stiff tunnel lining (megascale). The crystallisation pressure of gypsum (microscale) is determined from the above-mentioned thermodynamic model as a function of water activity, pore size etc. Subsequently, the thermodynamic model is used in combination with a simplified cavity expansion model and numerical rock models (with stochastic pore distributions) in order to estimate the macroscopic swelling pressure under volume constraint. These relatively simple models can explain why the swelling pressures in laboratory tests are lower by one order of magnitude than the crystallisation pressure of gypsum. Finally, the upper bound of the swelling pressure in the megascale is derived by taking into account the bearing capacity of existing intact linings of tunnels crossing heavily swelling rocks. This upper bound is considerably lower than the crystallisation pressure of gypsum, thus providing additional evidence of the significance of scale.

The swelling of anhydritic claystones is a markedly time-dependent process which may take several decades to complete in nature and is thus important for the design of the final lining. The present dissertation attempts to improve our understanding of the factors governing the time-dependency of swelling by investigating the kinetics of the underlying anhydrite dissolution and gypsum precipitation reactions. (The reaction kinetics are also important for the third part of the thesis, which deals with the interplay between chemical reactions and transport processes in open systems.) A kinetic model is formulated and calibrated by analysing existing experimental results for the individual reactions. In the next step, the model is verified using comparable experimental results from a closed system where anhydrite dissolution and gypsum precipitation take place simultaneously. The model is then used to investigate the effects of a range of parameters (e.g. the initial composition of the rock, the form and size of the rock particles) on the hydration duration. The results indicate that the time period for the transformation of anhydrite into gypsum is governed by the rate of anhydrite dissolution, if the anhydrite is present in the common form of veins with a thickness of 1 mm or more and there are sufficient nuclei for gypsum precipitation. A further interesting finding is that the hydration time in this dissolution-controlled process does not depend on the initial volume fraction of anhydrite.

In nature, gypsum may frequently seal an anhydrite surface, preventing further hydration. The existing kinetic models for the transformation of anhydrite into gypsum ignore this effect. The present thesis extends the standard kinetic model in order to take sealing into account. The computational results show that – depending on the thickness or size of the anhydrite veins or particles – sealing may be decisive for the evolution of the swelling process and may offer a theoretical explanation for the in situ observations that thick anhydrite layers (in the range of some cm) hardly swell at all.
The third part of the dissertation deals with the significance of advective and diffusive ionic transport. Understanding whether and under what conditions ion transport may be ignored is important both for the design of laboratory tests and for the formulation of manageable continuum-mechanical models (i.e. models that are not unnecessarily overloaded with irrelevant coupled processes). In order to investigate these effects, a coupled model is formulated to take account of the chemical reactions, diffusion and advective ionic transport. Since a chemo-mechanical coupling is not essential for the questions under investigation, a system under volume constraint is considered. The following two questions are analysed quantitatively on the basis of this model: (i) what is the effect of diffusion on oedometer swelling tests? (ii) what is the effect of advective ionic transport in situ?

The motivation for the first question is that ionic diffusion out of the oedometer (towards the distilled water in the container) might influence the test results, because part of the anhydrite would be dissolved and transported away instead of being transformed to gypsum. The idea behind the second question is that advective transport in situ might reduce the calcium and sulphate content in one rock region and increase it in another region. The consequence would be the leaching of anhydrite in the first region and gypsum growth in the second region, even if the latter was initially free of anhydrite. It is therefore evident that transport processes (advection and diffusion) may play a significant role in the swelling process. Computational results show, however, that diffusion is irrelevant in most cases. This is also true with respect to advective transport for the low seepage flow velocities prevailing in the Gypsum Keuper formation. The leaching of anhydrite (and precipitation of gypsum in other locations) can take place only under a combination of high flow velocity (greater than $10^{-5}$ m/s, e.g. in fracture zones) and low ion production rate (thick anhydrite veins, low anhydrite content).
Zusammenfassung


Es existieren erhebliche Wissenslücken bezüglich wichtiger Aspekte des makroskopisch beobachteten Verhaltens (z.B. die Wirkung eines Gegendruckes auf die Hebung) sowie auch bezüglich der mikroskopischen Mechanismen, die dem Quellverhalten zugrunde liegen. Das mangelnde Wissen ist auf die Komplexität der involvierten physikalischen und chemischen Prozesse (Auflösung von Anhydrit und Wachstum von Gipskristallen, Sickerströmung, I onendiffusion) und die Dauer des Quellprozesses zurückzuführen. Letztere ist selbst bei kleinen Proben und unter den optimalen Bewässerungsbedingungen von Laborversuchen sehr lang, was in Kombination mit der Heterogenität der Naturgesteine systematische experimentelle Untersuchungen erschwert. Fast alle bestehenden theoretischen und experimentellen Untersuchungen beschränken sich auf das mechanische Materialverhalten, was angesichts der beteiligten chemischen Reaktionen und Transportprozesse unbefriedigend ist.


meisten Fällen irrelevant ist. Das trifft auch für den advektiven Ionentransport zu, wenn man die niedrige Geschwindigkeit der Sickerströmung in Gipskeuper berücksichtigt. Eine Auslaugung von Anhydrit (und Bildung von Gips an anderen Stellen) könnte nur im Fall einer hohen Strömungsgeschwindigkeit (höher als $10^{-5} \, \text{m/s}$, wie z.B. in Bruchzonen) bei gleichzeitig niedriger Ionenproduktionsrate (dickere Anhydritader, kleiner Anhydritgehalt).
# Table of contents

1 Introduction ........................................................................................................................................... 19
   1.1 Tunnelling in swelling rocks ........................................................................................................ 19
   1.2 State of research ........................................................................................................................ 19
       1.2.1 Overview ......................................................................................................................... 19
       1.2.2 Theoretical models ....................................................................................................... 20
       1.2.3 Experimental investigations ......................................................................................... 23
   1.3 Objectives and structure of the dissertation ........................................................................... 24

2 Thermodynamic Fundamentals ...................................................................................................... 27
   2.1 Introduction ................................................................................................................................ 27
   2.2 Basic thermodynamic relations .............................................................................................. 30
       2.2.1 Gibbs free energy ............................................................................................................ 30
       2.2.2 Chemical potential ........................................................................................................ 31
       2.2.3 Activity ......................................................................................................................... 33
       2.2.4 Crystal-liquid interfacial effect ..................................................................................... 39
   2.3 Equilibrium concentrations ...................................................................................................... 41
       2.3.1 Gypsum ......................................................................................................................... 41
       2.3.2 Anhydrite ...................................................................................................................... 42
   2.4 Gypsum-Anhydrite equilibrium relationships ........................................................................ 43
       2.4.1 General case ................................................................................................................... 43
       2.4.2 Simplified model for the conditions in the ground ......................................................... 44
   2.5 Comparison between predicted solubilities and published data ............................................ 44
   2.6 Comparison of predicted equilibrium conditions with published data ................................ 46
       2.6.1 Anhydrite – gypsum equilibrium in pure water ............................................................. 46
       2.6.2 Anhydrite – gypsum equilibrium in NaCl solutions ...................................................... 47
   2.7 General equilibrium diagram .................................................................................................. 48
   2.8 Conclusions ............................................................................................................................... 50

3 Anhydrite in Gypsum Keuper at Shallow Depths ......................................................................... 51
   3.1 Introduction .............................................................................................................................. 51
   3.2 The small pore hypothesis ....................................................................................................... 56
       3.2.1 Introduction ................................................................................................................... 56
       3.2.2 Porosity and pore size distribution of anhydritic claystones .......................................... 57
1 Introduction

1.1 Tunnelling in swelling rocks

Swelling rocks experience a volume increase when interacting with water. In tunnelling, the swelling causes a heave of the tunnel floor which may impair the serviceability of the structure (Fig 1.1a). If attempts are made to prevent floor heave by means of an invert arch, however, so-called swelling pressure develops, which may damage the tunnel lining (Fig 1.1b).

Figure 1.1. Problems in tunnels crossing swelling rock: (a) tunnel floor heave, (b) development of swelling pressure (Kovári et al. 1988)

Swelling rocks are widely distributed in Switzerland and South-West Germany and have caused serious damage, lengthy disruptions and very costly repairs in many tunnels in the past (Amstad and Kovári 2001). This is particularly true for the anhydritic rocks of the Gypsum Keuper formation, which consist of a clay matrix containing finely distributed anhydrite. The swelling of these rocks can be traced back to osmosis-driven water uptake by the clay minerals and to gypsum growth from sulphate solutions ($\text{Ca}^{2+} + \text{SO}_4^{2-} + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

1.2 State of research

1.2.1 Overview

Research on the problem of swelling was triggered off in the early 70's by difficulties encountered in two road tunnels, the Wagenburg Tunnel in Germany and the Belchen Tunnel in Switzerland. Since then a series of research projects have been carried out which differ in the questions addressed and therefore also in the methods employed, the scale of the investigation and the scientific disciplines involved. At the microscale, mineralogists have carried out theoretical and experimental studies into
the interactions between clay particles, anhydrite and gypsum crystals (cf., e.g. Madsen and Nüesch 1991, Madsen and Vonmoos 1989). The scale of a geological formation (Dm to km) defines the other end of the spectrum. Here, ongoing hydrogeological research addresses the question of possible links between regional groundwater circulation systems and the spatial distribution of swelling phenomena observed in tunnelling. More specifically, Huggenberger (2008a, b) and Butscher et al. (2011a) investigated whether the observed variability of swelling intensity (which is often very large even within lithologically homogeneous geological units in one and the same tunnel) is due to differing water circulation conditions. Butscher et al. (2011b) employed numerical simulations to examine the effect of tunnel excavation on groundwater flow patterns that depend on the hydrogeological setting, suggesting tunnel induced processes which trigger the transformation of anhydrite into gypsum and thus the swelling of the rock.

In addition to investigations into processes at the extreme ends of the scale, considerable engineering research has been carried out into phenomena at the scale of the specimens used for geotechnical laboratory testing (‘macroscale’ i.e. some centimetre to decimetre) and at the scale of underground openings (‘megascale’ i.e. some meter to decametre). The following summarises existing theoretical models (Section 1.2.2) and experimental investigations (Section 1.2.3), while bearing in mind that interesting research has also been done on concerning the microstructure and mineralogical changes in swelling rocks (cf., e.g. Madsen 1976, Madsen and Nüesch 1991, Ko et al. 1997).

1.2.2 Theoretical models

Since 1972 many models have been proposed to describe the swelling behaviour of rock in tunnelling and to provide a rational basis for tunnel design. The process began with the formulation of relatively simple computational models which addressed only the mechanical response of the materials (purely mechanical models), and continued with the first attempts to simulate the interaction between mechanical behaviour, seepage flow and chemical reactions.

Simple mechanical models

Based on oedometer laboratory tests on clay rock, Grob (1972) proposed a semi-logarithmic stress-swelling strain relationship. In his 1-D model he also assumed linearly elastic rock behaviour immediately after excavation. The swelling heave in the centre of the tunnel floor is calculated from the integration of the vertical strains, which are determined from the results of oedometer tests and from the vertical stress distribution predicted by elasticity theory. Einstein et al. (1972) extended this model into three dimensions by assuming isotropic material behaviour with a constant ratio of principal stresses that is also based upon elasticity theory. The swelling strains in the principal stress directions are determined from the respective stresses and the semi-logarithmic relationship mentioned above. Wittke and Rissler (1976) modified the isotropic model of Einstein et al. (1972) by assuming that the first invariant of volumetric swelling strain depends on the first stress invariant according to
Grob’s law and that the distribution of the strains is proportional to the unloading caused by tunnel excavation. Gysel (1977, 1987) investigated analytically the case of circular tunnels in swelling rock under the assumption of a homogeneous, non-hydrostatic initial stress state and taking account of the constitutive assumptions of Einstein et al. (1972) and Wittke and Rissler (1976). Based on laboratory swelling tests, Fröhlich (1986) emphasized that the swelling behaviour of claystones is markedly anisotropic. He proposed a two-dimensional, transversally anisotropic material model (with swelling only perpendicular to the bedding).

Models addressing behaviour under triaxial stress conditions

Bellwald and Einstein (1987) proposed an isotropic, elasto-plastic, strain-softening model in order to investigate the influence of the stress path on the mechanical behaviour of shales under drained or undrained conditions. Swelling is treated as an inverse consolidation process, i.e. it occurs when the effective stress decreases (which may also happen through the dissipation of negative excess pore pressures). This model was extended by Aristorenas (1992) by incorporating elastic anisotropy and creep behaviour together with an associated flow rule. The material constants were also determined by triaxial drained and undrained tests on shale specimens. Barla (1999) enhanced the constitutive model of Aristorenas (1992) by a swelling-specific term (Barla et al. 2003, Barla 2008), which assumes a sigmoidal relationship between the excess pore pressure and the volumetric strain. The material constants were determined empirically by curve-fitting using the results of triaxial tests and of a swelling test.

Models addressing the time-dependency of swelling

Kiehl (1990) proposed an elasto-viscoplastic, isotropic model with the stress - swelling strain relationship developed by Grob (1972). The verification of the model was based on the test results of Pregl et al. (1980) on remoulded clay and on leached Gypsum Keuper (Wittke 1978). The rheological part of the model is described through Newton viscosity. Furthermore, it is assumed that the time-development of the swelling process takes place according to an exponential decay rate law as proposed by Overbeck (1981). In order to model the in situ swelling tests of the Freudenstein railway tunnel (Stuttgart, Germany), the model was extended by Wittke-Gattermann (1998) to include a specific watering stage. The time-water absorption relationship was calculated using Darcy’s law without a coupling to the mechanical response of the material. Wittke (2003) used diffusion theory for the water absorption of the solid, comparing the process with the one taking place in highly-compressed bentonite. Based on the saturation degree of the system, a dimensionless water content was introduced, which controls the activation of the swelling process.

Coupled models

Anagnostou (1991) developed a hydraulic-mechanical coupled model to investigate the effect of seepage flow on the deformation pattern around tunnels in swelling rocks. The material model is elasto-plastic, obeys Terzaghi’s principle of effective stress, and takes account of anisotropic swelling
based on Grob’s law. Seepage flow is simulated using Darcy’s law. The numerical results indicate the major importance of rock strength (the weaker the rock, the larger the floor heaves) and of the hydraulic boundary conditions (more specifically, the absence of significant swelling deformations above the tunnel floor can be explained as a consequence of the non-uniformity of the hydraulic head field).

Alonso and Olivella (2008) proposed a chemo-mechanical micro-model for crystal growth in a single rock fracture. The fracture is treated as being embedded as a discontinuity in an elastic continuum element. It is exclusively responsible for water transport in the system, i.e. the permeability of the system depends only on the aperture of the fracture according to Poisseuille’s model. A basic assumption of this model is that the water in the fracture is always saturated in sulphates. Evaporation is considered to be the only activator of the swelling process, i.e. oversaturation, precipitation and subsequent crystal growth will be caused only by changes in relative humidity. The model was developed in order to prove the plausibility of the assumption that evaporation was an activator of the swelling process in the case of the Lilla Tunnel (Spain). Since other processes such as dissolution of anhydrite and solute transport are not considered in this model, its applicability is limited to the specific problem studied.

Oldecop and Alonso (2012) investigated the degradation and swelling of clayey rocks containing calcium sulphate. More specifically, in order to reproduce the observed swelling phenomena in the case of the Lilla Tunnel in Spain, they developed a numerical model which addresses several mechanisms that might be crucial to the swelling process: evaporation, water seepage flow, stress changes, anhydrite dissolution and gypsum precipitation. In their model, the voids are assumed to be permanently saturated. A second order law is adopted for the dissolution of anhydrite and the precipitation of gypsum, while a first order kinetic equation is followed for the dissolution of gypsum. The model assumes that the mechanical stresses exerted on the anhydrite crystals vanish with time, as their size reduces during dissolution, thus becoming idle in the rock matrix. The anhydrite solubility is therefore considered to be constant during the swelling process and equal to the solubility corresponding to atmospheric pressure. On the other hand, as the growing gypsum crystals are under a considerable load, their solubility depends on the stress exerted on them. In order to calculate the swelling strains induced by the growth of the gypsum crystals, a coefficient which measures the bulking effect in the rock mass is introduced. The increase in volume consists of two parts: the volume increase due to gypsum growth and the volume increase related to the voids. Based on the model and contrary to Alonso and Olivella (2008), Oldecop and Alonso (2012) concluded that evaporation of the ground water is rather insignificant and the most likely mechanism for the swelling process is the dissolution of anhydrite and the precipitation of gypsum.
1.2.3 Experimental investigations

The goal of the first laboratory tests on samples of swelling rock was to determine their characteristics (magnitude of swelling strain or pressure, relationship between swelling stress and strain) under simple experimental setups (oedometer apparatuses). Huder and Amberg (1970) used the conventional oedometer apparatus from soil mechanics for running swelling tests, while special oedometer apparatuses were later developed specifically for rock specimens (ISRM 1989, 1999). Pimentel (1996, 2006) proposed a modified oedometer that enables the stress-strain relationship to be determined under triaxial conditions and he later improved this technique in order to be able to determine both the maximum swelling stress and the stress-strain relationship with just one test.

The effects of pore water pressure, radial stress and changes in strength and stiffness have been investigated by means of triaxial tests. Aristo renas (1992) performed such tests under drained as well as undrained conditions with pure shear stress paths in compression and extension on oriented anisotropic specimens in a specially designed apparatus. Pimentel (1996) has demonstrated through triaxial tests that swelling claystones experience a considerable loss of strength and stiffness when absorbing water, while Barla (1999) investigated the excess pore pressures developing under triaxial stress conditions.

It should be noted that most of the reported laboratory test results concern purely argillaceous rocks. Tests on sulphatic rocks have been carried out mostly within the framework of design activities for tunnelling projects and lack the quality needed for research purposes. As the duration of the swelling process is extremely long even under the optimum watering conditions prevailing in the laboratory, most of the tests were terminated before reaching a steady state. Reliable experimental results for sulphatic rocks are therefore very scarce. Systematic long-term observations are available from only one test series which was carried out on samples from the Freudenstein railway Tunnel (Pimentel 2006). It is interesting to note that the swelling process has not reached completion yet, although it is now more than 20 years since the tests were started. The test results indicate that swelling strain may be largely independent of pressure - a very important finding for the conceptual design of tunnel supports. Information on this aspect might probably be gained from a recently-launched research project (IGT 2006). Finally, Alonso et al. (2013) who investigated swelling phenomena in Lilla Tunnel (Spain), presented data of geotechnical investigations and monitoring of the tunnel, providing precious information concerning the swelling pressures exerted on the lining. In addition, they displayed results of large-scale wetting tests which were executed in three enlarged circular test sections constructed inside the tunnel. Alonso et al. (2013) came to the conclusion that the swelling process is due to the precipitation of gypsum crystals in the discontinuities. The growth of the crystals causes an opening of the rock which is followed by a mechanical degradation of the rock and an increase in the quantity of water in the claystone matrix.
1.3 Objectives and structure of the dissertation

Contrary to the swelling of purely argillaceous rocks, which is sufficiently well understood for all practical engineering purposes and can be satisfactorily mapped using existing mechanical or hydraulic-mechanical models, our knowledge concerning the swelling of anhydritic claystones is limited. The reasons for this are the duration of the swelling process (which takes several years, even under laboratory conditions, and, in combination with the large heterogeneity of natural rock, makes systematic experimental investigations very difficult) and the high complexity and diversity of the physico-chemical processes involved: seepage flow interacting with deformation processes and stress relief, ionic diffusion, dissolution of anhydrite and growth of gypsum crystals, evaporation, interactions of sulphate with the clay phase (in the absence of cracks and fissures the clay matrix governs water transport, while the clay minerals may affect the equilibrium of the anhydrite–gypsum–water system).

The present dissertation aims to improve our understanding of the fundamental mechanisms behind the macroscopic behaviour of the swelling of anhydritic claystones. Besides serving as a basis for further research (e.g. regarding the formulation of comprehensive continuum-mechanical models), the dissertation shall investigate quantitatively a series of scientifically relevant and interesting questions such as: why is anhydrite rather than gypsum present at shallow depths? why is the swelling pressure \textit{in situ} and in laboratory tests lower by one order of magnitude than the crystallisation pressure of gypsum? what is the effect on the rate of swelling when anhydrite is sealed by the formation of gypsum? is ionic transport really relevant or is it sufficient to consider anhydrite transformation as a relatively simple topochemical process?

The dissertation is structured in three major parts which deal with: (i) the thermodynamics of anhydrite dissolution and gypsum precipitation and their application to specific questions (Chapters 2 to 4); (ii) the kinetics of these chemical reactions and the time-development of the anhydrite transformation (Chapter 5); and (iii) the interplay of these reactions with the diffusive and advective ion transport (Chapter 6).

This dissertation starts by setting out the thermodynamic fundamentals of the mechanisms underlying the swelling of anhydritic claystones (Chapter 2). In contrast to earlier studies, the equilibrium state in the anhydrite–gypsum–water system is approached by starting from the underlying dissolution and precipitation equations. A thermodynamic model for estimating the individual anhydrite and gypsum solubilities is therefore formulated first. The resulting equations are thus more general than equations describing the anhydrite–gypsum equilibrium and can be incorporated into continuum-mechanical models that explicitly consider the two reactions together with ionic transport. Furthermore, apart from the factors commonly considered (pore water and solid pressure, temperature and the presence of foreign ions), the model considers two additional factors which have not been taken into account in the
past by any of the existing models and are important specifically for fine-porous argillaceous rocks: the effect of clay minerals and of liquid–solid interfacial energy on the thermodynamics of the anhydrite–gypsum–water system.

The results of Chapter 2 are applied to investigate two questions: the occurrence of anhydrite (rather than gypsum) at the relatively shallow depths of Gypsum Keuper tunnels (Chapter 3) and the relationship between the crystallisation pressure of gypsum and the swelling pressure observed macroscopically (Chapter 4). Understanding why anhydrite, rather than gypsum, occurs at shallow depths is not only interesting from a scientific point of view, but is also indispensable when it comes to the formulation of adequate initial conditions within the framework of continuum-mechanical models for the swelling of anhydritic claystones. The occurrence of anhydrite at shallow depths of Gypsum Keuper has been discussed in the past (see literature review in Chapter 3), but without providing a quantitatively supported explanation. Chapter 3 investigates quantitatively three possible explanatory hypotheses which are associated with the pore size distribution in sulphatic claystones, the crystallisation pressure in the pores and the thermodynamic state of the pore water in the presence of clay minerals, concluding that the latter is the most probable cause for the occurrence of anhydrite.

The thermodynamic model in Chapter 2 leads to crystallisation pressures in the order of several tens of MPa, which is significantly higher than the swelling pressures observed in oedometer tests or in situ. Chapter 4 explains that this due to the different scales considered (gypsum crystal–rock specimen–rock mass), analysing numerically the interaction between the gypsum crystals growing in the pores and the surrounding rock matrix and explaining why the swelling pressure is lower by one order of magnitude than the crystallisation pressure.

The swelling of anhydritic claystones is a markedly time-dependent process which may take several decades to complete in nature and is thus important for the design of the final lining. The second part of the dissertation aims to improve our understanding of the factors governing the time-dependency of swelling by investigating the kinetics of the underlying anhydrite dissolution and gypsum precipitation reactions. (The reaction kinetics are also important for the third part of the thesis, which deals with the interplay between chemical reactions and transport processes in open systems.) In nature, anhydrite surfaces are frequently seen to be sealed by gypsum, thus preventing further hydration. Sealing, however, is ignored by the existing kinetic models for the transformation of anhydrite into gypsum. Chapter 5 formulates a kinetic model for the individual reactions that takes the effect of sealing into account, estimating the kinetic constants by back-analysing existing experimental data and validating the model by means of comparisons with experimental results for a closed system where anhydrite dissolution and gypsum precipitation take place simultaneously. This model is used to study the effect on hydration duration of the initial rock composition and the form and size of the rock particles. Parametric studies show that it is the rate of anhydrite dissolution (rather than gypsum precipitation) that governs the time-development of the transformation, providing a theoretical explanation for the in situ observation that thick anhydrite layers (in the range of some cm) hardly swell at all.
The third part of the dissertation (Chapter 6) deals with the significance of advective and diffusive ionic transport. Understanding whether and under what conditions ion transport can be ignored is important both for the design of laboratory tests, and for the formulation of manageable continuum-mechanical models (\textit{i.e.} models that are not unnecessarily overloaded with irrelevant coupled processes). In order to investigate these effects, a coupled model is formulated addressing anhydrite dissolution, gypsum precipitation, diffusion and advective ionic transport. Based on this model the following two questions are quantitatively analysed: (i) what is the effect of diffusion in oedometer swelling tests? (ii) what is the effect of advective ionic transport \textit{in situ}? The motivation behind the first question is that ionic diffusion out of the oedometer (towards the distilled water of the container) might influence the test results, because part of the anhydrite would be dissolved and transported away instead of being transformed to gypsum. The idea behind the second question is that advective transport \textit{in situ} might reduce the calcium and sulphate content in one rock region and increase it in another region. The consequence would be leaching of anhydrite in the first region and gypsum growth in the second region, even if the latter was initially free of anhydrite. It is therefore evident that the transport processes (advection and diffusion) might play a significant role on the swelling process. The computational results of Chapter 6 show, however, that diffusive and advective ionic transport is rather irrelevant in most cases.
2 Thermodynamic Fundamentals

2.1 Introduction

Anhydritic claystones consist of a clay matrix with finely distributed particles, veins and layers of anhydrite (CaSO₄). The swelling of anhydritic claystones is attributed mainly to the chemical transformation of anhydrite to gypsum (CaSO₄·H₂O), which leads to an increase in the volume of sulphate by 61% (the molar volumes of anhydrite and gypsum are equal to 46 and 74 cm³, respectively). This transformation takes place via the solution phase, i.e. via anhydrite dissolution and gypsum precipitation. The chemical dissolution and precipitation reactions of gypsum and anhydrite as well as the masses involved are

\[
\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad (2.1)
\]

\[
\begin{align*}
0.136 \text{ kg/mol} & \quad 0.036 \text{ kg/mol} & \quad 0.172 \text{ kg/mol}
\end{align*}
\]

and

\[
\text{CaSO}_4 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} \quad (2.2)
\]

\[
\begin{align*}
0.136 \text{ kg/mol} & \quad 0.136 \text{ kg/mol}
\end{align*}
\]

respectively.

In a system where different minerals co-exist, the mineral with the lower equilibrium concentration (or solubility) represents the stable phase. Thus, the transformation takes place as a result of the anhydrite equilibrium concentration being higher than that of gypsum under the conditions normally prevailing when tunnelling through the Gypsum Keuper formation (rather low temperatures and pressures, cf. Section 3.1). More specifically, anhydrite in contact with water starts to dissolve into calcium and sulphate ions until the ionic concentration reaches its equilibrium concentration. Before this happens, however, the concentration reaches the solubility of gypsum with the consequence that gypsum starts to precipitate, thus consuming ions and maintaining a state of undersaturation with respect to anhydrite until all of the anhydrite is dissolved.

Van’t Hoff et al. (1903) were the first ones to investigate the conditions under which anhydrite and gypsum occur in salt deposits. Since then, the system CaSO₄ – H₂O (with or without other salts) has been examined by several authors both experimentally and theoretically based on the thermodynamic concept of Gibbs free energy. An extended review of the literature on the CaSO₄ – H₂O system can be found in Freyer and Voigt (2003). Nonetheless, most of the studies are outdated and many of them fail

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1 This Chapter is based on Serafeimidis and Anagnostou (2014a)
to provide all the necessary information. More specifically, the effect of crystal size, which may be particularly important in argillaceous rocks with very small pores, has never been investigated. Additionally, existing research results often appear to be controversial. For instance, the gypsum-anhydrite transition temperature is still quite uncertain, with extreme values of 38 and 63.5 °C proposed by Toriumi and Hara (1938) and Van’t Hoff et al. (1903), respectively. The difficulty of defining the transition temperature is attributed to the fact that at temperatures below 70 °C, anhydrite does not crystallise in water at rates that can be measured, even when anhydrite seed crystals are present (Freyer and Voigt 2003). Freyer and Voigt (2003) also calculated the transition temperature as a function of water activity, based on thermodynamic factors. The water activity reduces with the addition of non-common ions (cf. Section 2.2.3.2). In the case of a saturated NaCl solution, which corresponds to a water activity of 0.75, they determined different transition temperatures, depending on which thermodynamic data found in the literature was used. In the following, only some of the most relevant works are mentioned.

The following paragraphs summarise the most relevant work in this area. Posnjak (1938), Bock (1961), Zen (1965), Hardie (1967) and Innorta et al. (1980) investigated the role of temperature and salts on gypsum and anhydrite solubilities at atmospheric pressure experimentally. The salt which has been focused on in most studies is NaCl, as it is the most prominent foreign pore water constituent in evaporite deposits (MacDonald, 1953). Blount and Dickson (1973) performed experiments in order to estimate anhydrite and gypsum solubilities in aqueous and NaCl solutions at different temperatures and pressures up to 1000 bars. Based on their own experimental results and on experimental data found in the literature, they proposed empirical equations for the determination of anhydrite and gypsum solubilities. Nevertheless, according to Blount and Dickson (1973), the empirical equation proposed for the anhydrite equilibrium concentration does not provide reliable results at temperatures below 70 °C, as the results had to be extrapolated in this region.

Marsal (1952) studied the influence of water pressure on the CaSO4 – H2O system thermodynamically, treating the hydration of anhydrite into gypsum as a topochemical reaction. He additionally defined the temperature and pressure conditions under which anhydrite or gypsum is the stable phase. MacDonald (1953) also investigated the role of temperature, pressure and dissolved NaCl on the transition point based on the thermodynamics of a topochemical reaction. He treated the different pressures acting on the solid and liquid phases (lithostatic and hydrostatic pressure, respectively) in an innovative way and investigated which mineral is stable in pure water and NaCl solutions at different depths below the surface. Rolnick (1954) confirmed experimentally the theoretical predictions of MacDonald (1953) and extended their range towards extremely high pressures (up to 2000 bar which corresponds to an overburden of approximately 8.5 km). Similar investigations have been performed on NaCl-saturated solutions by Hanshaw and Bredehoef (1968). Raju and Atkinson (1990) developed a thermodynamic model for the separate prediction of anhydrite and gypsum solubilities in water and aqueous NaCl solutions at atmospheric pressure and up to a temperature of 250 °C and 110 °C for
anhydrite and gypsum, respectively. Kontrec et al. (2002) performed experiments studying the kinetics of anhydrite dissolution and gypsum dissolution and precipitation at temperatures between 10 and 40 °C. In addition, they proposed a mathematical model for the evolution of the transformation processes. Further details on the work of Kontrec et al. (2002) are presented in Chapter 5.

Despite the above-mentioned controversies found in the literature on the CaSO₄ – H₂O system (cf. also Freyer and Voigt 2003), the following qualitative conclusions are generally accepted: (i) an increase in pressure increases the equilibrium concentrations of anhydrite and gypsum to different extents; (ii) the presence of salts such as NaCl in the solution both increases the equilibrium concentrations and lowers the temperature at which anhydrite and gypsum coexist; (iii), the anhydrite equilibrium concentration decreases with increasing temperature, whilst the gypsum equilibrium concentration changes only slightly with temperature.

The existing theoretical models for the anhydrite-gypsum equilibrium take into account the temperature, the solid and liquid pressures and the effect of foreign ions in the solution. In the case of small pores, however, the crystal size is an additional important factor (Steiger 2005b, Scherer 1999, Flatt and Scherer 2008). More specifically, according to the Ostwald–Freundlich equation (also known as the Gibbs-Thomson and Kelvin equation), the equilibrium concentration increases with decreasing crystal size (Freundlich 1922). Another effect which should be considered in the case of claystones with finely distributed anhydrite is that clay minerals lower the chemical potential of the water, thus increasing the solubility of gypsum and shifting the thermodynamic equilibrium in favour of anhydrite. The present work incorporates these effects into the thermodynamic equations consistently and discusses the effects of clay minerals on water activity (Sections 2.2.3.3 and 2.2.4).

Almost all theoretical studies deal with the equilibrium between anhydrite and gypsum without investigating the anhydrite-water and the gypsum-water equilibria, i.e. without presenting theoretical estimates of the anhydrite and gypsum solubilities. An exception to this is the work of Raju and Atkinson (1990), which refers, however, only to sulphate dissolution/precipitation under atmospheric conditions. The intermediate stage can in fact be disregarded when investigating the anhydrite-gypsum equilibrium, i.e. it is sufficient to consider one single reaction for the anhydrite–gypsum transformation (CaSO₄ + 2H₂O ↔ CaSO₄·2H₂O), because both phases exhibit the same solubility at equilibrium and are in equilibrium with the pore solution. However, in contrast to existing studies, we approach the thermodynamic equilibrium problem starting from the two individual dissolution/precipitation reactions (Eqs. 2.1 and 2.2) and a determination of the equilibrium concentrations of anhydrite and gypsum (Section 2.3).

An analysis only in terms of thermodynamic stability is generally insufficient for investigating the rock-water interaction comprehensively, as the chemical dissolution and precipitation reactions occur simultaneously with diffusive and advective transport (seepage flow through the rock). Nonetheless, consideration of the equilibrium situations constitutes a starting point for further investigations into
systems which are not in equilibrium (Paterson 1973). The results are thus valuable also as a component of comprehensive claystone-sulphate-water interaction models which address the chemical dissolution and precipitation reactions simultaneously (cf. Chapter 6).

The present Chapter is organised as follows: Starting with an overview of the fundamental thermodynamic principles (Section 2.2), we derive mathematical relationships for the gypsum and anhydrite equilibrium concentrations (Section 2.3) and formulate the anhydrite–gypsum equilibrium condition in terms of temperature, pore water pressure, the pressure in the solid phase and crystal size (Section 2.4). Sections 2.5 and 2.6 compare, respectively, the predicted equilibrium concentrations and equilibrium conditions with existing experimental data and third party computations for pure water and NaCl solutions. Finally, Section 2.7 presents and discusses an equilibrium diagram covering a wide range of the parameters that govern the gypsum–anhydrite equilibrium.

In all derivations the geomechanics sign convention is adopted whereby pressures (compressive stresses) are positive. Furthermore, although the equations are given in a general form, attention will be paid to the pressure, temperature and salinity conditions that prevail when tunnelling through the Gypsum Keuper formation.

2.2 Basic thermodynamic relations

2.2.1 Gibbs free energy

We start with the fundamental thermodynamic relationships governing the anhydrite–gypsum–water system. For further details on thermodynamics within a geological context, the reader is referred to textbooks, e.g. Anderson (1996) and White (2005). According to the first law of thermodynamics, assuming for simplicity that the product of pressure and volume change is the only mechanical work done by the system, the internal energy differential can be written as

\[ dU = dQ - \sum_i P_i n_i \, dV_i + \sum_i \mu_i \, dn_i, \]

where \( dQ \) denotes the energy supplied to the system as heat. The subscript \( i \) denotes the \( i \).th constituents of the system. In the present case \( i = Ca^{2+}, SO_4^{2-}, H_2O, CaSO_4 \) and \( CaSO_4·2H_2O \). (For the sake of brevity, the subscripts A and G and W will be used in place of the chemical formulae of anhydrite, gypsum and water, respectively.) The second term on the right side of Eq. (2.3) denotes the mechanical work performed when \( n_i \) moles of the system-constituent \( i \) experience the molar volume change \( dV_i \) while being subject to the pressure \( P_i \). As in previous research works on the \( CaSO_4 – H_2O \) system (see references in Section 2.1), we limit ourselves to hydrostatic thermodynamics and this is why the mechanical work is given here only in terms of volume changes and pressures (mean stresses). The pressure \( P_i \) in Eq. (2.3) is equal to \( p_w + p_{air} \) for the water and the
ions, and to \( p_S + P_{\text{am}} \) for the solid phase, where \( p_W \), \( p_S \) and \( P_{\text{am}} \) denote the pore water pressure, the macroscopic solid pressure (Dahlen 1992) and the atmospheric pressure, respectively. (As usual in geomechanics, the stresses are taken in excess of atmospheric pressure, i.e. a stress of zero means that the medium is actually under atmospheric pressure.) The macroscopic solid pressure \( p_S \) represents the average pressure experienced by the grains (Dewers and Ortoleva 1989) and will be referred hereafter simply as “solid pressure”.

The last term of Eq. (2.3) represents the change in the internal energy due to chemical reactions, i.e. due to changes in the molar quantities \( n_i \). The symbol \( \mu_i \) denotes the molar chemical potential of constituent \( i \) and depends in general on the temperature \( T \) and on the pressure \( P_i \) (see Section 2.2.2).

According to the second law of thermodynamics,

\[
T \sum_i n_i dS_i \geq dQ ,
\]

(2.4)

where the equality sign applies to reversible processes while \( T \) and \( S_i \) denote the temperature and the molar entropy of constituent \( i \), respectively.

The Gibbs free energy

\[
G = U + \sum_i P_i n_i V_i - T \sum_i n_i S_i
\]

(2.5)

or, after integrating Eq. (2.3) at constant values of the intensive properties,

\[
G = \sum_i n_i \mu_i .
\]

(2.6)

For a reversible process we obtain from Eqs. (2.3), (2.4) and (2.5) the Gibbs free energy increment:

\[
dG = \sum_i \mu_i dn_i + \sum_i n_i V_i dP_i - \sum_i n_i S_i dT .
\]

(2.7)

According to this equation, the chemical potential \( \mu_i \) of the substance \( i \) is equal to the change of the Gibbs free energy \( G \) due to the formation of 1 mol of this substance under constant temperature and pressure. The direction of a chemical reaction depends on the difference in the Gibbs free energy \( G \) between the products and the reactants: Any transformation in a system takes place in order to minimize \( G \), i.e. a chemical reaction will occur spontaneously from a state of high Gibbs free energy \( G \) to a state of low \( G \). In a system at equilibrium, the Gibbs free energies \( G \) of the products and of the reactants are equal.

### 2.2.2 Chemical potential

The molar chemical potential \( \mu_i \) at arbitrary temperature \( T \) and pressure \( P_i \) can be expressed as a function of \( T, P_i \) and the chemical potential \( \mu_i \bigg|_{T_0, P_{\text{am}}} \) at standard temperature \( T_0 \) (298.15 K or...
25 °C) and atmospheric pressure $P_{\text{atm}}$. In order to do that, we consider a system consisting of one substance only. In the absence of chemical reactions, we obtain from Eqs. (2.6) and (2.7)

$$d \mu_i = dG = V_i dP_i - S_i dT.$$  \hspace{1cm} (2.8)

For a constant molar volume $V_i$ and entropy $S_i$, which is a reasonable simplification for the constituents of the gypsum–anhydrite–water system (without gases), the integration of Eq. (2.8) leads to

$$\mu_i = \left. \mu_i \right|_{T_0, P_{\text{atm}}} + V_i \left( P_i - P_{\text{atm}} \right) - S_i \left( T - T_0 \right).$$ \hspace{1cm} (2.9)

Under certain conditions, which will be detailed below, the chemical potential $\mu_i \bigg|_{T_0, P_{\text{atm}}}$ of the species $i$ at atmospheric pressure and standard temperature is identical to its standard Gibbs energy of formation, $\Delta_f G_i^0$, which can be determined from thermodynamic tables (see Table 2.1 for the constituents of the gypsum–anhydrite–water system). The conditions mentioned are: (i) the water and the dissolved ions are in their standard states; (ii) liquid-crystal interfacial effects can be neglected for the solids. In general, the chemical potential can be written as

$$\mu_i \bigg|_{T_0, P_{\text{atm}}} = \Delta_f G_i^0 + RT \ln a_i + \gamma_i \frac{dA_i}{dn_i},$$ \hspace{1cm} (2.10)

where $R$, $a_i$, $\gamma_i$, and $A_i$ denote the universal gas constant ($R = 8.31$ J/K/mol), the activity of the species $i$, the surface free energy of the crystal–water interface and the total interfacial area of the species $i$, respectively. The second and the third term on the right-hand side account for deviations from conditions (i) and (ii), respectively, and will be explained in detail in Sections 2.2.4 and 2.2.5.

Inserting $\mu_i \bigg|_{T_0, P_{\text{atm}}}$ from Eq. (2.10) into Eq. (2.9) leads to the following general expression for the chemical potential of species $i$:

$$\mu_i = \Delta_f G_i^0 + RT \ln a_i + \gamma_i \frac{dA_i}{dn_i} + V_i \left( P_i - P_{\text{atm}} \right) - S_i \left( T - T_0 \right),$$ \hspace{1cm} (2.11)

where the second term on the right-hand side is non-zero only for the water and the ions, while the third term is non-zero only for the solid species.
Table 2.1. Parameter values at standard state (after Anderson 1996, with the exception of $V^0_{SO_4^-}$ and $\gamma_G$ which are after Millero (1972) and Section 2.2.4, respectively)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_r,AG_0^0$</td>
<td>23680 J/mol</td>
</tr>
<tr>
<td>$\Delta_r,GG_0^0$</td>
<td>24930 J/mol</td>
</tr>
<tr>
<td>$\Delta_r,AS_0^0$</td>
<td>-139.7 J/K/mol</td>
</tr>
<tr>
<td>$\Delta_r,GAV_0^0$</td>
<td>-50.36 cm$^3$/mol</td>
</tr>
<tr>
<td>$\Delta_r,GAV_{Ca^+}^0$</td>
<td>-7.64 cm$^3$/mol</td>
</tr>
<tr>
<td>$\Delta_r,AG_{0}^{Ca^{2+}}$</td>
<td>-1250 J/mol</td>
</tr>
<tr>
<td>$\Delta_r,GG_{0}^{Ca^{2+}}$</td>
<td>-553.58 kJ/mol</td>
</tr>
<tr>
<td>$\Delta_r,GAV_{SO_4^{2-}}$</td>
<td>-7.64 cm$^3$/mol</td>
</tr>
<tr>
<td>$\Delta_r,AG_{0}^{SO_4^{2-}}$</td>
<td>-1321.79 kJ/mol</td>
</tr>
<tr>
<td>$\Delta_r,GG_{0}^{SO_4^{2-}}$</td>
<td>-1797.28 kJ/mol</td>
</tr>
<tr>
<td>$\Delta_r,GAV_{W}^0$</td>
<td>-237.12 kJ/mol</td>
</tr>
<tr>
<td>$\Delta_r,AG_{0}^{W}$</td>
<td>-553.58 kJ/mol</td>
</tr>
<tr>
<td>$\Delta_r,GG_{0}^{W}$</td>
<td>-744.53 kJ/mol</td>
</tr>
</tbody>
</table>

### Activity

#### 2.2.3.1 General

At standard state, the activity $a_i$ is by definition equal to 1 and the second term in Eq. (2.11) disappears. In addition to the conditions of atmospheric pressure and 25 °C temperature, standard state means with respect to a specific ion that its concentration amounts to $c_0 = 1 \text{ mol/l}$ and that there are no other ions in the solution. Water is in its standard state only if it is pure (or almost pure, i.e. a very dilute solution). High ionic concentrations or the presence of clay minerals decrease the water and ion activities and thus also their chemical potential. Details about the activities $a_i$ of water and ions are given in Sections 2.2.3.2-2.2.3.3 and 2.2.3.4, respectively. The standard state of the solid species is characterized solely by the conditions of atmospheric pressure and a temperature of 25 °C and, consequently, the activity of solids is equal to 1. Therefore, the second term on the right side of Eq. (2.11) disappears for the anhydrite and gypsum crystals.
2.2.3.2 Activity of water in the presence of ions

As mentioned above, the activity of pure water is equal to one. In the presence of ions, the water activity

\[ a_W = x_W \lambda_W, \]  

where \( x_W \) is the mole fraction of the water, defined as the amount of a water \( n_W \) divided by the total amount of all the system constituents, i.e.

\[ x_W = \frac{n_W}{\sum n_i}, \]  

and \( \lambda_W \) is the water activity coefficient. The latter accounts for the interactions among the ions in the solution and is in general \( \leq 1 \). For very dilute solutions, both \( \lambda_W \) and \( x_W \), and thus also \( a_W \), equal unity. The water activity coefficient \( \lambda_W \) can be determined by using the Pitzer (1973) or the Davies (1962) equations, for example. Due to the limitations of the theoretical models, experimental methods are often applied which are frequently based on the following relationship between the activity and the water’s vapour pressure \( p_V \) over the solution (Blandamer et al. 2005):

\[ a_W = \frac{p_V}{p_{V,0}}, \]  

where \( p_{V,0} \) is the vapour pressure of pure water at the same temperature. Data concerning the decrease in vapour pressure in salt solutions as a function of temperature and concentration can be found in the literature. For example, according to Washburn (1926-1933), \( a_W = 0.75 \) for a saturated NaCl solution \((c \approx 6 \text{ mol/l}, x_W \approx 0.89)\) at \( T = 30^\circ C \).

2.2.3.3 Effect of clay minerals on water activity

The pore water in a clayey material generally has an activity less than unity. The underlying causes on the micro-scale are the increased ionic concentration in the vicinity of the clay platelets and the intermolecular forces acting between the clay surface and the water. In general, water activity can be calculated by using the Kelvin equation (cf. Scanlon et al. 2002):

\[ a_W = \exp \left( \frac{\Psi V_w}{RT} \right), \]  

where \( \Psi < 0 \) is the soil-water potential, \( T \) the temperature in K, \( R \) the gas constant and \( V_w \) the molar volume of water.

The potential \( \Psi \) can be defined as ‘the work done on a unit mass of water, required to move it from a free water surface to a point in the soil’ (Yong and Warkentin 1975) and consists in its very general form of several components (Yong 1999). Nonetheless, the selection of the components is not
standardised and appears to be rather arbitrary in the literature. In the current study, the following general expression for the potential is considered (Passioura 1980, Yong 1999):

$$\Psi = \Psi_\pi + \Psi_m,$$  \hspace{1cm} (2.16)

where $\Psi_\pi$ and $\Psi_m$ denote the osmotic and the matric potential, respectively. It should be mentioned that the expression given by Passioura (1980) and Yong (1999) includes pressure potential as an additional term. This term was omitted here from Eq. (2.16) because the pore water pressure has been considered already in Eq. (2.11). The two components of the pore water potential according to Eq. (2.16) will be discussed next.

The osmotic potential $\Psi_\pi$ is associated with the ionic concentration in the soil water. The clay minerals carry negative electric charges. The pore water between the clay platelets is actually a salt solution in which the cations balance these negative electric charges (Dormieux et al. 2003). The clay platelets thus perform a similar function to a semipermeable membrane in a normal osmotic system, i.e. they restrain the ions (Atkins and De Paula 2006).

As the potential of the pore water is lower than that of the free water far away from the clay minerals, water flows towards the inter-platelet space and pushes the clay platelets apart. The swelling of the clay can thus be attributed to the activity difference between the free water and the pore water. The osmotic potential can either be calculated theoretically by considering the clay platelets in the micro-scale (Madsen and Müller-Vonmoos 1990) or determined experimentally (cf. Fermi 1936). Note that strains in a clayey rock also occur due to changes in the osmotic potential, i.e. the potential is “effective” in the sense of the soil mechanical principle of effective stress. Osmotic swelling occurs at water activities greater than 0.9, while at low water activities (unsaturated systems) intracrystalline swelling takes place (Bihannic et al. 2009, Mering 1946). The latter is associated with the hydration of the interlamellar spaces, which results in an increase in the crystal distance.

The matric potential $\Psi_m$ is made up of two components, the adsorptive component $\Psi_a$ and the capillary component $\Psi_c$ (Tuller et al. 1999, Philip 1977). In general, when a liquid comes in contact with a solid, a thin liquid film forms around the solid surface and surface forces (suction forces) develop (Chenevert 1969, Derjaguin et al. 1987). More specifically, the interfacial interactions between the clay surface and the water result in a decrease in the chemical potential of the water in the absorbed film. This decrease induces a further gradient between the chemical potentials of the water in the film and the water in the bulk, which in turn causes an additional water flow in the system and thus also additional swelling (Mitchell and Soga 2005). The adsorptive component $\Psi_a$ depends on the thickness of the water layer absorbed. According to Low and Margheim (1979), who provided a relationship for the swelling pressure of clays, the thinner the absorbed water layer (i.e. the less water), the higher the swelling pressure.
Chapter 2

The capillary component $\Psi_c$ applies to partly saturated porous media and results from the stresses transmitted to the water phase from pressures developed by concave menisci at the water–vapour interfaces, causing a decrease in the pore water pressure (Passioura 1980, Mitchell and Soga 2005). $\Psi_c$ depends on the mean curvature of the water–vapour interface and is given by the Young-Laplace equation (cf. Tuller et al. 1999).

Nevertheless, as verified by crystalline swelling tests, differences in the water content might result in gradients of matric potential and thus in water movement, even in saturated systems. Therefore, the term ‘capillary flow’ is used in the literature (Derjaguin et al. 1987). It is a common case for clays to exhibit high values of suction even under saturated conditions where capillary flow may take place due to suction differences (Yong and Warkentin 1975).

It is not possible to measure the two components ($\Psi_a$ and $\Psi_c$) of the matric potential separately (Yong and Warkentin 1975). Nonetheless, there are techniques both in the laboratory and in the field for the measurement of the matric potential $\Psi_m$ and the potential $\Psi$ of water. An extended overview of the different measuring methods can be found in Scanlon et al. (2002).

2.2.3.4 Activity of the ions

The activity of an ion $i$ is given by:

$$a_i = \gamma_i c_i / c_0,$$

where $c_i$ and $\gamma_i$ denote its concentration and activity coefficient, respectively, while $c_0$ is the concentration at standard state ($c_0 = 1$ mol/l). In a similar way to the water activity coefficient, the ion activity coefficient accounts for the interactions among the ions present in the solution. It depends on all of the ionic concentrations (including foreign ions) and is generally $\leq 1$. For an extremely dilute solution, $\gamma_i$ equals unity, i.e. the activity $a_i$ of the constituent $i$ is equal to its concentration $c_i$ in mol/l.

Activity coefficients can be measured experimentally only for salts, and not for single ions. Nonetheless, several theoretical approaches for determining $\gamma_i$ have been proposed in the literature (cf. e.g. Merkel and Planer-Friedrich 2008 for a general overview). For dilute solutions, the most common equations are the extended equations of Debye and Hückel (1923) and the equations of Davies (1962), while for highly saline waters the equations of Pitzer (1973) should be applied.

As explained later, salinities are rather low in the Gypsum Keuper formation. The activity coefficients $\gamma_i$ will therefore be calculated here according to the Davies equations:

$$\log_{10} \gamma_i = -A \cdot z_i^2 \left( \frac{\sqrt{I / c_0}}{1 + \sqrt{I / c_0}} - 0.3 I / c_0 \right),$$

where $z_i$ is the valence of the ions ($z_i = 2$ for calcium and sulphate ions) and $I$ is the ionic strength.
\[ I = 0.5 \sum c_i z_i^2 . \] (2.19)

The coefficient \( A \) depends on the temperature:

\[ A = \frac{1.82483 \times 10^9 \cdot \sqrt{\rho_W}}{(\varepsilon \cdot T)^{1/2}}, \] (2.20)

where \( T \), \( \rho_W \) and \( \varepsilon \) denote the temperature in Kelvin, the water density (in gr/cm\(^3\)) and the dielectric constant (dimensionless). For temperatures up to 80 °C, Gildseth et al. (1972) and Nordstrom et al. (1990) give the following expressions for the water density and for the dielectric constant, respectively:

\[ \rho_W = 1 - \frac{(T - 277.14)^2 \cdot (T + 15.79)}{508929.2 \cdot (T - 205.02)} + 0.011445 \cdot e^{-394.3(T - 273.15)} \] (2.21)

and

\[ \varepsilon = 2727.586 + 0.6224107 \cdot T - 666.9151 \cdot \ln T - \frac{52000.87}{T} \cdot \ln T. \] (2.22)

For the usual temperatures in Gypsum Keuper tunnels (15 - 30°C, cf. Section 3.3), the coefficient \( A \) amounts to 0.50 - 0.52. Figure 2.1 shows activity as a function of concentration and it was calculated based on Eqs. (2.18) to (2.22) for solutions containing only calcium and sulphate ions with \( c_{Ca^{2+}} = c_{SO_4^{2-}} = c \).

![Figure 2.1](image)

**Figure 2.1.** Activity of solutions containing only calcium and sulphate ions with \( c_{Ca^{2+}} = c_{SO_4^{2-}} = c \) as a function of concentration \( c \) according to the Davies equations

The Davies equations used above give proper results only if the ionic strength \( I < 500 \) mmol/l, which, as explained below, is true for the Gypsum Keuper formation. Chemical analyses of water from a number of Swiss tunnels crossing this formation indicate high values for sulphate content and variable
values for other ions such as sodium or chloride. For instance, water analyses from different sections of the Belchen Tunnel showed the presence of sodium, calcium, potassium, carbonate, sulphate, hydroxide and chloride ions (Table 2.2) as well as negligible quantities of magnesium, nitrite ($NO_2^-$), nitrate ($NO_3^-$) and phosphate ($PO_4^{3-}$) ions (not included in Table 2.2). The investigations on water from the Chienberg Tunnel and the Adler Tunnel revealed the presence of $Ca^{2+}$, $SO_4^{2-}$, $Na^+$, $Cl^-$ and in some cases also magnesium ions as shown in Table 2.2. In the Adler Tunnel, bromide ($Br^-$), fluoride ($F^-$), nitrate and nitrite ions were additionally detected, though in extremely low concentrations (not included in Table 2.2). Even if uncertainties exist as to whether the analysed water is identical to the water in the pores or even to the natural groundwater (the composition of which may have altered due to reactions with injection materials and concrete), the high sulphate content values are characteristic of water from the Gypsum Keuper formation (Noher and Meyer 2002) and agree with the results from chemical analyses of the pore water of Keuper marls (Pearson et al. 2003, Gimmi and Waber 2004).

The last row of Table 2.2 shows the ionic strength $I$, calculated simultaneously from the maximum values of the given concentration ranges (omitting the very low concentration ions mentioned above). Even in this extreme case, however, the ionic strength $I$ is less than 500 mmol/l, thus justifying the use of the Davies equations. Low ionic strength values were also determined for Keuper marls from the Mont Terri Rock Laboratory and from the Benken borehole of NAGRA (50 – 180 mmol/l according to Pearson et al. 2003 and Gimmi and Waber 2004).

A further conclusion from Table 2.2 is that the sodium and chloride concentrations are rather low. Relatively low concentrations were also observed in the pore water of Keuper marls from Mont Terri and Benken ($< 120$ mmol/l sodium and $< 15$ mmol/l chloride, Pearson et al. 2003, Gimmi and Waber 2004). Higher sodium and chloride concentrations (up to 300 and 350 mmol/l, respectively, Pearson et al. 2003) were measured in water squeezed out from the pores of Opalinus clay samples from Mont Terri. (Opalinus clay is a slightly younger, Jurassic marine claystone overlying the Keuper marls.) However, even this higher salinity results in ionic strengths lower than 400 mmol/l (Pearson et al. 2003). Opalinus clay specimens from Benken exhibit even lower ionic strengths (94 – 310 mmol/l, Voegelin and Kretzschmar 2002, Van Loon and Soler 2003).
Table 2.2. Ion concentrations and maximum ionic strength for three Swiss Tunnels in Gypsum Keuper

<table>
<thead>
<tr>
<th>Ion concentration [mmol/l]</th>
<th>Belchen Tunnel(^{(1)})</th>
<th>Chienberg Tunnel(^{(2)})</th>
<th>Adler Tunnel(^{(3)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (Ca^{2+})</td>
<td>0.18-18.8</td>
<td>0.78-21.5</td>
<td>1.7-15</td>
</tr>
<tr>
<td>Sulphate (SO_4^{2-})</td>
<td>0.14-95.9</td>
<td>0.29-36.5</td>
<td>0.4-19.4</td>
</tr>
<tr>
<td>Sodium (Na^+)</td>
<td>2.7-137.5</td>
<td>0-25.6</td>
<td>0.23-6.5</td>
</tr>
<tr>
<td>Chlorine (Cl^-)</td>
<td>0.11-186.4</td>
<td>0-2.5</td>
<td>0-5.5</td>
</tr>
<tr>
<td>Potassium (K^+)</td>
<td>0.6-13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxide (OH^-)</td>
<td>2.3-29.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate (CO_3^{2-})</td>
<td>1.7-8.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium (Mg^{2+})</td>
<td></td>
<td>0-11.1</td>
<td>0-6.9</td>
</tr>
<tr>
<td>Max. ionic strength (I) [mmol/l]</td>
<td>429</td>
<td>152</td>
<td>89</td>
</tr>
</tbody>
</table>

(2) after LPM (2000-6) and Lothenbach (2012)
(3) after Zehringer (1997) and Bachema (1995-7)

2.2.4 Crystal-liquid interfacial effect

Solid–liquid interfacial effects increase the chemical potential of crystals. This is taken into account by the third term on the right hand side of Eq. (2.11). This term applies only to the solid species (anhydrite and gypsum crystals in the present case) and corresponds to Eq. (7) of Steiger (2005a). Since \(dA_i/dn_i\) is directly related to the specific surface of the crystals, this term can be neglected for large crystals or plane interfaces, but is important for crystals with small curvature radii. Under the simplifying assumptions of spherical particles with radius \(r_i\) and isotropic surface free energy \(\gamma_i\), the third term of Eq. (2.11) is equal to \(V_i \frac{2\gamma_i}{r_i}\) (cf. Steiger 2005b), which means (as can be confirmed by inspecting Eq. 2.9) that the effect of the surface energy is equivalent to that of the pressure \(P_i\): The surface can be conceived of as a stretched membrane that encloses the crystal and exerts a confining pressure of \(2\gamma_i/r_i\) upon it. Figure 2.2 shows this apparent confining pressure \(2\gamma_i/r_i\) as a function of the particle radius \(r_i\) for the typical range of the interfacial tension \(\gamma_i\) (which is 10 – 150 mN/m according to Nielsen and Söhnel, 1971). The apparent confining pressure reaches very high values (several MPa) at small radii, decreases with increasing radius and becomes negligible for radii greater than 1 \(\mu\)m.
Anhydrite appears in natural rocks either in the form of particles or of layers of different thicknesses and spacings (cf. Section 5.2.1). The form of the particles may be closer to a sphere, or a rather prismatic form, while their size lies within a wide range, amounting from a few $\mu$m to a few cm. The solid-liquid interfacial effects are therefore practically negligible for anhydrite.

However, such effects may be important during gypsum growth inside the pores of anhydritic claystones, since the size of the pores in the rock sets an upper limit on the size of the growing gypsum crystals. According to the literature, both the porosity and the pore size of claystones may be extremely low, while the surface free energy $\gamma_G$ between gypsum and water is in the range $10 – 120$ mN/m (Tables 2.3 and 2.4). All calculations have been performed for $\gamma_G = 80$ mN/m.

Table 2.3. Pore size data for claystones

<table>
<thead>
<tr>
<th>Reference</th>
<th>Rock</th>
<th>Method</th>
<th>$r_p$ [nm]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borst (1982)</td>
<td>Pleistocene claystone from a depth of 453 m</td>
<td>MIP(1), nitrogen sorption</td>
<td>50</td>
<td>mean size</td>
</tr>
<tr>
<td>Stroes-Gascoyne et al. (2007)</td>
<td>Opalinus Clay</td>
<td>MIP</td>
<td>&lt; 20</td>
<td>mostly</td>
</tr>
<tr>
<td>Desbois et al. (2009)</td>
<td>Boom Clay</td>
<td>Cryo-SEM(2)</td>
<td>&lt; 100</td>
<td>40 % (3)</td>
</tr>
<tr>
<td>Muñoz et al. (2009)</td>
<td>Opalinus Clay</td>
<td>MIP</td>
<td>20 – 100</td>
<td>24.2 % (3)</td>
</tr>
<tr>
<td>Lima et al. (2010)</td>
<td>Boom Clay</td>
<td>MIP</td>
<td>10 – 20</td>
<td>42.5 % (3)</td>
</tr>
<tr>
<td>Lima et al. (2010)</td>
<td>Lilla claystone</td>
<td>MIP</td>
<td>&lt; 100</td>
<td>mostly</td>
</tr>
</tbody>
</table>

(1) Mercury intrusion porosimetry; (2) Scanning electron microscopy; (3) Fraction of the total porosity
## 2.3 Equilibrium concentrations

### 2.3.1 Gypsum

In order to determine the equilibrium concentration under a given temperature $T$ and pressure $P_i$, we apply Eq. (2.7) with $dP_i = dT = 0$, with chemical potentials according to Eq. (2.11) and with pressures as introduced in Section 2.2.1. Incorporating the stoichiometric relations $dn_{Ca^{2+}} = dn_{SO_4^{2-}} = 2dn_w = -dn_G$ of the gypsum dissolution/precipitation reaction (Eq. 2.1) as well, we obtain:

$$dG = \left( \mu_{Ca^{2+}} + \mu_{SO_4^{2-}} + 2\mu_w - \mu_G \right) dn_G = $$

$$\left( \Delta_{r,G}G^0 + RT \ln K_G + p_w \left( V_G^0 + \Delta_{r,G}V^0 \right) \right) - \left( p_G + \frac{2\gamma_G}{r_G} \right) V_G^0 - (T - T_0) \Delta_{r,G}S^0 \right) dn_G, \quad (2.23)$$

where $\Delta_{r,G}G^0$, $\Delta_{r,G}V^0$, $\Delta_{r,G}S^0$ and $K_G$ are the standard Gibbs energy, the standard volume, the standard entropy and the ion activity product of gypsum dissolution, respectively:

$$\Delta_{r,G}G^0 = \Delta_{f,G}G^0_{Ca^{2+}} + \Delta_{f,G}G^0_{SO_4^{2-}} + 2\Delta_{f,G}G^0_w - \Delta_{f,G}G^0_G, \quad (2.24)$$

$$\Delta_{r,G}V^0 = V_{Ca^{2+}}^0 + V_{SO_4^{2-}}^0 + 2V_{w}^0 - V_G^0, \quad (2.25)$$

$$\Delta_{r,G}S^0 = S_{Ca^{2+}}^0 + S_{SO_4^{2-}}^0 + 2S_{w}^0 - S_G^0, \quad (2.26)$$

$$K_G = \frac{a_{Ca^{2+}}a_{SO_4^{2-}}a_w^2}{a_G} = \gamma_{Ca^{2+}}\gamma_{SO_4^{2-}}^2 \frac{c_{Ca^{2+}}}{c_o} \frac{c_{SO_4^{2-}}}{c_o} a_w^2. \quad (2.27)$$

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\gamma_G$ [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nielsen (1964)</td>
<td>100</td>
</tr>
<tr>
<td>Nielsen and Söhnel (1971)</td>
<td>76 - 117 (1)</td>
</tr>
<tr>
<td>He et al. (1994)</td>
<td>12, 41.1 (2)</td>
</tr>
<tr>
<td>Lancia et al. (1999)</td>
<td>37</td>
</tr>
<tr>
<td>Pricandaro et al. (2001)</td>
<td>37.8</td>
</tr>
<tr>
<td>Lancia et al. (2002)</td>
<td>11 - 95 (1)</td>
</tr>
<tr>
<td>Alimi et al. (2003)</td>
<td>48.5, 14.3 (3)</td>
</tr>
<tr>
<td>Mahmoud et al. (2004)</td>
<td>8.4</td>
</tr>
<tr>
<td>Mishra (2012)</td>
<td>31 ± 4 (4)</td>
</tr>
</tbody>
</table>

(1) based upon literature review; (2) depending on the equation used; (3) for heterogeneous and homogeneous nucleation, respectively; (4) for one crystal plane only.
At equilibrium, \( \frac{dG}{d_n} = 0 \) (cf. Section 2.2.1) and, consequently, the last bracketed term in Eq. (2.23) is equal to zero, thus representing the equation for determining the equilibrium solubility product \( K_{eq,G} \) as a function of temperature \( T \), pore water pressure \( p_{W} \), gypsum pressure \( p_{G} \) and grain radius \( r_{G} \):

\[
RT \ln K_{eq,G} = -\Delta_{r,G} G^0 - p_{W} \left( V_{G}^0 + \Delta_{r,G} V^0 \right) + \left( p_{G} + \frac{2\gamma_{G}}{r_{G}} \right) V_{G}^0 + \left( T - T_{0} \right) \Delta_{r,G} S^0 .
\] (2.28)

Under the simplifying assumption that the calcium and sulphate ion concentrations are permanently equal during the chemical reaction \((c_{Ca^{2+}} = c_{SO_{4}^{2-}} = c)\), the equilibrium solubility product

\[
K_{eq,G} = \left( \frac{\gamma_{\pm} c_{eq,G}}{c_{0}} \right)^2 ,
\] (2.29)

where \( c_{eq,G} \) denotes the gypsum equilibrium concentration and \( \gamma_{\pm} \) the mean activity coefficient of the dissolved ions:

\[
\gamma_{\pm} = \sqrt{\gamma_{Ca^{2+}} \gamma_{SO_{4}^{2-}}} .
\] (2.30)

Equation (2.29) is a non-linear equation for the equilibrium concentration \( c_{eq,G} \), because the mean activity coefficient \( \gamma_{\pm} \) depends non-linearly on \( c_{eq,G} \).

### 2.3.2 Anhydrite

The anhydrite equilibrium concentration can be calculated analogously to that of gypsum (Section 2.3.1) with some minor modifications. More specifically, Eq. (2.28) becomes

\[
RT \ln K_{eq,A} = -\Delta_{r,A} G^0 - p_{W} \left( V_{A}^0 + \Delta_{r,A} V^0 \right) + \left( p_{A} + \frac{2\gamma_{A}}{r_{A}} \right) V_{A}^0 + \left( T - T_{0} \right) \Delta_{r,A} S^0 ,
\] (2.31)

where

\[
\Delta_{r,A} V^0 = V_{Ca^{2+}}^0 + V_{SO_{4}^{2-}}^0 - V_{CaSO_{4}^{2-}}^0 ,
\] (2.32)

\[
\Delta_{r,A} S^0 = S_{Ca^{2+}}^0 + S_{SO_{4}^{2-}}^0 - S_{CaSO_{4}^{2-}}^0 .
\] (2.33)

\[
K_{eq,A} = \left( \frac{\gamma_{\pm} c_{eq,A}}{c_{0}} \right)^2
\] (2.35)
and $K_{eq,A}$ and $c_{eq,A}$ denote the equilibrium solubility product and the anhydrite equilibrium concentration.

2.4 Gypsum-Anhydrite equilibrium relationships

2.4.1 General case

In order for gypsum and anhydrite to co-exist in a system, their equilibrium concentrations (Eqs. 2.28 and 2.31 with $K_{eq,G}$ and $K_{eq,A}$ according to Eqs. 2.29 and 2.35, respectively) must be equal. This condition leads to the following general equilibrium condition:

$$2RT \ln a_w + (T - T_0) \Delta_{r,Gd} S^0 = \Delta_{r,Gd} G^0 + p_w \left( V^0_A - V^0_G + \Delta_{r,Gd} V^0 \right) + \left( p_G + \frac{2\gamma_G}{r_G} \right) V^0_G - \left( p_A + \frac{2\gamma_A}{r_A} \right) V^0_A,$$

where

$$\Delta_{r,Gd} G^0 = \Delta_f G_G^0 - \Delta_f G_A^0 - 2\Delta_f G_w^0,$$

$$\Delta_{r,Gd} V^0 = V^0_G - V^0_A - 2V^0_w$$

and

$$\Delta_{r,Gd} S^0 = S^0_G - S^0_A - 2S^0_w.$$

Solving Eq. (2.36) with respect to $T$ yields the equilibrium temperature:

$$T_{eq} = T_{eq}^0 \left( \frac{p_w \left( V^0_w - V^0_G + \Delta_{r,Gd} V^0 \right) + \left( p_G + \frac{2\gamma_G}{r_G} \right) V^0_G - \left( p_A + \frac{2\gamma_A}{r_A} \right) V^0_A}{\Delta_{r,Gd} G^0 + T_0 \Delta_{r,Gd} S^0} \right),$$

where $T_{eq}^0$ denotes the equilibrium temperature under atmospheric pressure ($p_w = p_G = p_A$) without surface tension effects (i.e. for sufficiently large crystals):

$$T_{eq}^0 = \Delta_{r,Gd} G^0 + T_0 \Delta_{r,Gd} S^0 \frac{2R \ln a_w + \Delta_{r,Gd} S^0}{2R \ln a_w + \Delta_{r,Gd} S^0}.$$  

At temperatures above the equilibrium temperature $T_{eq}$, the thermodynamically stable phase is anhydrite. (Gypsum is stable, if $T < T_{eq}$.) According to Eq. (2.41), the equilibrium temperature depends linearly on the pressures of the constituents.
2.4.2 Simplified model for the conditions in the ground

Equation (2.40) will be used in order to determine the equilibrium temperature prevailing at depth \( H \) below the surface and to compare it with other theoretical predictions from the literature (Section 2.6). As in Marsal (1952) and MacDonald (1953), we assume that the solid pressure increases linearly with depth according to the lithostatic gradient (i.e. \( p_S = \gamma_s H \), where \( \gamma_s \) denotes the unit weight of the rock). This constitutes a good approximation. According to Dewers and Ortoleva (1989) the assumption is made that the total pressure \( p_S \) acting on a rock volume is undertaken partially by the solid phase and partially by the pores, i.e. \( p_S = (1-\phi)\gamma_s H + \phi p_W \) where \( \gamma_s H \) is the pressure on the solid phase and \( \phi \) the porosity. For very small porosities, which is the case in Gypsum Keuper, \( p_S \approx \gamma_s H \). Furthermore, as in the literature, we neglect surface energy effects, which is reasonable for sufficiently large crystals \( (r_A, r_G > 1 \, \mu m \) according to Fig. 2.2). For the pore water pressure, we will address the two cases investigated in the literature: it will be taken either as hydrostatic (i.e. \( p_W = \gamma_W H \), where \( \gamma_W \) denotes the unit weight of the water) or equal to the lithostatic pressure \( p_W = p_S \).

Equation (2.40) with \( p_A = p_G = p_S = \gamma_s H, r_G/r_A = r_A/r_A = 0 \) and the constants of Table 2.1 leads to the following expressions for the gradient of equilibrium temperature over depth:

\[
\frac{\partial T_{eq}}{\partial H} = T_{eq}^0 \gamma_W \frac{\Delta_{r,eq}G^0 - V_A^0}{\Delta_{r,eq}G^0 + T_0 \Delta_{r,eq}S^0} \left( \frac{\gamma_s - 2V_W^0}{\gamma_W - V_G^0 - V_A^0} \right) = -0.005 \frac{T_{eq}^0}{T_0} \left( \gamma_s - 1.27 \right) \degree C/m \quad (2.42)
\]

if the pore water pressure is hydrostatic, and

\[
\frac{\partial T_{eq}}{\partial H} = T_{eq}^0 \gamma_W \frac{\Delta_{r,eq}V^0}{\Delta_{r,eq}G^0 + T_0 \Delta_{r,eq}S^0} = 0.00135 \frac{T_{eq}^0}{T_0} \degree C/m \quad (2.43)
\]

if the pore water pressure is equal to the lithostatic pressure. It can easily be verified that in the first case the temperature gradient is negative for the relevant values of \( \gamma_s/\gamma_W \), i.e. the equilibrium temperature decreases with depth.

2.5 Comparison between predicted solubilities and published data

In the present Section we compare the predictions of the presented model with the published data for rather low temperatures and low NaCl molalites. Figure 2.3a shows the anhydrite equilibrium concentration in pure water under atmospheric pressure \( (p_W = p_A = 0) \) as a function of the temperature according to Eq. (2.31). The theoretical prediction generally agrees well with the literature data. Greater deviations are observed only at low temperatures, where little data exist (those of Kontrec et al. 2002). Similarly, Fig. 2.3b shows that the equilibrium concentration computed for gypsum (under
atmospheric pressure, i.e. $p_W = p_G = 0$, and water activity $a_W = 1$) is in good agreement with the literature data.

Blount and Dickson (1973) are among the few researchers to have studied the equilibrium concentrations of anhydrite and gypsum as a function of pore water pressure $p_W$, albeit at rather high temperatures. For a temperature of $T = 40 \, ^\circ\text{C}$ and pressure of $p_S = p_W = 500$ bar for instance, they calculated a value of $c_{eq,G} = 24$ mmol/l, based on their own empirical equations. A similar value of $c_{eq,G} = 27.8$ mmol/l can be derived from the present model.

Figure 2.4 shows the gypsum equilibrium concentration as a function of NaCl molality at $T = 30 \, ^\circ\text{C}$. Most existing investigations take the molality of NaCl between 0 and 6 mol/l, which is a common range for saline deposits. As the NaCl-molality is relatively low in Gypsum Keuper (Section 2.2.3.4), the model verification is restricted to low NaCl concentrations in this case. Experimental data for such low molalities exist only for gypsum (in Marshall and Slusher 1966). The predictions of Eq. (2.28) fit the experimental data well.

![Figure 2.3. (a) Anhydrite and, (b), gypsum equilibrium concentration in pure water at atmospheric pressure as a function of temperature](image)

![Figure 2.4. Gypsum equilibrium concentration at atmospheric pressure and 30 °C as a function of NaCl-molality](image)
2.6 Comparison of predicted equilibrium conditions with published data

2.6.1 Anhydrite – gypsum equilibrium in pure water

Figure 2.5 shows the equilibrium temperature between anhydrite and gypsum in pure water (a_w = 1, i.e. without foreign ions or interactions with clay minerals) as a function of the depth according to Section 4 as well as according to MacDonald (1953) and Marsal (1952). The dashed lines are based on Eq. (2.43), which assumes that the pore water pressure is equal to the lithostatic pressure (Marsal 1952 has studied only this case). The solid lines have been computed with Eq. (2.42), which assumes that the lithostatic pressure is higher than the pore water pressure by a factor that is equal to the ratio of the unit weights \( \gamma_r/\gamma_w = 2.4 \) (cf. MacDonald 1953).

Marsal (1952) determined the equilibrium temperature as a function of depth by using a thermodynamic expression which accounts for mineral solubilities. MacDonald (1953), however, used the empirical relationship of Kelley et al. (1941), which expresses the change in the Gibbs free energy \( \Delta G \) of the anhydrite to gypsum transformation as a function of the temperature, and calculated the equilibrium temperature by setting \( \Delta G \) equal to zero. Furthermore, he employed Eq. (2.7) in order to get the slopes of the lines in Fig. 2.5.

![Figure 2.5. Anhydrite – gypsum equilibrium temperature in pure water as a function of depth below surface](image)

All of the model predictions in Fig. 2.5 agree well concerning the slope of the equilibrium temperature over depth line, but present differences concerning the equilibrium temperature under atmospheric pressure. According to the relationship used by MacDonald (1953), anhydrite and gypsum co-exist under atmospheric pressure at a temperature of \( T = 40 \, ^\circ C \), while Marsal (1952) suggested a transition temperature of \( T = 42 \, ^\circ C \) using existing data of Posnjak (1938) for his model. The present model
predicts a transition temperature of approximately $T = 49 \, ^\circ C$ (Eq. 2.41). This value lies in the middle of the range of the transition temperatures usually found in the literature (42 – 60 °C, cf. Freyer and Voigt 2003). The discrepancy between the results of MacDonald (1953) and the present model is probably due to the different values that have been used for the thermodynamic parameters (more specifically, the formation of Gibbs free energies and entropies, cf. Eqs. 2.41 and 2.42). Unfortunately, MacDonald (1953) does not provide the assumed parameter values. At this point, it is worth mentioning that according to Zen (1965) the empirical relationship used by MacDonald (1953) was not consistent, leading to erroneous results. Zen (1965) recalculated this relationship but with revised data from Kelley (1960) and found a transition temperature of $T = 46 \, ^\circ C$ at atmospheric pressure, which is closer to the value proposed in the present study (see lines marked by rhombus in Fig. 2.4).

2.6.2 Anhydrite – gypsum equilibrium in NaCl solutions

MacDonald (1953) studied the gypsum – anhydrite equilibrium temperature in a NaCl - saturated solution (under the two above-mentioned assumptions concerning pore water pressure). In such a solution the salt concentration is approximately 6 mol/l H$_2$O, which in turn leads to a water activity of $a_W = 0.75$ (cf. Section 2.2.3). In order to take the dissolved salt into account, MacDonald (1953) supplemented the empirical equation of Kelley et al. (1941) with a term that deals with the change in Gibbs free energy $G$ caused by the decrease in water activity. Furthermore, Hanshaw and Bredehoeft (1968) studied the equilibrium conditions in a pressure-temperature graph for $a_W = 0.93$, which corresponds to a NaCl concentration of 2 mol/l H$_2$O, while assuming a unit weight of 23 kN/m$^3$ and of 10 kN/m$^3$ for the water (i.e. $p_S = 2.3p_W$). As with MacDonald (1953), they relied on the change in the Gibbs free energy during the anhydrite-gypsum reaction, but without providing all of the essential data. Figure 2.6 shows the equilibrium temperature in NaCl-solutions as a function of the depth according to the aforementioned studies (MacDonald, 1953; Hanshaw and Bredehoef, 1968), the relationship derived by Zen (1965) as mentioned in the previous paragraph (modified according to MacDonald 1953 in order to take account of decrease in water activity) and the model in Section 2.4. Comparing the results for $a_W = 0.75$, we see that the transition temperature at atmospheric pressure is 14 °C according to MacDonald (1953), while Zen (1965) predicts a higher temperature of about 20 °C, which is much closer to the transition temperature of 22 °C predicted by Eq. (2.41).

The influence of water activity on the equilibrium between anhydrite and gypsum has been investigated both theoretically (Freyer and Voigt 2003, MacDonald 1953, Raju and Atkinson 1990, Marshall and Slusher 1966, Møller 1988) and experimentally (Hardie 1967, Bock 1961, Blount and Dickson 1973) in terms of NaCl concentration. Figure 2.7 shows the gypsum–anhydrite equilibrium temperature as a function of water activity according to the literature and to the model in Section 2.4. Again, a satisfactory agreement can be observed.
The present Section presents a synthesis of the results of the previous Sections, illustrating in a single diagram the effect of the several parameters which influence the equilibrium between anhydrite and gypsum. According to Eq. (2.36), the latter is a function of the temperature $T$, the pore water pressure $p_w$, and the water activity $\alpha_w$.
thermodynamic fundamentals

$p_w$, the water activity $a_w$ (which takes into account the effects of the clay minerals and foreign ions in the pore solution according to Sections 2.2.3.2 and 2.2.3.3), the gypsum and anhydrite pressures $p_G$ and $p_A$ (Section 2.2.1) and the particle radii $r_G$ and $r_A$ (which determine whether the surface energy effects are relevant, Section 2.2.4). Under certain simplifying assumptions, the interaction between these parameters can be visualized by means of one single equilibrium diagram (Fig. 2.8).

The assumptions in question are: the pressures of the anhydrite and gypsum are equal, i.e. $p_G = p_A = p_S$; the solid-liquid interfacial effects are negligible for the anhydrite; the radius of the gypsum particles $r_G$ corresponds to the pore radius $r_p$ (cf. Section 2.2.4). Figure 2.8 shows the anhydrite-gypsum equilibrium diagram for the two boundaries of the relevant temperature range ($T = 15$ and $30 \, ^\circ C$), for different values of the water activity $a_w$ and for two assumptions concerning the pore water pressure: atmospheric pressure ($p_w = 0$) as well as a pore water pressure of $p_w = 3$ MPa, which corresponds to a cover depth of 300 m. The diagram has been calculated assuming a value of $\gamma_G = 80$ mN/m.

The stable phase above and below each curve is gypsum and anhydrite, respectively. According to Fig. 2.8, the pore water pressure has a negligible effect on the equilibrium condition for the depths concerned. The effect of the other parameters is, however, significant. A high water activity $a_w$, low solid pressure $p_S$, low temperature $T$ and big pore radius $r_p$ favour gypsum as the stable phase.

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![Figure 2.8](image)

Figure 2.8. Anhydrite – gypsum equilibrium condition in terms of pore radius and solid pressure at different temperatures, water activities and pore pressures
2.8 Conclusions

In the present chapter a rigorous thermodynamic model is put forward for determining the equilibrium conditions between anhydrite, gypsum and water. The model predictions are close to the measured solubilities reported in the literature and agree with older theoretical predictions with respect to the gradient of the equilibrium temperature over depth. The discrepancies among older theoretical estimations of the equilibrium temperature under atmospheric pressure can be attributed to the different thermodynamic data used.

In addition to the parameters usually considered (solid and fluid pressure, temperature, concentration of foreign ions), we discuss and incorporate into our model the effects of pore size and clay minerals. These two factors are important particularly in the case of claystones with very small pores (smaller than 1 μm) and finely distributed anhydrite. Small crystals have a higher chemical potential than big crystals and clay minerals reduce the chemical potential of water. Consequently, both factors – a small pore size and the presence of clay minerals – increase the solubility of gypsum, thus shifting the thermodynamic equilibrium in favour of anhydrite.

Furthermore, in contrast to earlier research, the anhydrite–gypsum equilibrium is approached starting from the underlying dissolution and precipitation equations. More specifically, account is taken of the anhydrite–water and gypsum–water equilibria; equations are derived for the gypsum and anhydrite solubilities and these equations are applied to the special case of the anhydrite–gypsum equilibrium.
3 Anhydrite in Gypsum Keuper at Shallow Depths\textsuperscript{2}

3.1 Introduction

In the present Chapter we apply the fundamentals presented in Chapter 2 in order to analyse the initial conditions prevailing in situ in Gypsum Keuper before tunnelling and, more specifically, the presence of calcium sulphate in the form of anhydrite which, as will be shown, seems at first glance to be thermodynamically abrupt. The following brief description of the geology of the Gypsum Keuper is based mainly on Amstad and Kováři (2001).

The Gypsum Keuper consists of alternating sequences of sandstones, limestones, dolomites and claystones containing finely distributed anhydrite and gypsum. Swelling phenomena are observed only in the anhydritic claystones which are encountered in tunnelling at depths of mostly 50 – 150 m. The swelling is attributed to the combined effect of the anhydrite to gypsum transformation ($\text{CaSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and to water uptake by expansive clay minerals such as corrensite, which are also present in Gypsum Keuper (Lippmann 1976, Jordan 1994).

The Gypsum Keuper in South-Western Germany (Baden-Württemberg) consists of three zones (Fig. 3.1a). In the leached Gypsum Keuper which lies above the so-called “gypsum level”, a large fraction of the sulphate has been dissolved and transported away. Therefore, the leached Gypsum Keuper consists of weathered rocks (marls and claystones) with gypsum residues, and these rocks are water-bearing and generally exhibit a high permeability. A transition zone separates the leached from the unleached Gypsum Keuper. Due to the low permeability of the transition zone, minor water flow is observed there (Krause and Wurm 1975, Krause 1976, Kuhn and Lorscheider 1979). The “anhydrite level” represents the upper boundary of the zone, where the calcium sulphate is present in its anhydrous form. In this zone, the rock permeability is very low and the seepage flow practically non-existent. It is interesting to note that the gypsum level and the anhydrite level approximately follow the morphology of the surface (cf., e.g. the geological profile of the Wagenburg Tunnel in Fig. 3.1b), exhibiting depressions beneath valleys or close to the tunnel portals (cf., e.g. Krause and Wurm 1975, Krause 1976, Prommersberger and Kuhn 1989, Paul and Wichter 1996).

\textsuperscript{2} This Chapter is an extended version of Anagnostou et al. (2014)
In the Jura Mountains of Switzerland, the Gypsum Keuper is divided into the Faltenjura and the Tafeljura (Jordan 1994). In the Faltenjura, the sedimentary gypsum had already been transformed into anhydrite before the beginning of the Jura folding (Jordan 1994). However, in the course of this folding, anhydrite was able partially to transform into gypsum, as the anhydrite came into contact with water in the folded regions (Jordan 1994). Gypsum is therefore expected to be present at greater depths in tectonically stressed rocks. In the Tafeljura, on the other hand, the structure of the rock mass is different due to the faults which created the so-called Gypsum Keuper blocks (Fig. 3.1c). At the boundaries of these blocks across the fault zones, the sulphatic rock was dissolved and subsequently transported away by the circulating water. Each Gypsum Keuper block in the Tafeljura is surrounded by a zone characterised by a variable degree of gypsification. Unlike the Gypsum Keuper formation of Baden Württemberg, the anhydrite- and gypsum-levels are not unique and do not follow the surface morphology very closely (Fig. 3.1d). These forms of Gypsum Keuper indicate the importance of water circulation for the gypsification process. The occurrence of anhydrite at the relatively small overburdens of Keuper tunnels is, however, surprising at first glance because one might expect
gypsum rather than anhydrite to be the stable phase at the pressure and temperature conditions prevailing at these depths.

More specifically, assuming that, (i) the solid-liquid interfacial effects are negligible (cf. Section 2.2.5), (ii) the pore water is thermodynamically free (i.e. the water activity $a_W = 1$), (iii) the solid pressures of anhydrite and gypsum are equal (i.e. $p_G = p_A$) and (iv) the solid pressures and the pore water pressure $p_W$ increase linearly with the depth $H$ (cf. Section 2.4.2), Eqs. (2.40) and (2.41) lead to the following linear relationship between the equilibrium temperature $T_{eq}$ and the depth of cover $H$:

$$T_{eq} = T_0 + \frac{\Delta r_G S^0}{\Delta r_G S^0} + \frac{(V_G^0 - V_A^0) \gamma_r - 2V_W^0 \gamma_W}{\Delta r_G S^0} H,$$

where $\gamma_r$ and $\gamma_W$ denote the total unit weight of the rock and the unit weight of the water, respectively (taken as $\gamma_r = 25$ kN/m$^3$ and $\gamma_W = 10$ kN/m$^3$ in all following computations); $T_0$ is the standard temperature (25 ºC); and the other symbols denote the common thermodynamic constants (see Table 2.1).

![Figure 3.2. Anhydrite – gypsum equilibrium diagram (for $a_W = 1$, neglecting solid-liquid interfacial effects) and the range of values for tunnels in Gypsum Keuper](image)

Figure 3.2 shows the anhydrite–gypsum equilibrium temperature as a function of the depth (solid straight line). By way of comparison, the diagram also shows the equilibrium temperature in the case of atmospheric pore pressure (dashed line, calculated by Eq. 3.1 without the $\gamma_W$ – term). Gypsum represents the stable phase at temperatures below the equilibrium temperature (i.e. at points on the left side of the straight lines). Anhydrite is stable at higher temperatures, i.e. on the right side of the lines.

The rectangle in Fig. 3.2 indicates the relevant range for tunnels in Gypsum Keuper. The depth range is based on Table 3.1, which shows the minimum and maximum overburden of a number of tunnels crossing the Gypsum Keuper formation. The minimum overburden encountered is 10 m (Adler Tunnel), while the maximum overburden is 370 m in the case of the Belchen Tunnel. The data
presented by Krause and Wurm (1975) also show that Gypsum Keuper is encountered at a maximum depth of 280 m in tunnelling. The temperature range of 15 – 30 °C takes account of the relevant depth range and geothermal gradient in Switzerland, which is equal to about 30 – 40 °C/km (Medici and Rybach 1995).

Table 3.1. Depth of tunnels in Gypsum Keuper

<table>
<thead>
<tr>
<th>Tunnel</th>
<th>minimum overburden in Gypsum Keuper [m]</th>
<th>maximum overburden in Gypsum Keuper [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wagenburg Tunnel (1)</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Schanz Tunnel (2)</td>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>Kappelesberg Tunnel (3)</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td>Hauenstein Base-Tunnel (4)</td>
<td>270</td>
<td>300</td>
</tr>
<tr>
<td>Belchen Tunnel (5)</td>
<td>45</td>
<td>370</td>
</tr>
<tr>
<td>Chienberg Tunnel (6)</td>
<td>20</td>
<td>120</td>
</tr>
<tr>
<td>Engelfberg Base-Tunnel (7)</td>
<td>40</td>
<td>85</td>
</tr>
<tr>
<td>Freudenstein Tunnel (8)</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Adler Tunnel (9)</td>
<td>10</td>
<td>110</td>
</tr>
<tr>
<td>Bözberg Tunnel (10)</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>Mont Terri (11)</td>
<td>115</td>
<td>360</td>
</tr>
<tr>
<td>Lilla Tunnel (12)</td>
<td>20</td>
<td>115</td>
</tr>
</tbody>
</table>


The literature contains few works dealing with observations of anhydrite at shallow depths, and these mainly concern massive anhydrite beds. So, for example, Rolnick (1954) discussed the findings from drill holes in evaporitic deposits in Nova Scotia and attributed the occurrence of anhydrite to chemical kinetics (extremely slow hydration of the anhydrite). In the following we focus on the literature dealing specifically with the case of finely distributed anhydrite. The latter is different from massive anhydrite in that it offers a large specific surface to hydration.

Lippmann and Schüle (1975) introduced the so-called “corrensite-anhydrite theory”, according to which the presence of anhydrite rather than gypsum in the rock provides an indication as to the thermodynamic characteristics of corrensite (see also Lippmann 1976). More specifically, corrensite cannot exist in its swollen, hydrated state, because this would imply the presence of free water, which would in turn lead to the gradual transformation of anhydrite into gypsum within a period of some years. The access of water (via the seepage flow which is triggered by tunnel excavation) has a twofold effect. It will cause both the swelling of corrensite and the transformation of anhydrite into
Anhydrite in Gypsum Keuper at Shallow Depths

gypsum. Since the latter is a rather slow process, the swelling of corrensite constitutes the main initial swelling mechanism and thus the main cause of heave of the tunnel invert in the early stages after tunnel excavation (Lippmann and Schüle 1975). Fecker (1981) provided support for the “corrensite-anhydrite theory” after performing in situ swelling tests in which the invert of an exploratory gallery (in the Wagenburg Tunnel near Stuttgart) was soaked with a saturated magnesium chloride solution. The dissolved magnesium chloride shifts the thermodynamic equilibrium in favour of anhydrite, i.e. it hinders the transformation of anhydrite to gypsum. Nevertheless, despite the suppression of the anhydrite transformation, considerable heave of the invert took place. According to Fecker (1981) this can only be attributed to the swelling of corrensite, thus proving the validity of the theory.

An interesting alternative hypothesis was put forward by Wichter (1989). He proposed that gypsum growth starts from existing – and possibly very small – cavities, thereby compressing the surrounding rock and retarding or stopping the transformation process. The question therefore arises as to whether the stresses developing during growth might shift the equilibrium in favour of anhydrite, thus explaining the fact that anhydrite occurs at shallow depths.

Hauber et al. (2005) also commented on the fact that anhydrite has been found at shallow depths during tunnel excavations in Gypsum Keuper. The point is made that, even assuming a high amount of dissolved salts in the circulating water (and thus low water activity, favouring thermodynamically stable anhydrite), the stability limit of anhydrite in terms of pressure and temperature is much higher than the actual values prevailing at the depths of the tunnels. Hauber et al. (2005) concluded that anhydrite should therefore actually be unstable at shallow depths.

These studies, even though based upon qualitative considerations, provide useful indications as to the possible reasons for the occurrence of anhydrite at relatively shallow depths. The present Chapter aims to close existing knowledge gaps by investigating a number of hypotheses on this phenomenon quantitatively.

One possible scenario is that gypsum is indeed the thermodynamically stable phase (as indicated by Fig. 3.2), but is not present in situ either because of a lack of water or because the hydration of anhydrite is an on-going process which proceeds extremely slowly in geological times. However, this scenario does not seem probable: On the one hand, anhydrite occurs in the form of veins or particles finely distributed in claystones, which may have a very low porosity (5-10%) but are nevertheless saturated. On the other hand, the hydration of finely distributed anhydrite (in contrast to that of massive anhydrite beds) occurs rapidly due to its large specific surface. It may take months or years (depending on the specific surface areas of the mineral particles) but certainly not geological times (cf. Grob 1972, Pimentel 2007, Rauh 2009, Oldecop and Alonso 2012 and also Chapter 6 of the present dissertation).

For these reasons we focus here on the alternative scenario that anhydrite is the thermodynamically stable phase. This would mean that one or more of the simplifying assumptions behind the
thermodynamic equilibrium diagram in Fig. 3.2, which implies that gypsum rather than anhydrite is the stable form, cannot be true. Therefore, we examine which deviations from the assumptions of Fig. 3.2 might explain why anhydrite is the stable phase. Specifically, we examine the assumptions concerning water activity, pore size and solid pressure, as a low water activity, small pore size and high solid pressure shift the thermodynamic equilibrium in favour of anhydrite (cf. Chapter 2). The underlying ideas are:

- The pore size may be extremely small (in the range of a few nm) with the consequence that solid-liquid interface effects become relevant, considerably increasing the chemical potential of gypsum.

- The growth of gypsum crystals may increase the stresses locally (in the close vicinity of the crystals) to values which are much higher than the ones corresponding to the overburden of the tunnels in Gypsum Keuper. (This hypothesis takes up Wichter’s 1989 idea.)

- The activity of the pore water may be considerably lower than 1 due to its interactions with the clay minerals. (This hypothesis is very close to that of Lippmann and Schüle’s, 1975, as it also focuses on the thermodynamic state of the water.)

These three hypotheses, herein referred to as the “small pore hypothesis”, the “high pressure hypothesis” and the “low water activity hypothesis”, will be examined in Sections 3.2, 3.3 and 3.4, respectively.

The investigations of the present Chapter indicate that the third hypothesis is the most probable one. The results of this Chapter, besides providing insight into an interesting observation, are also valuable for future research as they assist in the formulation of adequate initial conditions for continuum-mechanical models of the chemo-mechanical and transport processes in swelling anhydritic claystones.

3.2 The small pore hypothesis

3.2.1 Introduction

As explained in Chapter 2, small pores favour anhydrite as the stable phase, while large pores favour gypsum – all other conditions (pressure, temperature, water activity) being equal. This is due to the effect of surface energy, which is equivalent to that of a confining pressure. (The surface can be conceived of as a stretched membrane that encloses the crystal and exerts a confining pressure upon it.)

Consider, for instance, the solid line “a” in Fig. 3.3 which has been calculated for the pressure and temperature conditions of the Belchen Tunnel (given in Section 3.2.3). It shows the gypsum equilibrium concentration as a function of the pore radius (computed from Eq. 2.28). With increasing pore radius, the surface energy and thus also the gypsum equilibrium concentration decrease. Additionally, the diagram shows the anhydrite equilibrium concentration for the same solid pressure
and pore water pressure and temperature (line “b”, computed with Eq. 2.31). In pores with small radii \( r_p \) (hereafter referred to as “*subcritical pores*”), anhydrite exhibits a lower equilibrium concentration than gypsum and therefore represents the thermodynamically stable phase. In the pores with great radii \( r_p \) (hereafter referred to as “*supercritical pores*”), the opposite applies. The threshold pore size, i.e. the pore size where anhydrite and gypsum exhibit the same equilibrium concentration (intersection point \( O \) of the two lines), will be denoted from now on as the critical pore radius \( r_{cr} \). It can be calculated according to Eq. (2.36), i.e. by setting the equilibrium concentrations of anhydrite and gypsum equal. Taking the radius of the gypsum particles equal to the pore radius (\( r_G = r_p \)) and considering that the solid-liquid interfacial effects are practically negligible for anhydrite and that anhydrite and gypsum are subject to the same stress (\( p_G = p_A = p_{S,0} \)), we obtain:

\[
r_{cr} = \frac{2 \gamma_G V_G^0}{2RT \ln a_w + (T - T_0) \Delta S_G^0 - \Delta S_{G,A} G^0 + 2 \rho w V_w^0 - p_{S,0} \left( V_G^0 - V_A^0 \right)}
\]

where \( p_{S,0} \) denotes the lithostatic pressure and the other parameters already introduced in Chapter 2.

In the following Sections we investigate whether the actual pore sizes of the anhydritic claystones of Gypsum Keuper are bigger or smaller than the critical pore radius.

### 3.2.2 Porosity and pore size distribution of anhydritic claystones

The porosity and the pore size distribution of natural rock samples were determined by means of mercury intrusion porosimetry (MIP) in the Clay Mineralogy Lab of our Institute (Röthlisberger 2012) and in the Swiss Federal Laboratories for Materials Testing and Research (Leemann and Wyrzykowski 2012).

![Figure 3.3: Equilibrium concentrations of anhydrite and gypsum as a function of pore radius for the temperature and pore pressure conditions of the Belchen Tunnel, \( a_w = 1 \) and different stress values on the anhydrite and gypsum](image)

Figure 3.3. Equilibrium concentrations of anhydrite and gypsum as a function of pore radius for the temperature and pore pressure conditions of the Belchen Tunnel, \( a_w = 1 \) and different stress values on the anhydrite and gypsum
As can be seen from a number of works (Table 2.3), MIP is standard for the rock types we are interested in. MIP measures the volume of non-wetting liquid intruding into capillaries under pressure (Abell et al. 1999). The porous samples are introduced into a chamber which is then evacuated (Cook and Hover 1999). The samples are then surrounded by mercury on which a progressively increasing pressure is applied. The mercury first penetrates the larger and then the smaller pores of the sample. The relationship between the pressure and the capillary diameter is determined after Washburn (1921). The volume of the mercury intruding at each pressure increment is used to determine the pore size distribution. The porosity is equal to the ratio between the total intruded volume (i.e. the volume at the maximum pressure) and the bulk volume of the unintruded sample (Cook and Hover 1999).

A drawback of the MIP method is that it regards throat diameters as pore diameters where large internal pores are accessible via narrow throats (e.g. Abell et al. 1999, Moro and Böhni 2002, Renault 1988). This so-called “ink-bottle” effect tends to overestimate the percentage of small pores. Kaufmann et al. (2009) developed a novel procedure according to which a second mercury intrusion cycle is performed in order to eliminate this effect. This additional cycle was executed in the EMPA experiments, but only the results of the first intrusion are considered here, in order to be consistent with the results provided by the Clay Mineralogy Lab (which performed five out of the total of seven tests). The “ink-bottle” effect will be taken into account qualitatively in the discussion of the computational results.

The Gypsum Keuper samples were taken from the Belchen Tunnel and from the Chienberg Tunnel at depths of 200 m and 50-55 m, respectively. These tunnels are located in the Gypsum Keuper formation and have experienced serious damage due to swelling since or even during their excavation (Grob 1972, Chiaverio and Thut 2010). In total, four tests were conducted on samples from the Chienberg Tunnel (one by EMPA and three by the Clay Mineralogy Lab) and three tests on samples from the Belchen Tunnel (one by EMPA and two by the Clay Mineralogy Lab). Anhydritic claystones consist of different constituents and may be very heterogeneous in the scale of a specimen. In order to determine the pore size distribution of the claystone matrix, samples with a macroscopically high content of clay were selected. The mass of the samples was 1.6 to 5.1 gr.

Figure 3.4 shows the results of the seven MIP-tests. The abscissa depicts the pore radius \( r_p \) and the ordinate describes the pore percentage \( \pi \). (For example, a percentage of \( \pi = 20\% \) for a pore radius of 100 nm means that 20% of the total pore volume consists of pores with radius greater than 100 nm). According to Fig. 3.4, the samples of the Belchen Tunnel (solid lines) have smaller pores than the samples from the Chienberg Tunnel (dashed lines). This can be attributed to the greater overburden of the Belchen Tunnel (200 vs. 50 m). Furthermore, the Chienberg Tunnel crosses the so-called Tafeljura, while the rock in the Belchentunnel belongs to the intensively folded part of the Jura.
Anhydrite in Gypsum Keuper at Shallow Depths

Mountains (the so-called Faltenjura), where high tectonic stresses may have caused additional compaction (Huggenberger 2014).

Figure 3.4. Pore size distributions and porosities $\phi$ of samples from the Chienberg and the Belchen Tunnel with critical radii $r_{cr}$ calculated for different water activities

3.2.3 Discussion

Taking the sampling depth into account and assuming hydrostatic pore pressure distribution and a unit total weight of 25 kN/m$^3$ for the rock mass, we get $p_W = 2$ MPa and $p_{S,0} = 5$ MPa for the Belchen Tunnel, while for the Chienberg Tunnel the corresponding values read $p_W = 0.5$ MPa, $p_{S,0} = 1.25$ MPa. Furthermore, with regard to the geothermal gradient in Northern Switzerland (cf. Section 3.1), $T = 21$ and 15 °C for the Belchen and the Chienberg Tunnel, respectively. Under these considerations, Eq. (3.2) leads to critical radii $r_{cr}$ between 7 and 250 nm, depending on the pore water activity $\alpha_W$. These critical radii are shown also in Fig. 3.4 beneath the abscissa. One can readily verify that all samples contain a larger (Chienberg Tunnel) or smaller (Belchen Tunnel) quantity of supercritical pores.

As explained in the following, the presence of even a few supercritical pores is sufficient for the entire anhydrite to transform into gypsum – including the anhydrite in regions with small pores, where it represents the thermodynamically stable phase. The consequence would be a completely anhydrite-free rock.

Assume that the rock contains both subcritical and supercritical pores. In the subcritical pores, where anhydrite represents the thermodynamically stable phase, the concentration $c$ in the pore water would
be equal to the equilibrium concentration $c_{eq,A}$ of the anhydrite (given by the line AO in Fig. 3.3).

Analogously, in the supercritical pores, the concentration would be equal to the equilibrium concentration $c_{eq,G}$ of gypsum (given by the line Oa in Fig. 3.3). Such a non-uniform concentration field would be unstable: As the porosity of the claysones is interconnected, ions will migrate by diffusion from the subcritical pores to the supercritical pores, thus reducing the concentration in the former and increasing the concentration in the latter. This will trigger dissolution of anhydrite in the subcritical pores and gypsum growth in the supercritical pores. This process – mineral dissolution in the small pores, diffusion of the dissolved ions to the larger pores and crystal growth in the latter – will continue until the entire anhydrite is transformed. Such processes are well known from the literature (Flatt 2002, Scherer 2002, 2004).

In conclusion, the small pore hypothesis must be abandoned even in the case of the extremely fine porous claysones from the Belchen Tunnel and even under the favourable assumptions of spherical pore shape and of negligible “ink-bottle” effect which underestimate the supercritical porosity. The effect of surface energy is more pronounced in the case of spherical pores than with other shapes, for example, cylindrical pores. This is because the effect of the surface energy in the case of cylindrical pores is $\gamma/\tau_1$ (one radius of curvature tends to infinity, cf., e.g., Scherer 1999), while as already mentioned in Section 2.2.4, it equals $2\gamma/\tau_1$ for spherical pores. Finally, the “ink-bottle” effect underestimates the percentage of large pores.

### 3.3 The high pressure hypothesis

#### 3.3.1 Introduction

The present Section investigates whether, under the simplifying assumption of an isotropic state, the pressures which develop locally during the growth of gypsum in the supercritical pores are able to explain the occurrence of anhydrite (rather than gypsum) at shallow depths in Gypsum Keuper. In order to answer this question we must estimate: (i) the pressure which is required for the hydration to cease according to the thermodynamic equilibrium condition (this pressure will be hereafter referred to as the “required solid pressure”); (ii) the expansion-induced counterpressure of the matrix, i.e. the pressure that develops due to the confinement of gypsum by the surrounding claystone (this pressure will be hereafter referred to as the “mechanically possible pressure”). In order for the high stress hypothesis to be valid, the sum of the mechanically possible counterpressure and the pore water pressure must be higher than the required solid pressure.

An additional necessary condition is that the formation of only a small amount of gypsum is sufficient to mobilize the required counterpressure of the surrounding matrix. Otherwise, a considerable quantity of gypsum would also be present in situ. Thus, the validity of the high pressure hypothesis presupposes not only that the mechanically possible counterpressure reaches the required stress, but
Anhydrite in Gypsum Keuper at Shallow Depths

also that this happens with the formation of a small amount of gypsum. Obviously, the stiffer the matrix and the greater the pore expansion, the higher will be the mechanically possible counterpressure. Small quantities of gypsum can cause a considerable increase in pressure only if the surrounding matrix is sufficiently hard.

A third necessary condition is that the radial stress that must develop at the pore wall in order that gypsum growth stops may involve some cracking, but is not so high that tensile failure of an extended zone of the rock matrix occurs between the supercritical pores; if this were not the case, the rock at the scale of a specimen would appear completely disintegrated, resembling granular soil, which does not agree with the observed high quality of anhydritic claystones.

Section 3.3.2 determines the required solid pressure by means of thermodynamic computations. Subsequently, we estimate the mechanically possible counterpressure in Section 3.3.3 based on a simplified cavity expansion model which is widely used in geomechanics (Yu 2000). In Section 3.3.4 we apply this model to the pressure and temperature conditions of the Belchen Tunnel and the Chienberg Tunnel in order to investigate the validity of the high pressure hypothesis. Subsequently, the reliability and the limitations of the simplified cavity expansion model are discussed in Section 3.3.5 by means of numerical calculations. The results show that these limitations are substantial and that they call into question the validity of the high pressure hypothesis as they reveal that there are always pores which cannot develop pressures much higher than the initial in situ values and therefore, the required solid pressure is not reached. As will be shown in Section 3.3.5.5, the presence of even a few pores at a pressure lower than required would lead to the transformation of the entire amount of anhydrite into gypsum.

3.3.2 Required pressure

During gypsum growth towards the pore walls, the gypsum pressure $p_G$ increases, leading to an increase in the gypsum equilibrium concentration until the latter becomes equal to the anhydrite equilibrium concentration. The anhydrite equilibrium concentration depends, however, on the anhydrite pressure $p_A$, which may be variable: before growth, the anhydrite pressure is equal to the initial solid pressure $p_{S,0}$, but it may increase due to the pressure exerted by the growing gypsum. The anhydrite pressure obviously depends on the proximity of the anhydrite particles to the constrained gypsum growth. In this respect, two borderline cases can be considered which bound the range of possible anhydrite pressures. As explained below, the two borderline cases correspond to extreme rates of diffusive ion transport.

The calcium and sulphate ions that are necessary for the formation of gypsum crystals are supplied by the dissolution of the anhydrite. The dissolving anhydrite particles cause an increase in the ion concentration in adjacent pores. Should the ions stay in the adjacent pores (slow diffusion), then the
concentration in these pores would rise above the gypsum equilibrium concentration with the consequence that gypsum would start to precipitate close to the anhydrite particles.

However, the ions may also move by diffusion away from the anhydrite particles due to the fact that the ion concentration in the vicinity of the latter is higher than the concentration in the pores further away from them. Should the diffusion occur rapidly relative to the dissolution of anhydrite and the precipitation of gypsum, the concentration would then increase uniformly in the pores and gypsum growth would occur in all supercritical pores, as well as in pores further away from the anhydrite particles. In conclusion, the location where the crystals grow depends on whether diffusion occurs slowly or rapidly with regard to anhydrite dissolution and gypsum precipitation. The two limiting cases are the following: (1) gypsum growth in all supercritical pores (Fig. 3.5a) and (2) gypsum growth only in the supercritical pores very close to the anhydrite particles Fig. 3.5b).

![Figure 3.5.](image)

Let us consider the first case where gypsum crystals grow in all supercritical pores. In this case the pressure induced only affects the gypsum particles, while the anhydrite particles remain under the initial solid pressure, \( p_A = p_{S,0} \) (lower bound). As mentioned above, the gypsum equilibrium concentration also increases with increasing pressure \( p_G \). Therefore, in the diagram of Fig. 3.3, the equilibrium concentration – pore radius curve of gypsum will move upwards (dashed line “c” instead of line “a”), while the anhydrite equilibrium concentration will remain the same as before (solid line “b”), because we made the assumption that confined gypsum growth causes a higher pressure only in the gypsum particles. (Line “c” of Fig. 3.3 was calculated from Eq. 2.28, assuming that the solid pressure increases locally from \( p_G = p_{S,0} = 5 \) MPa to, e.g., \( p_G = 12 \) MPa, due to the growth of gypsum crystals.) As can be seen from Fig. 3.3, the intersection point of the two equilibrium concentration – pore radius curves moves to the right (from point O to point O1), which means that the critical radius becomes larger (\( r_{cr,1} \) instead of \( r_{cr} \)) and the range of pore sizes where anhydrite is the stable mineral becomes larger. For reasons explained in Section 3.5.3, the process of gypsification will continue as long as supercritical pores exist, i.e. as long as the critical pore radius (which, as mentioned above, increases with the solid pressure \( p_G \) that develops during gypsum crystal growth) is smaller than the largest pore in the rock. The process will stop when the critical pore radius becomes equal to the radius \( r_{max} \) of the largest pore, which will happen at a certain solid pressure \( p_G \) (the “required pressure”).
Where gypsum crystals grow close to anhydrite particles (case 2), the latter may also experience a certain pressure increase (i.e. \( p_G > p_A > p_{S,0} \)). The anhydrite solid pressure \( p_A \) depends on the distance between the supercritical pores and the anhydrite particles (or, more generally, on the spatial distribution of anhydrite and gypsum) as well as on the stiffness of the rock around the expanding gypsum crystals. In the 

borderline case (upper bound) both minerals will be subject to the same stress.

Then, the required solid pressure would be higher, because the increase in the anhydrite solid pressure would cause an increase in its equilibrium concentration. Therefore, line “b” in Fig. 3.3 would move upwards (to line “d” for the example of \( p_A = 12 \) MPa, calculated with Eq. 2.31) and the intersection point with the gypsum curve would move to the left (point \( O_2 \) instead of point \( O_1 \)). This means that the increase of the critical radius is less pronounced here (from \( r_{cr} \) to \( r_{cr,2} \) rather than to \( r_{cr,1} \)) or, in other words, that a higher stress must develop in order for the critical radius to reach the radius \( r_{max} \) of the largest pore.

The required solid pressure for equilibrium to be reached can be determined by setting the gypsum equilibrium concentration (Eq. 2.28) equal to that of anhydrite (Eq. 2.31) with \( \gamma_A/r_A = 0 \) and \( r_G = r_{max} \).

Taking the lower bound for the pressure exerted on anhydrite, (i.e. \( p_A = p_{S,0} \), \( p_G = p_{req} \)), the lower bound of the required pressure can be calculated as

\[
P_{req,LB} = \frac{2RT \ln a_w + (T - T_0) \Delta_{r,G,4} S_0^0 - \Delta_{r,G,4} G_0^0 + 2p_w V_w^0 - 2 \frac{\gamma_G}{r_{max}} V_G^0 + p_{S,0} V_A^0}{V_G^0},
\]

while in the case that \( p_A = p_G = p_{req} \), i.e. upper bound

\[
P_{req,UB} = \frac{2RT \ln a_w + (T - T_0) \Delta_{r,G,4} S_0^0 - \Delta_{r,G,4} G_0^0 + 2p_w V_w^0 - 2 \frac{\gamma_G}{r_{max}} V_G^0}{V_G^0 - V_A^0}.
\]

Figure 3.6 shows the required pressure as a function of temperature and water activity, while neglecting liquid-solid interface effects (i.e. for \( \gamma_G/r_{max} = 0 \)). The solid lines correspond to the lower bound and the dashed lines to the upper bound of the required pressure. The higher the temperature and the lower the water activity, the lower will be the required pressure. The diagram applies to specific values of initial solid and pore pressure. However, parametric studies have shown that the influence of these parameters is small within the relevant range of values for initial solid and pore pressure.
Figure 3.6. Required solid pressure \( (p_G = p_{req}) \) for the termination of the gypsum growth as a function of temperature and water activity \( (\phi \approx 0, p_{S,0} = 5 \text{ MPa}, p_w = 2 \text{ MPa}) \)

### 3.3.3 Mechanically possible pressure

#### 3.3.3.1 The effect of the spatial distribution of the pores

In general, the mechanically possible pressure which could be developed during crystal growth depends on the stiffness of the surrounding medium and on the spatial distribution of the supercritical pores. In order to illustrate the effect of the spatial distribution, let us consider a claystone layer at depth \( H \) below the ground surface (Fig. 3.7a) which contains sparsely distributed supercritical pores (Fig. 3.7b). The expansion of each pore changes the stresses in the surrounding matrix. More specifically, it mobilizes a counterpressure in the radial direction (the radial compressive stress increases), while the tangential stress decreases. With further pore expansion, the tangential stress becomes zero and then negative (tension). When it reaches the tensile strength of the claystone, cracks develop in the radial direction and the tangential stress drops to zero. (Figure 3.7c shows only the horizontal cracks.) Assume for the sake of simplicity that the tensile strength is equal to zero and consider the distribution of the vertical stress in a horizontal cross section through the rock (Fig. 3.7d). For the reasons explained above, the vertical stress will be higher at the locations of the expanding pores and lower (or even zero) in the spaces between the pores. Note that the vertical stress must fulfil equilibrium, \( i.e. \) counterbalance the weight of the overburden, which means that the average vertical stress over the considered section must be equal to the initial stress \( \sigma'_0 \) at the depth of the layer \( (\sigma'_0 = \gamma'_0 \cdot H) \). Pore expansion can only result in a high vertical stress locally if there is a space between the expanding pores where the vertical stress decreases to below the initial stress. This is only possible if the expanding pores are sparsely distributed: For simple equilibrium reasons, gypsum growth in densely spaced pores would occur under a practically constant vertical stress (the initial stress \( \sigma'_0 \)).
Figure 3.7. (a) In situ situation; (b) detail A with indicative distribution of the supercritical pores; (c) detail A with radial cracks due to pore expansion and, (d), corresponding distribution of the vertical stress $\sigma_y$; (e) detail A with tensile failure of the entire matrix between the expanding pores and, (f), corresponding distribution of the vertical stress $\sigma_y$; (g) horizontal cross section

The importance of the pore distribution becomes clearly evident when considering the extreme state of Fig. 3.7e, where the entire area between the expanded pores fails in tension and its vertical stress is equal to zero. In this case, the material in the expanded pores would bear the full weight of the
overburden and, consequently, the local stress would reach its highest possible value \( \sigma'_{\text{max}} \). (Figure 3.7f shows the corresponding stress distribution.) Due to the equilibrium condition in the vertical direction, the average vertical stress over the area of the supercritical pores reads as follows:

\[
\sigma'_{\text{max}} = \frac{F_{\text{tot}}}{F_p} \sigma'_o = \frac{F_{\text{tot}}}{N_p F_p} \sigma'_o,
\]

where \( \sigma'_o \) is the initial stress; \( F_{\text{tot}} \) is the total area of the horizontal cross section (Fig. 3.7g); \( F_p \) is the sum of the areas of the cross sections of the pores; \( N_p \) is the number of pores; and \( F_p \) is the average cross section area of the pores. According to Eq. (3.4), for a given pore size distribution (i.e. for a fixed average area \( F_p \)), the maximum stress increases with a decreasing number of pores or with increasing distances between the pores. Crystal growth in a few sparsely distributed large pores results in the same maximum local stress as crystal growth in many densely distributed small pores: The ratio of the pore distance to the pore size governs the maximum local stress.

Note that in the state of Fig. 3.7e, the rock in the scale of a specimen would be completely fractured, thus resembling granular soil. This does not agree with the actual quality of rock cores from tunnels in Gypsum Keuper. It is reasonable to assume that the stress developing due to crystal growth may involve some cracking, but this should happen only in a limited zone around the expanding pores. The high local stress according to Eq. (3.4) is thus only theoretically possible. The actual stress must be lower than the stress according to Eq. (3.4).

In Section 3.3.3.2, we formulate a simple spherical cavity expansion model for estimating the mechanically possible expansion-induced pressure, while the validity of the underlying simplifying assumptions and the effects of deviations from these will be investigated in Section 3.3.5.

### 3.3.3.2 Simplified spherical cavity expansion model

**Problem layout**

A spherical cavity model obeying spherical symmetry is formulated by taking a rock element (Fig. 3.8a) and introducing the following simplifying assumptions successively:

(i) the pores are spherical (Fig. 3.8b);

(ii) the pores have a uniform radius (Fig. 3.8c);

(iii) the pores are regularly distributed on a grid (Figs. 3.8d, 3.8e) presenting symmetry properties due to which zero displacement boundary conditions apply in the horizontal directions (Fig. 3.8f);

(iv) the prismatic computational domain of Fig. (3.8f) is replaced by a cylindrical domain exhibiting axial symmetry (Fig. 3.8g);
(v) the cylindrical computational domain of Fig. (3.8g) is replaced by a spherical domain. As a boundary condition, a uniform radial pressure (equal to the in situ stress) is prescribed at the outer surface of the sphere (Fig. 3.8h). The system thus exhibits spherical symmetry.

In addition to the spherical model, a rotationally symmetric model for regularly distributed, uniform cylindrical pores will be considered as well.

**Figure 3.8. Successive assumptions for defining the spherical cavity expansion model**

**Boundary conditions**

Selecting the boundary condition at the outer surface of the sphere involves a trade-off. The nature of the simplified boundary condition (assumption (v)) becomes evident when considering the cylindrical model of Fig. (3.8g): For symmetry reasons (Fig. 3.8f), a displacement boundary condition should be applied to its outer boundary in the horizontal direction. In the vertical direction, however, a stress boundary condition is more satisfactory as it takes account of the fact that the vertical stress is limited by the weight of the overburden. Prescribing a displacement boundary condition in the vertical direction of the model in Fig. 3.8h would allow the actual stress to increase unlimitedly. A uniform stress boundary condition (according to the in situ stress at the given depth of the rock specimen) underestimates horizontal stress, but is more satisfactory for the question under investigation because it limits the vertical stress developing during cavity expansion.

The simplified model therefore consists of a hollow thick-walled sphere (or a hollow thick-walled cylinder) with internal and external radii equal to \( r_p \) and \( b_p \), respectively, which is subjected to a uniform radial pressure (in relation to the initial pressure) and also to a gradually increasing, uniform radial displacement of its inner boundary (Fig. 3.9).
Figure 3.9. Cavity expansion model

Radius of the computational domain

As explained in qualitative terms in Section 3.3.3.1, the outer radius $b_p$ (which represents a measure of the distance between the pores, Fig. 3.8f) is important with respect to the stress which is mobilized by the rock as a reaction to the expansion of the growing gypsum crystals in the pores. The radius $b_p$ can be determined from the results of the porosimetry and simple geometric factors. More specifically, for a given porosity $\phi$, the volume of the supercritical pores per unit volume of rock (hereafter referred to as “supercritical porosity”) is equal to $\phi_{cr} = \phi \cdot \pi_{cr}$. Thus, under the assumption of uniform pore size (radius $r_p$) made above, the number $N_p$ of these pores per unit volume is given by the following equation:

$$N_p = \frac{3\phi_{cr}}{(\zeta + 2) \pi r_p^{\zeta+1}},$$  

(3.5)

where $\zeta$ denotes the type of cavity, being equal to one ($\zeta = 1$) for cylindrical cavities and equal to two ($\zeta = 2$) for spherical ones. (The variable $\zeta$, which allows the simultaneous treatment of two- and three-dimensional problems, is encountered frequently in the literature – cf. Yu 2000.) On the other hand, for the regular arrangement of cylindrical or spherical pores on a square or on a cubic grid, respectively (Fig. 3.10a), the number of pores per unit volume is equal to

$$N_p = \frac{1}{(2b_p)^{\zeta+1}}.$$  

(3.6)

From Eqs. (3.5) and (3.6) we obtain:

$$\frac{b_p}{r_p} = \left[ \frac{(\zeta + 2) \pi}{3 \cdot 2^{\zeta+1} \cdot \phi_{cr}} \right]^{\frac{1}{\zeta+1}}.$$  

(3.7)
As an alternative to the square or cubic arrangement of Fig. 3.8d-e, the densest sphere or cylinder packing may also be considered, according to which the contact points of the cylindrical or spherical domains form equilateral triangles in 2D and equilateral tetrahedrons in 3D, respectively (Fig. 3.10b). Taking the porosity of the densest packing into account (Gauss 1831), the number of pores per unit volume becomes

\[ N_p = \frac{1}{2\zeta \sqrt{4-\zeta} \cdot b_p^{\zeta+1}}, \]  

which in combination with Eq. (3.5) yields:

\[ \frac{b_p}{r_p} = \left[ \frac{(\zeta + 2)\pi}{6\zeta \sqrt{4-\zeta} \cdot \phi_{cr}} \right]^{\frac{1}{\zeta+1}}. \]  

According to Eqs. (3.9) and (3.7), the ratio between the outer radius \( b_p \) and the pore radius \( r_p \) depends only on the supercritical porosity \( \phi_{cr} \) and on the type of the pores. Figure 3.11a shows the normalized outer radius \( b_p/r_p \) as a function of the supercritical porosity for cylindrical or spherical pores and for the two considered arrangements (quadratic grid or densest packing).

**Figure 3.10.** Cylindrical pores: (a) quadratic grid and, (b), densest packing
Material behaviour

The rock around the expanding cavity is considered as a linearly elastic material which is brittle under tension, i.e. the stress drops suddenly to zero after reaching the tensile strength $f_t$. This model includes the special case of a no-tension material. For simplicity, the compressive strength of the rock and the possibility of an inner crushed zone (see Ladanyi, 1967) are ignored.

Stress analysis

The problem defined above can be solved analytically. The complete derivation and the closed-form expressions including the pressure-displacement relationships can be found in Appendix A1. The stress analysis considers a constant pore water pressure. According to Eq. (A28) (where the stresses $\sigma_{a,\text{max}}$ and $\sigma_0$ have been replaced by $p_{p,\text{max}} - p_w$ and the $p_{S,0} - p_w$, respectively), the following
relationship applies for the mechanically possible pressure \( p_{p,\text{max}} \) which can be developed during pore expansion:

\[
p_{p,\text{max}} = \left( \frac{b_p}{r_p} \right)^{\zeta} \left( p_{S,0} - p_w \right) + p_w.
\]  (3.10)

This equation leads, in combination with Eqs. (3.7) and (3.9), to the following relationships for the mechanically possible pressure in the case of the cubic or of the densest arrangement, respectively:

\[
p_{p,\text{max}} = \left[ \frac{(\zeta + 2) \pi}{3 \cdot 2^{\zeta+1}} \phi_{cr} \right]^{\frac{\zeta}{2^{\zeta+1}}} \left( p_{S,0} - p_w \right) + p_w,
\]  (3.11)

\[
p_{p,\text{max}} = \left[ \frac{(\zeta + 2) \pi}{6 \zeta \sqrt{4 - \zeta}} \phi_{cr} \right]^{\frac{\zeta}{4 - \zeta}} \left( p_{S,0} - p_w \right) + p_w.
\]  (3.12)

According to these equations, the mechanically possible pressure depends on the initial pressure (linearly), the pore water pressure, the supercritical porosity and on type of pores. It is independent from the radius \( r_p \) of the supercritical pores. Figure 3.11b shows the normalized mechanically possible pressure as a function of the supercritical porosity, assuming atmospheric pore water pressure, i.e. \( p_w = 0 \). The highest pressures develop, as expected, in the case of spherical pores (\( \zeta = 2 \)). The influence of the grid type (cubic or densest packing) is rather small. The lower the supercritical porosity, the higher will be the mechanically possible pressure. At supercritical porosities lower than 5%, the mechanically possible pressure may be higher than the far field stress by a factor of 5 – 15.

It should be noted that Eq. (3.10) gives an upper bound for the mechanically possible pressure as it presupposes tensile failure of the entire rock between the expanding pores, which does not agree with the observations. The mechanically possible pressure that can be developed in the more general and realistic case of partial failure of the rock can be determined by using Eqs. (A26) and (A27). By neglecting the tensile strength of the rock (i.e. \( f_t = 0 \)) and once again replacing the stresses similar with above (cf. Eq. 3.10), we obtain:

\[
p_p = \frac{(\zeta + 1) \left( b_p / r_p \right)^{\zeta+1}}{\zeta \left[ 1 + \lambda \left( b_p / r_p - 1 \right) \right]^{\zeta+1}} + \left( b_p / r_p \right)^{\zeta+1} \left( p_{S,0} - p_w \right) + p_w,
\]  (3.13)

where \( \lambda \) denotes the percentage of the cracked region around the pores (Fig. 3.9):

\[
\lambda = \frac{\rho - r_p}{b_p - r_p}.
\]  (3.14)

The values of the parameter \( \lambda \) lie between 0 and 1, with \( \lambda = 0 \) denoting the elasticity limit (where the tangential stress becomes equal to zero just at the pore wall and only there), while \( \lambda = 1 \) means that the entire rock between the pores has failed. Obviously, Eq. (3.13) simplifies to Eq. (3.10) for \( \lambda = 1 \).
remarks made above with respect to the factors influencing the mechanically possible pressure remain valid. It is worth mentioning that the pressure developing for a given extent of the failed zone does not depend on the elastic material properties. Figure 3.11c shows the effect of the parameter $\lambda$ on the normalized actual pressure for the case of a cubic grid (for $p_{W} = 0$). The actual pressure already reaches a multiple of the effective initial solid pressure at a failure point of $\lambda = 0.40$.

In order to obtain an indication as to the expansion associated with the development of these pressures, we consider the case of spherical pores ($\zeta = 2$) on a cubic grid. The displacement at the mechanically possible pressure $p_{p,\max}$, while assuming a zero tensile strength is obtained from Eq. (A30) (for $f_{t} = 0$):

$$u_{p} = \frac{P_{S,0} - p_{W}}{E} \left[ b_{p} / r_{p} \left( b_{p} / r_{p} - 1 + v \right) + 1 - 2v \right].$$

(3.15)

Taking Eq. (3.7) into account as well, we can express the normalized pore expansion as a function of the supercritical porosity (Fig. 3.11d).

### 3.3.4 Application to the Belchen and the Chienberg Tunnel

The models presented above will be applied in relation to the data from the Belchen Tunnel and the Chienberg Tunnel in order to investigate whether the high pressure hypothesis might explain the presence of anhydrite at shallow depths of cover.

#### Necessary pore expansion

As explained in Section 3.3.1, an initial condition for the validity of the high pressure hypothesis is that a minor pore expansion will be sufficient for mobilising expansion-induced pressure. We will see here that this condition is fulfilled in the present case. According to Eq. (3.15) the expansion which is needed in order to mobilize the mechanically possible pressure increases with an increasing in situ initial solid pressure $P_{S,0}$ and with a decreasing Young’s modulus $E$ of the rock. Consequently, an upper boundary for the necessary expansion can be obtained by assuming a high in situ solid pressure $P_{S,0}$ in combination with a low pore pressure and a low Young’s modulus $E$.

The Young’s modulus $E$ of the matrix is generally difficult to define due to the heterogeneity and anisotropy of the rock. Amann (2012) performed several uniaxial and triaxial compression tests on samples from the Belchen Tunnel. He measured values from 2 up to 85 GPa, depending on the composition and the orientation of the samples. Furthermore, according to more than 120 XRD-analyses on the core samples, it was shown that the clay content in most cases was greater than $10 – 15\%$ (and up to nearly $50\%$). Layers with lower clay content ($7 – 9 \%$) were also observed, but only at distances of a few meters and in a finite number of locations. The elastic moduli of these layers, which were greater than 50 GPa, are therefore not meaningful for the question under
investigation. The elastic moduli of the samples with a representative clay content lie within the range of \( E = 5 - 38 \) GPa. Moreover, according to Chiaverio (2012), the maximum Young’s modulus, as derived from several uniaxial compression tests including samples from the Belchen Tunnel, was \( E = 16 \) GPa. In the case of the Adler Tunnel the values lie in the range of \( E = 9 - 20 \) GPa, while tests performed on samples from the Chienberg Tunnel show a minimum modulus of \( E = 14 \) GPa (Chiaverio 2012). Taking all of these experimental results into consideration, a value of 2 GPa can be accepted as a lower bound of the Young’s modulus \( E \).

This value of \( E \) leads in combination with a normalized pore expansion \( (E_u/E_p_\text{up}/(p_{S,0} - p_W)r_p) \) of about 10 (Fig. 3.11d) and a high in situ stress of 7.5 MPa (corresponding to a depth of cover of about 300 m, cf. Table 3.1, and to the lowest possible pore pressure, i.e. atmospheric) to an expansion \( u_p/r_p \) of about 4%. In conclusion, even under the extreme assumptions made, the expansion which must occur in order to mobilize the mechanically possible pressure is in the range of only a few percent.

In the following we will focus on the second condition: Do the mechanically possible pressure and the pore water pressure reach the solid pressure that is required in order for anhydrite to represent the thermodynamically stable phase? The required solid pressure will be estimated according to Section 3.3.3 by neglecting solid-liquid interfacial effects (i.e. \( \gamma_G/r_G = 0 \)), which is reasonable in view of the size of the supercritical pores (several 100s nm, Fig. 3.4). The mechanically possible pressure will be determined from the simplified spherical cavity expansion model in Section 3.3.3.2, which also reproduces the average stress response of the pores, as will be shown in Section 3.3.5.

**Chienberg Tunnel**

Let us consider the pore size distribution of the Chienberg sample with porosity \( \phi = 4.75 \% \) (Fig. 3.4). For a water activity \( a_w = 1 \) the critical pore radius \( r_{cr} \) is equal to 9 nm (Eq. 3.2), which corresponds to a critical pore percentage \( \pi_{cr} = 96 \% \). With a square lattice arrangement of the pores, the mechanically possible pressure becomes \( p_{p,max} = p_p(\lambda = 1) = 4.3 \) MPa (cf. Eq. 3.11). Repeating this process for several water activity values, we obtain the pressure \( p_p(\lambda = 1) \) as a function of the water activity (Fig. 3.12a). This calculation is performed up to a water activity of 0.69. As will be shown in Section 3.4, this value corresponds to the equilibrium water activity \( a_{W,eq,0} \), i.e. the water activity at which anhydrite and gypsum co-exist in the system. Below this value, anhydrite will be the stable mineral.

According to Fig. 3.12a, the mechanically possible pressure increases with decreasing water activity, because the lower the water activity, the greater will be the critical pore radius, the lower will be the supercritical porosity and the greater will be the distances between the supercritical pores.

Figure 3.12a additionally shows the lower bound of the required pressure \( p_{req,LB} \) according to Eq. (3.3a) as a function of the water activity. Anhydrite will be stable if the mechanically possible pressure and the pore water pressure are higher than \( p_{req,LB} \). It is evident that this is only true at water activities below 0.755, which is only slightly higher than the equilibrium water activity of \( a_{W,eq,0} = 0.69 \). This
means that the pressures developing locally due to gypsum growth have a minor effect and in any case are not sufficiently high to prevent gypsum growth. The high pressure hypothesis fails to explain the presence of anhydrite under the small depth of cover of the Chienberg project area. If we had considered an upper bound for the required pressure $p_{\text{req.UB}}$, Eq. (3.3b) would apply, leading to even lower water activities, as in this case the required pressure is even higher (cf. Fig. 3.6).

Figure 3.12. Mechanically possible pressure (according to the simplified cavity expansion model) and required pressure as a function of water activity, (a), for the Chienberg Tunnel and, (b), for the Belchen Tunnel

Belchen Tunnel

We follow the same approach for the anhydritic claystones of the Belchen Tunnel, with a pore size distribution according to the upper Belchen curve of Fig. 3.4, which corresponds to a porosity $\phi = 5.65\%$. Figure 3.12b shows both of the required pressures $p_{\text{req.LB}}$ and $p_{\text{req.UB}}$, the mechanically possible pressure $p_p (\lambda = 1)$ (i.e. the pressure developing after tensile failure of the entire rock around the pore) and the pressure developing if $\lambda = 0.5$, i.e. if the cracked zone around each pore extends to a quarter of the distance between them.
On the one hand, Fig. 3.12b clearly shows that the maximum mechanically possible pressure exceeds the lower bound of the required pressure, even when assuming a water activity of unity and only a partial failure of the rock around the expanding pore ($\lambda = 0.5$). This means that the high pressure hypothesis would fully explain the presence of anhydrite in this case. The reason for this is the very large percentage of small pores in the claystones of Belchen, a consequence of which is a low supercritical porosity and rather high distances between the supercritical pores, thus allowing the local pressures to develop which are considerably higher than in the case of Chienberg (compare the two diagrams of Fig. 3.12). On the other hand, however, where gypsum and anhydrite particles experience the same pressure, anhydrite is stable for water activities below 0.885 for $\lambda = 1$ and 0.863 for $\lambda = 0.5$ (Fig. 3.12b). This leads to the conclusion that the high pressure hypothesis is not sufficient to explain the presence of anhydrite by itself. Nonetheless, one should bear in mind that as the two cases (lower and upper bound) constitute borderlines, the most likely situation in reality will be somewhere between these two.

### 3.3.5 Limitations of the simplified model

#### 3.3.5.1 Introduction

The current section investigates the adequacy of the simplified spherical cavity expansion model and the effects of deviations from the underlying simplifying assumptions. The successive approximations presented in Fig. 3.8 are examined here in detail through numerical calculations, following an inverse course from the last step (Fig. 3.8h) to the first step (Fig. 3.8b). More specifically, spherical symmetry idealization (Fig. 3.8h), the regular arrangement of the pores (Fig. 3.8d) and the assumption of a uniform radius (Fig. 3.8c) are investigated in the Sections 3.3.5.2, 3.3.5.3 and 3.3.5.4, respectively. It should also be noted, that the assumption of a spherical shape for the pores (Fig. 3.8b) is in itself an idealization. In fact, the pores neither possess a specific smooth shape nor constitute individual entities within the ground matrix. On the contrary, they form a complex network without any regularity. Nevertheless, the conclusions derived may be qualitatively extended to more complicated geometric structures.

#### 3.3.5.2 Deviation from spherical symmetry

**Numerical model**

This Section considers a regular grid (as in the simplified spherical cavity expansion model) but does not assume spherical symmetry or uniform far field boundary conditions. The predictions of the spherical cavity expansion model (Fig. 3.8h) will be compared with the results of numerical analyses of the axisymmetric model of Fig. 3.8g. Making use of the symmetry properties of the problem, a quarter of the cylindrical rock column is considered, with three equally spaced spherical cavities in the vertical direction. Parametric studies have confirmed that the number of cavities does not affect the
results. Figure 3.13 shows the computational domain. The initial solid stresses are equal to $\sigma_0 = 2.5$ MPa and remain constant. The nodes of the cylindrical surface are fixed in the horizontal direction. At the upper boundary of the model, the stress is kept constant and equal to its initial value. The expansion of the pores is induced numerically through a fictitious temperature increase. In order to obtain a uniform expansion, the Young’s modulus of the pore material is taken $10^3$ times higher than the modulus of the rock matrix. The rock is considered as a no-tension, linearly elastic material with the Young’s modulus $E = 5000$ MPa and the Poisson’s ratio $\nu = 0.30$. All numerical analyses were performed with the finite element code Abaqus (Dassault Systèmes 2011).

**Figure 3.13. Axisymmetric computational model**

**Numerical results**

Figure 3.14a shows the typical distribution of the vertical stresses developing along a horizontal section through the sphere centres at a cavity expansion of $E \cdot u_p/r_p = 12$ MPa for two pore spacings ($b_p/r_p = 6$ or $b_p/r_p = 3$). The stress is seen to be higher in the case of the larger pore spacing. Fig. 3.14b shows the stress distribution at a greater expansion ($E \cdot u_p/r_p = 18$ MPa). The developing stress is higher than before. For closely spaced pores ($b_p/r_p = 3$), the entire rock between the pores fails in tension. For a comparison with the predictions of the simplified spherical expansion model (Section 3.3.4.2), we take the average vertical stress at the horizontal equator plane of each sphere, estimated as follows:
\[
\bar{\sigma}_y = \frac{2}{r_p^2} \int_0^{r_p} \sigma_y r dr \approx \frac{2}{r_p^2} \sum_{i=1}^{N} \sigma_{y,i} r_i t_i, 
\]

(3.16)

where \(N\) is the number of points on the horizontal surface at which the vertical stress \(\sigma_y\) is evaluated, \(r\) represents the radius and \(t\) corresponds to the interval of influence (of each point) in the \(x\) direction.

Figure 3.15a and 3.15b show (for \(b_p/r_p = 3\) and \(b_p/r_p = 6\), respectively) actual stress as a function of cavity expansion according to the numerical analysis in the present Section (marked by circles) and the analytical solution in Section 3.3.3.2 (solid curves). The predictions of the simplified cavity expansion model agree well with the numerical results. The assumption of spherical symmetry is thus adequate.

Figure 3.14. Distribution of the vertical stresses \(\sigma_y\) along a horizontal section of the model for (a) \(E_u/r_p = 12\) and, (b), \(E_u/r_p = 18\). (The absolute values of \(r\) are irrelevant.)
Figure 3.15. Normalized cavity expansion curves for (a) \( b_p/r_p = 3 \) and, (b), \( b_p/r_p = 6 \) (in the numerical results, the stress \( \sigma_p \) is taken equal to the average vertical stress at the horizontal equator plane of the sphere)

3.3.5.3 Random spatial distribution of the pores

Numerical model

This Section assumes a uniform pore size (as in the previous Section) but does not assume that the pore grid is regular. As indicated by Fig. 3.8c, even if all the pores have the same radius \( r_p \), some of them may be close to each other, while others are isolated. Therefore, keeping Eq. (3.10) in mind, the actual maximum stress should be different for every pore. The three-dimensional numerical treatment of the problem is very time consuming with respect to pre-processing (mesh generation), finite element analysis and post-processing (interpretation of the results). Hence, a two-dimensional approach is adopted here (\( \zeta = 1 \)) for cylindrical pores under plane strain conditions. The results and conclusions derived can be extended to three-dimensions.
The numerical example of the present Section takes account of the lower porosimetric curve of the Belchen Tunnel (curve for $\phi = 7.19\%$ in Fig. 3.4, solid line in Fig. 3.16), which is the most favourable one for the high pressure hypothesis. For a water activity $a_w = 0.9$, the critical radius is $r_{cr} = 13.15$ nm (according to Eq. 3.2), which in combination with the porosimetric curve of Fig. 3.16 leads to $\bar{n}_{cr} \approx 20\%$. The numerical calculations have been carried out for a constant pore radius of 30 nm. (The dashed line ABCD in Fig. 3.16 represents the idealized porosimetric curve in the supercritical range.) With these assumptions, the number of pores per unit volume of rock can be calculated based upon Eq. (3.5) and amounts to 5.12 pores / $\mu m^2$ for the present example. The computational model for the investigation of the stress developing around the irregularly distributed, expanding pores consists of a square domain. Its side length $L_s$ is taken equal to 4.8 $\mu m$ (as big as in the numerical example of the next Section, where two different pore sizes are accounted for). This results in a total of 118 pores placed randomly inside the square domain with the aid of a uniform probability distribution function. Two restraints are applied during the placement of the pores in order to avoid intersecting or extremely closely spaced pores: the distance between the centre of a new pore and the centre of each existing one as well as the vertical distance between the centre of a new pore and each boundary surface should be greater than the diameter of the pores. Figure 3.17 shows the locations of the pores and the boundary conditions as well as a detail of the triangular finite element mesh of the model. The initial stress field is assumed to be isotropic and uniform (stress $\sigma_0$). The same material constants were taken as in the last Section. The expansion of the pores is induced exactly as in the previous axisymmetric numerical example by means of a fictitious in-plane thermal expansion.

Figure 3.16. Pore size distribution for the Belchen Tunnel (from Fig. 3.4, curve for $\phi = 7.19\%$ and idealization of uniform supercritical pores (dashed line ABCD)
Numerical results

For a comparison with the predictions of the simplified cavity expansion model in Section 3.3.3.2, we take the average minimum principal stress $\bar{\sigma}$ in each pore, which is calculated as follows:

$$\bar{\sigma} = \frac{1}{\pi r_p^2} \sum_{i=1}^{N} \sigma_i A_i$$  \hspace{1cm} (3.17)

where $N$ denotes the number of triangular finite elements within a pore, $\sigma$ represents the minimum principal stress at the integration point (centroid) of each finite element (note that linear finite elements are used) and $A$ corresponds to the area of each finite element.

Figure 3.18 shows the results of one simulation with 118 pores. Each thin curve corresponds to a pore and shows its minimum principal stress (averaged over the pore volume) as a function of expansion. The stress response exhibits a large scatter. Nevertheless, it is interesting that the simplified model in Section 3.3.3.2 (curves “s” and “t” in Fig. 3.18 apply to the distributions of Fig. 3.10a and 3.10b, respectively) predicts the average of all pores satisfactorily (curve “a” in Fig. 3.18). The reasons for the large scatter of the stress response can be explained by taking two specific pores (denoted by A and B in Fig. 3.17): The expansion of pore A generates a high stress locally, because this pore is far away from other pores; on the other hand, the stress is low in the case of pore B, because this pore forms a cluster with other pores.

In summary, the prediction of the simplified model agrees very well with the average for the numerical predictions. However, there are always pores which develop stresses much lower than the average value. As we will see later (Section 3.3.5.5), this is significant for the question under investigation.
Figure 3.18. Minimum principal in-plane stress as a function of the normalized cavity expansion for the 118 pores in the model of Fig. 3.17

3.3.5.4 Non-uniform pore size

Numerical model

The aforementioned process can be extended to include pores of several sizes. More specifically, in the general case of \( m \) discrete supercritical pore radii arranged in descending order, i.e. \( r_{p,1} > \ldots > r_{p,i} > \ldots > r_{p,m} (> r_{\text{crit}}) \), the number \( N_{p,i} \) of the pores with a specific radius \( r_{p,i} \) per unit volume is given (similarly to Eq. 3.5) by:

\[
N_{p,i} = \frac{3 \cdot \phi_{\text{v}} \cdot \Delta \bar{\pi}_i}{(\zeta + 2) \cdot \pi \cdot r_{p,i}^{\zeta+1}}, \tag{3.18}
\]

where the difference

\[
\Delta \bar{\pi}_i = \frac{\bar{\pi}_{i+1} - \bar{\pi}_{i-1}}{2}, \tag{3.19}
\]

with \( \pi_{m+1} = 2 - \pi_{m} \) and \( \bar{\pi}_0 = -\bar{\pi}_1 \).

In the numerical calculations of the present Section, the same data as in the previous example are used. The dashed line in Fig. 3.19 shows the idealized pore size distribution. Supercritical pores with radius equal to 200 nm are assumed in addition to the 30 nm large pores of the last Section.

One effect which does not appear in the case of uniform pores and which leads to highly different stresses around the pores is that large expanding pores (pore 1 in Fig. 3.20) do not allow small pores (pore 2 in Fig. 3.20) to develop a high stress because they produce radial cracks, causing the stress in the tangential direction (t-t in Fig. 3.20) to drop to zero. An expanding small pore thus increases the radial stress in its vicinity only as long as it is outside the cracked zone of a larger pore. In order to
illustrate this effect with the simplest possible model, we consider an example with just one large pore. The side length $L_s$ of the square domain is calculated by means of Eq. (3.24) so that one supercritical pore with radius equal to 200 nm fits within the square domain, which leads to the value of $L_s = 4.8 \, \mu m$. The number of pores with a radius of 30 nm can then be determined by using the same equation, providing a total of 74 pores. This number is smaller than before (118 pores), because some of the supercritical porosity (which is the same as in the last Section) is provided by the large pores. Figure 3.21a shows the pores generated and Fig. 3.21b the corresponding numerical model.

Figure 3.19. Pore size distribution for the Belchen Tunnel (from Fig. 3.4, curve for $\phi = 7.19 \%$ and idealization by supercritical pores of two radii (dashed line)

Figure 3.20. Presence of a small supercritical pore (2) within the cracked zone that is formed around a larger pore (1) during its expansion
Numerical results

The numerical results are processed in the same way as before (Fig. 3.22). It can be confirmed again that the stress exhibits a large scatter but the simplified cavity expansion model (curves “s” and “t”) agrees well with the average stress of all pores (curve “a”). For reasons explained before, none of the small pores around the large pore (and also the relatively remote pore B, Fig. 3.21, for example) can develop a high stress. On the other hand, the stresses are high in small pores which are isolated and outside the cracked zone of larger supercritical pores (e.g. pore A, Fig. 3.21).

As the pore placement process was probabilistic, 50 different models were analysed using the same parameters as above, leading to a sample of 3750 pores. An appropriate code was developed to automate the process, calling Abaqus software externally during the algorithm to perform the static numerical analyses. Figure 3.23a shows the resulting probability density function, while Fig. 3.23b depicts the corresponding cumulative distribution function for the minimum principal in-plane stresses at an expansion of 2%. For comparison, the diagrams include the stresses according to the simplified cavity expansion model.

In summary, the prediction of the simplified model also agrees well in this case with the average from the numerical predictions. Nevertheless, there are pores which cannot develop stresses much higher than the existing \textit{in situ} values, irrespective of the level of expansion or the progress of crystal growth.
Figure 3.22. Minimum principal in-plane stress as a function of normalized cavity expansion for the 75 pores of the model of Fig. 3.21

Figure 3.23. (a) Probability density and, (b), cumulative distribution function for the minimum principal in-plane stress at an expansion of $\mu_{0}/r_p = 2\%$ (3750 pores, 50 simulations)
### 3.3.5.5 Discussion

The numerical calculations showed the presence of a smaller or larger number of pores around which the developed stresses are much lower than the average stress (cf. Figs. 3.18, 3.22 and 3.23). The presence of even a few pores with pressure lower than the required solid pressure would be sufficient for all of the anhydrite to transform into gypsum. The reason for this is exactly the same as in Section 3.2.3, where it was explained that the presence of even a small number of supercritical pores is enough for the entire transformation of anhydrite to gypsum. The subcritical pores of Section 3.2.3 correspond to the pores in the present case which reach the required pressure during crystal growth, while the supercritical pores correspond to the pores where local pressure remains insufficiently low and gypsum continues to grow. In the present case, ions would diffuse from the pores that reach the required pressure towards the pores with lower local stresses. This calls into doubt the validity of the high pressure hypothesis: The hypothesis would explain the presence of anhydrite at shallow depths only for extremely fine-porous anhydritic rocks, and only under the unrealistic assumption of poorly graded and uniformly distributed pores.

### 3.4 The low water activity hypothesis

As shown in Chapter 2, a low water activity favours anhydrite as the stable phase. In order to estimate the water activity values at which anhydrite would represent the stable mineral at the depths and temperatures concerned we apply the thermodynamic model of Chapter 2 and in particular Eq. (2.36). The underlying assumptions of these equations are that porosity is very low, the solid pressures of anhydrite and gypsum are equal to the lithostatic pressure $p_{S,0}$ (i.e. $p_G = p_A = p_{S,0}$) and the solid-liquid interfacial effects are neglected. The water activity at which anhydrite and gypsum co-exist in a system reads as follows:

$$\left(\frac{\Delta r_{G,A} G^0 + \left(T_0 - T\right) \Delta r_{G,A} S^0 + \left(V_G^0 - V_A^0\right) p_{S,0} - 2V_w^0 P_w}{2RT}\right).$$

(3.20)

Anhydrite is stable if the water activity is lower than the one given by Eq. (3.20). Figure 3.24 shows the equilibrium water activity as a function of the temperature for two depths of cover ($H = 50$ m and $300$ m), assuming that total stress and pore pressure increase linearly with the depth $H$. In the relevant temperature range, the equilibrium water activity varies between $a_{W,eq} = 0.69 - 0.84$. Such low water activities might occur either due to high levels of dissolved ions in the pore water or due to interaction between the pore water and the clay minerals. Mineralogical analyses of water from the Gypsum Keuper show, however, that the actual ionic concentration is far too low to explain water activities as low as $0.70 - 0.80$ (cf. Section 2.2.3.4). The remainder of the present Section therefore deals with the second hypothesis. As discussed below, this scenario is entirely possible.
An assumption that the activity of the pore water is associated with its potential $\Psi$ according to Eq. (2.15) and Eq. (3.20) leads to the following expression for the potential at the anhydrite-gypsum equilibrium:

$$\Psi_{eq} = \frac{A_{G,G}G^0}{2\nu^0} + (T_0 - T)A_{G,G}S^0 + \left(\nu_0^G - \nu_1^G\right)\sigma_{WS,0} - P_w.$$  

(3.21)

According to this equation, the equilibrium potential $\Psi$ varies between -50 MPa and -25 MPa in the relevant depth and temperature range. Anhydrite would be stable under the conditions prevailing before tunnel excavation, provided the in situ pore water potential $\Psi_0$ is lower than the equilibrium potential, i.e. -50 to -25 MPa. It is well known from the literature that pore water in claystones often exhibits potentials as low as these, or very low activity values. Alonso and Olivella (2008), for example, measured potential values as low as -40 to -20 MPa by means of a transistor psychrometer (cf. Woodburn et al. 1993). Other studies supporting the hypothesis of very low water potential or activity values include those of Mitaritonna et al. (2009), Mohajerani et al. (2012) and Zhang et al. (2012).

At the same time, there is a possible objection to the low pore water potential argument. The case might be made that such high negative values for the water potential imply unrealistically high swelling pressures in the claystones: as shown by Anagnostou (1993) based upon the principle of effective stress in its classic form ($\sigma' = \sigma - (\Psi' + p_w)$), the so-called maximum swelling pressure $\sigma_s$, i.e. the pressure developing in a laboratory test while preventing the development of swelling strain (a so-called ‘‘swelling pressure’’ test after ISRM, 1999) is equal to the effective stress $\sigma'_0$ prevailing in situ, i.e. $\sigma_s = \sigma_0 - (\Psi'_0 + p_{w,0})$, where $\sigma_0$ and $(\Psi'_0 + p_{w,0})$ denote the in situ total stress and the in situ water pressure, respectively.

According to the principle of effective stress in its classic form, a change in $\Psi$ or $p_w$ is as effective (with respect to the mechanical response) as a change of the total stress, i.e. the effective stress $\sigma' = \sigma - (\Psi + p_w)$. Under ideal conditions, the sampling and specimen preparation for a swelling test should not alter the water content of the specimen (no
anhydrite in gypsum keuper at shallow depths

$situ$ total potential of the pore water, respectively. In this case, an $in\ situ$ pore water potential $\Psi_0$ of -25 to -50 MPa would lead to swelling pressure of more than 25 MPa. The fact that this value is much higher than the swelling pressures measured in oedometer tests on claystones (typically 1 – 3 MPa, cf. Anagnostou 1991) might be taken as evidence that the low water activity assumption is wrong.

The argument outlined above is not correct, however, as the measured swelling pressures $\sigma_s$ can indeed be lower than the value corresponding to the $in\ situ$ pore water potential $-\Psi_0$. In order to explain this, let us consider how swelling strain develops when water activity increases from extremely low values to 1. Figure 3.25 is based upon Mering (1946), who investigated the swelling of montmorillonite (a clay mineral exhibiting both osmotic and intracrystalline swelling$^4$) over the entire intracrystalline and osmotic range, and showed swelling strain schematically (normalized by its final value) as a function of water activity. Mering (1946) noticed that up to a water activity $\alpha_W$ of 0.90, i.e. in the range of extremely high negative values for the pore water potential $\Psi$, the volume of the particles increases significantly due to water absorption, but this occurs at the expense of the pore space and does not result in macroscopic swelling. In the next stage (0.9 < $\alpha_W$ < 0.96), the distance of the clay platelets slightly increases, resulting in clay swelling, which is nevertheless relatively moderate. About 30% of the swelling strain occurs in this intracrystalline phase (Fig. 3.25). The largest portion of the swelling strain occurs in the last (osmotic) stage, when the water activity rises above 0.96 (cf. also Norrish and Quirk 1954, Devineau et al. 2006, Boidin et al. 2009, Bihannic et al. 2009).

As changes in the total potential $\Psi + p_W$ during intracrystalline swelling at very low water activities do not result in any relevant strain, a possible interpretation of the behaviour illustrated in Fig. 3.25 is that these changes are not effective in the sense of Terzaghi, i.e. that they do not produce strains to the same extent that a change in the total stress $\sigma$ does. This can be expressed mathematically by taking the effective stress equal to $\sigma' = \sigma - b(\Psi + p_W)$, where the coefficient $b$, which governs the extent to

wetting or drying). This, in combination with the fact that the stress change induced by the sampling (complete unloading) does not involve shearing, means that the strains induced by sampling are negligible. In addition to this, the conditions of a swelling pressure test are by definition such that no strains develop. In conclusion, the entire process of sampling and testing takes place under practically zero strain conditions. According to the principle of effective stress, this means that the effective stress at the end of a swelling pressure test $\sigma'_i$ is equal to the initial, $in\ situ$ effective stress $\sigma'_0$, i.e. $\sigma'_i = \sigma'_0 - (\Psi_0 + p_{W,0})$. At the end of the swelling pressure test, the total stress $\sigma_i$ is (by definition) equal to the maximum swelling pressure $\sigma_s$, while the total potential $(\Psi_i + p_{W,i})$ of the water is equal to zero, because the pore water is in equilibrium with the free water outside the specimen. Consequently, $\sigma'_i = \sigma_i - (\Psi_i + p_{W,i}) = \sigma_s$ and, since, as explained before, $\sigma'_i = \sigma'_0$, the swelling pressure $\sigma_s = \sigma'_0 = \sigma_0 - (\Psi_0 + p_{W,0})$, i.e. the maximum swelling pressure $\sigma_s$ is equal to the in situ effective stress $\sigma'_0$.

Concerning the distinction between intracrystalline swelling and the osmotic swelling see, e.g., Madsen and Müller-Vonmoos (1989). In intracrystalline swelling, which occurs at low water activities, water dipoles and ions are incorporated in the clay platelets or in the first layers of water dipoles around the platelets. The hydration of the interlamellar spaces results in an increase of the clay platelet distance. In osmotic swelling, which occurs at higher water activities, water dipoles and ions are incorporated in the diffuse double layer around the clay platelets due to electrostatic interactions between them.
which a change in the total potential $\Psi + p_W$ is effective with respect to the macroscopic strain, would be close to unity at high activities and close to zero at very high negative values for the pore water potential $\Psi$. In this case, the maximum swelling pressure would be equal to $\sigma'_s = \sigma^*_o - b(\Psi^*_o + p^*_w)$, which means that the swelling pressure is considerably smaller than $-\Psi^*_o$.

A second possible interpretation of the behaviour in Fig. 3.25 is that the principle of effective stress is valid in its classic form (i.e. $\sigma' = \sigma - (\Psi + p_w)$), but the dependency of strain on effective stress is highly nonlinear, characterized by an extremely high stiffness under the high compressive effective stresses that prevail at low water activities. (Note that, according to Fig. 3.25, a change in water activity from 0.70 to 0.90 does not result in relevant strain despite the large change in effective stress of $\Delta \sigma' = -\Delta \Psi = 34$ MPa.) In this case too, the measured swelling pressure would be considerably smaller than $-\Psi^*_o$, because the common oedometric devices unavoidably allow some strain to occur due to their stiffness and to the positioning of the dial gauges (cf. Appendix B).

The first interpretation seems to be more convincing, as it additionally has a theoretical foundation: Coussy et al. (1999) formulated a poromechanical model with a non-constant coefficient $b$, which accounts for the interactions between the clay platelets according to the electric double layer theory\(^5\).

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\(^5\) The double layer theory considers a simplified one-dimensional setting of two parallel clay particles (cf. Israelachvilli 2011) and was used by Madsen (1976) in his theoretical treatment of the relationship between swelling pressure and swelling strain in Opalinus clay. As the clay platelets are negatively charged, they attract the cations of the dissolved salt, while at the same time pushing the anions away. The local concentration of anions close to the particles is thus considerably smaller than that far away, leading to a potential difference across the double layer.
They showed that the stronger these interactions are (i.e. the lower the water activity $a_W$), the lower will be the value of $b$ and consequently the more pronounced will be the deviation from Terzaghi’s original principle of effective stress; for an ideal pore solution (i.e. for $a_W = 1$) $b = 1$, while for non-ideal solutions (i.e. for $a_W < 1$) $b < 1$.

However, regardless of which interpretation of the behaviour in Fig. 3.25 is true (deviation from Terzaghi’s principle of effective stress vs. a highly nonlinear effective stress – strain relationship), both interpretations lead – for different reasons – to the same conclusion: the occurrence of very high negative $\Psi_0$ – values in situ, which is a prerequisite for the low water activity hypothesis, is not excluded by the fact that the measured swelling pressures of claystones are relatively moderate.

## 3.5 Conclusions

Based on the thermodynamic model developed in Chapter 2, an attempt was made to explain quantitatively the occurrence of anhydrite in Gypsum Keuper at low depths prior to tunnel excavation. Three effects were quantitatively investigated: the size of the pores; the local stresses generated due to gypsum growth in the pores; the thermodynamic state of water in the presence of the clay phase.

In order to determine the role of the pore size of anhydritic claystones, MIP experiments were performed on samples from the Gypsum Keuper. Natural anhydritic rocks were found to contain not only extremely small pores, where anhydrite would be stable and gypsum growth thermodynamically impossible, but also larger pores, where gypsum would precipitate, thus sustaining a process of anhydrite dissolution and ionic diffusion from the small pores to the large pores. The consequence would be a complete transformation of anhydrite into gypsum. The so called “small pore hypothesis” must therefore be abandoned as it does not provide a general and robust explanation for the occurrence of anhydrite under the in situ conditions.

The hypothesis of high local stresses, initially proposed in relation to the Gypsum Keuper formation by Wichter (1989), has also proved deficient, except for the unusual combination of extremely fine-porous rocks with uniform, regularly distributed pores. In general, the stress developing locally does not reach the level thermodynamically required for anhydrite to be stable in all pores, which would cause a complete transformation of anhydrite to gypsum via dissolution and diffusion.

The low activity hypothesis, which, following Lippmann and Schüle (1975), emphasises the role of clay minerals with respect to the thermodynamic state of the pore water, provides the most convincing explanation for the occurrence of anhydrite at shallow depths. Although no experimental confirmation has yet been made specifically for the anhydritic claystones of the Gypsum Keuper, the low water lower than the concentration in the outside solution, whereas the contrary holds for the cations. From a thermodynamical point of view, the interaction between the solid and the ions implies that the solid-salt mixture is not ideal, i.e. that water activity is lower than one.
activity hypothesis does not make any unrealistic assumptions. In addition, it provides a consistent explanation of the processes taking place when anhydritic claystones come into contact with water: Swelling starts with water uptake by the clay minerals. During this first phase, the pore water activity gradually increases, eventually reaching the gypsum – anhydrite equilibrium activity. From this point on, anhydrite to gypsum transformation takes place, consuming water and thus maintaining the water deficiency of the clay and sustaining the water uptake until all of the anhydrite is transformed into gypsum. At the end of the swelling process the water activity reaches unity (the fully swollen state of the clay).
4 Maximum Swelling Pressure of Anhydritic Claystones

4.1 Introduction

In tunnelling, swelling causes a long term heave of the tunnel floor which affects the serviceability of the tunnel. If an attempt is made to prevent heave by installing an invert arch, then a swelling pressure develops which can either damage the lining or lift the tunnel as a whole. In order to cope with the swelling phenomenon in tunnelling, two basic options are available (Kovári et al. 1988): According to the so-called yielding principle, a hollow space is provided between the carriageway and the surface of the rock. The tunnel floor is thus allowed to heave without affecting tunnel operation. According to the so-called resistance principle, on the other hand, a stiff and strong lining is installed with the aim of completely preventing floor heave. The design of the lining presupposes knowledge of the swelling pressure. The present Chapter focuses on the swelling pressure that would develop under a practically constant rock volume, as this is approximately the case with the resistance principle.

The microscopic mechanism behind the development of the swelling pressure in situ is the growth of gypsum crystals inside the rock matrix: If a crystal is in equilibrium with an oversaturated solution and its growth is completely prevented by the surrounding matrix, then it exerts so-called crystallisation pressure (Correns and Steinborn 1939). However, the pressure which is necessary in order to keep the overall volume of the rock constant must be lower than the crystallisation pressure. The reason is that the latter acts only locally within the rock matrix and, in addition, the matrix may, depending on its stiffness, allow a certain amount of crystal growth. Obviously, swelling pressure as well as the notion of “complete volume constraint” depends on scale. Therefore, a distinction between the micro-, the macro- and the megascale is indispensable (Fig. 4.1).

Figure 4.1. Scales examined in the swelling process

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6 This Chapter is an extended version of Serafeimidis and Anagnostou (2014b) and Serafeimidis et al. (2014)
The microscale refers to the scale of the individual gypsum crystal. Complete volume constraint at this scale means that the matrix does not allow the gypsum to grow. (The pressurized crystal is in thermodynamic equilibrium with the pore solution.) The swelling pressure at the microscale comprises the above-mentioned crystallisation pressure.

The term “macroscale” refers to the scale of a rock specimen containing gypsum crystals. Complete volume constraint at this scale means that the volume of the rock specimen is kept constant. This is the condition applied in the standardized oedometer test for determining axial swelling stress (ISRM 1999).

The megascale refers to the scale of a tunnel. Complete volume constraint at this scale means that the heave of the tunnel floor is completely constrained. The swelling pressure at the megascale is the pressure developing \textit{in situ} upon a stiff invert arch. The distinction between macro- and megascale is necessary for the following reasons: (i) The boundary conditions \textit{in situ} are different from those in laboratory test (a stiff invert arch does not completely prevent an increase in rock volume). (ii) The rock mass generally contains non-swelling layers as well, which, depending on their stiffness, may allow some increase in the volume of the swelling layers. (iii) The water circulation conditions \textit{in situ} are in general less favourable than under laboratory conditions, where the specimens are constantly supplied with water (Anagnostou 2007).

The structure of the present Chapter is based around these three scales. Section 4.2 (microscale) begins with a critical discussion of existing thermodynamic estimates of the crystallisation pressure of gypsum. A rigorous thermodynamic model for the crystallisation pressure is then presented and the influencing factors are discussed, with an emphasis on the ion concentration in closed or open systems. Section 4.3 (macroscale) starts with a review of existing results from laboratory swelling pressure tests, showing that the swelling pressures measured are considerably lower than the computed crystallisation pressure. A model similar to the model in Chapter 3 is formulated for estimating the macroscopic swelling pressure and understanding the underlying mechanisms. The model accounts in a simplified way for the mechanical interaction between the growing crystals and the surrounding matrix. It leads to swelling pressures of the same order of magnitude as the laboratory values. Finally, Section 4.4 (megascale) reviews investigations on the swelling pressure \textit{in situ} and estimates an upper limit for this pressure based upon an analysis of existing tunnels with intact linings. This analysis also indicates that the swelling pressure \textit{in situ} cannot be higher than 4 – 5 MPa, which is considerably lower than the crystallisation pressure.
4.2 Microscale

4.2.1 Critical review of previous theoretical estimates of crystallisation pressure

Winkler and Singer (1972) and Winkler (1973) estimated the crystallisation pressure of gypsum by applying Correns and Steinborn’s (1939) theory, according to which the crystallisation pressure \( p_c \) of a crystal in equilibrium with a solution of concentration \( c \) reads as follows:

\[
p_c = \frac{RT}{V_G^0} \ln \left( \frac{c}{c_{eq,G}} \right),
\]

where \( c_{eq,G} \) is the gypsum equilibrium concentration at standard conditions (i.e. dilute solutions under atmospheric pressure and at \( T = 25 \, ^\circ\text{C} \)); \( c \) is the actual ion concentration (and, at the same time, the equilibrium concentration when the gypsum is subjected to the pressure \( p_c \)); \( R \) is the universal gas constant; \( T \) is the temperature; \( V_G^0 \) is the molar volume of gypsum. According to Eq. (4.1), the supersaturation \( \frac{c}{c_{eq,G}} \) is the driving force for the development of crystallisation pressure. Winkler and Singer (1972) and Winkler (1973) calculated the crystallisation pressure of gypsum as a function of supersaturation for different temperatures (0, 25 and 50 °C). However, they erroneously considered a molar volume of gypsum of \( V_G^0 = 54.8 \, \text{cm}^3/\text{mol} \) instead of the correct value (74.3 cm\(^3\)/mol).

In addition, Eq. (4.1) does not take into account the activities of the reacting substances. The concentrations in Eq. (4.1) should be replaced by the solubility products (cf. Ping and Beaudoin 1992a):

\[
p_c = \frac{RT}{V_G^0} \ln \frac{K}{K_{eq,G}},
\]

where \( K \) denotes the ion activity product of the solution and \( K_{eq,G}^0 \) the equilibrium solubility product of gypsum at standard conditions (see Section 2.3.1).

The results of Winkler (1973) were later adopted by Wichter (1989). Assuming that supersaturation in Gypsum Keuper rarely exceeds 2, he concluded that the crystallisation pressure amounts to about 30 MPa at \( T = 25 \, ^\circ\text{C} \). Nevertheless, Wichter (1989) did not substantiate the assumption concerning supersaturation, either empirically or theoretically.

Figure 4.2 shows crystallisation pressure as a function of supersaturation for \( T = 25 \, ^\circ\text{C} \) and atmospheric pressure: Curve 1 is according to Winkler (1973), i.e. it does not take account of the activities and assumes an excessively low value for the molar volume; Curve 2 takes the correct value of the molar volume but neglects the effect of activity; Curve 3 is based upon Eq. (4.2) with the
correct molar volume value. The incorrect assumption about molar volume (Curve 1) leads to a considerable overestimation of crystallisation pressure (compared with Curve 2), but when combined with the simplifying assumption mentioned above (activity equal to unity) leads coincidentally to results which are close to the correct values (Curve 3).

Figure 4.2. Crystallisation pressure $p_c$ of gypsum as a function of the supersaturation $c / c_{eq,G}^0$ $(T = 25 \, ^\circ C, \text{atmospheric pore water pressure } p_W)$

Another theoretical estimate can be found in Flückiger (1994) and Flückiger et al. (1994), who used thermodynamic calculations to determine a value of 3.7 MPa for the crystallisation pressure of gypsum at room temperature ($T = 20 \, ^\circ C$). This value was later used by Steiner et al. (2010), who investigated the role of brittle fractures on the swelling of anhydritic claystones. The value of 3.7 MPa is lower than all previous thermodynamic estimates and also lower than the swelling pressures that are frequently measured in swelling pressure tests under volume constraint (see Pimentel, 2007, and Section 4.3.1). The value is based, however, upon erroneous thermodynamic considerations and questionable assumptions. More specifically, Flückiger et al. (1994) used the relationship

$$p_c = \frac{RT}{V_G^0} \ln \frac{K_{sp}}{K_{sp}^0}, \quad (4.3)$$

which resembles (Eq. 4.2), but, rather than considering the actual ionic concentration, they determined the solubility products needed in Eq. (4.3) as follows:

$$K_{sp} = \exp \left( -\frac{\Delta G_c(T)}{RT} \right), \quad (4.4)$$

$$K_{sp}^0 = \exp \left( -\frac{\Delta G_c(T_0)}{RT_0} \right), \quad (4.5)$$
Maximum Swelling Pressure of Anhydritic Claystones

where $\Delta G_r$ (the free energy of the transformation of anhydrite to gypsum at temperature $T$) was calculated by applying the following empirical relationship (Kelley et al. 1941, Gmelin 1961):

$$
\Delta G_r [\text{J/mol}] = 10439 + 273T \log_{10} T - 0.09 T^2 - 686 T \quad (T \text{ in [K]})
$$

(4.6)

Flückiger et al. (1994) did not explicitly mention the application of Eqs. (4.4) and (4.5), but these equations lead, in combination with Eq. (4.6), exactly to their numerical values for the solubility product $K_{sp}$ (1.57 and 1.40 at $T = 20$ and 25 °C, respectively). As shown in Appendix C, the pressure calculated by Flückiger et al. (1994) is not the crystallisation pressure at 20 °C. It is the increase in crystallisation pressure that would occur if the temperature dropped from $T_0 = 25°$ to $T = 20 °C$ with the solution being continuously saturated with respect to anhydrite. The value of 3.7 MPa thus lacks practical relevance.

### 4.2.2 Crystallisation pressure

The crystallisation pressure $p_c$ depends on the concentration $c$ of calcium and sulphate ions in the solution, the quantity of foreign ions, the presence of clay minerals, the pore water pressure $p_w$, the temperature $T$ and the geometry and size of the pores and crystal grains (Scherer 1999, Flatt 2002, Steiger 2005b). Based on Eqs. (2.27) and (2.28) and also replacing the solid pressure $p_G$ with the crystallisation pressure $p_c$ (which is the notation commonly used in literature) these dependencies can be written in the following form:

$$
p_c = \frac{2RT \ln a_w}{V_G^o} - \frac{2\gamma_G}{r_G} + RT \ln \left( \frac{c_0 c_s}{c_{G_0} \gamma_{G_0}} \right) + \Delta_{r,G}G^0 - (T - T_0) \Delta_{r,G}S^0
$$

(4.7)

Based on Eq. (4.7) and taking atmospheric pore pressure into account ($p_w = 0$), the factors that affect crystallisation pressure are as follows: the concentration of the ions, the radius of the gypsum $r_G$ (which coincides with the pore radius $r_p$), the water activity $a_w$, the presence of foreign ions and the temperature $T$. The effect of these factors is investigated in the following Sections. More specifically, in the parametric analyses of Section 4.2.3, the concentration of the sulphate and calcium is taken as an independent, given parameter. The actual concentration in a closed system is a result of anhydrite dissolution and gypsum precipitation, while an open system also involves transport processes (advection and diffusion). Sections 4.2.4 and 4.2.5 deal with the value of the ion concentration in closed and open systems, respectively.
4.2.3 Relationship between crystallisation pressure and concentration

Figure 4.3 shows the relationship between crystallisation pressure and concentration $c$ (assuming equal calcium and sulphate concentrations, \textit{i.e.} $c_{Ca^{2+}} = c_{SO_4^{2-}} = c$) for different values of the other parameters.

\textbf{Effect of the radius of the gypsum particles}

Figure 4.3a shows the effect of the solid-liquid interface, which is expressed by the term $2\gamma_G/r_G$ in Eq. (4.7). It decreases with increasing $r_G$ and can be totally neglected for radii greater than 1 $\mu$m. For small radii $r_G$, however, it is relevant: The surface of the crystal can be conceived of as a stretched membrane which exerts a pressure upon the crystal, thus taking over some of the crystallisation pressure; crystallisation pressure therefore decreases with decreasing radius $r_G$ (Scherer 1999, Steiger 2005). This can also be seen from Eq. (4.7), according to which the surface energy effect reduces crystallisation pressure by $2\gamma_G/r_G$.

\textbf{Effect of water activity}

Clay minerals or a high ionic concentration may substantially reduce the ability of water to take part in chemical reactions. This is taken into account by the activity coefficient $a_W$ (\textit{cf.} Section 2.2.3.3). Figure 4.3b shows the effect of the water activity $a_W$. The lower its value, the lower will be the crystallisation pressure. As can be verified from Eq. (4.7), a water activity less than 1 decreases crystallisation pressure by $2RT \ln a_W/V_G^0$.

\textbf{Effect of the presence of foreign ions}

Foreign ions (\textit{e.g.} sodium or chloride) decrease the activities of all reactants (water, calcium and sulphate ions) that participate in the growth of gypsum and thus also in its crystallisation pressure. This is taken into account in Eq. (4.7) via the water activity $a_W$ and the ion activity coefficients $\gamma_{Ca^{2+}}$ and $\gamma_{SO_4^{2-}}$ (\textit{cf.} Sections 2.2.3.2 and 2.2.3.4). Figure 4.3c compares the crystallisation pressure in the case of a NaCl solution of 0.2 mol/l H$_2$O with the crystallisation pressure without foreign ions. For the sake of simplicity, the activity of the water, which is slightly lower than 1 at this NaCl concentration (Washburn 1926-1933), was taken equal to 1. The presence of foreign ions clearly decreases crystallisation pressure.

\textbf{Effect of temperature}

As the temperature affects several terms of Eq. (4.7), its effect cannot be seen immediately. According to Figure 4.3d, temperature has a minor effect on crystallisation pressure. It should be noted that this conclusion is true only for given concentration $c$, \textit{i.e.} under the assumption that the actual concentration itself does not depend on the temperature. However, as we will see in Section 4.2.4, in a closed system containing gypsum, anhydrite and water, the concentration $c$ is equal to the equilibrium
Maximum Swelling Pressure of Anhydritic Claystones

concentration \( c_{eq,A} \) of anhydrite, which is sensitive to temperature (Marsal 1952, Blount and Dickson 1973). In this particular case, the crystallisation pressure of the gypsum also depends to a considerable extent on the temperature (see end of Section 4.2.4).

**Figure 4.3.** Crystallisation pressure \( p_c \) of gypsum as a function of the ion concentration \( c \): (a) effect of the pore radius; (b) effect of the water activity; (c) effect of foreign ions; (d) effect of temperature

### 4.2.4 Ion concentration in a closed system containing anhydrite and gypsum

Let us first consider the concentrations and the corresponding crystallisation pressures that would develop in a closed system, i.e. a system where water and ions cannot flow in or out. In this case, anhydrite is the only supplier of ions. Anhydrite dissolution increases the concentration of ions in the pore water until it reaches the equilibrium concentration \( c_{eq,A} \) of anhydrite. The latter can be determined by means of Eqs. (2.31) and (2.35). Under atmospheric pressure \( (p_A = 0) \) and \( T = 20 \, ^\circ C \), it is equal to 23.4 mmol/l. As this concentration is higher than the gypsum equilibrium concentration
under the same conditions (15 mmol/l, determined from Eqs. (2.28) and (2.29) with $p_G = 0$, neglecting the effects of water activity and surface energy), gypsum will develop a crystallisation pressure of about 20 MPa (see, e.g., Fig. 4.3 for $c = c_{eq,A} = 23.4$ mmol/l and $a_W = 1$). The development of this pressure will also cause a certain increase in the pressure $p_A$ acting on the anhydrite particles. The increase in pressure depends on the spatial distribution of the anhydrite and the gypsum particles, whose growth is constrained by the surrounding medium. In the borderline case where the constrained gypsum crystals are very closely spaced and located close to the anhydrite grains (cf. Fig. 3.5b), the pressure developing upon the latter can be taken approximately equal to the crystallisation pressure of the gypsum.

The increased anhydrite pressure will cause an increase in the anhydrite equilibrium concentration to a value that is higher than the equilibrium concentration under atmospheric pressure (23.4 mmol/l). This in turn will further increase the crystallisation pressure of gypsum to more than 20 MPa, which will again further increase the anhydrite equilibrium concentration. The process of a successive pressure-induced increase in the equilibrium concentration of the dissolving mineral is well known from petrography (cf. Merino and Dewers 1998). It can be illustrated graphically by plotting in one and the same diagram the following two curves (Fig. 4.4): (i) the crystallisation pressure $p_c$ of the gypsum as a function of the actual concentration $c$ (determined by Eq. 4.7 with $c_{Ca^{2+}} = c_{SO_4^{2-}} = c$) and (ii) the relationship between the pressure $p_A$ acting upon the anhydrite particles and the anhydrite equilibrium concentration, determined according to Eq. (2.31) and taking atmospheric pressure into account, i.e. $p_W = 0$, by:

$$p_A = \frac{1}{V_A} \left[ RT \ln \left( \gamma_{Ca^{2+}} \gamma_{SO_4^{2-}} \frac{c_{Ca^{2+}}}{c_0} \frac{c_{SO_4^{2-}}}{c_0} \right) + \Delta_{r,A}G^0 - (T - T_0) \Delta_{r,A}S^0 \right], \tag{4.8}$$

where the general equation $K_A = \gamma_{Ca^{2+}} \gamma_{SO_4^{2-}} \frac{c_{Ca^{2+}}}{c_0} \frac{c_{SO_4^{2-}}}{c_0} / c_0^2$ (similar to Eq. 2.27 which applies for gypsum) has been used for the ion activity product of anhydrite.

Points 1 and 2 in Fig. 4.4 show the anhydrite equilibrium concentration under atmospheric pressure and the corresponding crystallisation pressure of gypsum, respectively. Point 3 shows the increased anhydrite equilibrium concentration assuming that the crystallisation pressure of 20 MPa also acts upon the anhydrite particles. At this higher concentration, the crystallisation pressure of gypsum would also be higher (about 30 – 35 MPa, point 4), which would in turn increase the anhydrite equilibrium concentration (point 5) and so on. The system reaches equilibrium only at the intersection point of the two curves. At this point, the anhydrite equilibrium concentration amounts to about 46 mmol/l (about twice the equilibrium concentration under atmospheric pressure) and the crystallisation pressure of gypsum to 53 MPa.
In general, the crystallisation pressure at equilibrium can be obtained by setting $p_A = p_c$ in Eq. (2.36) and solving with respect to $p_c$ (taking into account that $p_c = p_G$)

$$p_c = \frac{2RT \ln a_G + (T - T_0) \Delta_{r,G,4} S^0 - \Delta_{r,G,4} G^0 - \frac{2\gamma_G V_G^0}{r_G}}{V_G^0 - V_A^0}, \quad (4.9)$$

As mentioned above, Eq. (4.9) assumes that the anhydrite pressure is equal to the pressure developed by the gypsum crystals. If the latter are sparsely distributed within the rock matrix and located at greater distances from the anhydrite grains, the anhydrite will experience a smaller pressure increase than the walls of the pores constraining the gypsum growth. In the borderline case, where the anhydrite pressure remains equal to atmospheric pressure, the crystallisation pressure of gypsum can be determined by setting $p_A = 0$ in Eq. (2.36) resulting in

$$p_c = \frac{2RT \ln a_G + (T - T_0) \Delta_{r,G,4} S^0 - \Delta_{r,G,4} G^0 - \frac{2\gamma_G V_G^0}{r_G}}{V_G^0}, \quad (4.10)$$

Let us revisit now the question of Section 4.2.3, i.e. study the effect of temperature, water activity and pore size, taking into account the specific conditions prevailing in a closed system. Figure 4.5a, 4.5b and 4.5c show crystallisation pressure as a function of these parameters for the two bounds of anhydrite pressure ($p_A = 0$ or $p_A = p_c$). It is evident that in a system where anhydrite is the only ion supplier, the anhydrite pressure significantly influences the crystallisation pressure of gypsum.

As the anhydrite equilibrium concentration depends on temperature, both the supersaturation with respect to gypsum and the crystallisation pressure of gypsum also depend on temperature (Fig. 4.5a). More specifically, with increasing temperature, the crystallisation pressure decreases by 1 – 2 MPa/°C depending on the anhydrite pressure.

Figure 4.4. Relationship between gypsum crystallisation pressure and the ion concentration, and between pressure and the anhydrite equilibrium concentration

In general, the crystallisation pressure at equilibrium can be obtained by setting $p_A = p_c$ in Eq. (2.36) and solving with respect to $p_c$ (taking into account that $p_c = p_G$)

$$p_c = \frac{2RT \ln a_G + (T - T_0) \Delta_{r,G,4} S^0 - \Delta_{r,G,4} G^0 - \frac{2\gamma_G V_G^0}{r_G}}{V_G^0 - V_A^0}, \quad (4.9)$$

As mentioned above, Eq. (4.9) assumes that the anhydrite pressure is equal to the pressure developed by the gypsum crystals. If the latter are sparsely distributed within the rock matrix and located at greater distances from the anhydrite grains, the anhydrite will experience a smaller pressure increase than the walls of the pores constraining the gypsum growth. In the borderline case, where the anhydrite pressure remains equal to atmospheric pressure, the crystallisation pressure of gypsum can be determined by setting $p_A = 0$ in Eq. (2.36) resulting in

$$p_c = \frac{2RT \ln a_G + (T - T_0) \Delta_{r,G,4} S^0 - \Delta_{r,G,4} G^0 - \frac{2\gamma_G V_G^0}{r_G}}{V_G^0}, \quad (4.10)$$

Let us revisit now the question of Section 4.2.3, i.e. study the effect of temperature, water activity and pore size, taking into account the specific conditions prevailing in a closed system. Figure 4.5a, 4.5b and 4.5c show crystallisation pressure as a function of these parameters for the two bounds of anhydrite pressure ($p_A = 0$ or $p_A = p_c$). It is evident that in a system where anhydrite is the only ion supplier, the anhydrite pressure significantly influences the crystallisation pressure of gypsum.

As the anhydrite equilibrium concentration depends on temperature, both the supersaturation with respect to gypsum and the crystallisation pressure of gypsum also depend on temperature (Fig. 4.5a). More specifically, with increasing temperature, the crystallisation pressure decreases by 1 – 2 MPa/°C depending on the anhydrite pressure.

99
Figure 4.5. Crystallisation pressure $p_c$ of gypsum as a function of (a) temperature $T$; (b) water activity $\alpha_W$; (c) gypsum particle radius $r_G$.

According to Fig. 4.5c, the surface energy effect is relevant only for pore radii of up to 100 nm. Figure 4.5d gives an idea of the pore sizes of sulphatic claystones. More specifically, the diagram indicatively shows the two curves of the MIP results presented in Fig. 3.4, one on a sample from the Chienberg Tunnel and one from the Belchen Tunnel. The diagram can be read in combination with the overlying diagram (Fig. 4.5c). Consider, for example, the curve for the sample from the Belchen Tunnel and a percentage of $n = 20\%$. The corresponding pore radius and crystallisation pressure amount to about 12 nm (point A in Fig. 4.5d) and $8 - 21$ MPa (points B and C in Fig. 4.5c), respectively. This means that in $80\%$ of the total pore space (which consists of pores smaller than 12 nm) the crystallisation pressure amounts to $8 - 21$ MPa, which is significantly lower than the pressure in the remaining larger pores ($20 - 52$ MPa, Fig. 4.5c). The effect of the surface energy is thus significant in the case of the Belchen Tunnel. By the same line of argument, it can easily be seen from Fig. 4.5c and 4.5d that this effect is less important in the case of Chienberg Tunnel. The sample from this tunnel has considerably larger pores, probably due to the smaller depth of sampling (cf. Section...
3.2.2). Furthermore, the Chienberg Tunnel crosses the so-called Tafeljura, while the rock in the Belchen Tunnel belongs to the intensively folded part of the Jura mountains, the Faltenjura (cf. Section 3.1), where high tectonic stresses may have caused additional compaction (Huggenberger 2014).

In conclusion, the thermodynamically possible range for the crystallisation pressure of gypsum is very wide even under the relatively simple conditions of a closed system. In the absence of surface energy effects or of interactions with clay minerals, the crystallisation pressure is equal to 20 – 50 MPa (Fig. 4.5a for $T = 20 \, ^\circ\mathrm{C}$), depending on how much the pressure on the anhydrite particles increases due to the pressure exerted by the gypsum crystals upon the pore walls.

### 4.2.5 Ion concentration in open systems

In an open system, additional uncertainties exist with respect to the actual ion concentration. Consider, for example, the relatively simple conditions of a rock sample that is placed in an oedometer device and immersed in a container filled with distilled water. Under the conditions of a swelling pressure test, the volume of the specimen is kept constant and consequently water uptake by and seepage flow towards the specimen is negligible. However, even in the absence of advection, it is possible under certain conditions (cf. Section 6.4) that the ions produced by the dissolution of anhydrite can move by diffusion out of the oedometer, towards the water of the container. The ion concentration in the sample is governed by the combined effect of the anhydrite dissolution rate and the ion diffusion rate. If the diffusion rate is very high compared to the rate of anhydrite dissolution, then the actual ion concentration and thus the crystallisation pressure of gypsum will be very low or even zero. On the other hand, if the diffusion is very slow, then the situation will be close to that of the closed system discussed above.

In general, ion transport may also occur by advection (cf. Section 6.5). This is particularly true in situ due to seepage flow around the tunnel. Seepage flow introduces an additional source of uncertainty making a theoretical determination of the ion concentration and thus also of the crystallisation pressure in situ extremely difficult. The ion concentration in a rock element might vary from practically zero to values even higher than the anhydrite equilibrium concentration. Theoretically, anhydrite should then also start to precipitate or – if crystal growth is constrained – exert a crystallisation pressure. However, according to Klepetsanis and Koutsoukos (1991), who investigated the precipitation of calcium sulphate within the temperature range $T = 20 – 60 \, ^\circ\mathrm{C}$, the only phase forming under these conditions is gypsum. The reason is that anhydrite precipitates much more slowly than gypsum. According to Fletcher and Merino (2001), who evaluated the experimental results of Liu and Nancollas (1970), the kinetic rate constant of anhydrite precipitation is lower than that of gypsum precipitation by a factor of about 200.
Table 4.1. Measured ion concentrations and calculate crystallisation pressures for three Swiss tunnels in the Gypsum Keuper formation

<table>
<thead>
<tr>
<th>Tunnel</th>
<th>Sample</th>
<th>Source</th>
<th>Sulphate $SO_4^{2-}$ [mg/l]</th>
<th>Calcium $Ca^{2+}$ [mg/l]</th>
<th>Natrium $Na^+$ [mg/l]</th>
<th>Chlorine $Cl^-$ [mg/l]</th>
<th>$p_c$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belchen</td>
<td>Collecting box 1 (19.6.02)</td>
<td>Noher and Meyer (2002)</td>
<td>2174.4</td>
<td>566.1</td>
<td>638</td>
<td>335.6</td>
<td>3.27</td>
</tr>
<tr>
<td></td>
<td>Collecting box 1 (21.8.02)</td>
<td>Noher and Meyer (2002)</td>
<td>2774.2</td>
<td>553.8</td>
<td>808</td>
<td>484.1</td>
<td>7.25</td>
</tr>
<tr>
<td></td>
<td>Collecting box 3 (24.7.01)</td>
<td>Noher and Meyer (2002)</td>
<td>2565</td>
<td>752.9</td>
<td>2628</td>
<td>2319</td>
<td>6.16</td>
</tr>
<tr>
<td>Adler</td>
<td>Sample Nr. 9505819</td>
<td>Bachema (1995)</td>
<td>1864</td>
<td>602</td>
<td>42</td>
<td>196</td>
<td>4.73</td>
</tr>
<tr>
<td></td>
<td>Sample Nr. 95002582</td>
<td>Bachema (1995)</td>
<td>1686</td>
<td>577</td>
<td>64</td>
<td>103</td>
<td>1.61</td>
</tr>
<tr>
<td>Chienberg</td>
<td>Field Nr. O1 (Tm 1003)</td>
<td>LPM (2000-3)</td>
<td>2000</td>
<td>620</td>
<td>16</td>
<td>20</td>
<td>7.83</td>
</tr>
<tr>
<td></td>
<td>Field Nr. O2 (Tm 1059)</td>
<td>LPM (2000-3)</td>
<td>1800</td>
<td>580</td>
<td>15</td>
<td>34</td>
<td>3.79</td>
</tr>
<tr>
<td></td>
<td>Field Nr. O10 (Tm 1160)</td>
<td>LPM (2000-3)</td>
<td>1600</td>
<td>610</td>
<td>14</td>
<td>18</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>Field Nr. O12 (Tm 1196)</td>
<td>LPM (2000-3)</td>
<td>3500</td>
<td>550</td>
<td>420</td>
<td>84</td>
<td>14.50</td>
</tr>
<tr>
<td></td>
<td>Field Nr. 15 (Tm 862)</td>
<td>LPM (2000-3)</td>
<td>1750</td>
<td>860</td>
<td>200</td>
<td>41</td>
<td>10.80</td>
</tr>
<tr>
<td></td>
<td>Field Nr. 16 (Tm 862)</td>
<td>LPM (2000-3)</td>
<td>2050</td>
<td>750</td>
<td>244</td>
<td>71</td>
<td>11.74</td>
</tr>
</tbody>
</table>

In view of the practical difficulties of producing a reliable estimate of ion concentrations in situ, we will estimate the crystallisation pressure based upon the concentrations measured in the three Swiss tunnels crossing the Gypsum Keuper formation mentioned in Chapter 3. Table 4.1 focuses only on the most common ions identified in water chemical analyses, i.e. calcium- ($Ca^{2+}$), sulphate- ($SO_4^{2-}$), sodium- ($Na^+$) and chloride- ($Cl^-$) ions. Data from a number of chemical analyses were available for the present study. However, in order to get meaningful results we considered only measurements that included data for all of the aforementioned ions (not just for some of them). As mentioned above, crystallisation pressure increases with the concentration of calcium and sulphate ions and decreases with the concentration of foreign ions (i.e. mainly natrium and chloride in the present case). Based
upon the concentrations of Column 4 to 7 of Table 4.1 and assuming, for all three tunnels, that the 
temperature \( T = 20 \, ^\circ\text{C} \), water activity is equal to 1, pore water pressure is atmospheric and the 
interface effects are negligible, Eq. (4.7) leads to crystallisation pressures up to 7.25 MPa for the 
Belchen Tunnel, 14.5 MPa for the Chienberg tunnel and 4.73 MPa for the Adler Tunnel (Column 8 of 
Table 4.1). For comparison, the results from the last Section showed crystallisation pressure in a 
closed system amounting to 20–50 MPa.

The circulation of ions by advection and/or diffusion may clearly be significant for crystallisation 
pressure, as it appears to reduce ion concentrations to values lower than the anhydrite equilibrium 
concentration (which prevails in closed systems), thereby also reducing the driving force for gypsum 
precipitation (cf. Section 5.2.1.1).

Table 4.2. Measured swelling pressures at the scale of a specimen

<table>
<thead>
<tr>
<th>Sampling place</th>
<th>Test duration [months]</th>
<th>Swelling pressure [MPa]</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belchen Tunnel, Switzerland</td>
<td>8-9</td>
<td>&lt; 3.8</td>
<td></td>
<td>Grob (1972)</td>
</tr>
<tr>
<td>Belchen Tunnel, Switzerland</td>
<td>( \approx 24 )</td>
<td>&gt; 5</td>
<td></td>
<td>Madsen et al. (1995)</td>
</tr>
<tr>
<td>Hauenstein Tunnel, Switzerland (30-70% anhydrite, 5-20% clay and &lt; 25% quartz, dolomite, magnesite)</td>
<td>&gt; 24</td>
<td>4.7</td>
<td>Maximum swelling pressure developed perpendicular to the foliation plane in a sample with clay content 5%</td>
<td>Nüesch et al. (1995)</td>
</tr>
<tr>
<td>Adler Tunnel, Switzerland</td>
<td>( \approx 60 )</td>
<td>( \leq 7.1 )</td>
<td></td>
<td>Vögltli and Jordan (1996)</td>
</tr>
<tr>
<td>Belchen, Adler and Chienberg Tunnel, Switzerland</td>
<td></td>
<td>&lt; 4.6</td>
<td>Maximum swelling pressure developed for clay content of 10-15%</td>
<td>Ko et al. (1997)</td>
</tr>
<tr>
<td>Nagra-borehole Weiach, Switzerland</td>
<td>( \approx 24 )</td>
<td>&lt; 4.5</td>
<td>Maximum swelling pressure developed for 10-15% clay and 70-75% anhydrite</td>
<td>Madsen and Nüesch (1990, 1991)</td>
</tr>
<tr>
<td>Exploration gallery of the B-14 Heslach Tunnel, Germany</td>
<td>48</td>
<td>6.8</td>
<td></td>
<td>Beiche (1991)</td>
</tr>
<tr>
<td>Freudenstein Tunnel, Germany</td>
<td>48</td>
<td>&gt; 7</td>
<td>Tests not completed</td>
<td>Kirschke (1987)</td>
</tr>
<tr>
<td>Freudenstein Tunnel, Germany</td>
<td>7 - 10</td>
<td>Swelling pressure could not be determined explicitly</td>
<td>Pimentel (2007)</td>
<td></td>
</tr>
<tr>
<td>Freudenstein Tunnel, Germany</td>
<td>240</td>
<td>9.6</td>
<td></td>
<td>Wahlen and Wittke (2009)</td>
</tr>
<tr>
<td>Artificial sulphatic claystones (15% clay, 85% anhydrite)</td>
<td>&lt; 7.9</td>
<td></td>
<td></td>
<td>Ko et al. (1997)</td>
</tr>
<tr>
<td>Artificial anhydrite-montigel (a swelling clay) and anhydrite-gypsum mixtures</td>
<td>5</td>
<td>Maximum swelling pressure developed for 15% montigel - 85% anhydrite</td>
<td>Flückiger et al. (1994)</td>
<td></td>
</tr>
<tr>
<td>Massive anhydritic rock with sulphates as accelerators</td>
<td>1.6</td>
<td>Swelling pressure determined by extrapolation of the results of dilatometer tests.</td>
<td>Sahores (1962)</td>
<td></td>
</tr>
</tbody>
</table>
4.3 Macroscale

4.3.1 Measured swelling pressures in laboratory tests

The macroscopic swelling pressure is the pressure developing at the scale of a rock specimen. Table 4.2 provides an overview of measured values reported in the literature. All the tests have been performed in oedometer devices under volume constraint, except for the early laboratory investigations by Sahores (1962), who used dilatometers.

According to Table 4.2, swelling pressures of up to 10 MPa were measured in laboratory tests, with the mean value being less than 6 MPa. The clay and anhydrite content seem to be significant for pressure. In spite of the optimum watering conditions prevailing in the laboratory, the testing times were usually very long. For example, the tests on samples from the Freudenstein Tunnel took more than 20 years (Pimentel 2007a). As a consequence of the long testing times, relatively few tests have been performed, thereby raising doubts as to how representative the results are for an entire rock mass. In addition, tests were often terminated before reaching a steady state, which means that the pressures measured may not be the maximum ones.

4.3.2 Model for the theoretical estimation of macroscopic swelling pressure

4.3.2.1 Introduction

Even with the above-mentioned experimental uncertainties, it is remarkable that the measured macroscopic swelling pressures $\sigma_s$ are in general significantly lower than the crystallisation pressure $p_c$ of gypsum (a few MPa versus tens of MPa in a closed system). This can be attributed either to the presence of foreign ions (cf. Section 4.2.5) or to the interaction between the growing crystals and the surrounding matrix. We will examine here the second effect by means of a computational model for macroscopic swelling pressure. The model accounts in a simplified way (similar to that of the model in Chapter 3) for the interaction between the growing gypsum crystals and the surrounding matrix.

The model takes up an idea developed by Ping and Beaudoin (1992b) in relation to sulphate expansion in cement that the pressure macroscopically observed represents only a fraction of the local crystallisation pressure because crystal growth takes place only in isolated locations within the sample. Ping and Beaudoin (1992b) proposed the general relationship $\sigma_s = x_c \cdot p_c$, where $x_c$ denotes the ratio between the contact area (of the growing crystal and the surrounding matrix) and the total specimen section area. The parameter $x_c$ depends on the porosity of the specimen, and the number, size and geometry of the crystals. The greater the porosity, the greater will be the number of crystals that may grow and the higher will be the value of $x_c$. Another potentially relevant factor is the stiffness of the
matrix around the growing crystals. A soft matrix acts as a buffer allowing some gypsum growth while keeping the overall volume of the specimen constant. The softer the matrix, the lower will be the swelling pressure that develops in a specimen under volume constraint. Fletcher and Merino (2001) also emphasised the generation of a local stress state around a growing crystal, the associated modification of macroscopic stress due to the growth of many dispersed crystals and the effects of host rock stiffness.

4.3.2.2 Thermodynamic equilibrium

Under atmospheric pressure and room temperature, gypsum is the thermodynamically stable phase, because its equilibrium concentration is lower than that of anhydrite (cf. Fig. 4.4). However, the stresses in the rock specimen increase during gypsum growth (due to the confinement) and, consequently, the difference between the equilibrium concentrations, i.e. the driving force of hydration, becomes smaller (Fig. 4.4). We assume here that gypsum growth will continue until reaching thermodynamic equilibrium, i.e. it will cease only when the stresses developing are sufficiently high that the equilibrium concentrations of anhydrite and gypsum become equal. This assumption will be discussed later in Section 4.3.2.6, where it will be shown that the transformation of anhydrite into gypsum may end earlier for other reasons.

Taking into account the fact that (i) the solid-liquid interfacial effects are negligible for the anhydrite particles, and (ii) the pore water pressure at steady state is equal to the pressure outside the oedometer, i.e. atmospheric, and (iii) the activity of the pore water is equal to one, i.e. clay–water interactions are not significant, the condition for thermodynamic equilibrium based on Eq. (2.36) reads as follows:

\[
p_c = p^0 + \frac{V^0}{V^0_G} \left( T - T_0 \right) \Delta r_{G,G}^S - \frac{\Delta r_{G,G}^G}{V^0_G} - 2 \frac{\gamma}{r^0_G}.
\] (4.11)

4.3.2.3 Cavity expansion model

The interaction between the growing gypsum and the surrounding matrix will also be studied with the aid of an analytical cavity expansion model, where the expanding cavity and the solid represent the growing gypsum and the surrounding rock matrix, respectively. In a similar way to the simplified cavity expansion model in Section 3.3.3.2, a model obeying spherical symmetry is formulated by taking a rock specimen (Fig. 4.6a) and successively introducing the following simplifying assumptions: the expanding cavities are spherical (Fig. 4.6b), they have a uniform initial radius \( a \) (Fig. 4.6c), they are regularly distributed on a grid in a densest packing lattice (Fig. 4.6d-e) and they expand uniformly, i.e. their boundaries experience the same radial displacement \( u_r \). Furthermore, the matrix enclosing each expanding cavity (Fig. 4.6e) will be approximated by a spherical computational domain of radius \( b \) (Fig. 4.6f). In this case, a zero radial displacement is prescribed at the outer surface of the sphere as a boundary condition. The model of the rock specimen as a densely packed array of
microscopic representative volume elements (RVE), each of which consists of an expanding cavity of radius $a$ surrounded by a spherical domain from the rock matrix with outer radius $b$, is geometrically identical to the model proposed by Fletcher and Merino (2001) for studying the mechanism of mineral growth by replacement.

![Figure 4.6. Assumptions underlying the spherical cavity expansion model](image)

Figure 4.6. Assumptions underlying the spherical cavity expansion model

It is apparent (Fig. 4.6f) that the ratio of cavity size ($2a$) to cavity distance ($2b$) depends only on the ratio of the volume of the expanding cavities to the total volume of the specimen. In a similar way to Eq. (3.3.9), replacing the term $\phi_c$ with the volume fraction of the expanding cavities, denoted here as $\delta$, we get the following for the densest packing arrangement:

$$\frac{b}{a} = \left(\frac{\pi}{3\sqrt{2}\delta}\right)^{\frac{1}{3}}. \quad (4.12)$$

![Figure 4.7. Cavity expansion model](image)

Figure 4.7. Cavity expansion model
The imposition of cavity expansion $u_a$ causes an increase in the radial stress both at the cavity boundary ($r = a$) and at the outer boundary ($r = b$) of the spherical domain (Fig. 4.7). The stress $\sigma_b$ at the outer boundary of the model corresponds to the macroscopic swelling pressure $\sigma_s$ that develops under volume constraint, while the stress $\sigma_a$ at the cavity boundary is equal to the pressure exerted by the growing gypsum upon the surrounding matrix.

Assuming that the rock matrix behaves like a linearly elastic material with zero tensile strength, the macroscopic swelling pressure $\sigma_s$, the radial stress $\sigma_a$ at the cavity boundary (i.e. the pressure exerted by the growing gypsum upon its vicinity) and the cavity expansion (expressed by the radial displacement $u_a$ of the cavity boundary) are linked by the following equations (cf. Eqs. A51 and A53 in Appendix A2):

$$\sigma_s = \frac{\sigma_a}{(b/a)^2}, \quad (4.13)$$
$$\sigma_a = \frac{b/a}{b/a - 1} \frac{u_a}{E}, \quad (4.14)$$

where $E$ denotes the Young’s modulus of the matrix around the growing gypsum. Inserting $\sigma_a$ from Eq. (4.14) into Eq. (4.13) and taking account of Eq. (4.12) gives the macroscopic swelling pressure $\sigma_s$ as a function of the cavity expansion ($u_a/a$), of the Young’s modulus $E$ of the matrix and of the volume fraction $\delta$ of the expanding cavities:

$$\sigma_s = E \frac{u_a}{a} \left( \frac{\pi}{3\sqrt{2}} \right)^{1/3} \left( \left( \frac{\pi}{3\sqrt{2}} \right)^{1/3} - \delta^{1/3} \right). \quad (4.15)$$

According to this equation, the macroscopic swelling pressure $\sigma_s$ increases with the cavity expansion $u_a/a$, with the stiffness of the matrix and with the volume fraction of the expanding cavities (Fig. 4.8).

**Figure 4.8.** Normalized macroscopic swelling pressure $\sigma_s / (E u_a/a)$ as a function of volume fraction $\delta$ of the expanding cavities.
4.3.2.4 On the adequacy of the assumptions in the simplified cavity expansion model

The adequacy of the simplified cavity expansion model (which assumes that the expanding cavities have a uniform size and are distributed on a regular grid) was verified by comparative numerical analyses which consider randomly distributed cavities of different sizes. For the sake of simplicity, only the two-dimensional problem is examined ($\zeta = 1$). As we will see, the predictions of the simplified model in Section 4.3.2.3 agree well with the macroscopic swelling pressure determined numerically.

Numerical model

The comparative analyses take the cavity size distribution in the lower porosimetric curve of Fig. 3.4, which relates to the Belchen Tunnel. The volume fraction $\delta$ of the cavities is equal to the porosity, i.e. $\delta = \phi = 7.19\%$. The numerical model approximates the continuous line of Fig. 3.4 by a step-like distribution, i.e. by an arbitrary number $m$ of discrete pore radii $a_i$. For reasons of computational economy, the numerical analyses considered three pore sizes (4 nm, 8 nm and 20 nm, dashed line in Fig. 4.9).

![Figure 4.9. Distribution of the cavity radii (\(\delta = \phi = 7.19\%\) and idealization by a step-like distribution with cavities of three radii)](image)

Arranging the radii in descending order, i.e. so that $a_1 > ... > a_i > ... > a_m$, the volume fraction $\delta_i$ of the cavities of a specific radius $a_i$ can be estimated as follows:

$$\delta_i = \frac{\bar{n}_i - \bar{n}_{i+1}}{2}, \quad (4.16)$$

where $\bar{n}_{mi} = 2 - \bar{n}_m$ and $\bar{n}_b = -\bar{n}_1$. Dividing the volume fraction $\delta_i$ by the volume of one cavity yields the number $N_i$ of cavities of radius $a_i$ per unit volume:
\[ N_i = \frac{\delta_i}{\xi + 2 \pi a_i^{\xi+1}}. \]  

(4.17)

The computational model consists of a square domain with side length \( L_s \) equal to 281.1 nm, which is calculated by means of Eq. (4.17) so that one of the largest size pores fits within it. The number of cavities with radii equal to 8 nm and 4 nm can then be determined in an analogous manner, providing a total of 6 and 60 cavities, respectively. These 67 cavities are placed randomly within the square area based upon a uniform probability distribution function. Two restraints are applied during placement in order to avoid intersecting or extremely closely spaced pores: the distance between the centre of a new cavity and the centre of any existing one, as well as the vertical distance between the centre of a new cavity and each boundary surface, should be greater than the cavity’s diameter. Figure 4.10 shows the cavity locations and the boundary conditions as well as a detail of the triangular finite element mesh for a specific example. The initial stresses are taken equal to zero, whereas the expansion of the cavities is induced numerically through a fictitious temperature increase (setting the out-of-plane thermal coefficient equal to zero). In order to obtain a uniform expansion (i.e. a constant \( u_{ai}/a_i \), where \( u_{ai} \) is the radial displacement of the boundary of the cavity of radius \( a_i \)), the Young’s modulus \( E \) of the cavity material is taken \( 10^3 \) times higher than the modulus of the rock matrix, which in turn is considered as a no-tension, linearly elastic material with \( E = 5 \) GPa (cf. Section 3.3.4) and a typical Poisson’s ratio \( \nu = 0.30 \). All numerical analyses were performed by means of the finite element code Abaqus (Dassault Systèmes 2011).

![Figure 4.10](image.png)

**Figure 4.10.** (a) 2D computational model and, (b), detail of the finite element mesh for randomly distributed cylindrical cavities of non-uniform size

**Numerical results**

As the cavity placement process was probabilistic, 200 different models were analysed. For the comparison with the predictions of the simplified cavity expansion model (see Section 4.3.2.3), the average boundary pressure \( \bar{p} \) is calculated for each numerical model:
\[ p = \frac{1}{4L_i} \sum_{i=1}^{N} F_i, \quad (4.18) \]

where \( N \) denotes the total number of boundary nodes restrained (either horizontally or vertically) and \( F \) is the reaction force at each node (defined as positive when directing the domain inwards). Figure 4.11 shows this average pressure as a function of the imposed cavity expansion \( u_{ii}/a_t \) (200 practically coinciding dashed lines) as well as the pressure – expansion relationship according to the analytical solution of the cavity expansion model for a square or a triangular lattice (two solid lines). The numerical results are very close to the analytical ones. In conclusion, as the cavity expansion model provides adequate predictions, it will be adopted for the following investigations into macroscopic swelling pressure.

**Figure 4.11.** Macroscopic swelling pressure as a function of the cavity expansion

### 4.3.2.5 **Synthesis of static and thermodynamic equilibrium**

The condition of static equilibrium between the growing gypsum and the surrounding matrix (Eq. 4.13) must be handled simultaneously with the condition of thermodynamic equilibrium between gypsum and anhydrite (Eq. 4.11). In order to solve the system of Eqs. (4.11) and (4.13), we need additional relationships linking the crystallisation pressure \( p_c \) and the anhydrite pressure \( p_A \) appearing in Eq. (4.11) with the macroscopic swelling pressure \( \sigma_s \) and the stress \( \sigma_a \) at the boundary of the expanding cavities appearing in Eq. (4.13). These relationships will be established for the two borderline cases that have been introduced in Section 3.3.2.

As explained in Section 3.3.2, in the case of very rapid diffusion (the first borderline case), gypsum growth will theoretically occur in all pores (including pores far away from anhydrite particles). The expanding cavities are then identical with the pores, and their volume fraction \( \delta \) (Eq. 4.12) is equal to the porosity \( \phi \). In the second borderline case (very slow diffusion), the gypsum will grow very close to the anhydrite particles. For the sake of simplicity, we consider the expanding gypsum-filled pores as
being “smeared” over the surface of the anhydrite particles. The expanding cavities then represent the spaces that are occupied by the anhydrite particles and their gypsum “coating” (thick black line in Fig. 4.12a). In this case the volume fraction \( \delta \) is equal to the volume fraction \( \phi_A \) of the anhydrite particles.

Let us consider next the relationships between the pressures \( p_c \) and \( p_A \) appearing in Eq. (4.11) and the pressures \( \sigma_s \) and \( \sigma_a \) in the cavity expansion model. The first borderline case is rather trivial. The crystallisation pressure \( p_c \) is identical to the radial stress \( \sigma_a \) at the pore boundaries, while the pressure \( p_A \) acting upon the anhydrite particles can be taken equal to the macroscopic swelling pressure \( \sigma_s \), because the gypsum crystals are assumed to grow everywhere in the porous matrix around the anhydrite particles. Equations (4.11) and (4.13) lead (with \( p_c = \sigma_a, p_A = \sigma_s \) and \( b/a \) according to Eq. 4.12 with \( \delta = \phi \)) to the following expression for the macroscopic swelling pressure:

\[
\sigma_{s,P} = \left[ \left( \frac{\pi}{3\sqrt{2} \cdot \phi} \right)^{\frac{1}{2}} V_A^0 - \frac{V_G^0}{V_G^0} \right] \left[ \frac{(T-T_0)\Delta_{r,G}S^0 - \Delta_{r,G}G^0}{V_G^0} - \frac{2\gamma_G}{r_G} \right], \tag{4.19}
\]

where the subscript \( P \) was added to \( \sigma_s \) in order to indicate that we are considering the case of gypsum growth in all pores.

**Figure 4.12.** (a) Smeared model with gypsum coats around the anhydrite particles, (b) relationship between the crystallisation pressure \( p_c \) and the equivalent cavity expansion pressure \( \sigma_a \)

In the second borderline case some averaging must be made with respect to the stress that acts upon the anhydrite particles because the cavity expansion model smears the expansion of the pores next to the anhydrite particles across the entire surface of the particles (Fig. 4.12a). (Remember that the expanding cavities of the spherical cavity expansion model in this case represent the anhydrite particles with a uniform gypsum “coating”.) As the individual growing pores on the anhydrite surface develop the crystallisation pressure \( p_c \) (Fig. 4.12b), without actually covering the entire anhydrite surface, the radial pressure \( \sigma_a \) at the cavity boundary of the cavity expansion model will be lower than \( p_c \). The ratio of \( \sigma_a \) to \( p_c \) can be taken equal to the percentage of the anhydrite surface area, that is in contact with the growing crystals, *i.e.* – assuming densest packing – equal to \( \pi/(2\sqrt{3}) (r_p/h_p)^2 \), where
\( r_p \) and \( b_p \) are equal to the pore radius and to the half distance of the pore centres, respectively (cf. Fig. 3.10). Their ratio \( r_p / b_p \) is given by Eq. (4.12) with \( \delta = \phi, a = r_p \) and \( b = b_p \). Finally, we obtain:

\[
\sigma_a = p_c \left( \frac{\pi \sqrt{3}}{4} \right)^{\frac{1}{2}} \phi^{\frac{\sqrt{2}}{3}}.
\] (4.20)

This equation together with Eq. (4.11) (with \( p_A = \sigma_A \)) and Eq. (4.13) (with \( b/a \) according to Eq. 4.12 with \( \delta = \phi_A \)) leads to the following expression for the macroscopic crystallisation pressure:

\[
\sigma_{s,A} = \left[ \frac{3\sqrt{2} \cdot \phi_A}{\pi} \right]^{\frac{1}{2}} \left[ \left( \frac{4}{\pi \sqrt{3}} \right)^{\frac{1}{2}} \phi^{\frac{\sqrt{2}}{3}} - \frac{V_A}{V_G} \phi^{\frac{\sqrt{2}}{3}} \right]^{\frac{1}{2}} \left[ \frac{(T - T_0) \Delta \gamma_{G,A} S_0 - \Delta \gamma_{G,A} G^0}{V_G} - \frac{2 \gamma_G}{r_G} \right]^{\frac{1}{2}},
\] (4.21)

or, considering Eq. (4.19),

\[
\sigma_{s,A} = \sigma_{s,P} f(\phi_A, \phi),
\] (4.22)

where

\[
f(\phi_A, \phi) = \left( \frac{3\sqrt{2} \cdot \phi_A}{\pi} \right)^{\frac{1}{2}} \left[ \left( \frac{\pi}{3\sqrt{2}} \right)^{\frac{1}{2}} \phi^{\frac{\sqrt{2}}{3}} - \frac{V_A}{V_G} \phi^{\frac{\sqrt{2}}{3}} \right]^{\frac{1}{2}} \left[ \frac{4}{\pi \sqrt{3}} \phi^{\frac{\sqrt{2}}{3}} - \frac{V_A}{V_G} \phi^{\frac{\sqrt{2}}{3}} \right]^{\frac{1}{2}}.
\] (4.23)

It should be noted that the condition \( b/a > 1 \) leads, based on Eq. (4.12), to \( \delta < \pi / (3\sqrt{2}) \approx 0.74 \). The right side of this inequality corresponds to the densest possible packing and marks the validity limit of the cavity expansion model (Section 4.3.2.3). Thus, the model cannot be applied, if the porosity \( \phi \) (first borderline case) or the volume fraction \( \phi_A \) of the anhydrite particles (second borderline case) are higher than about 0.74.

One can readily verify that for \( \phi < 0.74 \) the right side of Eq. (4.23) is always less than one (Fig. 4.13). Consequently, Eq. (4.22) shows that the macroscopic pressure predicted by the second model (the borderline case of gypsum growth only close surface of the anhydrite particles) is always lower than the pressure predicted by the first one (the borderline case of gypsum growth in all pores). The lower the anhydrite content \( \phi_A \), the greater will be the difference between the two models. This is because gypsum growth will occur in only a few pores (the ones which are very close to the anhydrite particles) if the amount of anhydrite is small.
Figure 4.13. Ratio of the macroscopic swelling pressure $\sigma_{s,A}$ that develops in the borderline case of gypsum growth only in pores beside anhydrite particles to the pressure $\sigma_{s,P}$ that develops in the borderline case of gypsum growth in all pores, as a function of the volume fraction of the anhydrite $\phi_A$ and the porosity $\phi$.

4.3.2.6 Remarks concerning the termination of swelling pressure development

As already mentioned in Section 4.3.2.2, the model assumes that the growth of gypsum crystals and the development of swelling pressure will continue until thermodynamic equilibrium is reached. It should be noted, however, that the development of swelling pressure may terminate earlier (before reaching thermodynamic equilibrium) for one of the following reasons:

(i) The entire anhydrite in the specimen is transformed into gypsum.
   As explained below, this may happen only if the matrix around the growing crystals is very soft (softer than natural claystones) or if the anhydrite content is very low (lower than about 15%).

(ii) The entire pore water is consumed.
   This might happen in a closed system if the anhydrite content is high and the water content (porosity) low. In an oedometer test, the system is open because the sample is permanently in contact with water. Nevertheless, hydration might also cease due to lack of water in an open system if the growing gypsum plugs the pores, thus reducing permeability to practically zero.

(iii) The dissolution rate of anhydrite becomes practically zero.
   This may happen if the surfaces of the anhydrite particles have been sealed by gypsum, and it is relevant particularly for very coarse anhydrite particles or veins with a small specific surface area (see Section 6.4.5).

(iv) The transformation of anhydrite to gypsum proceeds without volume change.
   Swelling pressure develops due to the volume constraint imposed by the oedometer device. As a consequence of the stresses developing during the mineral transformation and of the ion concentration in the pore water, the dissolution rate of the anhydrite and the precipitation rate of
gypsum may become such that the volume fraction of anhydrite decreases at the same rate as the volume fraction of gypsum increases. In this case the volume of the solids, and consequently the swelling pressure as well, would cease to grow in spite of the on-going hydration. The mechanism of replacement of a mineral by another one under constant volume is known from petrography (cf. Merino and Dewers 1998).

Since Eqs. (4.21) and (4.22) are based solely upon the thermodynamic equilibrium, neglecting these effects, they tend to overestimate the macroscopic swelling pressure, i.e. the pressure predicted by the model in Section 4.3.2.5 represents an upper bound of the swelling pressure.

Concerning the above-mentioned point (i), we will show in the following that the transformation of a relatively small quantity of anhydrite causes a cavity expansion which is sufficient to mobilize the stress required for thermodynamic equilibrium between anhydrite and gypsum. In order to show this we will determine an upper limit of the required expansion. The cavity expansion that must occur for the stresses to increase to a level where anhydrite and gypsum are in thermodynamic equilibrium can be determined from Eq. (4.15):

\[ \frac{u_a}{a} = \frac{\sigma_s}{E} \left( \frac{\pi}{3\sqrt{2}\, \delta} \right)^{3/2} \left( \frac{\sigma_s}{\left( \frac{\pi}{3\sqrt{2}\, \delta} \right)^{3/2}} - 1 \right). \] (4.24)

where \( \delta = \phi \) and \( \sigma_s = \sigma_s,P \) (Eq. 4.19), in the borderline case that gypsum growth occurs in all pores, and \( \delta = \phi_t \) and \( \sigma_s = \sigma_s,A \) (Eq. 4.23), in the other borderline case of gypsum growth only in the pores next to anhydrite particles. It can readily be verified that

\[ \sigma_{s,A} < \sigma_{s,P} \] (see last Section), the inequality (4.25) is true for the macroscopic swelling pressure \( \sigma_s \) also in the borderline case that gypsum growth occurs only close to the surface of the anhydrite particles. In order to determine an upper bound for the cavity expansion \( u_a/a \) we consider, in addition to Eq. (4.25) the lowest values for the Young’s modulus \( E \) of the matrix reported in the literature (cf. Section 3.3.4). Considering all of the experimental results, a value of 2 GPa can be regarded as a lower bound of the Young’s modulus of the matrix. Taking into account that \( E > 2 \) GPa we obtain from Eq. (4.24) and Eq. (4.25), which, as mentioned above, applies both to \( \sigma_{s,A} \) and \( \sigma_{s,P} \), the following upper bound for the cavity expansion:

\[ \frac{u_a}{a} < 0.0315 \left( \frac{\pi}{3\sqrt{2}\, \delta} \right)^{3/2} \left( \frac{\sigma_s}{\left( \frac{\pi}{3\sqrt{2}\, \delta} \right)^{3/2}} \right)^{3/2} \] (4.26)

The cavity expansion \( u_a/a \) is associated with the hydration of a certain amount of anhydrite. Subsequently, the relationships between the volume fraction of the transformed anhydrite \( \Delta \phi_A \) and the
cavity expansion $u_a/a$ is derived for the borderline case that gypsum crystals grow in all pores and for the borderline case that gypsum grows next to anhydrite particles.

**Borderline case of crystal growth in all pores**

We consider the borderline case where the growing gypsum crystals theoretically fill both the space generated by the anhydrite dissolution and the initially existing pores completely, causing a subsequent uniform expansion of the latter. The volume change of the pore $\Delta V_p \ (= V_p - V_{p,0})$ can then be written as follows:

$$\Delta V_p = V_G - \Delta V_A - V_{p,0}, \quad (4.27)$$

where $V_G$ and $\Delta V_A$ denote the volume of gypsum and the volume change of anhydrite, respectively. Dividing both sides with the initial total volume we get:

$$\frac{V_p}{V_{p,0}} \phi = \frac{V_G^0}{V_A^0} \Delta \phi_A - \Delta \phi_A, \quad (4.28)$$

where $\Delta \phi_A$ is defined as the volume fraction of the transformed anhydrite. The assumptions of spherical pores and uniform gypsum crystal growth lead to:

$$\Delta \phi_A = \frac{\phi}{V_G^0 / V_A^0} \left(1 + \frac{u_a}{a}\right)^3. \quad (4.29)$$

Equation (4.29) in combination with Eq. (4.26) (with $\delta = \phi$) yields the upper limit of the amount of anhydrite $\Delta \phi_A$ that must be transformed to gypsum in order to reach thermodynamic equilibrium, if the gypsum growth takes place in all pores. Figure 4.14 shows this upper limit as a function of the porosity $\phi$ (solid line). For the typical porosities of anhydritic claystones ($5 – 10\%$, cf. Section 3.2.2), the volume fraction of the anhydrite that must be transformed to gypsum amounts to $10 – 20\%$ at most. If the anhydrite content is higher than $10 – 20\%$, then the macroscopic swelling pressure will increase until thermodynamic equilibrium is reached. If, on the other hand, the anhydrite content is lower than $10 – 20\%$, the process may stop before reaching equilibrium and the macroscopic swelling pressure will be lower than predicted by Eq. (4.17). This would also happen in the theoretical case of an extremely soft matrix (dashed line in Fig. 4.14) because a large expansion of the cavity would be necessary (and consequently a large amount of anhydrite should transform into gypsum) in order to mobilize the pressure thermodynamically required in order the transformation process to stop.
Borderline case of gypsum growth in pores close to anhydrite particles

In this borderline case, only the pores which are close to anhydrite particles and the space induced by the dissolution of anhydrite are filled with gypsum crystals. Neglecting the filling of the volume of the pores next to the anhydrite particles, the volume change of the anhydrite particles \( \Delta V_{AG} \) (\( = V_{AG} - V_{A,H} \), where \( V_{AG} \) is the volume of the particle composed of anhydrite and gypsum) is given by:

\[
\Delta V_{AG} = V_{G} - \Delta V_{A}. \tag{4.30}
\]

Dividing both sides with the initial total volume we get:

\[
\left( \frac{V_{G}}{V_{A,0}} - 1 \right) \phi_A = \frac{V_{G}^0}{V_{A}^0} \Delta \phi_A - \Delta \phi_A. \tag{4.31}
\]

The assumptions of spherical particles and uniform expansion due to the gypsum crystal growth result in:

\[
\Delta \phi_A = \frac{\phi_A}{V_{G}^0 / V_{A}^0 - 1} \left( \frac{1 + \frac{u}{a}}{1} \right)^3 - 1. \tag{4.32}
\]

Equation (4.32) in combination with Eq. (4.26) (with \( \delta = \phi_A \)) yields the upper limit for the amount of anhydrite \( \Delta \phi_A \) that must be transformed to gypsum in order to reach thermodynamic equilibrium in the borderline case that gypsum grows only close to the surface of the anhydrite particles. In this case, the volume fraction of the anhydrite that must be transformed into gypsum amounts to only few percent (Fig. 4.15, solid line), which means that the macroscopic swelling pressure is governed by the thermodynamic equilibrium for the relevant range of matrix stiffness \( E \). (The dashed line in Fig. 4.15 applies to an extremely low \( E \)–value and is presented only for comparison.)
4.3.2.7 Computational results

According to Eqs. (4.19) and (4.22) the macroscopic swelling pressure $\sigma_s$ depends on the porosity $\phi$, on the volume fraction $\phi_A$ of the anhydrite particles, on the temperature $T$ and, in the case of a fine-porous matrix with relevant liquid-solid interface effects, also on the pore radius $r_P (= r_G)$.

Figure 4.16 shows the swelling pressure $\sigma_s$ as function of porosity $\phi$ for $T = 15 – 25 \, ^\circ C$ without taking into account liquid-solid interface effects. The solid lines apply to the borderline case of crystal growth in all pores, and they were computed by means of Eq. (4.19). For the typical porosity range of anhydritic claystones ($4 – 10\%$, shaded area in Fig. 4.14) the swelling pressure is equal to $3 – 7 \, \text{MPa}$. The role of temperature is not negligible, as an increase of only $5 \, ^\circ C$ leads to a decrease in the swelling pressures of about $1 \, \text{MPa}$, which is significant from the standpoint of the structural design of a tunnel lining. (The reason for the temperature-dependency is that the solubility of gypsum depends only slightly on temperature, but the solubility of anhydrite and thus the oversaturation increases considerably with decreasing temperature.) The dashed lines correspond to the other borderline case, i.e. that crystal growth occurs only in pores close to the surfaces of anhydrite particles and that the volume fraction $\phi_A$ of the anhydrite is equal to $25\%$ or $50\%$. They were computed by using Eq. (4.22).

In this case the swelling pressure is about half as high as in the other model (see also reduction factor in Fig. 4.13).
Figure 4.16. Macroscopic swelling pressure $\sigma_s$ as a function of the porosity $\phi$, neglecting liquid-solid interfacial effects (dashed lines: gypsum growth close to the anhydrite particles, solid lines: gypsum growth in all pores, shaded area: porosity range of six samples from the Belchen Tunnel and the Chienberg Tunnel).

Figure 4.17. Macroscopic swelling pressure $\sigma_s$ as a function of the porosity $\phi$ and the pore radius $r_G$ (gypsum growth in all pores, $T = 20^\circ C$, shaded area: porosity range of six samples from the Belchen Tunnel and the Chienberg Tunnel).
As can be seen from the last term of Eq. (4.19), the surface free energy of the gypsum-water interface decreases the macroscopic swelling pressure in particular for small pore radii $r_G$. Figure 4.17 shows the swelling pressure as a function of the porosity for different pore radii $r_G$. The dashed line applies to large pores without a liquid-solid interfacial effect. The liquid-solid interfacial effect is highly relevant for rocks with very fine pores (pore radius smaller than about 100 nm). It is evident that the smaller the pore radius, the lower will be the macroscopic swelling pressure.

In the following we will show the significance of the pore radius with reference to the MIP results presented in Section 3.2.2. Figure 4.18 shows the porosimetric curves of two samples (one from the Belchen Tunnel and one from the Chienberg Tunnel). As the actual pores vary in size, the application of the simplified model in Section 4.3.2, which takes a uniform size, is not straightforward. However, Eq. (4.19) provides a rough indication as to the magnitude of the interfacial effect: Let us choose the pore radius value in Eq. (4.19) so that only 20% of the pores have a bigger radius. With this choice, Eq. (4.19) tends to overestimate the swelling pressure because the great majority (80%) of the pores have a radius smaller than the assumed value, and therefore favour less crystal growth than the assumed pore. The 20% - fractile amounts to 14 nm for the Belchen sample and to 490 nm for the Chienberg sample (points B and C in Fig. 4.18, respectively). These pore radii in combination with the measured porosities of the two samples (7.19% and 9.03%, respectively) lead to swelling pressures of about 2 MPa and 5.5 MPa, respectively (see points B and C in Fig. 4.17). The solid-liquid interfacial effect is thus negligible for the Chienberg sample, but significant for the Belchen sample: Without this effect the swelling pressure would be equal to about 4.7 MPa (point B in Fig. 4.17).

In any case, the simplified model in Section 4.3.2 predicts macroscopic swelling pressures which lie within the range of the experimental values for anhydritic claystones (cf. Table 4.2) and are significantly lower than the microscopic crystallisation pressures in Section 4.2.
4.4 Megascale

The term “megascale” refers to the scale of a tunnel. The swelling pressure at this scale is the pressure that would develop on a stiff invert lining. In contrast to the conditions in swelling pressure oedometer tests, the development of swelling strains cannot be completely prevented in situ. Even a stiff lining may experience certain heave. In addition, intercalated non-swelling rock layers may allow some expansion of the swelling layers even if the overall volume of the rock mass remains practically constant.

This can be seen, for example, from the results of field measurements in the Belchen Tunnel. Figure 4.19 shows the distribution of axial strain along four measuring lines. (“Axial strain” means the strain in the direction of every line. It was measured piecewise, over intervals of 1 m, by means of sliding micrometers.) The zero measurement was taken in September 1986, 18 years after completion of the tunnel. The solid and dashed lines show the strain profiles 6 and 12 months, respectively, after the zero measurement. It is evident that the development of swelling strains is accompanied by a heave of the invert arch and also by a partial compression of non-swelling layers.

![Figure 4.19. Strain profiles measured in the Belchen Tunnel (after Kovári et al. 1988)](image)

A well-known property of clays and claystones is that development of a swelling strain leads to a lower swelling pressure (Kovári et al.1988). This property, in combination with the swelling strains observed (Fig. 4.19), suggests that the swelling pressure in situ must be lower than the pressure developing under volume constraint in oedometer tests. It is, nevertheless, still uncertain whether and to what extent anhydritic claystones, the expansion of which is also due to gypsum crystal growth, exhibit the same property and whether the unavoidable development of some swelling in situ is thus really significant with respect to the swelling pressure at the megascale (Anagnostou 2007).
Table 4.3 gives an overview of measured or estimated values for swelling pressure in situ. The given values are fraught with smaller or larger uncertainties concerning both the interpretation of the monitoring results and the reliability of the measurements themselves.

In many cases the data refer to tunnels in which a stiff invert arch was constructed only after the occurrence of considerable heave and after repeated reconstruction work (e.g. Belchen Tunnel, Hauenstein Base Tunnel, Wagenburg Tunnel). Therefore, measurements of the pressure acting upon the invert arch in situ or back-calculations of the swelling pressure based on the bearing capacity of the installed lining probably underestimate the swelling pressure that would develop on an intact lining under the condition of practically complete prevention of deformation.

With respect to the reliability of the measurements, it should be noted that pressure cells, which are often used for the direct measurement of the contact pressure between the lining and the rock, are particularly problematic. Experience shows that they may fail within few years of installation, which also calls into question their pre-failure reliability. In addition, depending on their stiffness and on the stiffness of the embedding mortar, they may significantly underestimate or overestimate the actual pressure (Amstad and Kováři 2001). As a consequence, the measured values often exhibit considerable scatter, which is hard to interpret.

Figure 4.20. (a) Time-development of the floor heave $u$ under a constant support pressure $\sigma_s$ of 0.10, 0.25, 0.50 or 0.75 MPa and, (b), floor heave as a function of the support pressure $\sigma_s$ (5, 10, 15 and 20 years after test begin) in blocks XI to XIV of the exploratory gallery of the Freudenstein Tunnel (data from Kováři 1996 and Geotechnisches Ingenieurbüro 2007, referred by Wahlen 2009)
### Table 4.3. Swelling pressures measured or estimated in situ

<table>
<thead>
<tr>
<th>Project</th>
<th>Measuring period</th>
<th>Swelling pressure [MPa]</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belchen Tunnel, Switzerland (1967)</td>
<td>1967-1972</td>
<td>0.5 – 3.5 (average 1.75)</td>
<td>Measured by pressure cells. Large scatter of measured values. Most cells destroyed within 2 years.</td>
<td>Grob (1972, 1976)</td>
</tr>
<tr>
<td>Hauenstein Base Tunnel, Switzerland (1916, reconstr. 1923, 1986)</td>
<td>1988</td>
<td>1.6 (average, standard deviation 1.3)</td>
<td>Back-calculated from the tangential stress in the lining (measured by flat jacks)</td>
<td>Steiner et al. (1989)</td>
</tr>
<tr>
<td>Adler Tunnel, Switzerland (1999)</td>
<td>1999 - 2006</td>
<td>≤ 1.8 (15 sensors), 4 (1 sensor)</td>
<td>Measured by special sensors that were incorporated into the segmental lining. Irregular distribution of measured values.</td>
<td>Noher et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>1987-2007</td>
<td>0.8 – 5.5</td>
<td>Dto.</td>
<td>Geotechnisches Ingenieurbüro (2007), Wahlen (2009)</td>
</tr>
<tr>
<td>Freudenstein Tunnel (exploratory gallery blocks XI to XIV), Germany (1987)</td>
<td>1987-2007</td>
<td>1.2</td>
<td>Extrapolated from measured floor heave (Fig. 15)</td>
<td>Geotechnisches Ingenieurbüro (2007), Wahlen (2009)</td>
</tr>
<tr>
<td>Heslach II Tunnel, Germany</td>
<td>1987</td>
<td>3.3</td>
<td>9.5 month long, large scale swelling pressure test in situ (sample ø 600 mm). Test stopped before reaching final state.</td>
<td>Kiehl and Wittke (1991)</td>
</tr>
<tr>
<td>Lilla Tunnel, Spain (2003)</td>
<td>2005-2011</td>
<td>&lt; 6 (mostly 3 – 4)</td>
<td>Measured by pressure cells. Extremely irregular distribution of the measured values in the cross-sections and along the tunnel.</td>
<td>Alonso et al. (2013)</td>
</tr>
</tbody>
</table>

Large scale swelling tests, such as the one conducted in blocks XI to XIV of the Freudenstein exploratory gallery (Kovári et al. 1986, Amstad and Kovári 2001), allow for a straightforward determination of the maximum swelling pressure in situ. In the Freudenstein field test, a support pressure was applied to the floor by means of prestressed anchors and the time development of the heave was monitored (Fig. 4.20a). Figure 4.20b shows the measured floor heave $u$ as a function of the applied support pressure $\sigma_s$ at different times from the start of the test. The extrapolations of the four
lines tend to converge to a single point on the stress axis at about 1.2 MPa. This is the stress that would prevent floor heave completely, i.e. the swelling pressure in situ.

An upper bound of the swelling pressure in situ can be determined by considering the bearing capacities of the linings of tunnels that cross heavily swelling rock but do not exhibit signs of overstressing. A similar approach was followed by Amstad and Kovári (2001) in their evaluation of the lining of the Belchen Tunnel, as well as by Kovári (2010) and Kovári and Vogelhuber (2014) who analysed a number of tunnels crossing the Gypsum Keuper formation.

As examples we consider here the Adler Tunnel (Jedelhauser 2008) and the Chienberg Tunnel (Chiaverio and Thut 2010). The Adler Tunnel has a circular cross-section with a radius of approximately 6 m and 0.65 – 0.70 m thick concrete lining. The Chienberg Tunnel has an almost circular cross-section also with a radius about 6 m and a concrete lining 0.70-1.10 cm thick. They were analysed by applying the computational model in Fig. 4.21a, according to which the lining is conceived of as an elastically embedded circular ring. The ring is loaded at the invert by a vertical swelling pressure (cf. Amstad and Kovári 2001). The interface between the ground and the lining was modelled using appropriate contact elements, preventing penetration (but allowing separation) in the normal direction as well as providing a slight sliding resistance. The lining thickness was taken equal to 0.70 m (Adler Tunnel) or 1.00 m Chienberg Tunnel). Both the rock and the concrete were considered as linearly elastic materials. In order to obtain an upper bound for the swelling pressure, a high Young’s modulus was assumed for the rock mass (7.5 GPa) in combination with a low Young’s modulus for the concrete lining (15 GPa). The Poisson’s ratio was taken equal to 0.20 for both materials. The numerical solution was obtained by the finite element method (Plaxis 2012).

Figure 4.21b shows the internal forces of the lining computed for a unit load and for a lining thickness of 0.70 m (solid lines) or 1.00 m (dashed lines). Lining sections A and B present the highest moments $M$ and, considering that the axial force $N$ is almost uniform at the lower part of the tunnel, they are chosen as the control positions for failure assessment. Figure 4.21c shows the $(M, N)$ – pairs for these two lining sections as well as the axial force-bending moment interaction diagram for the case of a 0.70 m thick lining (Adler Tunnel) assuming strong reinforcement (steel bars ø25 / 125 mm). Figure 16d shows the results for a 1.00 m thick, unreinforced concrete lining (Chienberg tunnel). Due to the linearity of the problem, the swelling pressure that must be applied in order to reach the bearing capacity of a cross section can be estimated by a simple linear extrapolation, amounting in the cases of Figs. 4.21c and 4.21d to about 4.6 MPa and 5.5 MPa, respectively. As there is no sign of overstressing in these tunnels, it can be concluded that the actual swelling pressure in situ must be considerably lower than these values. It should be noted that the lining of the Chienberg tunnel is not exactly circular. If the actual geometry were taken into account, the result would be higher bending moments (Kovári 2013) and an even lower back-calculated swelling pressure than the one indicated by Fig. 4.21.
In conclusion, the existing observations seem to support the hypothesis that the swelling pressure *in situ* (megascale) is lower than the pressures developing in laboratory swelling tests (macroscale), although the difference is not as pronounced as the difference between the microscale and the macroscale.

Figure 4.21. (a) Computational model for a tunnel subjected to swelling pressure; (b) axial force and bending moment diagrams for the lining; (c) axial force - bending moment interaction diagram as well as tunnel response ($M, N$) assuming linear behaviour for the rock and the lining for a 0.70 m thick, reinforced concrete lining and (d) for a 1.00 m thick, unreinforced concrete lining (both with concrete quality C50/60)

### 4.5 Conclusions

The swelling pressure depends on the scale considered. In this respect a distinction must be made between: (i), the pressure at the microscale (*i.e.* the crystallisation pressure of a single constrained crystal); (ii), the pressure at the macroscale (*i.e.* the pressure of a specimen in an oedometer test); and, (iii), the pressure the megascale (*i.e.* the pressure developing upon a stiff invert lining *in situ*).
The factors affecting crystallisation pressure were investigated by means of thermodynamic computations. We considered different scenarios with respect to oversaturation for both closed and open systems and concluded that crystallisation pressure can vary across a very wide range.

In order to study the macroscopic pressure we used the cavity expansion model, which accounts in a simplified manner for the interaction between a growing crystal and the surrounding matrix. This model is able, in spite of its simplicity, to explain why the swelling pressures observed in laboratory tests are lower by one order of magnitude than the crystallisation pressure. The computations indicate, furthermore, that the development of swelling pressure in most cases does not cease until thermodynamic equilibrium is reached. The process may stop before reaching thermodynamic equilibrium (at a lower swelling pressure) only if the volume fraction of anhydrite is very low or if the rock matrix around the growing gypsum crystals is extremely soft. Finally, the data about the swelling pressure in situ are fraught with uncertainties, but seem to indicate that the in situ swelling pressures are in general lower than the pressures at the macroscale.
5 Time Development of Sulphate Hydration

5.1 Introduction

The swelling of anhydritic claystones is a markedly time-dependent process. It may take several decades to complete in nature and is therefore important for the design particularly of the final tunnel lining. The present Chapter aims to improve our understanding of the factors governing the time-dependency of swelling by investigating the kinetics of the underlying anhydrite dissolution and gypsum precipitation reactions.

The Chapter begins with an overview of common formulations of dissolution and precipitation rates found in the literature (Section 5.2.1) and continues with an estimate of the kinetic parameters based on the published experimental data. Additional equations are subsequently presented in order to take the effect of the sealing of anhydrite by a layer of gypsum into account, which, according to existing investigations and observations, is decisive for the evolution of the swelling process under certain conditions (Section 5.2.2). Section 5.2.3 formulates the equations that govern the evolution of a closed system with simultaneous anhydrite dissolution and gypsum precipitation.

Section 5.3 checks the predictive capacity of the computational model on the basis of the existing experimental data from Kontrec et al. (2002). Section 5.4 investigates the effect of the initial composition of the system and of the surface areas of any minerals on the time-development of hydration in a closed system, showing that anhydrite dissolution (rather than gypsum precipitation) is the governing factor for transformation durations in most cases and developing a simplified equation for estimating the hydration durations. The Chapter finishes with parametric studies on the effect of anhydrite sealing (Section 5.5).

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7 This Chapter is based on Serafeimidis and Anagnostou (2012a,b) and Serafeimidis and Anagnostou (2013)
5.2 Kinetic model

5.2.1 Dissolution and precipitation rates

5.2.1.1 Reaction rate expressions

In the literature, different formulations can be found for dissolution and precipitation rates (e.g. Appelo and Postma 2005; Lasaga 1986 and 1998; Mullin 2001; Nancollas and Purdie 1964; Steefel and Van Cappellen 1990; Steefel and Lasaga 1994). Generally, the rates depend on the reactive surface area of the mineral, the temperature and the distance of the system from thermodynamic equilibrium. A general formulation for the mass change rate of a mineral in contact with water due to dissolution or precipitation is (Mullin 2001):

\[
dM / dt = k \cdot A \cdot f(c).
\]  

(5.1)

where \( dM/dt \) [kg/s] is the mass change rate of the mineral (positive for precipitation and negative for dissolution); \( A \) [m²] denotes the surface area of the mineral in contact with water (note that \( A \) may vary over time); \( k \) [kg/m²/s] is the reaction rate constant (increasing with temperature according to the equation of Arrhenius, cf., e.g. Atkins and De Paula 2006); and \( f(c) \) is a function of the ion concentration \( c \). It is given here as a function of the relative supersaturation (Mullin 2001):

\[
f(c) = \text{sgn}(c - c_{eq}) \cdot \left| (c - c_{eq})/c_{eq} \right|^\delta.
\]  

(5.2)

where \( \delta \) represents the order of the chemical reaction, \( c_{eq} \) is the equilibrium concentration of the mineral and, consequently, \((c - c_{eq})/c_{eq}\) expresses the degree of oversaturation, i.e. the driving force for dissolution and precipitation. For solutions that are supersaturated with respect to the mineral, i.e. \( c > c_{eq} \), \( f(c) \) the mass change rate is therefore positive and precipitation takes place. In contrast to this, in the case of undersaturated solutions \( (c < c_{eq}) \), the mass change rate is negative and the mineral dissolves.

At this point, two definitions that are necessary for the remainder of this work are introduced. Specifically, the mass of constituent \( i \) of a mixture per unit volume of the mixture will subsequently be denoted by:

\[
m_i = M_i / V_{tot},
\]  

(5.3)

where \( M_i \) [kg] denotes the mass of the \( i \)-th constituent at a given time and \( V_{tot} \) [m³] is the volume of the mixture which (for small volume changes) can be taken approximately equal to the initial mixture volume \( V_{tot,0} \). Additionally, the volume fraction of the mixture constituents are denoted by

\[
\phi_i = V_i / V_{tot} = m_i / \rho_i.
\]  

(5.4)
where $V_i$ and $\rho_i$ are the volume and density of constituent $i$, respectively.

From Eqs. (5.1), (5.3) and (5.4) we obtain the following equation for the mass change of a mineral per unit volume of a mixture:

$$\frac{dm}{dt} = \rho \frac{d\phi}{dt} = k \phi F f(c), \tag{5.5}$$

where $F$ [$\text{m}^{-1}$] is the specific surface area of the mineral, while the product of $\phi$ by $F$ is equal to the surface area of the dissolving or precipitating mineral per unit volume of the mixture.

The rates of anhydrite dissolution and gypsum precipitation can then be expressed as follows:

$$\frac{dm_A}{dt} = -k_A \phi_A F_A \left( \frac{c_{eq,A} - c}{c_{eq,A}} \right)^{\delta_A} \tag{5.6}$$

and

$$\frac{dm_G}{dt} = k_G \phi_G F_G \left( \frac{c - c_{eq,G}}{c_{eq,G}} \right)^{\delta_G}, \tag{5.7}$$

where $\delta_A$ and $\delta_G$ denote the orders of reaction for anhydrite dissolution and gypsum precipitation, respectively, while $F_A$ and $F_G$ [$\text{m}^{-1}$] are the specific surface areas (particle surface per particle volume) of the anhydrite and gypsum particles, respectively. For spherical or cubical particles, the specific surface area is equal to $3 \cdot (\text{radius})^{-1}$ or $6 \cdot (\text{side length})^{-1}$, respectively. As mentioned above, the terms $\phi_A F_A$ and $\phi_G F_G$ represent the area of the rock surface which is in contact with the pore water per unit volume of mixture. It should be noted that the specific surfaces $F_A$ and $F_G$ generally change during the dissolution and precipitation process (cf. Section 5.2.1.2-5.2.1.5).

The anhydrite surface per unit volume ($\phi_A F_A$) can be expressed as a function of the anhydrite mass in the following way:

$$\frac{\phi_A F_A}{\phi_{A0} F_{A0}} = \left( \frac{m_A}{m_{A0}} \right)^{\nu} = \left( \frac{\phi_A}{\phi_{A0}} \right)^{\nu}, \tag{5.8}$$

where $\phi_{A0} F_{A0}$, $\phi_{A0}$ and $m_{A0}$ are the initial anhydrite surface, volume and mass (per unit mixture volume), respectively, while the exponent $\nu$ accounts for changes to reactive surface sites caused by changes in crystal size or changes in the distribution of the crystal population during dissolution or precipitation (Appelo and Postma 2005). It can readily be verified that $\nu = 2/3$ for uniformly dissolving, cubical or spherical anhydrite particles. This is because the volume of each particle is proportional to the cube of its radius (or of the edge length in the case of cubical particles), while its surface area is proportional to the square of the radius or side length. From Eqs. (5.6) and (5.8), we obtain the following expression for the mass rate of anhydrite in the case of spherical or cubical particles:
\[
\frac{dm}{dt} = -k_A \phi_{A0} F_{A0} \left( \frac{m_A}{m_{A0}} \right)^{2/3} \left( \frac{c_{eq,A} - c}{c_{eq,A}} \right)^{\delta_A},
\]

where \( F_{A0} = 3 \text{-(radius)}^{-1} \) for spherical particles and \( F_{A0} = 6 \text{-(side length)}^{-1} \) for cubical particles.

For the case of growth on spherical or cubical gypsum particles a similar equation to Eq. (5.9) applies:

\[
\frac{dm_G}{dt} = k_G \phi_{G0} F_{G0} \left( \frac{m_G}{m_{G0}} \right)^{2/3} \left( \frac{c - c_{eq,G}}{c_{eq,G}} \right)^{\delta_G},
\]

while for gypsum crystal growth on inert minerals of spherical or cubical particles Eq. (5.10) takes following form:

\[
\frac{dm_G}{dt} = k_G \phi_s F_S \left( \frac{m_G}{m_{G0}} \right)^{2/3} \left( \frac{c - c_{eq,G}}{c_{eq,G}} \right)^{\delta_G},
\]

where \( F_S \) and \( \phi_s \) denote the specific surface area and the volume fraction, respectively, of the inert mineral on which gypsum growth takes place.

An alternative way to express the dissolution and precipitation rates is in terms of the distance \( s \) of the surface of a mineral at time \( t \) from the initial mineral surface (see Fig. 5.1 for the definition and the sign of \( s \)). Equation (5.1) is equivalent to the following equation for the rate of \( s \):

\[
\frac{ds}{dt} = \frac{k}{\rho} f(c),
\]

where \( f(c) \) is given by Eq. (5.2). For mineral dissolution, \( f(c) < 0 \) and consequently \( s \) decreases, while for mineral precipitation \( f(c) > 0 \) and \( s \) increases.

Figure 5.1. Movement of mineral surface due to dissolution or precipitation

5.2.1.2 Shape and size of anhydrite in claystones

The anhydrite surface in contact with water (which, according to Eq. 5.1, is decisive for the mass change rate) depends on the anhydrite content \( \phi_A \) and on the specific surface \( F_A \) of the particles, \( i.e. \) on their size and shape. Langbein et al. (1982) presented a qualitative classification of anhydrite with
respect to these two factors (Fig. 5.2). Despite the lack of values concerning size, the classification of Fig. 5.2 provides an overview of the possible occurrence of anhydrite in natural rocks.

![Classification of anhydrite in natural rocks (after Langbein et al. 1982) and order of particle size (left to right decreasing size, top to down different shapes)](image)

A first impression of the size of the particles can be gained from the typical examples in Fig. 5.3. Photographs 5.3a and 5.3b are from Murray (1964), who studied the diagenesis of anhydrite and gypsum. The particles seem to belong to the nodular type of the classification of Langbein et al. (1982) (second and third row of Fig. 5.2) and their sizes vary from a few mm to a few cm. Azam et al. (1998) studied the behaviour of expansive soil formations containing anhydrite and gypsum in Eastern Saudi Arabia. Figure 5.3c shows the results of scanning electron microscopy (SEM) performed on anhydrite samples. The photograph shows the presence of thin, prismatic, anhydrite particles of a few μm in size which belong to the two groups on the right in the bottom row of Fig. 5.2. Figure 5.3d shows a typical sedimentary deposit from close to Dammam (Azam 2007) containing anhydrite layers of a few cm thickness (as indicated by the pencil), which can be classified as ‘massive’ or ‘fine-layered’ in Langbein et al.’s (1986) classification (top row of Fig. 5.2). Figures 5.3e and 5.3f are from the Chienberg tunnel. The samples were collected within the framework of an on-going research project on the long-term relationship between swelling strain and pressure (Pimentel and Anagnostou 2010). Sample 935/3/1/1 (Fig. 5.4e) contains (at the top) anhydrite as a white strip of a few mm thickness which belongs to the first two types of the first row in Fig. 5.2. The SEM analysis of sample 2040 (12) revealed the presence of anhydrite, gypsum and other constituents, such as dolomite, quartz, clay (with visible cracks) etc. (Fig. 5.3f). The anhydrite particles (white in the SEM image) are nodular and up to 200 μm in size.

In conclusion, anhydrite appears, roughly speaking, either in the form of layers of different thicknesses and spacings (Fig. 5.3d, 5.3e) or as particles. The latter may have a form closer to a sphere (nodules,
Fig. 5.3a, 5.3f) or a rather prismatic form (Fig. 5.3b, 5.3c). Their size lies within a wide range (a few \( \mu \text{m} \) to a few \( \text{cm} \)).

Figure 5.3. a) Bed of nodular anhydrite (Murray 1964); b) Anhydrite types in reflected light (Murray 1964); c) SEM micrograph of anhydrite (Azam et al. 1998); d) Layered anhydrite near Dammam (Azam 2007); e) Claystone with a remarkable anhydrite vein (sample 935/3/1/1 from Chienberg tunnel); f) SEM image of anhydritic claystone (sample 2040 (12) from Chienberg tunnel)

5.2.1.3 Kinetic constants for the dissolution of anhydrite

Barton and Wilde (1971) investigated the dissolution of anhydrite at \( T = 25^\circ \text{C} \) by a rotating disc method, performing experiments with different rotation speeds. The role of the preparation temperature was investigated as well. The application of different temperatures introduces the heterogeneity that anhydrite might have in crystal structure as a consequence of its genesis. In order to avoid the erosion of the rotating disc, less than 2% of the total reaction was studied and the maximum concentration reached was approximately a hundred times less than the solubilities of the minerals (i.e. \( c << c_{eq,A} \)). Therefore, a linearization of the results was possible, i.e. a zero-order reaction rate could be used (\( \delta t = 0 \)). The rotation of the disc initiates transport of the ions due to advection and diffusion, resulting in reaction rate constants \( k_d \) as a function of the rotation speed. (In diffusion controlled dissolution, high flow velocities tend to reduce the thickness of the diffusion layer of the reaction surface, increasing the concentration gradient and thus leading to higher reaction rate constants.) However, for the present study, the reaction rate constant \( k_d \) will be estimated only for the
case of no transport processes (closed system), \textit{i.e.} for a zero rotation speed. In order to achieve this, an extrapolation of the existing results to zero rotation speed was performed (Appendix D1) leading to rate constants $k_A$ for the dissolution of anhydrite which vary within the range $k_A = 2.7 \text{ – } 5.4 \cdot 10^{-6} \text{ kg/m}^2/\text{s}$.

James and Lupton (1978) studied the dissolution of anhydrite at $T = 23^\circ\text{C}$ as a cause for deteriorating foundations of hydraulic structures. They performed three different kinds of experiments in order to determine the reaction rate constants of the chemical reactions as a function of the flow velocity of the water. As in Barton and Wilde (1971), advective and diffusive transport occurred simultaneously with the chemical reactions (increasing the reaction rate constants as mentioned above). For the dissolution of anhydrite a second order law was proven to be valid, \textit{i.e.} $\delta_A = 2$.

In the first experiment, distilled water was able to flow with different flow velocities through a small hole which was drilled through rock samples containing anhydrite. The ion concentration in the circulating solution was measured by atomic absorption spectroscopy and was taken as a measurement of the dissolved calcium sulphate in the water. As already mentioned, for the current study the reaction rate constants corresponding to zero flow velocities are of interest. After applying some minor transformations shown in Appendix D2 to account for differences in the definitions of the material constants between James and Lupton (1978) and the present formulation, a reaction rate constant of $k_A = 4.8 \cdot 10^{-6} \text{ kg/m}^2/\text{s}$ was obtained.

In the second series of experiments, glass tubes were filled with dry mixtures of crushed massive calcium sulphate and sand. Water was pumped through the tubes at a controlled rate and the conductivity was measured in order to follow the evolution of the ion concentration over time. The reaction rate constant of anhydrite was then calculated to be $k_A = 3.2 \cdot 10^{-6} \text{ kg/m}^2/\text{s}$.

In the third experiment, holes were drilled through massive anhydrite and gypsum and the changes in the shape of the hole were measured by slicing the specimen and measuring the diameter of the hole. For low flow velocities, the reaction rate constant of anhydrite is $k_A = 2.4 \cdot 10^{-6} \text{ kg/m}^2/\text{s}$.

Kontrec \textit{et al.} (2002) studied the kinetics of anhydrite dissolution at temperatures between $T = 10 – 40 ^\circ\text{C}$ by injecting anhydrite particles into a solution. Changes in the liquid and the solid phase were recorded by either monitoring the conductivity or by measuring the concentration of the calcium ions in the solution. A mathematical model was also developed, in which the calibration indicated a second order reaction ($\delta_A = 2$). The initial masses of anhydrite used in the experiments and the specific surface area of the anhydrite particles were given in the paper. The particles had a specific surface area of $3.78 \pm 0.04 \text{ m}^2/\text{g}$. The mass balance equation for the ions in a closed system consisting of anhydrite (subscript A) and gypsum (subscript G) and water (subscript W) which in the general case is given by:

$$m_t = m_{t0} + (m_{t0} - m_A) - 136 (m_G - m_{G0})/172,$$

(5.13)
where \( m_{A0}, \ m_{W0}, \ m_{G0} \) and \( m_{I0} \) denote the initial masses per unit volume was then used in combination with Eq. (5.9) for an aqueous solution (i.e. assuming a very high porosity) and applying a second order law. The general best fit with the experimental results at \( T = 20^\circ C \) which were performed for \( m_{A0} = 1.60, \ 2.28 \) and \( 4.00 \ kg/m^3 \) appeared to be for \( k_A = 5.4 \times 10^{-7} \ kg/m^2/s \). This value is lower by a factor of 5 to 10 than the values proposed by Barton and Wilde (1971) and James and Lupton (1978). The difference may be due to the aforementioned uncertain assumption concerning the particle shape and to a lesser degree the slightly lower temperature of \( T = 20^\circ C \), compared to the temperatures of \( T = 25^\circ C \) and \( 23^\circ C \) used in the other studies. From a theoretical perspective, however, this small temperature difference alone cannot explain the relatively large deviations between the rate constants.

### 5.2.1.4 Peculiarities of the precipitation process

In dissolution processes, the surface area \( A \) appearing in Eq. (5.1) is clearly defined and expresses the surface of the mineral per unit volume which is in contact with water. However, in the case of precipitation, a difficulty arises with the surface area \( A \) or with the term \( \phi_G F_G \) in Eq. (5.7) if the precipitating mineral is initially absent from the system. According to the theory of nucleation, (e.g. Lasaga 1998, Mullin 2001), as soon as the supersaturation of a mineral is reached, nuclei start to form and crystal growth subsequently takes place on these nuclei. The time required for the first stable nucleus to form is defined as the induction time. A distinction can be drawn here between homogeneous and heterogeneous crystal growth. In the former the crystals grow on the same mineral, while in the latter they grow on other minerals.

Homogeneous growth rarely occurs in nature (Mullin 2001) and it presupposes the presence of a number of nuclei which operate as centres for crystallisation. The surface \( A \) is then the surface of the nuclei, and the mass change rate is given by Eq. (5.7). In order to circumvent the aforementioned difficulty in modelling homogeneous nucleation, Steefel and Lasaga (1994) suggest that once a solution becomes supersaturated with a mineral that is initially absent, the mineral instantaneously acquires a radius of \( 10 \ \mu m \) which then develops over time. Nonetheless, the initial surface area does not depend only on the initial radius but also on the number of nuclei formed and thus on the nucleation rate (Lasaga and Rye 1993). A common way to deal with this difficulty is to assume a constant number of nuclei and to vary their radius. For an initially absent mineral, the radius of the nuclei is set to zero, although their number is not. A constant update of the radius during the modelling of crystal growth is essential.

In heterogeneous nucleation, crystals can grow, apart from on the nuclei, also on foreign bodies such as the surfaces of the different constituents of the rock. In this case the induction time vanishes, with nucleation and crystal growth occurring simultaneously (Nancollas and Purdie 1964). The surface area \( A \) in Eq. (5.1) is then the total surface area available for crystal growth, which is very difficult to determine, however, introducing considerable uncertainties into the model. A number of powerful
analytical techniques allow us to investigate and quantify the mineral surface (Brantley et al. 2008). Nonetheless, in order to fully understand the processes taking place at the interface between water and mineral, investigations must be performed at different scales. Direct observations of the changes on the surface of a mineral due to dissolution and precipitation at the atomic scale, however, are extremely difficult, if not impossible.

Simultaneous mineral dissolution and precipitation takes place in many geochemical systems. Normally, dissolution takes place more slowly than precipitation and therefore constitutes the limiting mechanism in the system. In such cases, assumptions concerning the precipitation rate are not necessary and the system will be close to the equilibrium concentration of the precipitating mineral (Mäder 2011). Therefore, the aforementioned difficulties do not necessarily constitute a problem from the practical point of view. In Section 5.4 we investigate the conditions under which this is also true for the anhydrite–gypsum–water system.

The precipitation of gypsum is investigated assuming the presence of an initial mass of gypsum or an inert mineral on which gypsum growth takes place. A phenomenon also observed in nature is the growth of gypsum crystals on particles of anhydrite (the sealing of anhydrite by gypsum delays or completely stops its dissolution and this is extensively investigated in Section 5.5). The complex process of nucleation is then omitted.

5.2.1.5 Kinetic constants for the precipitation of gypsum

Liu and Nancollas (1970) studied the kinetics of gypsum crystal growth in supersaturated solutions with added seed crystals experimentally, suggesting a second order rate law, i.e. \( \delta_G = 2 \). Their equation for the gypsum growth rate does not include a term for the change in the surface area of the crystals during crystallisation but it does include a term for the number of active growth sites added as seed crystals. From their experimental results they concluded that no new growth sites are formed during crystallisation. If the number of seed crystals is reduced, or the supersaturation is increased, nucleation also takes place after a corresponding induction time and new growth sites are thus generated. The rate constants for the crystal growth of gypsum then become higher. Plots were presented for some of the experiments performed, describing the concentration change of the sulphate ions as a function of time. Based on Eqs. (5.13) and (5.10), and using a second order law for gypsum precipitation in a suspension with an initial gypsum mass \( m_{G0} = 2.52 \text{ kg/m}^3 \), a specific surface area for the gypsum particles of approximately 0.15 m\(^2\)/g and an initial ion concentration \( c_0 = 39 \text{ mol/m}^3 \), a back calculation has been performed. The reaction rate constant has been varied in order to get a curve that best fits the measured data of their experiments at \( T = 25^\circ\text{C} \), which was found to be for \( k_G = 5.19 \cdot 10^{-7} \text{ kg/m}^2/\text{s} \).

Smith and Sweett (1971) studied gypsum crystallisation at \( T = 30^\circ\text{C} \) experimentally in distilled water by stirring the suspension in a magnetic stirrer. As no details are provided for the stirring rate, the
analysis of the results contains an uncertainty. The crystallisation kinetics were investigated by
monitoring the conductivity of the suspension. The experimental results indicate a second order law.
Both for unseeded and seeded crystallisation the change in surface area was measured at the beginning
and at the end of the experiments by dye adsorption. Assuming geometrically similar particles with a
known surface area, estimates of their numbers could be made for different supersaturations. High
 supersaturations did not lead to an increase in particle numbers, indicating heterogeneous nucleation.
The short induction periods observed in unseeded crystallisation tests also indicate heterogeneous
 nucleation. No induction periods were observed in the seeded experiments, as a sufficient initial area
was available for growth. The growth rate was proportional to the crystal surface area. Once the
necessary transformations had been performed in order to get the reaction rate constant in the desired
units (Appendix D3), a value of $k_G = 5.35 \cdot 10^{-6}$ kg/m$^2$/s was derived. This value is considerably higher
than that of Liu and Nancollas (1970). Possible reasons are associated with the unknown stirring rate
and the higher temperature in the investigations of Smith and Sweett (1971), as both of these factors
accelerate gypsum growth.

In addition to the anhydrite dissolution tests mentioned above (Section 5.2.1.3), Kontrec et al. (2002)
also studied gypsum precipitation at temperatures $T = 10 – 40 \, ^\circ C$ experimentally. Crystal growth was
initiated by adding gypsum seed crystals to the solution. No additional nucleation of gypsum or any
other calcium sulphate modification was observed in the experiments. The particles had a specific
surface area of $0.3 \pm 0.05$ m$^2$/g. Using Eqs. (5.16) and (5.10), a back calculation of the test results for
$T = 20 \, ^\circ C$, $m_{G0} = 2.28$ kg/m$^3$ and an initial concentration of $c_0 = 33$ mol/ m$^3$ has been performed.
Adopting a second order law, the equation best fits the experimental results with a reaction rate
constant of $k_G = 3.75 \cdot 10^{-7}$ kg/m$^2$/s which agrees reasonably well with the value resulting from the tests

Further literature

Several other works have been published in the past investigating the nucleation and crystallisation of
gypsum at temperatures of interest. However, these studies cannot be used to determine the reaction
rate constant, due to the absence of important data or the use of methods for accelerating gypsum
growth. For the sake of completeness, a short summary of some of these works is presented in the
following.

Schierholtz (1958) studied the nucleation and crystallisation of gypsum at $T = 25 ^\circ C$. The initial rate of
nucleus formation was found to be proportional to the supersaturation. The results showed that the
crystallisation of gypsum follows a first order rate law, rather than the commonly accepted second
order law. The effects of the pH of the solution and the crystal surface area were investigated, and also
the effects of accelerators and retarders.

Liu and Nancollas (1973) examined the induction periods and linear crystallisation rates of well-
formed crystallites of gypsum from a supersaturated solution for different temperatures starting from
25°C by applying a second order law. The scale of the reaction was monitored by photographing the growing crystals at various times, and the linear growth rate (expressed in mm per hour) was taken as the average length change of three or four crystals during each experiment. For a given initial concentration, increases in temperature resulted in a remarkable shortening of the induction period.

Van Rosmalen et al. (1981) studied the crystal growth of gypsum for different initial supersaturations and amounts of added seed crystals using three different methods at \( T = 25°C \). The overall growth rate of the crystals, defined as the increase in crystal volume per time unit, was given as a function of the linear rate of normal displacement of each crystal face relative to a fixed point in the crystal.

Christoffersen and Christoffersen (1982) investigated the growth of gypsum at low supersaturations \((c/c_{eq,G} < 1.2)\) at \( T = 25°C \) for three different preparations of gypsum seed crystals by recording the conductance of the solution as a function of time. Gypsum crystal growth was found to be of second order.

Amathieu and Boistelle (1988) studied the kinetics of gypsum crystallisation. Supersaturations were initiated from the dissolution of calcium sulphate hemihydrate in dense suspensions. The processes of dissolution and crystallisation were studied separately and were followed by monitoring the variation in conductivity as a function of time.

Finally, Niemann (2004) examined the kinetic parameters during precipitation of gypsum in a flow-through experiment. He identified that the reaction rate constant changes at a supersaturation of 1.8, while at supersaturations of up to 4.1 the reaction follows a second order rate law. Conductivity was also measured in order to control the concentration over time.

### 5.2.2 Sealing of anhydrite by the formed gypsum

Gypsum growth may also take place on an anhydrite surface, forming a layer of gradually increasing thickness. According to Böhringer et al. (1990), this happens within a few months. The gypsum layer can be up to a few millimetres thick and may, depending on its thickness and porosity, slow down or even stop anhydrite dissolution, due to the fact that the dissolving ions must diffuse through this layer in order to reach the macropores. At the same time, the gypsum seals the anhydrite by clogging communicating pores and fissures, which also leads to a significant deceleration or even a halt in anhydrite dissolution and thus also in the hydration process (Müller and Briegel 1977). This is why massive anhydrite, *i.e.* compact rock consisting mainly of anhydrite, does not swell. Amstad and Kovári (2001) concluded on the basis of a synthesis of various observations that anhydrite layers do not swell within the usual service life of tunnels (100 years) if they are thicker than 20 mm.

The sealing effect of gypsum was noticed by Wiesmann (1914) during the construction of Hauenstein Base Tunnel in Switzerland. Similar observations were made in the Simplon tunnel, where massive anhydrite with some insignificant dolomite inclusions was encountered in the bottom adit over a 100
m long section (Amstad and Kováři 2001). According to Andreae (1956), this part of the adit (km 9.7 – 9.8 from the Northern portal) remained unlined for about 10 years. However, no swelling was observed although the relative humidity of the air was practically 100%, due to a nearby spring of natural steaming hot water. Gassmann et al. (1979) mentioned that anhydrite sealing was also observed on the tunnel walls and in boreholes in the exploration gallery of Val Canaria. Existing fissures were sealed by a gypsum layer within 50 years. Additional evidence on the negligible swelling potential of massive anhydrite can be found in a number of South German tunnels crossing Gypsum Keuper (Grob 1972; Henke and Kaiser 1975; Henke et al. 1975).

Similar observations were made by Sahores (1962) who investigated masonry built with anhydrite quarry stones. The masonry remained in very good condition despite being exposed to temperature changes and rainwater for more than 50 years. Sahores (1962) attributed this to a thin gypsum layer formed on the surface of the anhydrite blocks, and confirmed this hypothesis in laboratory tests.

Madsen and Nüesch (1990) experimentally investigated the behaviour of massive anhydrite from the Weiach borehole. After almost two years of testing, rock samples consisting of 99 weight-% anhydrite and 1 weight-% clay and carbonate, developed swelling pressures of up to 0.05 MPa and swelling strains of up to 1% only. These figures are negligible relative to those of claystones with finely distributed anhydrite, which exhibit swelling pressures and strains of up to 7 – 8 MPa and up to 30 – 40%, respectively.

Sievert et al. (2005) studied the hydration of anhydrite in a ball mill as a function of time and temperature. Based on the experimental results, they proposed the following mechanism for the sealing of anhydrite by the formed gypsum. Anhydrite starts to dissolve into its ions according to Eq. (2.2) and the solution becomes saturated with respect to these. The ions are rapidly absorbed at the surface of the anhydrite and form a layer around it, the thickness of which increases with time. The adsorbed layer hinders both the circulation of the ions towards the solution and the tendency of water to interact with the surface of the anhydrite. As the layer increases in thickness, cracks are formed after a certain limit. Although this is a slow process, the ball mill accelerates it considerably. The molecules of water enter through the cracks and come into contact with particles of anhydrite. Nuclei of gypsum start to form when enough sulphate and calcium ions are present, along with water molecules. If the nucleus has a radius greater than the critical length (cf. Mullin 2001), gypsum starts to crystallise. Once a sufficient amount of gypsum has precipitated on the anhydrite particle, the further hydration of the latter becomes effectively impossible.

We model here the sealing effect of the gypsum layer in a similar way to Bezjak and Jelenic (1980), Pignat et al. (2005) and Bishnoi and Scrivener (2009), who investigated the transformation of tricalcium silicate (C₃S) to calcium silicate hydrate (C-S-H) in the context of cement technology. The similarity to the sealing effect of gypsum is due to the fact that diffusion through the C-S-H layer
(which covers the C₃S grains) represents – in addition to nucleation/growth and phase boundary reactions – one of the mechanisms governing the time evolution of the C₃S hydration.

In the absence of a gypsum sealing layer, anhydrite dissolution would occur according to Eqs. (5.2) and (5.12), i.e. the dissolution front would move at the following rate:

$$\frac{ds_A}{dt}igg|_{DIS} = -\frac{k_A}{\rho_A} \left( \frac{c_{eq,A} - c}{c_{eq,A}} \right)^{\delta_A}.$$  \hfill (5.14)

The sealing effect of the gypsum layer on anhydrite dissolution can be taken into account by considering that the diffusive flow of the calcium and sulphate ions through the gypsum may be the limiting mechanism. According to Fick’s law, the diffusive flux

$$J = -D n_G T_G \frac{c - c_{eq,A}}{s_G},$$  \hfill (5.15)

where $D$ [m²/s], $T_G$ [-], $n_G$ [-] and $s_G$ [m] denote the molecular diffusion coefficient, the tortuosity through the gypsum layer, the porosity and the thickness of the gypsum layer, respectively.

Concerning the tortuosity, it is a dimensionless parameter (always less than unity) showing how tortuous the flow path is through a porous medium (in this case the gypsum) and it generally varies in the three directions. However, as tortuosity is hard to measure, it is often assumed to be isotropic and is expressed by a single parameter (Fitts 2002). With increasing thickness of the gypsum layer, the diffusive flow may become slower than the flow predicted by Eq. (5.14) and may become the decisive factor for the rate of the anhydrite dissolution. In this case, the anhydrite surface will retreat at the following rate:

$$\frac{ds_A}{dt}igg|_{DIF} = -\frac{J}{\rho_A} = -n_G T_G \frac{D}{\rho_A} \frac{c_{eq,A} - c}{s_G}.$$  \hfill (5.16)

Equation (5.14) applies for the initial stage of the dissolution process, i.e. as long as it leads to lower values than Eq. (5.16). According to Eq. (5.16) the sealing effect of the gypsum layer depends essentially on how dense this layer is, i.e. on its porosity. Porosity probably decreases over time as more and more crystals grow. More specifically, a denser layer should develop if gypsum growth in the pore space is constrained (cf. Bezjak and Jelenic 1980; Bishnoi 2008). In the absence of experimental data, we make the simplifying assumption of a constant porosity $n_G$ and investigate its effect quantitatively.

### 5.2.3 Governing equations for a closed system

From Eqs. (5.2), (5.12), (5.14) and (5.16), the following dimensionless relationships can be obtained for the movement rate of the dissolution and precipitation front $s_A$ and $s_G$, respectively:
\[
\frac{d\bar{c}}{d\bar{\tau}} = -\min\left[(1-\bar{c})^\gamma; n_G T_G D \frac{c_{eq,G}}{k_A S_{A0}} (1-\bar{c})\right]
\]

(5.17)

and

\[
\frac{d\bar{c}_{eq,G}}{d\bar{\tau}} = \Lambda \left(\frac{\bar{c}}{c_{eq,G}} - 1\right)^{\delta_c} \frac{1}{1-n_\phi}
\]

(5.18)

where

\[
\bar{c} = c / c_{eq,A},
\]

(5.19)

\[
\bar{c}_{eq,G} = c_{eq,G} / c_{eq,A},
\]

(5.20)

\[
\bar{\tau} = \frac{k_A}{S_{A0} \rho_A},
\]

(5.21)

\[
\Lambda = \frac{k_G \rho_A}{k_A \rho_G},
\]

(5.22)

\[
\bar{s}_A = s_A / S_{A0}
\]

(5.23)

and

\[
\bar{s}_G = s_G / S_{A0}.
\]

(5.24)

The last term in Eq. (5.18) accounts for the porosity of the sealing layer (Section 5.2.2). The variable \(\bar{\tau}\) denotes a dimensionless time, while \(S_{A0}\) is a characteristic length (e.g. the initial diameter of the anhydrite particles in the case of spherical anhydrite particles) used here for normalizing \(s_A\) and \(s_G\).

Equation (5.17) applies only under the following conditions:

\[
c < c_{eq,A}, \quad \phi_A > 0, \quad \phi_G < \frac{172 \rho_W \phi_{W0}}{36 \rho_G \phi_{G0}}.
\]

(5.25)

The last inequality follows from the condition \(\phi_W > 0\) and the mass balance equation for the water:

\[
m_W = m_{W0} - 36 (m_G - m_{G0}) / 172.
\]

(5.26)

It must also be fulfilled (in addition to \(c > c_{eq,G}\)) due to Eq. (5.18).

Equations (5.17) and (5.18) are coupled via the dimensionless concentration \(\bar{c}\) which is a function of the ion concentration \(c\) (Eq. 5.19). The ion concentration \(c\) can be expressed as a function of the ion and water masses per unit volume as follows:

\[
c = \frac{M_i}{V_w} = \frac{\rho_w m_i}{m_w}.
\]

(5.27)
From Equations (5.27), (5.26) and (5.13) we obtain \( \bar{c} \) as a function of the volume fractions of anhydrite and gypsum:

\[
\bar{c} = \bar{c}_0 + \frac{\phi_A \phi_w}{\phi_w c_{eq,A}} \frac{136}{172} \frac{\rho_A}{\rho_w} \phi_G,
\]

(5.28)

where the porosity

\[
\phi_w = \phi_{w0} \frac{36}{172} \frac{\rho_A}{\rho_w} \phi_G,
\]

(5.29)

the initial porosity

\[
\phi_{w0} = 1 - \phi_{A0} - \phi_{G0} - \phi_S
\]

(5.30)

and

\[
\bar{c}_0 = \frac{c_0}{c_{eq,A}}.
\]

(5.31)

In order to calculate the concentration \( c \) in Eq. (5.28), the volume fractions of anhydrite and gypsum are needed. These depend on the shape and size of the anhydrite and gypsum particles and thus on the thicknesses \( s_A \) and \( s_G \). Two shapes for the mineral particles will be considered here: parallelepipeds and spheres. The initial side lengths of the parallelepipeds are \( s_0, aS_0 \) and \( bS_0 \) (Fig. 5.4a), while the spherical particles have an initial diameter \( S_0 \) (Fig. 5.4b). The characteristic length \( S_{0i} \) used for normalizing \( s_A \) and \( s_G \) is thus equal to the initial particle diameter (in the case of spherical anhydrite particles) or to the smallest side length if the anhydrite occurs in the form of parallelepipeds.

![Figure 5.4](image)

(a) Parallelepiped and (b) spherical particle

Gypsum may grow on pre-existing gypsum particles, on anhydrite particles or on other inert minerals. Therefore, the volume fraction of gypsum \( \phi_G \) consists of the initial fraction \( \phi_{G0} \) and three additional terms:

\[
\phi_G = \phi_{G0} + \phi_{G,A} + \phi_{G,S}.
\]

(5.32)
where $\phi_{G,G}$, $\phi_{G,A}$ and $\phi_{G,S}$ are the volume fractions of the gypsum that precipitates on gypsum, anhydrite and on other solids, respectively. For simplicity, we assume that gypsum growth occurs at the same rate on all particles in the system.

The geometric relationships expressing the volume fractions $\phi_A$, $\phi_{G,G}$, $\phi_{G,S}$ and $\phi_{G,A}$ in terms of the primary variables $s_A$ and $s_G$ are given in the Appendix E. A code has been developed in Mathematica 9 (Wolfram 2003) for solving the system.

### 5.3 Comparison of predictions with tests involving simultaneous anhydrite dissolution and gypsum precipitation

The model in Section 5.2 was tested by taking the results of Kontrec et al. (2002), who performed experiments on anhydrite dissolution, gypsum precipitation and simultaneous anhydrite dissolution and gypsum precipitation. They also investigated gypsum dissolution, which is out of the scope of the present study.

Kontrec et al. (2002) additionally performed a back analysis of their experiments, but without giving a complete mathematical formulation of their model. More specifically, they presented the equations for anhydrite dissolution and gypsum precipitation, but not the equations needed for the simultaneous process. Furthermore, their equations apply only to spherical or cubical particles, despite the fact that the anhydrite particles used had an irregular shape and the gypsum particles were platelets. Moreover, the rate constants used in their work were not material specific but applied only to the particle sizes considered. The model in the present work (Section 5.2) is more general in that it considers different particle shapes and accounts explicitly for their specific surface area. In spite of the uncertainties over the mathematical formulation used by Kontrec et al. (2002), their model must be similar to the present model as it leads to similar predictions.

In the absence of information on anhydrite particle shapes, spherical particles are assumed for the calculations with a corresponding surface area (3.78 m$^2$/g). Gypsum particles are elongated platelets with approximate proportions of 21:8:2 and a specific surface area of 0.3 m$^2$/g. Table 5.1 shows the orders of reactions used, as well as the rate constants for anhydrite dissolution and gypsum precipitation.

The first test used to check the model involves the dissolution of anhydrite for three different initial masses of anhydrite in the solution ($m_{A0} = 1.60, 2.28, 4.00$ kg/m$^3$). The initial ion concentration was 15.5 mol/m$^3$, i.e. equal to the gypsum equilibrium concentration at $T = 20$°C (Table 5.1). Figure 5.5a shows the computed ion concentration (solid line) over time and the measured values. The computational results generally agree with the experimental results of Kontrec et al. (2002), although with some deviations which can be attributed to the uncertainties over particle shape mentioned above.
The second test concerns the precipitation of gypsum with an initial mass of $m_{G_0} = 2.28 \text{ kg/m}^3$ and initial ion concentration $c_0 = 33 \text{ mol/m}^3$. Figure 5.5b depicts the computed ion concentration (solid line) as a function of time. The measured values (dots) correspond to a temperature of 20 °C. The model check was performed for this temperature, despite the fact that Kontrec et al. (2002) provided measured values for different temperatures as well, since the reaction rate constants considered (Table 5.1) have been derived for temperatures around $T = 20 \, ^\circ\text{C}$ (cf. Sections 5.2.1.3 and 5.2.1.5). A good correlation was found between the results.

Finally, the model in Section 5.2 was tested in relation to the experimental results for simultaneous anhydrite dissolution and gypsum precipitation. The initial anhydrite and gypsum masses in the solution were equal in the test ($m_{A_0} = m_{G_0} = 2.312 \text{ kg/m}^3$). The initial ion concentration $c_0$ was 16 mol/m$^3$, i.e. slightly higher than the gypsum equilibrium concentration (cf. Table 5.1).

Figure 5.5c shows the computed ion concentration over time (solid line) and the measured values (dots). The computational results agree to a great extent with experimental results from Kontrec et al. (2002) (the uncertainty over anhydrite particle shapes should also be considered here). The distinct non-linearity obtained in the concentration over time can be explained as follows: At the very initial stage of the process, the concentration is close to the gypsum equilibrium concentration and therefore only anhydrite dissolution takes place. Consequently, a steep increase in the concentration is observed. The effect of the increasing concentration is twofold: On the one hand, anhydrite dissolution slows down due to the fact that the difference between the actual concentration and the anhydrite equilibrium concentration decreases. On the other hand, as the solution becomes more and more oversaturated with gypsum, crystal growth starts to occur and consumes ions. Therefore, the concentration reaches a maximum and decreases thereafter. The second characteristic feature of the curve of concentration over time is the turning point at approximately $t = 33$ h. The turning point marks the termination of the anhydrite dissolution process (Fig. 5.5d).
Figure 5.5. Back-analysis of the experimental data from Kontrec et al. (2002) - ion concentration over time for the following processes: (a) anhydrite dissolution, (b) gypsum precipitation, (c) simultaneous anhydrite dissolution and gypsum precipitation and (d) anhydrite and gypsum mass over time.
5.4 Factors governing the time development of hydration

5.4.1 Introduction

In the present Section we discuss the results of parametric studies on a porous medium with gypsum growth on inert minerals (no sealing of anhydrite). More specifically, we identify the parameters that govern the duration of the hydration process and parameters that determine whether the transformation of anhydrite into gypsum is dissolution- or precipitation-controlled.

In tackling these questions, it is advantageous to formulate the governing equations in terms of the volume fractions of anhydrite and gypsum, instead of $s_A$ and $s_G$. From Eqs. (5.4), (5.6) and (5.7) we obtain:

\[
\frac{d\phi_A}{d\tau} = -\frac{\phi_A F_A}{\phi_{A0} F_{A0}} (1 - c)^{\delta_A},
\]

\[
\frac{d\phi_G}{d\tau} = A \frac{\phi_G F_P}{\phi_{G0} F_{G0}} \left( \frac{c}{c_{eq,G}} - 1 \right)^{\delta_G},
\]

where the dimensionless parameter

\[
A = \frac{k_G F_S}{k_A F_{A0} \phi_{A0} \rho_A \rho_G}
\]

expresses how quickly gypsum precipitation occurs relative to anhydrite dissolution (i.e. it provides a measure of the relative speed of the two processes), while the dimensionless time is:

\[
\tau = t \frac{k_A F_{A0} \phi_{A0}}{\rho_A}.
\]

The symbols $\phi_P$ and $F_P$ denote the volume fraction and the specific surface area of the particles that are available for gypsum precipitation (an inert mineral on which gypsum may form). At $t = 0$, $\phi_P$ and $F_P$ are equal to the volume fraction $\phi_S$ and to the specific surface $F_S$ of the inert particles, respectively.

In general, $F_A$ and $F_P$ change with time and are related to $\phi_A$ and $\phi_P$ in a more or less complex way, depending on the shape of the particles. The advantage of the formulation of Section 5.2 is that it allows for a more consistent treatment of different particle shapes and of different precipitation cases (precipitation on gypsum, on inert minerals and on anhydrite). However, the formulation of the current Section is useful, particularly for the case of spherical particles, as in this special case the equations simplify considerably. More specifically, for spherical particles Eqs. (5.33) and (5.34) (and bearing in mind Eq. 5.8) take the following form:
\[
\frac{d\phi_A}{d\tau} = \left( \frac{\phi_A}{\phi_{m0}} \right)^\gamma (1 - \bar{\varepsilon})^\delta 
\]

(5.37)

and

\[
\frac{d\phi_G}{d\tau} = A \left( 1 + \frac{\phi_G}{\phi_S} \right)^\gamma \left( \frac{\bar{\varepsilon}}{\bar{\varepsilon}_{eq,G}} - 1 \right)^\delta 
\]

(5.38)

Equations (5.37) and (5.38), with the concentration \( \bar{\varepsilon} \) according to Eq. (5.28), represent a system of two non-linear ordinary differential equations for the evolution of the volume fractions of anhydrite and gypsum over time. The solution of this system can be expressed as follows:

\[
\phi_A, \phi_G, \phi_W, \frac{c}{c_{eq,A}} = f \left( \tau, \phi_{A0}, \phi_{G0}, c_a, c_{eq,G}, c_{eq,A}, \frac{\rho_{G}}{\rho_A}, \frac{\rho_{G0}}{\rho_{A0}} \right). 
\]

(5.39)

The equations of this Section also apply to the case where gypsum growth occurs on gypsum particles that pre-exist in the system (the only difference being that \( \phi_p, F_P, \phi_S \) and \( F_S \) should be replaced by \( \phi_G, F_G, \phi_{G0} \) and \( F_{G0} \), respectively).

### 5.4.2 Evolution over time

We investigate the time development of hydration by means of a parametric study into mixtures consisting initially of anhydrite, inert minerals and distilled water (\( c_0 = 0 \) mol/m\(^3\)). For simplicity, all particles are assumed to be spherical and therefore Eqs. (5.37) and (5.38) can be used.

The last five parameters on the right side of Eq. (5.39) represent material constants. The initial water content \( \phi_{W0} \) will be kept equal to 0.15. Therefore, the evolution of the hydration process over time (represented by the dimensionless time \( \tau \)) is governed only by the dimensionless parameter \( \Lambda \) and by the initial anhydrite fraction \( \phi_{A0} \) (cf. Eq. 5.39).

During the hydration process, pore water may be consumed while anhydrite is still present in the system. Hydration of the entire anhydrite presupposes the presence of sufficient water or, for a given water content, that the anhydrite content does not exceed a critical value. The following relationship gives the critical volume fraction of anhydrite:

\[
\phi_{A0,crit} = \frac{136}{36} \frac{\rho_m}{\rho_A} \phi_{W0} \cong 1.276 \phi_{W0}.
\]

(5.40)

For the assumed initial water content \( \phi_{W0} = 0.15 \), hydration will end prematurely if the anhydrite content exceeds \( \phi_{A0,crit} = 0.19 \).

Figures 5.6a and 5.6b show the ion concentration and the anhydrite volume fraction, respectively, over the dimensionless time \( \tau \), for \( \Lambda = 1 \) and an initial anhydrite content \( \phi_{A0} \) of 7.7%, 14.2%, 28.3% or
42.5%. In the last two cases, hydration remains incomplete due to consumption of the whole amount of water. It is interesting that the maximum concentration attained during the process does not depend on the initial anhydrite fraction (all curves in Fig. 5.6a reach the same maximum). As all $\phi_{A0}$ over $\tau$ curves exhibit about the same gradient (Fig. 5.6b), the initial anhydrite content $\phi_{A0}$ determines the time needed for the system to reach equilibrium: The duration of the process increases practically linearly with $\phi_{A0}$.

The diagrams in Figs. 5.6c and 5.6d show the time development of the concentration $c$ and the volume fraction of anhydrite $\phi_A$, respectively, for a fixed initial mixture composition. Every curve corresponds to another value of the dimensionless parameter $\Lambda$. This parameter expresses the speed of gypsum formation relative to anhydrite dissolution. At high values of $\Lambda$, gypsum crystals grow much more quickly than anhydrite dissolves and, consequently, ion consumption (which is associated with gypsum formation) occurs rapidly relative to ion production by anhydrite dissolution. Therefore, the concentration cannot increase very much and remains slightly above the gypsum equilibrium concentration (see curve for $\Lambda = 10$ in Fig. 5.6c). On the other hand, for low values of $\Lambda$, the precipitation of gypsum and the consumption of ions occur relatively slowly. In this case, anhydrite dissolution causes a pronounced oversaturation with respect to gypsum (Fig. 5.6c). Therefore, it is evident that the value of the dimensionless parameter $\Lambda$ determines the maximum value of the concentration $c_{\text{max}}$: The higher the parameter $\Lambda$, the lower will be the maximum oversaturation with respect to gypsum.

In conclusion, the anhydrite content determines the duration of the hydration process for a given value of $\Lambda$, while $\Lambda$ determines whether the process is dissolution- or precipitation-controlled. Further investigations have shown that these results also remain valid for other mixtures, including dilute aqueous solutions (cf. Serafeimidis and Anagnostou 2012b).

### 5.4.3 Limiting mechanism

As mentioned earlier, the maximum concentration $c_{\text{max}}$ shows whether anhydrite dissolution or gypsum precipitation will determine the duration of the hydration process. If anhydrite dissolution represents the limiting mechanism, the concentration will be close to the gypsum equilibrium concentration. If, however, the process is governed by gypsum precipitation, the concentration will reach values closer to the anhydrite equilibrium concentration.

As explained in Section 5.3, a steep increase in the concentration can be observed at the beginning of the process, where anhydrite dissolution alone takes place (Fig. 5.6a and 5.6c). The increasing concentration slows down the anhydrite dissolution and accelerates the gypsum growth with the consequence that the curve of concentration over time exhibits a maximum.
Figure 5.6. (a) Ion concentration $c$ and, (b), volume fraction of anhydrite $\phi_i$ over dimensionless time $\tau$ for different initial anhydrite fractions $\phi_{i0}$. (c) Ion concentration $c$ and, (d), volume fraction of anhydrite $\phi_i$ over dimensionless time $\tau$ for different values of the dimensionless parameter $\Lambda$.

Figure 5.6c indicates that the maximum concentration $c_{\text{max}}$ depends solely on the dimensionless parameter $\Lambda$. This can also be shown in the governing equations. Considering the fact that the quantity of anhydrite that has to be dissolved in order for $c_{\text{max}}$ to be reached is so low that $\phi_A = \phi_{A0}$, $F_A = F_{A0}$ and $\phi_G = 0$ can be assumed in Eqs. (5.33) and (5.34), the condition $dc/dt = 0$ (which applies when $c = c_{\text{max}}$) leads to an algebraic equation for $c_{\text{max}}$, whose solution reads as follows:

$$c_{\text{max}} = c_{eq,G} \frac{\Lambda^* + 1}{\Lambda^* + c_{eq,G}/c_{eq,A}}, \quad (5.41)$$

where

$$\Lambda^* = \frac{\sqrt{136\frac{\rho_G}{\rho_A} A}}{\sqrt{172}} = \frac{136 k_{G0} F_0 \phi_{G0}}{172 k_A F_{A0} \phi_{A0}}, \quad (5.42)$$
This equation confirms that the maximum concentration $c_{\text{max}}$ that develops during the hydration process depends only on the dimensionless parameter $\Lambda$. Figure 5.7 shows the maximum concentration $c_{\text{max}}$ as a function of $\Lambda$ (the abscissa also contains the term $F_s\phi_s/F_{\text{A0}}\phi_\text{A0}$). It can be seen that for high $\Lambda$-values, \textit{i.e.} for rapid gypsum precipitation, the $c_{\text{max}}$-values are only slightly higher than the gypsum equilibrium concentration $c_{\text{eq,G}}$. In this case, anhydrite dissolution constitutes the limiting mechanism.

On the other hand, for very low values of $\Lambda$, the maximum concentration $c_{\text{max}}$ approaches the anhydrite equilibrium concentration $c_{\text{eq,A}}$. In this case, gypsum precipitation is considerably slower than anhydrite dissolution, and it governs the time-development of the hydration process.

![Figure 5.7. Maximum concentration $c_{\text{max}}$ over dimensionless parameter $\Lambda$](image)

We assume that the process occurs close to gypsum equilibrium (\textit{i.e.} its time development is controlled by the dissolution of anhydrite) when $\Lambda$ is higher than about 5, where $c_{\text{max}} \approx 17 \text{ mol/m}^3$ (\textit{cf.} Fig. 5.7). Taking the definition of $\Lambda$ (Eq. 5.35) into account, this criterion leads to the following inequality:

$$F_{\text{A0}}\phi_\text{A0} < \frac{k_G \rho_A}{5k_s \rho_G} F_s \phi_s.$$  \hspace{1cm} (5.43)

Figure 5.8 illustrates this condition graphically. The two lines correspond to extreme combinations of the reaction rate constants for anhydrite dissolution and gypsum precipitation found in the literature (\textit{cf.} Chapter 5.2.1.3 and 5.2.1.5). Points below the lower line clearly satisfy inequality (5.43), thus indicating conditions under which the dissolution of anhydrite constitutes the limiting mechanism. For points lying between the upper and the lower line, it is not possible to make a clear statement about the limiting mechanism due to the uncertainty related to the rate constants. According to Fig. 5.8,
anhydrite dissolution governs the overall process if the anhydrite surface area $\phi_A F_{A0}$ amounts to a maximum of $10 - 100 \, \text{m}^2/\text{m}^3$ of rock. This will be the case where anhydrite is in the form of veins at least 10 mm thick, spaced about 200 mm apart, with the gypsum crystals growing on spherical particles with a maximum radius of 1 mm (Point A in Fig. 5.8).

![Figure 5.8. Surface area of anhydrite over surface area available for gypsum growth per unit volume of rock](image)

### 5.4.4 Duration of the hydration process

According to Fig. 5.6b, after the very short initial period of rapidly increasing concentration, the volume fraction of anhydrite decreases at an approximately constant rate that does not depend on $\phi_S / \phi_{A0}$ over a long period of time. This rate can be derived from Eq. (5.33), by substituting $\phi_A \approx \phi_{A0}$, $F_A = F_{A0}$ and $c \approx c_{\text{mat}}$. Assuming the presence of a sufficient quantity of water (i.e. that $\phi_{A0} < \phi_{A0,\text{crit}}$), we obtain the following approximation for the hydration time:

$$t_h \approx \frac{\rho_d}{k_d F_{A0}} \left( \frac{c_{\text{eq},d}}{c_{\text{eq},d} - c_{\text{eq},G}} \right)^2 \left( 1 + \frac{c_{\text{eq},G}}{c_{\text{eq},d}} \right)^2. \tag{5.44}$$

Due to the slight curvature of the $\phi_A$ over $\tau$ curve, this equation gives the lower bound for hydration time. Figure 5.9 is based on Eq. (5.44) and shows the hydration time $t_h$ as a function of the initial specific surface area $F_{A0}$ of the anhydritic particles for different ratios of the initial surfaces areas $\phi_{A0} F_{A0} / \phi_S F_S$. Depending on the initial specific surface area of the anhydrite $F_{A0}$ and on the available surface area for gypsum precipitation $\phi_S F_S$, hydration takes from a few hours to several years.

If the process is dissolution-controlled (i.e. for large $\Lambda$ values), the last right side term of Eq. (5.44) becomes equal to 1. The hydration time is then inversely proportional to the specific surface of anhydrite $F_{A0}$ and does not depend on its volume fraction $\phi_{A0}$. This result emphasizes the importance of
anhydrite distribution for the intensity of swelling. For the cases of practical interest where \( A > 5 \), the parameter values of Table 5.1 and anhydrite particle radii of 0.1 to 10 mm, Eq. (5.44) gives hydration times between 5 days and 18 months. This result does not take the sealing effect into account.

![Figure 5.9. Hydration time \( t_h \) over initial specific surface area of anhydrite](image)

**5.5 The effect of sealing**

As explained in Section 5.2.2, the kinetics of anhydrite dissolution in the presence of a gypsum coating will be governed by the slowest mechanisms of dissolution and diffusion under Eqs. (5.14) and (5.16), respectively. Figure 5.10 shows the retreat rate of the dissolution front as a function of the ion concentration \( c \). Curve 5 is the second order dissolution equation (Eq. 5.14) for the values of Table 5.1. The straight lines 1 to 4 were calculated according to the diffusion equation (Eq. 5.16) for different porosities \( n_G \) and thicknesses \( s_G \) of the gypsum layer. The tortuosity and the diffusion coefficient for sulphate ions through a gypsum layer (Table 5.1) were taken from Böhm et al. (1998) and Li and Gregory (1974), respectively. Li and Gregory (1974) give a range of \( 6 \times 10^{-10} \) m²/s for the diffusion coefficient at \( T = 20 \) °C.

The behaviour of the model can be explained by considering the example of a 2 mm thick gypsum layer with 10% porosity (line 2 of Fig. 5.10). For concentrations to the right of the intersection of line 2 with curve 5 (point A), dissolution (curve 5) constitutes the slowest mechanism and therefore governs the process. The transition from one mechanism to the other occurs when the two rates become equal (point A). For lower concentrations (to the left of point A), diffusion through the gypsum layer limits the dissolution rate (line 2).

The porosity \( n_G \) of the gypsum layer has a major effect as can be seen by comparing line 1 with line 4. The two lines apply to a 5 mm thick gypsum layer with a porosity \( n_G \) of 0.5 or 0.01. The denser
gypsum layer controls dissolution over practically the entire concentration range (line 4). The porosity \( n_G \) is considered here as an independent parameter, but must depend essentially on the pressure conditions prevailing during growth. It will be larger or smaller depending on whether gypsum growth occurs freely or is constrained by the surrounding rock matrix. We do not investigate this aspect in detail, but note that the porosity \( n_G \) could be measured with the experimental technique of Neveux et al. (2013), who investigated dissolution and precipitation processes in the deep burial diagenesis of carbonate reservoirs.

At the beginning of the dissolution process, the gypsum layer is still thin and its porosity is probably high, so that diffusion is not relevant in relation to the kinetics of anhydrite dissolution. Over time, the gypsum thickness \( s_G \) increases, with the result that the diffusion rate decreases and becomes the governing mechanism, particularly in the region of low supersaturation, i.e. at concentrations close to the gypsum equilibrium concentration \( c_{eq,G} \) which are characteristic for dissolution-controlled hydration.

Figure 5.11a shows how the hydration of an anhydrite layer that is initially 100 mm thick proceeds over time, assuming that gypsum crystals grow only on anhydrite and form a layer of thickness \( s_G \). The two solid curves show the location of the gypsum – anhydrite interface (curve "\( S_A/2 \)") and the gypsum surface (curve "\( S_{G,A}/2 \)") according to the standard second order anhydrite dissolution and gypsum precipitation equations, i.e. disregarding the sealing effect of the gypsum layer on anhydrite dissolution. The distance of the two curves corresponds to the thickness \( s_G \) of the gypsum layer. It can be seen that the anhydrite core shrinks, but the total thickness of the layer increases by about 60% due to the higher molar volume of gypsum.

**Figure 5.10.** Retreat rate of the anhydrite dissolution front over concentration according to second order reaction kinetics (curve 5) and the diffusion equation (lines 1 to 4)
The dashed curves incorporate the effect of sealing, i.e. they assume that the retreat rate of the dissolution front is given by Eq. (5.16) if it yields a lower value than Eq. (5.14). It can be seen that sealing delays hydration by more than one order of magnitude. However, this result is true only for thick anhydrite layers. Figure 5.11b is obtained for a 1 mm thick anhydrite vein and shows that sealing is irrelevant for this particular case. For thick anhydrite layers, sealing plays a prominent role, because only a very small percentage of the anhydrite will have hydrated by the time the gypsum thickness reaches the critical value above which diffusion retards dissolution. This actually happens so rapidly that diffusion can be regarded as the governing mechanism for almost the entire hydration process. On the other hand, for finely distributed anhydrite (Fig. 5.11b), most of the anhydrite will already have dissolved before the gypsum layer reaches the critical thickness (time $t_d$). Therefore, the effect of sealing is almost negligible.

Figure 5.12 shows the reduction in the volume fraction of layered anhydrite over time for different gypsum porosities $n_G$ and anhydrite layer thicknesses $S_{d0}$, assuming that gypsum growth takes place both on the anhydrite layers and on other spherical particles of inert minerals. The initial volume fractions of anhydrite and inert minerals are $\phi_A = 0.2$ and $\phi_S = 0.5$, respectively. Under these conditions, the quantity of water available is sufficient for hydration of the entire quantity of anhydrite (cf. Eq. 5.40). Lines 3 to 6 apply to a 100 mm thick anhydrite layer. Line 3 disregards the effect of sealing, while lines 4, 5 and 6 take sealing into account and apply to layer porosities of 0.5, 0.1 and 0.01, respectively. In the absence of sealing, total hydration of the anhydrite would take approximately 38 years. Sealing increases the hydration time to 57 years if the gypsum layer has a porosity of $n_G = 0.5$, and to 147 years for a porosity of $n_G = 0.1$. At lower porosities, hydration would be practically irrelevant for tunnelling because it would take several centuries.

Line 1 in Fig. 5.12 corresponds to the case of finely distributed anhydrite ($S_{d0} = 1$ mm). For gypsum layer porosities $n_G$ of 0.1 or more, sealing does not affect the hydration duration. However, for a very low porosity ($n_G = 0.01$, line 2), the hydration time amounts to more than 5 years, i.e. three times more than without sealing (line 1). To summarise, sealing is important for thick anhydrite layers. In the case of finely distributed anhydrite, sealing plays a role only if the formed gypsum is very dense.

Finally, Fig. 5.13 shows the total hydration time $t_h$ as a function of the initial anhydrite layer thickness for different gypsum porosities $n_G$, with and without anhydrite sealing being taken into account. In this case as well, gypsum grows both on the layers of anhydrite and on spherical particles of inert minerals. Figure 5.13 once more illustrates the importance of gypsum porosity and particle size for the sealing effect and thus for the time evolution of the hydration process.

The modelling results agree with (and provide an explanation for) the general observation made in tunnelling that thicker anhydrite veins and layers do not swell (cf. Section 5.2.2).
Chapter 5

Figure 5.11. Thickness of anhydrite and gypsum layer over time $t$, (a), for a $S_{A0} = 100$ mm thick anhydrite layer and, (b), for a $S_{A0} = 1$ mm thick layer with sealing taken into account (dashed lines) and not taken into account (solid curves).

Figure 5.12. Volume fraction of anhydrite over time for different anhydrite layer thicknesses and gypsum layer porosities.
5.6 Conclusions

In the present Chapter a model has been developed for the simultaneous dissolution of anhydrite and precipitation of gypsum in a closed system. The model accounts for the sealing effect caused by the precipitation of gypsum onto the anhydrite mineral. The model predictions were compared with the experimental results of Kontrec et al. (2002). Furthermore, back calculations were performed in respect of existing experimental data from the literature in order to estimate the kinetic constants of anhydrite dissolution and gypsum precipitation. An extended review of the literature also showed that both reactions are of second order. The reaction rate constants were found to lie within the ranges $k_A = 0.54 - 5.4 \times 10^{-6} \text{ kg/m}^2/\text{s}$ for anhydrite dissolution and $k_G = 0.52 - 5.35 \times 10^{-6} \text{ kg/m}^2/\text{s}$ for gypsum precipitation at temperatures between 20 and 30 °C. However, as the reaction rate constants have been calculated by means of back calculations, extrapolations from existing data and assumptions concerning the specific shape of spherical particles, the values derived clearly contain uncertainties.

After performing parametric studies for the case of simultaneous anhydrite dissolution and gypsum precipitation omitting the sealing effect, a simple relation has been proposed in order for anhydrite dissolution to represent the limiting mechanism. The investigations have shown that this is the case if anhydrite occurs in the form of larger particles or thicker veins (> 1 mm) and there are sufficient nuclei for gypsum growth (e.g. precipitation takes place on the surfaces of inert minerals). It has also been shown that the time required for the whole amount of anhydrite to hydrate may vary by orders of magnitude. Moreover, for systems where dissolution is the governing mechanism, the initial volume fraction of anhydrite does not play any role in terms of the hydration time.

The effect of sealing has been shown to be decisive for the time evolution of the hydration process where gypsum with low porosity precipitates on thick layers of anhydrite. Depending on the gypsum porosity and the thickness of the anhydrite layers, the hydration time of anhydrite may increase by

Figure 5.13. Hydration time of an anhydrite layer as a function of its initial thickness
many orders of magnitude and far exceed the usual service life of tunnels (100 years). The quantitative results provide a theoretical explanation for the well-known observation that anhydrite layers of at least a few cm thick hardly swell at all.

It should be borne in mind that the investigations were performed under the assumption that a sufficient quantity of water was available. However, this is not always the case in nature, as the flow of water to the anhydrite surface may be hindered either by pores becoming clogged due to the precipitation of gypsum, or by the existence of a clay matrix that tends to absorb water. Consequently, the actual hydration times may be considerably higher. Transport processes and interaction between the anhydrite and the clay matrix are probably important in this respect.
6 On the Role of Transport Processes

6.1 Introduction

In a closed system, i.e. a system where water and ions cannot flow in or out, anhydrite is the only supplier of ions. In addition, anhydrite can only be consumed by the precipitation of gypsum. Consequently, the transformation of anhydrite into gypsum can be considered practically as a topochemical reaction (see Section 5). In an open system, however, the ions may circulate by advection (with the pore water) and, in the presence of ionic concentration gradients, also by diffusion. So, with the exception of closed systems, anhydrite dissolution and gypsum precipitation are usually coupled with transport. This raises the question as to whether and under what conditions advection or diffusion are relevant in relation to the time-dependent processes of sulphate dissolution or precipitation. Identifying the conditions under which transport might play a role is valuable for the formulation of manageable continuum-mechanical models (i.e. models that are not unnecessarily overloaded with irrelevant coupled processes), for planning the respective validation experiments and for conducting meaningful laboratory tests and interpreting their results correctly.

For example, in an oedometer swelling test, the ions produced by the dissolution of anhydrite can move by diffusion out of the oedometer if the container contains distilled water. On the other hand, if a saturated sulphate solution is used in the swelling test, then ions would be supplied to the rock specimen by advection and possibly also by diffusion. It is therefore obvious that quantifying the role of transport is important for the interpretation of the test results.

As another practical example illustrating the potential role of advective transport, in situ conditions may be considered where seepage flow occurs either from the rock towards the tunnel or vice versa (cf. Anagnostou 1995a, b). Depending on the seepage flow velocity relative to the rate of the chemical dissolution and precipitation reactions, it is at least theoretically possible that the flowing water transports the anhydrite dissolution products away before gypsum precipitates. In this case, seepage flow would decrease the calcium and sulphate content in a zone of the rock mass and increase the ion concentration in another zone, thus leading to rock leaching in the first zone and gypsum formation in the second zone – even if the latter did not initially contain anhydrite. Such phenomena have in fact been observed in the field, e.g. in the Schanz Tunnel (Schaeetherle 1929). The invert of this tunnel experienced an average yearly heave of 1.6 cm in the period 1880 - 1972, i.e. a cumulative heave of 1.50 m (Erichsen and Kurz 1996). Mineralogical investigations in 1990 (110 years after construction of the tunnel) showed, however, that the rock contained no sulphate up to a depth of 3 m beneath the tunnel floor. Beneath this zone, the rock contained both gypsum and anhydrite. The anhydrite percentage increased with depth; at depths greater than about 10 m beneath the tunnel the sulphate was
present only as anhydrite. The fact that the zone with the largest swelling deformations was gypsum-free is surprising at first sight, but it shows that advective transport may indeed be important.

The velocity of the seepage flow depends on rock permeability as well as on the hydraulic boundary conditions at the far field and at the tunnel boundary. The hydraulic boundary conditions also determine the extent of the water table drawdown as well as the potential development of an unsaturated zone (Anagnostou 1995a, b). The latter may be important for the swelling process, since a reduction in the saturation degree may lead to local supersaturation and, therefore, to gypsum growth (cf. Alonso and Olivella 2008).

The present dissertation analyses simple one-dimensional systems in order to investigate the conditions under which the seepage flow rate or the diffusion rate are so high (relatively to the rate of the chemical reactions) that these transport processes must be taken into account in continuum-mechanical modelling and in the planning and interpretation of laboratory tests. The question under investigation can also be formulated inversely: What are the conditions under which it is possible to ignore transport and consider swelling as a purely chemo-mechanical process?

Other potentially relevant effects, such as the subsequent leaching of the formed gypsum (as in the Schanz Tunnel), evaporation of pore water and development of an unsaturated zone, will not be investigated. Furthermore, since a full chemo-mechanical coupling is not essential for the questions under investigation, only the simplified case of a constrained system is considered (i.e. zero volumetric strain, as under the conditions prevailing in oedometer swelling pressure tests).

This Chapter is structured as follows:

- **Section 6.2** formulates the governing equations for the advection-diffusion problem in the presence of dissolution and precipitation (the “HC model”), taking account of the kinetic properties in accordance with Section 5 but without considering the effect of sealing. The latter is significant only for thicker anhydrite veins (Section 5.6).
- **Section 6.3** illustrates the basic behaviour of the HC model and shows that, depending on the composition of the system (anhydrite content, porosity etc.), the HC process may terminate either because all of the anhydrite has been hydrated (Section 6.3.2) or because the pores have filled up (clogging, Section 6.3.3).
- **Section 6.4** investigates whether diffusion may cause a significant loss of sulphate in oedometer swelling tests performed with distilled water. Section 6.4.2 describes the problem layout and presents the overall model behaviour. The effect of diffusion is quantified by introducing a so-called “leaching coefficient”, which is by definition equal to the fraction of the sulphate that moves out of the system (Section 6.4.3). The LC is obviously equal to 0 in the case of a closed system and constitutes a measure of the difference between the behaviour of an open system (with diffusion) and that of a closed system. A high LC-value means that the influence of diffusion is significant. The computations of Section 6.4 were carried-out without considering the seepage
flow of the distilled water towards the specimen. They showed that diffusion is relevant only in very exceptional cases. As the effect of diffusion would be even smaller in the presence of advection, it was not necessary to perform a coupled advection-diffusion analysis.

- Section 6.5 investigates the seepage flow rates for which advection significantly interferes with the anhydrite dissolution and gypsum precipitation process. Based on the results of Section 6.4, according to which diffusion is not significant, only advective flow is considered. Its effect is quantified, as in Section 6.4, by means of the $LC$.

### 6.2 Governing equations of the advection-diffusion model

#### 6.2.1 Mass balance and geometric equations

We consider a system consisting of a solid phase and a liquid phase under isothermal conditions. In the most general case the constituents of the solid phase are anhydrite (subscript $A$), gypsum (subscript $G$), and inert minerals, i.e. minerals that do not participate in the chemical reactions (e.g. dolomite). The liquid phase contains water (subscript $W$), as well as calcium and sulphate ions (I). The chemical reactions and the masses involved are given by Eqs. (2.2) and (2.1) for anhydrite and gypsum, respectively. In the forthcoming equations, these two chemical reactions will be denoted by the subscripts “$R1$” and “$R2$”.

In the most general case of an open system, mass changes in respect of the ions, water, anhydrite and gypsum may take place due to chemical reactions (dissolution and precipitation of anhydrite or gypsum), diffusion or advection (seepage flow). The general equation for the mass change rate of the $i$-th constituent reads as follows (the dot notation is applied hereinafter for time derivatives):

$$
\dot{m}_i = \dot{m}_{i,R1} + \dot{m}_{i,R2} + \dot{m}_{i,\text{dif}} + \dot{m}_{i,\text{adv}},
$$

(6.1)

where the subscripts “$R1$”, “$R2$”, “$\text{dif}$” and “$\text{adv}$” denote the mass change rates due to anhydrite dissolution or precipitation, gypsum dissolution or precipitation, diffusion and advection, respectively. Subsequently, Eq. (6.1) will be applied to the different constituents of the system.

The mass change of the solid phase (anhydrite and gypsum) is due to dissolution and precipitation only. The anhydrite and gypsum mass change rates read as follows:

$$
\dot{m}_A = \dot{m}_{A,R1} = -\dot{m}_{I,R1},
$$

(6.2)

$$
\dot{m}_G = \dot{m}_{G,R2} = -\dot{m}_{I,R2} - \dot{m}_{W,R2}.
$$

(6.3)

On account of the stoichiometry of gypsum precipitation (Eq. 2.1) the following equations apply:

$$
\dot{m}_{I,R2} = -\frac{136.14}{172.14} \dot{m}_G
$$

(6.4)
and
\[ m_{w,R2} = -\frac{36}{172.14} \cdot \dot{m}_G. \]  
(6.5)

For the ion mass change rate all components of Eq. (6.1) must be taken into account:
\[ \dot{m}_I = \dot{m}_{I,R1} + \dot{m}_{I,R2} + \dot{m}_{I,adv} + \dot{m}_{I,dif}. \]  
(6.6)

Additionally, assuming for the following investigations that \( c_{eOe} = c_{SO4} = c \), and considering a saturated porous medium, the ion mass depends on the concentration \( c \) (defined as ion mass \( M_I \) per water volume \( V_w \)) according to:
\[ M_I = \frac{M_I}{V_{tot,0}} = \frac{M_I}{V_w} \cdot \frac{V_w}{V_{tot,0}} = c \cdot \phi. \]  
(6.7)

where \( \phi \) is the porosity, defined as the pore volume \( V_p \) per unit of total volume.

The mass of water may change due to advection (seepage flow), gypsum growth or dissolution:
\[ \dot{m}_w = \dot{m}_{w,R2} + \dot{m}_{w,adv}. \]  
(6.8)

Moreover, the water mass per unit rock volume is related to the porosity \( \phi \) according to:
\[ m_w = \frac{M_w}{V_{tot,0}} = \rho_w \cdot \frac{V_w}{V_{tot,0}} = \rho_w \cdot \phi. \]  
(6.9)

Differentiating Eq. (6.9) with respect to time gives:
\[ \dot{m}_w = \dot{\rho}_w \cdot \phi + \phi \dot{\rho}_w. \]  
(6.10)

Taking the water compressibility \( c_w \) into account leads to the following relationship for the water mass balance:
\[ \frac{\dot{m}_w}{\rho_w} = \dot{\phi} + \gamma_w \cdot \phi \cdot c_w \cdot \dot{h}, \]  
(6.11)

where \( \gamma_w \) is the unit weight of the water and \( h \) the hydraulic head.

Under the condition of zero volumetric strain, the porosity changes only due to the chemical reactions, \( i.e. \) at the following rate:
\[ \dot{\phi} = -\frac{\dot{m}_A - \dot{m}_G}{\rho_A - \rho_G}. \]  
(6.12)
6.2.2 Transport

6.2.2.1 Advection

For the advective flux, the common formulation of Darcy’s law is adopted (cf. e.g. Bear 1972), according to which the seepage flow velocity depends on the hydraulic head gradient:

\[ q_i = -K_{ij} \frac{\partial h}{\partial j}, \quad (6.13) \]

where \( q_i \) is the seepage flow velocity, \( h = z + p/(\rho g) \) denotes the hydraulic head, \( p \) the pore pressure, \( \rho \) the density of water, \( g \) the gravitational acceleration \((\approx 10 \text{ m/s}^2)\), \( z \) the geodetic head and \( K_{ij} \) the hydraulic conductivity tensor, given by:

\[ K_{ij} = \frac{\rho g}{\mu} k_{ij}, \quad (6.14) \]

with \( k_{ij} \) denoting the intrinsic permeability tensor and \( \mu \) the dynamic viscosity of the water, which is constant under the assumption of isothermal conditions. Assuming isotropic behaviour, \( K_{ij} = \delta_{ij} K \).

The hydraulic conductivity depends in general on the porosity and on the pore structure, as well as on the occurrence of fractures, which either pre-exist in the rock or may be induced by swelling (cf. Anagnostou 1991). Sulphate leaching increases porosity and thus also permeability, while gypsum growth may either increase permeability (by opening up fractures) or decrease it (by clogging up pores). These effects are not taken into account in the present thesis.

Due to advective flux (Eqs. 6.6 and 6.8), the masses of water and ions change at the following rates:

\[ \dot{m}_{W,\text{adv}} = -\rho_w \frac{\partial h}{\partial j} q_k, \quad (6.15) \]

and

\[ \dot{m}_{i,\text{adv}} = -\partial_k \left( \alpha q_k \right), \quad (6.16) \]

6.2.2.2 Diffusion

The ions circulate in a solution from regions with high concentration towards regions with lower concentration due to diffusion, with a magnitude proportional to the concentration gradient (cf. e.g. Cussler 1997). The diffusive mass flux in a porous medium is given by Fick’s law which reads, in its general form, as follows:

\[ J_{k}^{\text{diff}} = -\phi \cdot T_k^* \cdot D \cdot \partial_k c, \quad (6.17) \]

where \( D \) is the molecular diffusion coefficient (cf. Section 5.2.3) and \( T_k^* \) is the tortuosity of the porous medium. The negative sign in Eq. (6.17) is attributed to the fact that the ions move towards decreasing
concentrations, in the opposite direction to that of the concentration gradient. As already mentioned in Section 5.2.3, tortuosity is a dimensionless parameter (< 1) that depends on how tortuous the flow path is through the porous medium. Typical values for different media can be taken from Marsily (1986) and Bear (1972). In the present case, we assume isotropic tortuosity and a value of $T^* = 0.1$.

The mass change of the ions due to diffusive flux is then given in its general form by:

$$\dot{m}_{i,df} = -\nabla \cdot \vec{j}_{i,k}. \quad (6.18)$$

### 6.2.2.3 Set of equations

Equations (6.2), (6.4), (6.6) and (6.7) lead to the balance equation of the ions (advection-diffusion equation):

$$\frac{\partial (\phi c)}{\partial t} = -\frac{\partial}{\partial x} \left( cq_s \right) + \frac{\partial}{\partial x} \left( \phi T^* D \frac{\partial c}{\partial x} \right) - \dot{m}_A - \frac{136.14}{172.14} \dot{m}_G. \quad (6.19)$$

Furthermore, Eqs. (6.5), (6.8), (6.11), (6.12) and (6.15) result in the water balance equation:

$$\gamma_w \cdot \phi \cdot c_w \cdot \dot{h} = -\frac{36}{172.14} \frac{\dot{m}_G}{\rho_w} - \frac{\partial q_x}{\partial x} - \dot{\phi}. \quad (6.20)$$

Finally, the seepage flow velocity in one dimension is given by (cf. Eq. 6.13):

$$q_s = -K \frac{\partial h}{\partial x}. \quad (6.21)$$

The chemically-induced mass change rates of anhydrite and gypsum are given by Eqs. (5.9) and (5.11), neglecting the dependency of the dissolution rate on the flow velocity (cf. Section 5.2.1.4). This effect is irrelevant for the relatively slow flow velocities in natural rocks. As in Section 5, spherical mineral particles are considered. Furthermore, we assume that gypsum grows only on the surfaces of inert particles. As mentioned in Section 6.1, the sealing effect is not considered in the following investigation.

Equations (6.19)-(6.21), (6.12), (5.9) and (5.11) represent a system of 6 equations with 6 unknown parameters, which are functions of time and space: $m_G(x,t)$, $m_A(x,t)$, $c(x,t)$, $q_s(x,t)$ and $h(x,t)$. For the solution of the system, a code has been developed in Mathematica 9 (Wolfram 2003). Depending on the specific findings in the following sections, some terms of the equations may vanish. Since we focus specifically on the effect of the seepage flow rate (Section 6.1), the flow velocity $q_s$ actually represents an independent input parameter for the questions under investigation. The assumption of a constant seepage flow rate means that the process is steady with respect to seepage flow. This is materialized computationally by considering a one-dimensional model of length $L = 1$ m, of small storativity and of hydraulic conductivity $K = q_s$ under a unit hydraulic head gradient.
6.3 Model behaviour

6.3.1 Introduction

In the present section we illustrate the basic behaviour of the model from Section 6.2. The parameter values are chosen in a manner, which makes it possible to show different modes of behaviour. More specifically, in the first investigation (Section 6.3.2), we choose a low initial volume fraction of anhydrite in combination with a sufficiently high porosity so that the process terminates when the total amount of anhydrite has dissolved. In Section 6.3.3, a high initial volume fraction of anhydrite is selected; in this case, the process ceases when the gypsum crystals fill the pores (clogging), which happens before all of the anhydrite is transformed. The indicative investigations of the present section assume a flow velocity of $10^{-5}$ m/s.

6.3.2 Low anhydrite content

We investigate the time-development of hydration for a mixture consisting initially of a low content of anhydrite ($\phi_A = 0.1$), inert minerals ($\phi_S = 0.8$) and distilled water ($\phi_W = 0.1$, $c(x, 0) = 0$ mol/m$^3$). The boundary conditions for the ion concentration comprise a value of $c(0, t) = 0$ mol/m$^3$ at boundary A (Fig. 6.1), while the ions are allowed to flow free at boundary B. The latter is implemented in the model by the so-called no-diffusive flow boundary condition $c \bigg|_{x=L} = 0$.

![Figure 6.1. System and boundary conditions](image)

For spherical mineral particles, the specific surface areas $F_{A0}$ and $F_S$ appearing in Eqs. (5.9) and (5.11) are related to the initial radius $r_{A0}$ of anhydrite and the radius $r_S$ of the inert minerals ($F_{A0} = 3/r_{A0}$ and $F_S = 3/r_S$). The investigation will be performed for $r_{A0} = 0.5$ mm and $r_S = 0.1$ mm. The other parameter values are given in Table 5.1.

Figure 6.2a shows the spatial distribution of the ion concentration $c$ at different times. As the initial ion concentration is everywhere equal to zero, anhydrite will start to dissolve, thus increasing the ion concentration. In general, once the gypsum equilibrium concentration $c_{eq,G}$ (15.5 mmol/l) is reached, gypsum crystals will start to precipitate on the inert mineral particles. As shown in Section 5.4.2 the maximum concentration attained depends on the dimensionless parameter $\mathcal{A}$ (Eq. 5.35). The higher
the value of $A$, the lower will be the maximum oversaturation with respect to gypsum. In the current investigation the maximum concentration, as can be seen from Fig. 6.2a, is always close to the equilibrium concentration $c_{eq,G}$ of gypsum, which characterizes a dissolution controlled system. This is attributed to the very high content of inert minerals in the system which leads to a high value of $A$ (Eq. 5.35) and thus, to a high gypsum production rate (Eq. 34).

At the same time, however, the dissolved ions move towards the right boundary due to the seepage flow. Therefore, the concentration at the left end of the system will always be lower than that at the right. On one hand, this leads to a higher anhydrite dissolution rate at regions of low $c$ (bearing in mind that the driving force for the dissolution is the term $(c_{eq,A} - c)/ c_{eq,A}$, cf. Section 5.2.1). This is verified by Fig. 6.2b, which shows the mass of anhydrite as a function of $x$ at different times; anhydrite clearly dissolves faster at lower $x$-values. The absence of gypsum at low $x$-values (Fig. 6.2c) is due to advective transport, which makes it impossible to reach the gypsum equilibrium concentration (Fig. 6.2a). The amount of gypsum increases close to boundary B because, due to ion transport, the mixture remains close to the gypsum equilibrium concentration in this region (Fig. 6.2a) – at least until the total amount of anhydrite dissolves. Figure 6.2c additionally shows the mass of gypsum $m_{G,CS}$ for a closed system (dashed line, cf. also Section 6.4.2). The process of anhydrite dissolution and gypsum precipitation continues until the total amount of anhydrite has been dissolved. In contrast to the behaviour of a closed system, where the concentration at equilibrium would be equal to the gypsum equilibrium concentration (cf. Section 5.4.2), $c = 0$ at any $x$ (Fig. 6.2a) because the ‘last’ ions (i.e. the ones corresponding to the gypsum equilibrium concentration) are transported away by the flowing water.

It should be noted at this point that, in reality, the gypsum that forms would start to dissolve once the ion concentration drops below the gypsum equilibrium concentration (leaching of gypsum) and the dissolution products would be transported away by the flowing water. The consequence would be a completely sulphate-free system. Even if the simulation does not consider gypsum dissolution, it is obvious that the model in the last Section is able to reproduce the observations made in the Schanz Tunnel (anhydrite transformation to gypsum followed by dissolution of the gypsum and transport of the sulphate out of the system, Section 6.1).

Figure 6.2d shows the spatial distribution of the porosity at different times. Initially ($t = 0$), the porosity $\phi = 0.1$ at any $x$ (straight line). As explained above, anhydrite dissolves faster at lower $x$ - values, while gypsum does not precipitate in this region. This leads to a local increase of the porosity. Furthermore, as the anhydrite dissolution and the gypsum precipitation proceed, porosity decreases with increasing $x$ as a result of the gypsum growth (as shown before in Fig. 6.2c, the amount of gypsum increases with increasing $x$, thus filling the pores). At the very first $x$ - values, i.e. in the vicinity of boundary A, where no gypsum precipitates, the porosity ultimately increases by the pore volume fraction created by anhydrite dissolution (the final porosity is equal to $\phi_{A0} + \phi_{W0} = 0.2$).
Figures 6.3a-d show the time development of the concentration, of the anhydrite and gypsum mass and of the porosity at different locations. As can be seen in Fig. 6.3a, and as explained above, the concentration close the right boundary of the model \( L = 1 \) m remains close to the gypsum equilibrium concentration over a long period (until all the anhydrite dissolves); this also explains the fact that this zone contains the greatest amount of gypsum (Fig. 6.3c). Furthermore, Fig. 6.3b confirms that anhydrite dissolves faster at low \( x \)-values. Finally, Fig. 6.3d, apart from making it clear once again that porosity is lower at high \( x \)-values, also illustrates a very interesting result of the non-monotonous evolution of the porosity over time. At low \( x \)-values, anhydrite dissolves and gypsum precipitates (thus reducing the porosity), while at the same time ions are transported towards the right. Once the concentration becomes lower than the gypsum equilibrium concentration and gypsum precipitation is no longer possible, the porosity starts to increase as a result of further anhydrite dissolution.

Finally, Fig. 6.3d shows that this effect becomes less important with increasing values of \( x \), as gypsum continues to precipitate there (the ion concentration there is greater than the gypsum equilibrium concentration for a longer period of time).

### 6.3.3 High anhydrite content

The mixture in the present investigation consists of anhydrite with a volume fraction of \( \phi_{A0} = 0.4 \), inert minerals \( \phi_S = 0.5 \) and distilled water \( \phi_W = 0.1 \). The initial conditions, boundary conditions and permeability are the same as in Section 6.3.2. The radii of the anhydrite and the inert particles are taken equal to \( r_{A0} = 5 \) mm and \( r_S = 0.05 \) mm, respectively. Neglecting once again the leaching of gypsum, Figs. 6.4a-d illustrate the spatial distribution of the ion concentration, the anhydrite mass, the gypsum mass and the porosity, respectively, at different times.

The evolution of the different parameters is, as expected, similar to that in Section 6.3.2. In the present numerical example, however, the process stops when the gypsum crystals fill the pores (clogging). Seepage flow and ion circulation are not possible after the pores fill up. Due to numerical accuracy problems, the numerical solution stops not at zero porosity, \( \phi = 0 \), but when the porosity value drops below a threshold of \( \phi = 0.005 \) (Fig. 6.4d). In the present numerical example, this happens close to the right boundary \( x > 0.8 \) m, Fig. 6.4d), because of the large amount of gypsum forming in this region (Fig. 6.4c).

At the end of the process, three zones can be observed in Fig. 6.4b and 6.4c. The first zone is free of sulphate; the second zone contains only gypsum; the third zone \( x > 0.4 \) contains both anhydrite and gypsum. This pattern resembles the one observed in situ: leached Gypsum Keuper, unleached gypsum-containing Keuper - transition zone from top to bottom (\textit{cf}. Fig. 3.1).
Figure 6.2. Spatial distribution of (a) ion concentration, (b) mass of anhydrite, (c) mass of gypsum and (d) porosity at different times
On the Role of Transport Processes

Figure 6.3. Time development of (a) ion concentration, (b) mass of anhydrite, (c) mass of gypsum and (d) porosity at different locations

(a)

1. x = 0.2
2. x = 0.4 m
3. x = 0.6 m
4. x = 0.8 m
5. x = 1.0 m

(b)

1. x = 0.2
2. x = 0.4 m
3. x = 0.6 m
4. x = 0.8 m
5. x = 1.0 m

(c)

1. x = 0.2
2. x = 0.4 m
3. x = 0.6 m
4. x = 0.8 m
5. x = 1.0 m

(d)

1. x = 0.2
2. x = 0.4 m
3. x = 0.6 m
4. x = 0.8 m
5. x = 1.0 m
Figure 6.4. Spatial distribution of (a) ion concentration, (b) mass of anhydrite, (c) mass of gypsum and (d) porosity at different times
6.3.4 Discussion

The computational model discussed above is actually nothing more than a conceptual model of the conditions that prevail in constrained systems (e.g. in the rock in the vicinity of a tunnel with a stiff lining which does not allow significant deformations to occur, or in an oedometer swelling pressure test where no volumetric strain is allowed). It considerably simplifies reality as it shows what happens in a one-dimensional system under a fixed seepage flow velocity; it does not consider a combination of effects such as variation of the hydraulic head and the seepage flow rate over time, the non-linearity imposed by porosity-dependent permeability, hydro-mechanical coupling (consolidation) or chemo-mechanical coupling (development of strains due to the dissolution or precipitation of the minerals).

However, it is remarkable that some features of the behaviour of this simplified model resemble certain conditions observed in situ. At the same time, even this relatively simple model exhibits a highly complex and nonlinear behaviour; differences in the initial conditions result in completely different behavioural patterns regarding development over time and the spatial distribution of the fields. The inclusion of the above-mentioned effects (hydro-chemo-mechanical coupling, non-linearity of seepage flow etc.) in the mathematical model formulation and with arbitrary two- or three-dimensional systems is possible in principle, but would increase the complexity of the model behaviour even more. Therefore, it is valuable for future theoretical and experimental investigations to check the conditions under which diffusion and/or advection can be omitted. The next two Sections deal with this question.

6.4 The role of diffusion in oedometer tests

6.4.1 Introduction

As mentioned in Section 6.1, it is at least theoretically possible that the ions produced by the dissolution of anhydrite within the rock specimen move out of the oedometer due to diffusion. The present section will show by means of numerical computations that the effect of ion diffusion out of the specimen can be neglected in most cases, even if the advective flow towards the specimen is slow. Taking the advective flow into account, the effect of diffusion would be even smaller, as the inflowing water would transport the ions towards the specimen, thus partially compensating for ion loss due to diffusive transport.

The ion concentration in the sample is governed by the combined effects of the anhydrite dissolution rate, the gypsum precipitation rate and the ion diffusion rate. If the diffusion is very slow relative to the chemical reactions, the anhydrite to gypsum transformation will proceed as a practically topochemical reaction (i.e. as in a closed system, Chapter 5). If, however, ion production and consumption by the chemical reactions is slow, the effect of diffusive transport may be significant.
The lower the initial anhydrite content, the slower will be the ion production rate (Eq. 5.9) and the more pronounced the effect of diffusion. A small specific surface (or a large size) in respect of the anhydrite particles will have the same effect, as it decelerates the dissolution process.

The present Section is organized as follows: Section 6.4.2 outlines the model assumptions and discusses, in a similar way to Section 6.3, the general model behaviour. Section 6.4.3 investigates the conditions under which diffusion might play a role, based on the parametric study results.

### 6.4.2 Model description and behaviour

The computations are based upon the model in Section 6.2 without the advective terms. We consider a rock sample consisting of anhydrite, inert minerals and water which is immersed in a container with distilled water. The height of the rock sample is 30 mm while its diameter is not of interest, because ion diffusion occurs towards the filter plates of the oedometer, i.e. only in the axial direction. Taking account of the symmetry of the watering conditions (filter plates at both specimen ends), only a half of the specimen is modelled with the boundary conditions \( \frac{\partial c}{\partial t} \bigg|_{x=0} = 0 \) and \( c (L, t) = 0 \) at points A and B, respectively (Fig. 6.5). The boundaries A and B correspond to the mid-plane of the specimen and to its drained end, respectively. We assume, furthermore, that the pore water is initially ion-free (\( c (x, 0) = 0 \)).

![Figure 6.5. System and boundary conditions](image)

In order to get an idea of the evolution of the different field variables over time, a specific example is presented, addressing a mixture of low anhydrite content (\( \phi_{A0} = 0.1, \phi_S = 0.8 \) and \( \phi_{W0} = 0.1 \)). Figure 6.6a shows the spatial distribution of the ion concentration at different times assuming rather large anhydrite particles (\( r_{A0} = 1 \) mm) and inert particles of radius \( r_S = 0.1 \) mm. (According to Section 5.2.1.2 the size of the anhydrite particles may generally vary from some \( \mu m \) to a few cm. The effect of this parameter will be investigated in the next Section.) As anhydrite starts to dissolve, the concentration increases uniformly over the entire specimen, apart from the zone close to the drained boundary B, where diffusive transport occurs due to the prescribed boundary condition \( c = 0 \). Once the mixture reaches the gypsum equilibrium concentration \( c_{eq,G} \), gypsum starts to precipitate almost everywhere, i.e. with the exception of the zone close to boundary B where the mixture cannot reach equilibrium concentration \( c_{eq,G} \) (Fig. 6.6b). In order to facilitate the comparisons, Fig. 6.6b also shows
(as a straight line) the final mass of gypsum in the case of a closed system, \textit{i.e.} without diffusive transport. The ions produced by the anhydrite dissolution close to the drained boundary \( B \) diffuse to the distilled water with the consequence that the gypsum quantity is less than in a closed system. The faster the diffusion and the slower the anhydrite dissolution, the more extended will be the zone where gypsum does not precipitate at all.

Figure 6.6. Spatial distribution of (a) ion concentration, (b) mass of gypsum and (c) mass of anhydrite, at different times
As expected, the ion concentration close to the mid-plane of the specimen (point A) drops more slowly than close to the drained boundary (point B). The reason is that the diffusive flux in the middle part of the specimen is slow due to the low concentration gradient. Close to the drained boundary the anhydrite dissolution occurs more quickly than elsewhere (Fig. 6.6c) due to the higher driving force \((c_{eq,A} - c)/ c_{eq,A}\); in this zone, however, the effect of diffusion dominates due to contact with the distilled water.

The system reaches equilibrium when the concentration becomes zero everywhere. In the case of higher anhydrite content, the process would stop at the time that the pores were filled with gypsum (cf. Section 6.3.3).

### 6.4.3 Parametric study

The effect of diffusion (and of advection in Section 6.5) can be quantified by considering the leaching coefficient \((LC)\), defined as follows:

\[
LC = \frac{m_{A0} - \int_0^L \left[ m_A(x) + m_L(x) + \frac{136}{172} m_G(x) \right] \, dx}{m_{A0}} \in [0,1],
\]  

where the integral denotes the mass of the calcium and sulphate within the system (calculated in Mathematica Software using the Riemann sum by dividing the region into 30 intervals) and \(m_{A0}\) is the initial mass of anhydrite. Figures 6.7a, b and c show the \(LC\) as a function of the anhydrite particle radius for different inert particle radii and initial anhydrite contents (volume fractions) \(\phi_{A0}\) of 0.1, 0.2, and 0.4, respectively. The numerical simulations show that in the first case \((\phi_{A0} = 0.1)\) the total amount of anhydrite dissolves, while in the other two cases \((\phi_{A0} = 0.2\) and 0.4) the process terminates sooner because the pores are filled with gypsum.

A high \(LC\) value means that the effect of diffusion is significant. Figures 6.7a-c show that this happens only under very specific conditions. The following conditions must be fulfilled cumulatively: low initial anhydrite content \((\phi_{A0} < 0.2)\); large anhydrite particles \((r_{A0} > 1\) mm); small specific surface of the inert particles (which means that the surface area where gypsum precipitates is small).

In the interpretation of an oedometer swelling test, the possible effect of diffusion should be borne in mind. Significant diffusion (characterized by a high \(LC\) value) would cause an underestimation of the swelling pressure or swelling strain by an amount which can be quantified either in comparative tests using sulphate-saturated water or computationally in a fully coupled HMC-model. The results of the present section indicate, however, that the diffusion effect can be neglected in most cases. More specifically, the \(LC\) is less than 0.1, i.e. the error caused by neglecting the diffusive transport is less than 10%, if the initial volume fraction of anhydrite is approximately greater than 0.2 and the anhydrite particles have a radius smaller than 1 mm. The error would be even smaller if advective
transport towards the specimen was considered, as the inflow water would transport the ions to the specimen.

Figure 6.7. $LC$ coefficient for (a) $\phi_{A0} = 0.1$, (b) $\phi_{A0} = 0.2$ and (c) $\phi_{A0} = 0.4$
6.5 The role of advection

6.5.1 Problem layout

At the scale of a tunnel, it is at least theoretically possible that transport processes reduce the calcium and sulphate content in one mass region while increasing it in another region. In the first region, anhydrite leaching would take place, while in the second region gypsum would precipitate, even if this region was initially free of anhydrite (Fig. 6.8). The one dimensional system and boundary conditions are the same as in Section 6.3.2 (Fig. 6.1). More specifically, a zero ion concentration is prescribed at boundary A, while the ions can flow away at boundary B (Fig. 6.1). Furthermore, as the flow velocity is actually the independent input parameter and the process is steady with respect to seepage flow, a length of 1m and a hydraulic head gradient of unity are considered (cf. Section 6.2.2.3). As already shown in Section 6.3, the process of anhydrite dissolution and gypsum precipitation terminates either due to dissolution of all the anhydrite or due to the pores filling up with gypsum crystals in specific regions of the system. As diffusive transport is relatively insignificant, the numerical examples in the present Section are based upon the model in Section 6.2 without the diffusion terms.

![Figure 6.8. Anhydrite dissolution and gypsum precipitation in an anhydrite-free region](image)

6.5.2 Parametric study

Figure 6.9 shows the $LC$ as a function of the seepage flow velocity for different radii $r_A$ of the anhydrite particles and $r_S = 1 \mu m$ for the inert minerals. This low value for the radius of the inert minerals indicates a high available specific surface area for the precipitation of gypsum and therefore a high precipitation rate. In the case of a low precipitation rate, the effect of advection would be more significant because the ions would stay longer in the solution and could thus be transported out of the system. Figures 6.9a, b and c have been calculated for an initial anhydrite volume fractions of $\phi_{A0} = 0.1$, 0.2 and 0.4, respectively. As expected, the leaching coefficient increases with increasing seepage flow velocity. Furthermore, the diagrams show that the larger the anhydrite particles are, the wider will be the range of seepage flow velocities where advection might play a role ($LC$ is also less...
than 1 for lower velocities). The reason for this behaviour is the same as in Section 6.4: if the anhydrite particles are large (or if their specific surface is small), then ion production will be slow and the mixture will take longer to reach gypsum equilibrium concentration (where precipitation would start to occur). Consequently, there is more time available for the flowing water to transport the ions out of the system. In the presence of larger particles, the effect of transport would be even more pronounced as they offer a smaller specific surface for precipitation.

In addition, according to Fig. 6.9, the higher the initial anhydrite content, the lower will be the leaching coefficient and the smaller will be the effect of advection (other parameters being constant).

6.5.3 Discussion based on the results of Butscher et al. (2011a, b)

Finally, let us consider the actual seepage flow velocities in the Gypsum Keuper formation. Butscher et al. (2011a, b) employed numerical simulations to investigate the hydrogeological conditions in the Gypsum Keuper formation before and after tunnel excavation. They found that tunnel excavation can increase flow rates by a factor of up to 30. Their study is very interesting for the question under investigation in the present section, particularly because it considered a series of hydrogeological models (homogeneous, hydrostratigraphic and aquifer-aquitard) with or without considering fault zones or a fractured zone around the tunnels. In the most extreme case (i.e. that of fractured zones), they determined high inflow rates of up to 623 l/m/d. For the diameter of the tunnel (11 m), the inflow rate of 623 l/m/d corresponds to a maximum seepage flow velocity of $q_x = 2 \times 10^{-7}$ m/s. This value is at the far left boundary of the diagrams in Fig 6.9, where advective transport has practically no effect on the dissolution and precipitation reactions. Therefore, even under the extreme assumptions behind an inflow value of 623 l/m/d, the effect of advective ionic transport can be neglected, which means that it is reasonable to consider the transformation of anhydrite to gypsum as a topochemical process. This result is very valuable for future research as it shows that continuum-mechanical formulations can be simplified.

6.6 Conclusions

In the present Chapter, a coupled HC model was formulated which takes account of anhydrite dissolution and gypsum crystal growth as well as advective and diffusive ion transport through a porous medium. After presenting the general behaviour of the model in one dimension, we examined the role of diffusion in oedometer swelling tests and concluded that it was rather insignificant in most cases. Finally, the effect of advective transport was quantified in terms of the so-called leaching coefficient. Gypsum growth was assumed to take place on particles with a small radius (1 μm), i.e. relatively quickly. The computational results indicate that for the low seepage flow velocities prevailing in the Gypsum Keuper formation, advective ion transport is rather insignificant. The leaching of anhydrite and precipitation of gypsum can occur in other locations only under the
combination of a high flow velocity (greater than $10^{-5}$ m/s, e.g. in fracture zones), slowly dissolving large particles or veins of anhydrite and low initial anhydrite contents.

Figure 6.9. Leaching coefficient as a function of seepage flow velocity for (a) $\phi_{40} = 0.1$, (b) $\phi_{40} = 0.2$ and (c) $\phi_{40} = 0.4$ ($r_s = 1 \mu m$)
7 Conclusions and Outlook

The scientific achievements of the present thesis can be summarized as follows:

- A thermodynamic model was developed for determining anhydrite and gypsum solubilities. The model coherently incorporates solid and fluid pressures, temperature, the effect of foreign ions, pore size and the effect of clay minerals (Chapter 2). The proposed solubility equations are valuable for future continuum-mechanical models that consider chemo-mechanical coupling simultaneously with transport processes.

- By combining the resulting solubility equations, the conditions were established for thermodynamic equilibrium between anhydrite, gypsum and water (Chapters 2.4 and 2.6), and the crystallisation pressure of gypsum was determined for arbitrary temperatures, pore sizes and water activities (Chapter 4.2).

- Based on the equations of Chapter 2, several hypotheses concerning the presence of anhydrite (rather than gypsum) at relatively shallow depths in Gypsum Keuper were quantitatively checked and partially dismissed (Chapter 3). It was shown that the presence of anhydrite must be due to the thermodynamic state of the pore water, which probably has a very low activity due to its interaction with the clay minerals. This result, besides being scientifically interesting, is also valuable for future modelling research, because it makes possible the formulation of consistent initial conditions. (In order to confirm this so-called “low water activity” hypothesis, plans are in place for experimental measurements using a transistor psychrometer.)

- The equations of Chapter 2, in combination with a simple pore expansion model for the interaction between the growing crystals and the surrounding rock matrix, made it possible to explain satisfactorily why the swelling pressure observed macroscopically is lower by one order of magnitude than the crystallisation pressure of gypsum (Chapter 4).

- The kinetic constants in respect of anhydrite dissolution and gypsum precipitation were determined by back-analysis of a large series of existing experimental results (Chapter 5).

- A kinetic anhydrite dissolution model was developed that incorporates the effect of the anhydrite surface being sealed by gypsum (Chapter 5). This model is able to explain quantitatively the well-known observation that thicker anhydrite veins hardly swell at all. (Experimental investigations into the effects of sealing are already being performed at the ETH Zurich.)

- Numerical analyses by means of a coupled HC model showed that ion transport by diffusion or advection is insignificant, apart from exceptional cases (Chapter 6). As ion transport does not interfere significantly with dissolution and precipitation reactions, anhydrite transformation can, for all practical purposes, be regarded as a topochemical process. This result is also very valuable for future research.
In the opinion of the author, future fundamental research in this field should focus on the following two questions: (i) the contribution of the clay matrix to the swelling process; (ii) the relationship between swelling pressure and swelling strain in sulphatic claystones.

In the present thesis, only one particular effect of the clay matrix has been considered – that of reducing water activity and shifting the thermodynamic equilibrium in favour of gypsum. Field observations indicate, however, that a relevant portion of the observed swelling may be due to water uptake by clay minerals rather than anhydrite transformation (Anagnostou et al. 2010). The contribution of clay (relative to that of anhydrite) is the subject of ongoing experimental research at the ETH Zurich.

The second question is important for the conceptual design of tunnel supports (Anagnostou et al. 2010). It is investigated by long-term swelling tests on sulphatic claystones (Pimentel and Anagnostou 2013). Isotropic compression tests are also currently being planned in order to study the chemo-mechanical behaviour. In a second stage, anisotropic loading conditions will be considered as well, i.e. triaxial tests and oedometer tests will be conducted. The results of these tests, in combination with the results of the present PhD research, will provide a basis for formulating and calibrating a coupled hydraulic-mechanical-chemical (HMC) model for the swelling of sulphatic claystones.
Appendix A. Closed-form solutions for cavity expansion

This Appendix presents the analytical solutions to the cavity expansion models used within the main body of the dissertation. The cylindrical cavity problem is analysed together with the spherical problem by introducing a variable $\zeta$, which is equal to 1 or 2, respectively. A hollow cylinder/sphere is taken, with internal radius $a$ and external radius $b$. The material is isotropic linearly elastic with Young’s modulus $E$ and Poisson’s ratio $\nu$, exhibiting a brittle tensile behaviour. More specifically, the peak tensile strength is equal to $f_t$ (negatively defined, i.e. $f_t \leq 0$), whereas the residual (or post-failure) tensile capacity is taken equal to zero. Cylindrical ($r, t, z$) and polar ($r, t \equiv z$) coordinates are used for the formulation of the mathematical equations with the origin being placed at the centre of the cavity. It shall be noted that the convention of positive compression is adopted in combination with positive radial displacements outwards. Finally, plane strain conditions are taken into consideration for the two-dimensional case (with the out-of-plane stress being the intermediate principal stress throughout loading).

A1. Cavity expansion model with stress boundary condition at the outer surface

A1.1. Problem statement

The initial stress field is assumed to be uniform and isotropic, corresponding to the in situ stress $\sigma_0$ at the depth of the rock element. Concerning the boundary conditions of the problem, a radial displacement $u_a$ is applied at the inner surface and a pressure equal to the in-situ stress $\sigma_0$ is considered at the outer radius $b$:

$$u(r = a) = u_a, \quad (A1)$$

$$\sigma_t(r = b) = \sigma_0. \quad (A2)$$

A1.2. Purely elastic response

The model geometry in combination with the symmetric loading and boundary conditions allow for the one dimensional mathematical treatment of the problem with respect to the radial coordinate $r$, forcing the radial (major) and the tangential (minor) axes to be the principal ones throughout loading. Considering the equilibrium equation:
Appendix A

\[ \frac{d\sigma_r}{dr} + \zeta \frac{\sigma_r - \sigma_t}{r} = 0, \quad (A3) \]

the constitutive equations:

\[ \sigma_r = \frac{E}{(1 + v)(1 - 2v)} \left[ (1 - v)\epsilon_r + \zeta v \epsilon_t \right], \quad (A4) \]

\[ \sigma_t = \frac{E}{(1 + v)(1 - 2v)} \left[ \epsilon_r + \left[ 1 - v(2 - \zeta) \right] \epsilon_t \right], \quad (A5) \]

the small strain kinematic relations:

\[ \epsilon_r = -\frac{du}{dr}, \quad (A6) \]

\[ \epsilon_t = -\frac{u}{r}, \quad (A7) \]

where \( \sigma_r, \sigma_t, \epsilon_r, \epsilon_t \) and \( u \) correspond to the radial and tangential stress and strain and the radial displacement, respectively, and the boundary conditions (A1) and (A2) correspond to the familiar solution of Lamé for the expansion of hollow cylinders and spheres (Yu 2000), giving:

\[ \sigma_a - \sigma_0 = C_1 \frac{E u_a}{a}, \quad (A8) \]

\[ \sigma_{t,a} - \sigma_0 = -C_1 \frac{E u_a}{a}, \quad (A9) \]

where \( \sigma_a \) and \( \sigma_{t,a} \) denote the radial and the tangential stress at the inner radius \( a \) of the model. The positive definite constants \( C_1 \) and \( C_2 \) depend on the Poisson’s ratio and the radii ratio \( b/a \):

\[ C_1 = \frac{\zeta \left[ 1 + (\zeta - 1)v \right] \left[ (b/a)^{\zeta+1} - 1 \right]}{(1 + v) \left[ 1 + (\zeta - 1)v \right] \left[ (b/a)^{\zeta+1} + \zeta (1 - 2v) \right]} > 0, \quad (A10) \]

\[ C_2 = \frac{\left[ 1 + (\zeta - 1)v \right] \left[ (b/a)^{\zeta+1} + \zeta \right]}{(1 + v) \left[ 1 + (\zeta - 1)v \right] \left[ (b/a)^{\zeta+1} + \zeta (1 - 2v) \right]} > 0. \quad (A11) \]

As \( u_a \) increases, the radial stresses around the cavity increase (cf. Eq. A8), while the circumferential ones decrease (Eq. A9). Hence, by setting the elastic tangential stress equal to the tensile strength of the material \( f_t \), a critical displacement which defines the onset of tensile failure can be calculated:

\[ \frac{E u_a}{a} = \frac{\sigma_0 - f_t}{C_2} . \quad (A12) \]
A1.3. Response after tensile failure

For displacements greater than this critical value, an inner cracked zone with radius $\rho$ will develop (Fig. 3.9). The response of the medium in the outer elastic region is given from Eqs. (A8)-(A11) substituting $a$, $\sigma_{a}$, $\sigma_{ta}$ and $u_{a}$ by $\rho$, $\sigma_{r}$, $\sigma_{tr}$ and $u_{r}$, respectively, as well as setting the tangential stress at the interface equal to the tensile strength of the material (i.e. $\sigma_{tr} = f$):

$$\sigma_{r} - \sigma_{o} = C_{1}' \frac{Eu_{r}}{\rho},$$  \hspace{1cm} (A13)

$$\frac{Eu_{r}}{\rho} = \frac{\sigma_{o} - f_{t}}{C_{2}'},$$  \hspace{1cm} (A14)

where

$$C_{1}' = \frac{\zeta \left[ 1 + (\zeta - 1)\nu \right] \left( b/\rho \right)^{\zeta + 1} - 1}{(1+\nu) \left[ 1 + (\zeta - 1)\nu \left( b/\rho \right)^{\zeta + 1} + \zeta (1-2\nu) \right]} > 0,$$  \hspace{1cm} (A15)

$$C_{2}' = \frac{\left[ 1 + (\zeta - 1)\nu \right] \left( b/\rho \right)^{\zeta + 1} + \zeta}{(1+\nu) \left[ 1 + (\zeta - 1)\nu \left( b/\rho \right)^{\zeta + 1} + \zeta (1-2\nu) \right]} > 0.$$  \hspace{1cm} (A16)

The response of a cracked material can be found in Ladanyi (1967), but will be presented briefly here for the sake of completeness. The tangential stress of each material point is equal to zero throughout this zone ($\sigma_{t} = 0$). The incorporation of the equilibrium condition (see Eq. A3):

$$\frac{d\sigma_{r}}{dr} + \zeta \frac{\sigma_{r}}{r} = 0,$$  \hspace{1cm} (A17)

the constitutive equation in the radial direction (elastic response):

$$\varepsilon_{r} = \frac{1 - \nu^{2}}{E} \left( 2 - \zeta \right) \left[ \sigma_{r} - \frac{1-2\nu}{1-\nu(2-\zeta)^{2}} \sigma_{o} \right],$$  \hspace{1cm} (A18)

and the kinematic relation (A6), in combination with the displacement boundary conditions (A1) and (A14), leads to a determination of the radial stresses at the inner and the failure radius respectively:

$$\sigma_{a} = K_{1} \frac{Eu_{a}}{a} - K_{3} \frac{Eu_{a}}{a} + K_{2},$$  \hspace{1cm} (A19)

$$\sigma_{r} = K_{1} \frac{Eu_{r}}{\rho} - K_{3} \frac{Eu_{r}}{\rho} + K_{2},$$  \hspace{1cm} (A20)

where the constants $K_{1}$-$K_{4}$ may be expressed for the cylindrical case ($\zeta = 1$) through:

$$K_{1} = K_{3} = \frac{1}{(1+\nu)(1-\nu)\ln(\rho/a)},$$  \hspace{1cm} (A21)
Appendix A

\[ K_2 = \left( \frac{\rho}{a} \right) K_4 = \frac{(1-2\nu)\sigma_0 (\rho/a-1)}{(1-\nu)\ln(\rho/a)}, \quad (A22) \]

and for the spherical case (\( \zeta = 2 \)):

\[ K_1 = \left( \frac{\rho}{a} \right) K_3 = \frac{\rho}{\rho/a-1}, \quad (A23) \]

\[ K_2 = \left( \frac{\rho}{a} \right)^2 K_4 = (1-2\nu)\sigma_0 (\rho/a). \quad (A24) \]

It is rather inconvenient to express the above coefficients through unified expressions using the variable \( \zeta \).

The continuity of stresses at the interface is used for determining the relationship between the radius \( \rho \) of the tensile failure zone and the cavity wall displacement \( u_a \). Accounting for Eq. (A13) and Eq. (A20) in conjunction with Eq. (A14), the next formula is derived:

\[ \frac{Eu_a}{a} = \frac{\rho}{a} K_3 \left[ \sigma_0 - K_4 + \frac{C'_1 + K_4}{C'_2} (\sigma_0 - f_i) \right]. \quad (A25) \]

As a result, for a given radius \( \rho \), the inner radial displacement and pressure can be evaluated by means of Eqs. (A25) and (A19), correspondingly.

It is helpful, however, to define a variable \( \lambda \), which represents the percentage of the cracked zone around the cavity, instead of the failure radius \( \rho \). This variable varies between zero (no tensile failure, \( \rho = a \)) and one (total tensile failure, \( \rho = b \)):

\[ \lambda = \frac{\rho - a}{b - a}. \quad (A26) \]

Then, the internal radial pressure becomes (Eq. A19):

\[ \sigma_a = \frac{\left( \zeta + 1 \right)\sigma_0 (b/a)^{\zeta+i} + \zeta f_i \left[ 1 + \lambda (b/a-1)^{\zeta+i} - (b/a)^{\zeta+i} \right]}{\zeta \left[ 1 + \lambda (b/a-1)^{\zeta+i} + (b/a)^{\zeta+i} \right]} \left[ 1 + \lambda (b/a-1) \right]^\zeta. \quad (A27) \]

Finally, when the extent of the cracked zone reaches the external radius \( b \) of the hollow cylinder/sphere, the inner pressure \( \sigma_a \) takes its maximum value, indicating that the reaction at the cavity wall remains constant for larger inner displacements. By setting \( \lambda = 1 \), Eq. (A26) gives

\[ \sigma_a^{\max} = \left( \frac{b}{a} \right)^\zeta \sigma_0. \quad (A28) \]

The necessary expansion is calculated from Eq. (A25), which for \( \zeta = 1 \) yields
Closed-form solutions for cavity expansion

\[
\frac{Eu_a}{a} = (1 + v) \left( 1 - 2v + \frac{b}{a} \left( 1 - v \right) \ln \left( \frac{b}{a} \right) + v \right) \sigma_0 - \frac{b}{a} \left( 1 - v^2 \right) f, \tag{A29}
\]

while for \( \zeta = 2 \) it leads to

\[
\frac{Eu_a}{a} = \left( \frac{b}{a} \right)^2 \sigma_0 - \frac{b}{a} \left( 1 - v \right) \left( \sigma_0 + f \right) + (1 - 2v) \sigma_0. \tag{A30}
\]

A2. Cavity expansion model with displacement boundary condition at the outer surface

A2.1. Problem statement

A zero initial stress field is assumed for the entire medium in the current case. Concerning the boundary conditions of the problem, a radial displacement \( u_a \) is applied at the inner surface and the outer boundary is fixed:

\[
u(r = a) = u_a, \tag{A31}
\]
\[
u(r = b) = 0. \tag{A32}
\]

A2.2. Purely elastic response

A second-order ordinary differential equation is derived from the equilibrium equation (A3), the constitutive equations (A4) and (A5) and the kinematic relationships (A6) and (A7) with respect to the radial displacement \( u(r) \), the solution of which, under the boundary conditions (A31) and (A32) is

\[
u(r) = \left( \frac{b}{a} \right)^{v+1} - 1 \left( \frac{r}{a} \right) u_a. \tag{A33}
\]

The radial stress \( \sigma_a \) and the tangential stress \( \sigma_{ta} \) at the inner radius \( a \) of the model are then equal to

\[
\sigma_a = \frac{1 + (\zeta - 1)v + \zeta(1 - 2v)(b/a)^{v+1}}{(1 + v)(1 - 2v)(b/a)^{v+1} - 1} \frac{Eu_a}{a}, \tag{A34}
\]
\[
\sigma_{ta} = \frac{1 + (\zeta - 1)v - (1 - 2v)(b/a)^{v+1}}{(1 + v)(1 - 2v)(b/a)^{v+1} - 1} \frac{Eu_a}{a}, \tag{A35}
\]

whereas the radial stress \( \sigma_b \) and tangential stress \( \sigma_{tb} \) at the outer radius \( b \) become

\[
\sigma_b = \frac{(\zeta + 1)(1 - v)}{(1 + v)(1 - 2v)(b/a)^{v+1} - 1} \frac{Eu_a}{a}, \tag{A36}
\]
Appendix A

\[ \sigma_{t,b} = \frac{(\zeta+1)v}{(1+v)(1-2v)} \frac{E u_a}{a} - \frac{1}{(b/a)^{\zeta+1} - 1} \]  

(A37)

All these stresses are positive (i.e. compressive) except for the tangential stress at the cavity wall, the value of which becomes negative (i.e. tensile) as long as

\[ b/a > \left[ \frac{1+(\zeta-1)v}{1-2v} \right]^{1/\zeta+1} . \]  

(A38)

Assuming a Poisson’s ratio equal to 0.30, the critical ratio \( b/a \) is equal to \( \sim 1.58 \) and \( \sim 1.48 \) for the two and three dimensional cases, respectively. These values are quite low (increasing only for unrealistically high values of \( v \)) and the scenario of pure compression is therefore rather theoretical. For ratios \( b/a \) greater than the limit value of Eq. (A38), in fact, some of the medium around the opening is subjected to tension. The circumferential stress at the cavity wall becomes negative (Eq. A35) and as \( u_a \) increases, it decreases until reaching the tensile strength \( f_t < 0 \). Therefore, by setting them equal to \( f_t \), a critical displacement \( u_a^{cr} \) can be calculated which defines the onset of tensile failure:

\[ \frac{E u_a^{cr}}{a} = \frac{(1+v)(1-2v)}{1+(\zeta-1)v-(1-2v)(b/a)^{\zeta+1}} \frac{f_t}{f_t}, \]  

(A39)

A2.3. Response after tensile failure

For displacements greater than this critical value (Eq. A39), an inner cracked zone with radius \( \rho \) develops (Fig. 4.10). The response of the medium in the outer elastic region is given from Eqs. (A34) - (A37) substituting \( a, \sigma_a, \sigma_{t,a} \) and \( u_a \) by \( \rho, \sigma_\rho, \sigma_{t,\rho} \) and \( u_\rho \) respectively, as well as setting the tangential stress at the interface equal to the tensile strength of the material \( (\sigma_{t,\rho} = f_t) \):

\[ \frac{E u_\rho}{\rho} = \frac{(1+v)(1-2v)}{1+(\zeta-1)v-(1-2v)(b/\rho)^{\zeta+1}} \frac{f_t}{\rho}, \]  

(A40)

\[ \sigma_\rho = \frac{1+(\zeta-1)v+\zeta(1-2v)(b/\rho)^{\zeta+1}}{(1+v)(1-2v)(b/\rho)^{\zeta+1} - 1} \frac{E u_\rho}{\rho}, \]  

(A41)

\[ \sigma_b = \frac{(\zeta+1)(1-v)}{(1+v)(1-2v)(b/\rho)^{\zeta+1} - 1} \frac{E u_\rho}{\rho}, \]  

(A42)
Closed-form solutions for cavity expansion

\[ \sigma_{t,b} = \frac{(\zeta + 1)v}{(1+v)(1-2v)} \frac{E_{u,\rho}}{\rho}. \]  \hfill (A43)

Concerning the stress state within the cracked zone, the radial stress at the inner and the failure radius are given by Eqs. (A19) and (A20), respectively (note that \( K_2 = K_4 = 0 \) due to the zero initial stress field). The continuity of stresses at the interface is used for determining the relationship between the radius \( \rho \) of the failure zone and the cavity wall displacement \( u_c \). Equations (A20) and (A41) in combination with Eq. (A40) and Eq. (A21) lead to the following formula for the 2D case (\( \zeta = 1 \)):

\[ \frac{E_{u_a}}{a} = \frac{1 + (1-2v)\left(\frac{b/a}{\rho/a}\right)^2}{1-(1-2v)\left(\frac{b/a}{\rho/a}\right)^2} \left(\frac{b/a}{\rho/a}\right) \ln \left(\frac{\rho/a}{a}\right) + (1+v)(1-2v) \left(\frac{b/a}{\rho/a}\right)^2 - (\rho/a)\eta. \]  \hfill (A44)

while the use of Eq. (A23) instead of Eq. (A21) for the 3D case (\( \zeta = 2 \)) results in

\[ \frac{E_{u_a}}{a} = \frac{1 + v + 2(1-2v)\left(\frac{b/a}{\rho/a}\right)^2}{1 + v - (1-2v)\left(\frac{b/a}{\rho/a}\right)} \left(\frac{b/a}{\rho/a}\right)^2 - (\rho/a)\eta. \]  \hfill (A45)

The radial stresses at the inner (Eq. A19) and the outer radius (Eq. A42) are equal to

\[ \sigma_a = \frac{1 + (\zeta -1)v + \zeta(1-2v)\left(\frac{b/a}{\rho/a}\right)^{\zeta+1}}{1 + (\zeta -1)v - (1-2v)\left(\frac{b/a}{\rho/a}\right)^{\zeta+1}} \eta; \]  \hfill (A46)

\[ \sigma_b = \frac{(\zeta +1)(1-v)}{1 + (\zeta -1)v - (1-2v)\left(\frac{b/a}{\rho/a}\right)^{\zeta+1}} \eta. \]  \hfill (A47)

It should be noted that the extent of the cracked zone is limited to a specific radius. More specifically, Eq. (A40) provides positive values in order to satisfy the consistency of radial displacements inside the failure zone, leading to the inequality

\[ \frac{\rho}{a} < \frac{\rho_{\text{max}}}{a} = \sqrt[1-\zeta v]{1 - 2v} \left(\frac{b}{a}\right)^{\zeta+1}. \]  \hfill (A48)

which is obviously equivalent to Eq. (A38). Note that this value is approached asymptotically.
A2.4. Special case: material with zero tensile strength \((f_t = 0)\)

If Eq. (A38) is satisfied, which means that tensile stresses develop, the inner critical displacement (Eq. A39) is equal to zero in the case of no tensile strength in the material, indicating that cracking occurs immediately upon cavity expansion. The extent of the failure zone is constant throughout loading and equal to the maximum obtained from Eq. (A48), which implies that the entire domain \([a, \rho_{\text{max}}]\) fails in tension, whereas the ground within the region \([\rho_{\text{max}}, b]\) is subjected to pure compression, irrespective of the magnitude of expansion. Equations (A41) - (A42) (outer elastic zone) as well as Eqs. (A19) - (A20) (inner cracked zone) are still valid. Hence, the displacement at the elastoplastic interface can be evaluated to account for the continuity of radial stresses through Eqs. (A20) and (A41) as follows:

\[
\left(1 + \frac{1 + (\zeta - 1)\nu}{v(1 + \nu)} \right)^{-1} \sigma_a, \tag{A49}
\]

Afterwards, the boundary radial stresses are calculated using Eqs. (A42) and (A19), while the unique relationship between these can be deduced throughout loading as follows:

\[
\sigma_b = \frac{\sigma_a}{(b/a)^v} \left\{(1 - \nu)(1 - 2\nu)\left[1 + \left(\frac{\zeta}{v}\right)^{2}\right]^{-1}\right\} \tag{A50}
\]

The influence of tensile strength on the ground response during cavity expansion proved to be negligible for values of \(f_t\) less than \(-E/10000\) (which is common for rock-like materials); thus the present solution assuming zero tensile strength can be used.

A2.5. Approximate solution: tensile failure of the entire medium

An even simpler solution can be obtained by assuming that the entire ground has failed in tension, \(i.e.\rho = b\). Eqs. (A19) and (A20) then yield

\[
\sigma_b = \frac{\sigma_a}{(b/a)^v}, \tag{A51}
\]

which is obviously lower than \(\sigma_b\) after Eq. (A50), because the outer compressive elastic zone provides greater stiffness. This is expressed through the bracketed term on the right side of Eq. (A50). This coefficient is close to unity for low and moderate values of \(\nu\) (Fig. A1a) and consequently the error arising from the use Eq. (A51) is small.

The corresponding linear radial stress-displacement expression at the cavity wall can be obtained from Eq. (A19). The following relationships apply for the two- and the three-dimensional problems, respectively:
\[ \sigma_a = \frac{1}{(1+\nu)(1-\nu)\ln(b/a)} \frac{Eu_0}{a}, \]  
(A52)

\[ \sigma_a = \frac{b/a}{b/a-1} \frac{Eu_0}{a}. \]  
(A53)

The Poisson’s ratio appears in the former case due to the plane strain restraint applied in the longitudinal direction, which results in a compressive axial stress. On the other hand, a uniaxial stress state takes place in the latter case, owing to spherical symmetry, i.e. \( \sigma_z = \sigma_r = 0 \).

The deviation from the exact solution is very small for both the cylindrical and the spherical cavity (Fig. A1b). As a result, Eqs. (A52) and (A53) can be used instead of the exact equations, as they will provide an acceptable degree of accuracy.

**Figure A1.** Effect of neglecting the outer compressive zone: (a) Relationship between exact and approximate radial stress \( \sigma_b \) at the outer boundary; (b) Comparison of the approximate (solid lines) with the exact (dashed lines) radial stress \( \sigma_a \) at the inner boundary.
Appendix B. Effect of oedometer stiffness

Following Anagnostou (1991) we show that the usual oedometer equipment tends to underestimate the swelling pressure which would occur under total volume constraint, i.e. $\varepsilon = 0$. Figure B1 shows an oedometer device schematically. The swelling-induced increase in the specimen height is monitored by the dial gauge and is permanently reduced to zero throughout a successive load increase. Nonetheless, the dial gauge measures the total axial displacement, which consists of expansion of the specimen and compression of several device components (denoted in Fig. B.1 by the spring with an overall axial stiffness $K$). If the stiffness $K$ is not infinitely high, the measured displacement $\mathbf{u}'$ will be different to the relevant displacement $\mathbf{u}$. Under the conditions of a swelling pressure test (i.e. for $\mathbf{u}' = 0$), the device components will generally experience compression under the increasing axial force $F$, while at the same time the sample will expand by the same amount. In order to eliminate this effect, it is important that the dial gauge is kept as close as possible to the sample. Anagnostou (1991) showed quantitatively that changes of just some hundredths of a millimetre can be responsible for a significant underestimation of swelling pressure. As we will see, this is particularly true in the present case due to the extremely nonlinear stress-strain behaviour in intracrystalline swelling (cf. Fig. 3.25)

\[ F = \frac{K}{h} \pi D^2 \sigma, \quad \text{(B1)} \]

with $K$, $D$ and $h$ being the stiffness of the testing equipment and the diameter and height of the rock, while $\sigma$ is the swelling pressure. Assuming that the testing equipment has a stiffness of $K = 150$ kN/mm (which is typical at least for older oedometer apparatuses, cf. Fröhlich 1986) and that

![Figure B1. Oedometer device (schematic)]
the diameter $D$ and height $h$ of the rock sample are equal to 80 mm and 20 mm, respectively, then curve 1 in Fig. B2 shows the stress-strain relationship of the oedometer device. Furthermore, curve 2 in Fig. B2 (which has been calculated for a maximum swelling strain of $\varepsilon_{\text{max}} = 10\%$ - a typical value for claystones, Anagnostou 1991) depicts the dependency of strain on stress based on the considerations finding of Mering (1946) (cf. Fig. 3.25), i.e. with about 30% of the total swelling strain taking place in the intracrystalline phase at a water activity of $a_w = 0.96$ which corresponds for $T = 20\,^\circ\text{C}$ to a pressure of $\sigma = -\varphi = 5.5\,\text{MPa}$ (point A). Furthermore, according to Mering (1946) at $a_w = 0.90$ (which corresponds to as stress of $\sigma = -\varphi = 14\,\text{MPa}$) the strain is practically zero (in curve 2 of Fig. B2 we assume a very small swelling strain value for this stress, at point B). The interaction of curve 1 with curve 2 (point C) corresponds to the swelling pressure that would be observed in the laboratory. It is evident that swelling pressure is considerably underestimated in swelling tests performed in oedometer devices due to the finite stiffness of the apparatus.

Figure B2. Relationship between swelling stress and swelling strain and the characteristic line of the oedometer equipment
Appendix C. Derivation of Flückiger et al. (1994)

From Eqs. (4.3) to (4.6) we obtain the following expression for the crystallisation pressure according to Flückiger et al. (1994):

\[ p_c = \frac{\Delta G_r(T) - \Delta G_r(T_0)}{V_G^0}. \]  

(C1)

The nominator on the right side is equal to the change in the Gibbs energy \( \Delta G_r \) of the anhydrite hydration reaction due to a temperature change from the standard temperature \( T_0 \) to another temperature \( T \). According to White (2005), for example,

\[ \Delta G_r(T) - \Delta G_r(T_0) = -(T - T_0) \Delta r_{GA,0} S^0, \]  

(C2)

where the standard entropy \( \Delta r_{GA,0} S^0 \) of the anhydrite hydration reaction can be determined from the molar entropies of the reaction product (gypsum) and reactants (anhydrite and water):

\[ \Delta r_{GA,0} S^0 = S_G^0 - S_A^0 - 2S_W^0. \]  

(C3)

Taking the values of the molar constants into account according to Anderson (1996) (see Table 2.1), Eqs. (C1) to (C3) lead to

\[ p_c = \frac{(T - T_0)(S_G^0 - S_A^0 - 2S_W^0)}{V_G^0} \approx 3.6 \text{ MPa}. \]  

(C4)

This value is close to Flückiger’s et al. (1994) result (3.7 MPa). The difference is due to rounding errors and to the fact that Flückiger (1994) used Kelley et al.’s (1941) empirical equation rather than the molar constants of Anderson (1996).

In the following, we will show that the pressure according to Eq. (C4) is equal to the increase in the crystallisation pressure of the gypsum that would occur if the solution was permanently saturated with respect to anhydrite, the anhydrite was under atmospheric pressure and the temperature decreased from the standard temperature of \( T = T_0 = 25 \text{ °C} \) (hereinafter referred to as “state 1”) to \( T = 20 \text{ °C} \) (hereinafter referred to as “state 2”). The decreasing temperature causes an increase in the crystallisation pressure of the gypsum because the solubility of anhydrite increases with decreasing temperature (cf. Freyer and Voigt 2003) and, consequently, the supersaturation with respect to gypsum in state 2 is higher than in state 1.

At state 1, the crystallisation pressure of gypsum reads as follows:
Appendix C

\[ p_{c1} = \frac{RT}{V_G} \ln \frac{K^0_{\text{eq,A}}}{K^0_{\text{eq,G}}}, \]  
\[ (C5) \]

where \( K^0_{\text{eq,A}} \) and \( K^0_{\text{eq,G}} \) denote the equilibrium solubility products of anhydrite and gypsum, respectively, at standard conditions. Equation (C5) follows directly from Eq. (4.2) when the solution is saturated with respect to anhydrite and, therefore, \( K = K^0_{\text{eq,A}} \). The crystallisation pressure \( p_{c2} \) at an arbitrary temperature \( T \) can be calculated from the following equation (cf. White 2005):

\[ RT \ln \frac{K}{K^0_{\text{eq,G}}} = V_G^0 \left( p_{c2} + (T - T_0) \Delta_{r,G} S^0 \right), \]  
\[ (C6) \]

where the standard entropy of gypsum dissolution \( \Delta_{r,G} S^0 \) can be determined from the molar entropies:

\[ \Delta_{r,G} S^0 = S^0_{\text{CaSO}_4} + 2S^0_{\text{H}_2O} - S^0_G. \]  
\[ (C7) \]

If the solution is always saturated with respect to anhydrite and the anhydrite is under atmospheric pressure, then the solubility product \( K \) can be obtained (analogously to Eq. C6) from the following equation:

\[ RT \ln \frac{K}{K^0_{\text{eq,A}}} = (T - T_0) \Delta_{r,A} S^0, \]  
\[ (C8) \]

where the standard entropy of anhydrite dissolution

\[ \Delta_{r,A} S^0 = S^0_{\text{CaSO}_4} + S^0_{\text{SO}_4^{2-}} - S^0_A. \]  
\[ (C9) \]

Inserting \( K \) from Eq. (C8) into Eq. (C6) and taking account of Eqs. (C5), (C7) and (C9) leads to the following expression for the crystallisation pressure of gypsum in state 2:

\[ p_{c2} = p_{c1} + (T - T_0) \frac{S^0_G - S^0_A - 2S^0_{\text{H}_2O}}{V_G^0}. \]  
\[ (C10) \]

The last term on the right side of this equation is identical to Eq. (C4). This means that the value determined by Flückiger et al. (1994) is equal to the change in the crystallisation pressure \( (p_{c2} - p_{c1}) \) that would occur if the temperature decreases from \( T_0 = 25 \, \text{°C} \) to \( T = 20 \, \text{°C} \).
Appendix D. Reaction rates

D1. Reaction rate constant for anhydrite dissolution according to Barton and Wilde (1971)

Barton and Wilde (1971) conducted the rotation disc experiment with different rotation speeds. The results are therefore a function of the rotation speed (rev/min). As we are interested in the reaction rate constants in the case of no transport, an extrapolation of their results for zero rotation speed is necessary.

Figure D1 depicts the reaction rate constant for anhydrite dissolution (according to the definition of Barton and Wilde 1971) as a function of the rotation speed for anhydrite prepared at $T = 400$, $500$ and $700$ °C (the last two are identical and are given by the same curve). An extrapolation of the existing results to zero rotation speed gives values within the range $k_{A(BW)} \approx 0.2 - 0.45 \cdot 10^{-8}$ mol/cm$^2$/s.

In order to calculate the reaction rate constant in the desired units, we will first start from Eq. (5.9) which in combination with Eq. (5.4) gives the following expression for the mass change rate of anhydrite per unit volume:

\[
\frac{dm_A}{dt} = -k_A \frac{m_{A0}}{\rho_A} F_{40} \left( \frac{m_A}{m_{A0}} \right)^{2/3} \left( \frac{c_{eq,A} - c}{c_{eq,A}} \right)^{\delta_A}.
\]  

(D1)

Barton and Wilde (1971) studied the chemical reaction at a very initial state, i.e. the reaction is of zero-order ($\delta_A = 0$) and, furthermore, the ion concentration in the solution is approximately zero ($c \approx 0$). Therefore,

\[
\left( \frac{c_{eq,A} - c}{c_{eq,A}} \right)^{\delta_A} \approx 1.
\]  

(D2)

Moreover, taking into account that the presence of ions in the solution is due to the dissolution of anhydrite, $c = m_{A0} - m_A$. Equation (D1) then becomes (taking Eq. D2 into account):

\[
\frac{d(m_{A0} - c)}{dt} = -k_A \frac{m_{A0}}{\rho_A} F_{40} \left( \frac{m_{A0} - c}{m_{A0}} \right)^{2/3}.
\]  

(D3)

Considering once again that $c \approx 0$, we get

\[
\frac{dc}{dt} = k_A \frac{m_{A0}}{\rho_A} F_{40}.
\]  

(D4)

According to Barton and Wilde (1971),

\[
\frac{dc}{dt} = k_{4(BW)} \frac{A}{V_w},
\]  

(D5)
where $A$ is the apparent area of the disc in cm$^2$ and $V_W (= V_{tot,0})$ is the volume of water in the reaction vessel in cm$^3$. Bearing in mind that the term $m_{A0}F_{A0}/\rho_A = \phi_{A0}F_{A0}$ in Eq. (D4) denotes the initial area of anhydrite in contact with water (which in the present case remains constant and equal to $A$), per unit volume of mixture (cf. Section 5.2.1.1), it can readily be verified that according to Eqs. (D4) and (D5) $k_{A,(BW)} = k_A$. The transformation of the reaction rate constants into the desired units leads to $k_A = 2.7 - 5.4 \times 10^{-6}$ kg/m$^2$/s.

![Figure D1](image.png)

**Figure D1.** Reaction rate constant according to Barton and Wilde (1971) as a function of the rotation speed for different preparation temperatures of anhydrite

### D2. Reaction rate constant for anhydrite dissolution according to James and Lupton (1978)

In the present section, the necessary transformations are set out for deriving the reaction rate constant for the dissolution of anhydrite. According to James and Lupton (1978), the mass change rate of anhydrite during its dissolution per unit volume is given by:

$$\frac{dm_A}{dt} = -k_{A,(IL)} \frac{A}{V_{tot,0}} (c_{eq,A} - c)^2,$$

(D6)

Where $k_{A,(IL)}$ is the reaction rate constant of anhydrite dissolution in m/s, and $A$ (m$^2$) is the area of anhydrite in contact with water (which is variable for the second series of experiments performed by James and Lupton 1978), $V_{tot,0}$ is the total volume of the mixture, while $c$ and $c_{eq,A}$ are in kg/m$^3$. In the present study, Eq. (D1) applies for the mass change rate of anhydrite. Taking into account that

$$\frac{A}{V_{tot,0}} = \frac{m_{A0}F_{A0}}{\rho_A} \left( \frac{m_A}{m_{A0}} \right)^{2/3},$$

(D7)

the reaction rate constant in the present study (which is in kg/m$^2$/s) is related to the reaction rate constant of James and Lupton (1978) by the following relationship:
Reaction rates

\[ k_d = k_{d,SS} c_{eq,A}^2. \]  

(D8)

Attention must be paid to the fact that the units of concentration in the transformation Eq. (D8) are kg/m³.

D3. Reaction rate constant for gypsum precipitation according to Smith and Sweett (1971)

The transformations required for deriving the reaction rate constant for the dissolution of anhydrite in the desired units are derived here. According to Smith and Sweett (1971), the following relationship applies for the time evolution of ion concentration during gypsum growth:

\[ \frac{dc}{dt} = -k_{G(SS)} A \left( c - c_{eq,G} \right)^2, \]  

(D9)

where \( k_{G(SS)} \) is the reaction rate constant according to Smith and Sweett (1971) in l/mol·cm²·s and \( A \) is the surface area of the crystals in cm². The concentrations are given in mol/l. Equation (D9) reads as follows in kg/m³/s:

\[ \frac{dc}{dt} = -\frac{1000}{0.136} k_{G(SS)} A \left( c - c_{eq,G} \right)^2. \]  

(D10)

Based on Eqs. (5.1), (5.3), (5.4) and (5.13), the ion concentration change over time is given by the following equation in the present study:

\[ \frac{dc}{dt} = -\frac{136}{172} k_G \frac{A}{V_{tot,0}} \left( c - c_{eq,G} \right)^2, \]  

(D11)

where \( V_{tot,0} = 80 \) ml in the specific case. According to Eqs. (D10) and (D11) and taking a value of 15.5 mol/m³ = 2.108 kg/m³ for the gypsum equilibrium concentration \( c_{eq,G} \), the reaction rate constants of the present study and the paper of Smith and Sweett (1971) are related by:

\[ k_G = 9300 \cdot V_{tot,0} \cdot c_{eq,G}^2 \cdot k_{G(SS)} = 3.3 \cdot k_{G(SS)}. \]  

(D12)
Appendix E. Volume fraction

The volume fraction of anhydrite

$$\phi_a = \frac{\phi_{ao}}{a_0 b_a} \overline{S}_a \left( \overline{S}_a + a_0 - 1 \right) \left( \overline{S}_a + b_a - 1 \right)$$  \hspace{1cm} (E1)

in the case of parallelepipeds (Fig. E1a), while for spherical particles (Fig. E1b)

$$\phi_a = \phi_{ao} \overline{S}_a^3,$$  \hspace{1cm} (E2)

where

$$\overline{S}_a = S_a / S_{ao} = 1 + 2 \overline{s}_a.$$  \hspace{1cm} (E3)

In the case of parallelepipedic gypsum particles (Fig. E1c),

$$\phi_{G,G} = \phi_{G0} \left( \frac{\overline{S}_{G,G} + a_G - 1}{a_G} \left( \frac{\overline{S}_{G,G} + b_G - 1}{b_G} \right) - 1 \right) \left( 1 - n_G \right),$$  \hspace{1cm} (E4)

while for spherical gypsum particles (Fig. E1d):

$$\phi_{G,G} = \phi_{G0} \left( \overline{S}_{G,G}^3 - 1 \right) \left( 1 - n_G \right),$$  \hspace{1cm} (E5)

where

$$\overline{S}_{G,G} = S_{G,G} / S_{G0} = 1 + 2 \overline{s}_G.$$  \hspace{1cm} (E6)

The volume fraction $\phi_{G,A}$ of the gypsum growing on parallelepipedic or spherical anhydrite particles (Fig. E1e and E1f) is given by the following equations:

$$\phi_{G,A} = \frac{\phi_{G0}}{a_0 b_a} \left[ \overline{S}_{G,A} \left( \overline{S}_{G,A} + a_a - 1 \right) \left( \overline{S}_{G,A} + b_a - 1 \right) - \overline{S}_a \left( \overline{S}_a + a_a - 1 \right) \left( \overline{S}_a + b_a - 1 \right) \right] \left( 1 - n_G \right),$$  \hspace{1cm} (E7)

$$\phi_{G,A} = \phi_{G0} \left[ \overline{S}_{G,A}^3 - \overline{S}_a^3 \right] \left( 1 - n_G \right),$$  \hspace{1cm} (E8)

where

$$\overline{S}_{G,A} = S_{G,A} / S_{G0} = \overline{S}_a + 2 \overline{s}_G.$$  \hspace{1cm} (E9)

Finally, the volume fraction of gypsum $\phi_{G,S}$ formed on inert solids of spherical shape (Fig. E1g) is equal to:

$$\phi_{G,S} = \phi_{S} \left( \overline{S}_{G,S}^3 - 1 \right) \left( 1 - n_G \right),$$  \hspace{1cm} (E10)
where

\[ \bar{\bar{S}}_{G,5} = \frac{S_{G,5}}{S_{A0}} = \bar{\bar{S}}_g + 2\bar{\bar{S}}_G \]  \hspace{1cm} (E11)

and

\[ \bar{\bar{S}}_s = \frac{S_s}{S_{A0}}. \]  \hspace{1cm} (E12)

Figure E1. (a), (b) Anhydrite particles during dissolution; (c), (d) gypsum particles during precipitation; (e), (f) anhydrite particles sealed by a gypsum layer; (g) inert solid particle with precipitated gypsum
Appendix F. Notation

\[ A \] mineral surface area in contact with water
\[ A \] parameter of Davies equation
\[ A \] triangular finite element area
\[ A_i \] total interfacial area of species \( i \)
\[ a \] shape factor of parallelepipedic particles
\[ a_a \] shape factor of parallelepipedic anhydrite particles
\[ a_g \] shape factor of parallelepipedic gypsum particles
\[ b \] half radial distance between the centres of the expanding cavities
\[ b \] shape factor of parallelepipedic particles
\[ b_a \] shape factor of parallelepipedic anhydrite particles
\[ b_g \] shape factor of parallelepipedic gypsum particles
\[ b_i \] half distance between the centres of expanding cavities
\[ b_p \] half distance between the centres of pores
\[ c \] concentration
\[ \tilde{c} \] normalized concentration
\[ c_{Ca^{2+}} \] concentration of calcium ions
\[ c_{eq,A} \] anhydrite equilibrium concentration
\[ c_{eq,G} \] gypsum equilibrium concentration
\[ \tilde{c}_{eq,G} \] normalized gypsum equilibrium concentration
\[ c_{eq,G}^0 \] gypsum equilibrium concentration at standard state
\[ c_i \] concentration of constituent \( i \)
\[ c_{SO_4^{2-}} \] concentration of sulphate ions
\[ c_0 \] concentration at standard state
\[ c_0 \] initial concentration
\[ \tilde{c}_0 \] normalized initial concentration
\[ C_1, C_2 \] constants
Appendix F

\(C_1, C_2\)  
constants

\(D\)  
sample diameter

\(D\)  
diffusion coefficient

\(E\)  
Young’s modulus

\(f\)  
a function

\(F\)  
axial force

\(F\)  
specific surface area

\(F_A\)  
anhydrite specific surface area

\(F_{A0}\)  
initial anhydrite specific surface area

\(F_G\)  
gypsum specific surface area

\(F_{G0}\)  
initial gypsum specific surface area

\(F_S\)  
inert solid specific surface area

\(F_i\)  
reaction force

\(F_p\)  
pore area

\(F_P\)  
mean pore area

\(f_t\)  
tensile strength

\(F_{tot}\)  
total area

\(g\)  
gravitational acceleration

\(G\)  
Gibbs free energy

\(h\)  
sample height

\(h\)  
hydraulic head

\(H\)  
depth of cover

\(I\)  
ionic strength

\(J\)  
diffusive flux

\(k\)  
reaction rate constant

\(K\)  
ion activity product

\(K\)  
stiffness of the swelling test device components

\(k_A\)  
reaction rate constant for anhydrite dissolution

\(k_{ABW}\)  
reaction rate constant for anhydrite dissolution according to Barton and Wilde (1971)

\(k_{AJL}\)  
reaction rate constant for anhydrite dissolution according to James and Lupton (1978)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{eq,A}$</td>
<td>equilibrium solubility product of anhydrite</td>
</tr>
<tr>
<td>$K_{eq,A}^0$</td>
<td>equilibrium solubility product of anhydrite at standard temperature and atm. pressure</td>
</tr>
<tr>
<td>$K_{eq,G}$</td>
<td>equilibrium solubility product of gypsum</td>
</tr>
<tr>
<td>$K_{eq,G}^0$</td>
<td>equilibrium solubility product of gypsum at standard temperature and atm. pressure</td>
</tr>
<tr>
<td>$k_G$</td>
<td>reaction rate constant for gypsum precipitation</td>
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<tr>
<td>$K_G$</td>
<td>ion activity product of gypsum</td>
</tr>
<tr>
<td>$k_{G(SS)}$</td>
<td>reaction rate constant for gypsum precipitation according to Smith and Sweett (1971)</td>
</tr>
<tr>
<td>$k_{ij}$</td>
<td>permeability</td>
</tr>
<tr>
<td>$K_{ij}$</td>
<td>hydraulic conductivity</td>
</tr>
<tr>
<td>$K_{sp}$</td>
<td>solubility product in Flückiger’s (1994) model</td>
</tr>
<tr>
<td>$K_{sp}^0$</td>
<td>solubility product at standard state in Flückiger’s (1994) model</td>
</tr>
<tr>
<td>$K_1, K_2$</td>
<td>constants</td>
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<td>$K_1-K_4$</td>
<td>constants</td>
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<td>$LC$</td>
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<td>$L_s$</td>
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<td>$L_s$</td>
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<td>$m$</td>
<td>mass per unit volume of mixture</td>
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<tr>
<td>$m$</td>
<td>number of cavity radii in the discretized numerical model</td>
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<tr>
<td>$m$</td>
<td>number of discrete supercritical pore radii</td>
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<tr>
<td>$M$</td>
<td>bending moment</td>
</tr>
<tr>
<td>$M$</td>
<td>mass</td>
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<td>initial anhydrite mass per unit volume of mixture</td>
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<td>$m_G$</td>
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<td>$m_{G,CS}$</td>
<td>gypsum mass per unit volume of mixture which forms in a closed system</td>
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<td>$m_{w0}$</td>
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<td>$\Pi$</td>
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<td>$\Pi_p$</td>
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<td>$n_{i}$</td>
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<td>$\Pi_i$</td>
<td>percentage of cavities of radius $a_i$</td>
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<td>$N_{i}$</td>
<td>number of expanding cavities of radius $a_i$</td>
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<td>$N_p$</td>
<td>number of pores</td>
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<td>gypsum pressure</td>
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<td>$P_i$</td>
<td>pressure of constituent $i$</td>
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<td>pressure exerted in the pore by crystal growth</td>
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<td>required pressure</td>
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<td>solid pressure</td>
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<td>$p_{S,0}$</td>
<td>initial solid pressure</td>
</tr>
<tr>
<td>$p_V$</td>
<td>vapour pressure of a solution</td>
</tr>
<tr>
<td>$p_{V,0}$</td>
<td>vapour pressure of pure water</td>
</tr>
<tr>
<td>$p_W$</td>
<td>pore water pressure</td>
</tr>
<tr>
<td>$p_{1}$</td>
<td>pore pressure after swelling test</td>
</tr>
</tbody>
</table>
Notation

\( Q \)  heat
\( q_i \)  seepage flow velocity
\( r \)  radial co-ordinate
\( R \)  universal gas constant
\( r_A \)  radius of anhydrite particles
\( r_{cr} \)  critical pore radius
\( r_G \)  radius of inert mineral particles
\( r_i \)  radius of particle \( i \)
\( r_{max} \)  largest pore radius
\( r_p \)  pore radius
\( s \)  distance of the mineral surface from its initial surface
\( S_A \)  characteristic length of anhydrite particles
\( s_A \)  thickness of dissolved anhydrite
\( \overline{s}_A \)  normalized thickness of dissolved anhydrite
\( \overline{S}_A \)  normalized characteristic length of anhydrite particles
\( S_A^0 \)  molar entropy of anhydrite at standard state
\( S_{i0} \)  initial characteristic length of anhydrite particles
\( S_{Ga^2+}^0 \)  molar entropy of \( Ca^{2+} \) at standard state
\( s_G \)  gypsum layer thickness
\( \overline{s}_G \)  normalized gypsum layer thickness
\( S_G^0 \)  molar entropy of gypsum at standard state
\( S_{GA,A} \)  characteristic length of gypsum particles growing on anhydrite
\( \overline{S}_{GA,A} \)  normalized characteristic length of gypsum particles growing on anhydrite
\( S_{GG} \)  characteristic length of gypsum particles growing on gypsum
\( \overline{S}_{GG} \)  normalized characteristic length of gypsum particles growing on gypsum
\( S_{GS} \)  characteristic length of gypsum particles growing on inert minerals
\( \overline{S}_{GS} \)  normalized characteristic length of gypsum particles growing on inert minerals
\( S_{G0} \)  initial characteristic length of gypsum particles
\( s_i \)  molar entropy of constituent \( i \)
$S_i^0$ molar entropy of constituent $i$ at standard state

$S_S$ diameter of inert solid particles

$S_{S_k}$ normalized diameter of inert solid particles

$S_{SO_4}^0$ molar entropy of $SO_4^{2-}$ at standard state

$S_{W}^0$ molar entropy of water at standard state

$S_{0}$ characteristic length (thickness and diameter for parallelepipedic and spherical particles, respectively)

$t$ tangential co-ordinate

$t$ thickness

$t$ time

$T$ temperature

$T_0$ temperature at standard state

$t_d$ time at which sealing becomes the relevant mechanism

$T_{eq}$ equilibrium temperature

$T_{eq}^0$ equilibrium temperature under atmospheric pressure

$T_{gi}$ tortuosity of the gypsum layer

$t_h$ hydration time

$T^*_k$ tortuosity of the porous medium

$u$ radial displacement

$U$ internal energy

$\bar{u}$ real displacement in a swelling test under volume constraint

$\vec{u}$ measured displacement in a swelling test under volume constraint

$u_a$ radial displacement of the boundary of the expanding cavity

$u_{a}^{cr}$ critical radial displacement of the expanding cavity

$u_p$ radial displacement of the pore wall

$u_p^{cr}$ critical radial displacement of the pore wall

$V$ volume

$V_A^0$ molar volume of anhydrite at standard state

$V_{Ca^{2+}}^0$ molar volume of $Ca^{2+}$ at standard state
Notation

\( V^0_G \) molar volume of gypsum at standard state

\( V_i \) molar volume of constituent \( i \)

\( V^0_i \) molar volume of constituent \( i \) at standard state

\( V_{SO_4^2-}^0 \) molar volume of \( SO_4^{2-} \) at standard state

\( V_{tot} \) total volume of mixture

\( V_{tot,0} \) initial total volume of mixture

\( V_w \) molar volume of water

\( V_w^0 \) molar volume of water at standard state

\( x_c \) Ratio of the contact area to the total area

\( x_w \) mole fraction of water

\( z \) geodetic head

\( z \) axial co-ordinate

\( z_i \) ion valence of constituent \( i \)

Greek Symbols

\( a \) radius of the expanding cavities

\( \alpha_{Ca^{2+}} \) activity of \( Ca^{2+} \)

\( \alpha_G \) activity of gypsum

\( a_i \) radius of the \( i \).th group of expanding cavities in the discretized numerical model

\( \alpha_i \) activity of constituent \( i \)

\( \alpha_{SO_4^{2-}} \) activity of \( SO_4^{2-} \)

\( \alpha_w \) water activity

\( a_{w,eq} \) equilibrium water activity

\( \gamma_A \) surface free energy of the anhydrite-water interface

\( \gamma_{Ca^{2+}} \) activity coefficient of \( Ca^{2+} \)

\( \gamma_G \) surface free energy of the gypsum-water interface

\( \gamma_i \) activity coefficient of constituent \( i \)

\( \gamma_i \) surface free energy of the interface of between constituent \( i \) and the water

\( \gamma_r \) total unit weight of rock
Appendix F

\[ \gamma_{SO_4} \] activity coefficient of \( SO_4^{2-} \)

\[ \gamma_w \] unit weight of water

\[ \gamma_z \] mean activity coefficient

\[ \delta \] order of chemical reaction

\[ \delta_i \] order of reaction for anhydrite dissolution

\[ \delta_o \] order of reaction for gypsum precipitation

\[ \delta_i \] volume fraction of the expanding cavities of radius \( a_i \)

\[ \Delta \phi_A \] volume fraction of transformed anhydrite

\[ \Delta r G_A^0 \] standard Gibbs energy of formation of \( Ca^{2+} \)

\[ \Delta r G_{SO_4}^0 \] standard Gibbs energy of formation of \( SO_4^{2-} \)

\[ \Delta r G_A^0 \] standard Gibbs energy of formation of anhydrite

\[ \Delta r G_i^0 \] standard Gibbs energy of formation of constituent \( i \)

\[ \Delta r G_G^0 \] standard Gibbs energy of formation of gypsum

\[ \Delta r G_W^0 \] standard Gibbs energy of formation of water

\[ \Delta G_r \] free energy of the transformation of anhydrite to gypsum in Flückiger’s (1994) model

\[ \Delta r,A G^0 \] standard Gibbs energy of anhydrite dissolution

\[ \Delta r,A V^0 \] standard volume of anhydrite dissolution

\[ \Delta r,A S^0 \] standard entropy of anhydrite dissolution

\[ \Delta r,G G^0 \] standard Gibbs energy of gypsum dissolution

\[ \Delta r,G V^0 \] standard volume of gypsum dissolution

\[ \Delta r,G S^0 \] standard entropy of gypsum dissolution

\[ \Delta r,G,A G^0 \] standard Gibbs energy of the transformation of anhydrite to gypsum

\[ \Delta r,G,A V^0 \] standard volume of the transformation of anhydrite to gypsum

\[ \Delta r,G,A S^0 \] standard entropy of anhydrite hydration

\[ \varepsilon \] swelling strain

\[ \varepsilon \] dielectric constant (Davies equation)
<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_a$</td>
<td>normalized radial expansion of the anhydrite particle due to gypsum growth</td>
</tr>
<tr>
<td>$\varepsilon_{\text{max}}$</td>
<td>maximum swelling strain</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>radial strain</td>
</tr>
<tr>
<td>$\varepsilon_t$</td>
<td>tangential strain</td>
</tr>
<tr>
<td>$\varepsilon_z$</td>
<td>longitudinal (axial) strain</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>variable that defines the type of cavity ($\zeta = 1$ for cylindrical and $\zeta = 2$ for spherical)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>percentage of cracked zone around the cavity</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>dimensionless parameter</td>
</tr>
<tr>
<td>$\Lambda^*$</td>
<td>dimensionless parameter</td>
</tr>
<tr>
<td>$\overline{\Lambda}$</td>
<td>dimensionless parameter</td>
</tr>
<tr>
<td>$\lambda_w$</td>
<td>water activity coefficient</td>
</tr>
<tr>
<td>$\mu_A$</td>
<td>chemical potential of formation of anhydrite</td>
</tr>
<tr>
<td>$\mu_G$</td>
<td>chemical potential of formation of gypsum</td>
</tr>
<tr>
<td>$\mu_{\text{Ca}^{2+}}$</td>
<td>chemical potential of formation of $\text{Ca}^{2+}$</td>
</tr>
<tr>
<td>$\mu_i$</td>
<td>chemical potential of constituent $i$</td>
</tr>
<tr>
<td>$\mu_{\text{SO}_4^{2-}}$</td>
<td>chemical potential of formation of $\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>$\mu_w$</td>
<td>chemical potential of formation of water</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>$\rho$</td>
<td>radius of the cracked zone</td>
</tr>
<tr>
<td>$\rho_a$</td>
<td>anhydrite density</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>gypsum density</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>density of the constituent $i$</td>
</tr>
<tr>
<td>$\rho_{\text{max}}$</td>
<td>maximum radius of the cracked zone</td>
</tr>
<tr>
<td>$\rho_r$</td>
<td>rock density</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>inert solid density</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>water density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>total stress</td>
</tr>
<tr>
<td>$\sigma_a$</td>
<td>radial stress at the boundary of the expanding cavity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>$\sigma_a$</td>
<td>equivalent cavity expansion pressure</td>
</tr>
<tr>
<td>$\sigma_{a_{\text{max}}}$</td>
<td>maximum radial stress at an expanding cavity with radius $a$</td>
</tr>
<tr>
<td>$\sigma_b$</td>
<td>radial stress at distance $b$</td>
</tr>
<tr>
<td>$\sigma_\rho$</td>
<td>radial stress at the outer boundary of the cracked zone</td>
</tr>
<tr>
<td>$\sigma_p$</td>
<td>radial stress at the pore wall</td>
</tr>
<tr>
<td>$\sigma_r$</td>
<td>radial stress</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>macroscopic swelling pressure</td>
</tr>
<tr>
<td>$\sigma_{s,A}$</td>
<td>macroscopic swelling pressure when gypsum grows only in pores on the surfaces of anhydrite particles</td>
</tr>
<tr>
<td>$\sigma_{s,P}$</td>
<td>macroscopic swelling pressure when gypsum grows in all pores</td>
</tr>
<tr>
<td>$\sigma_t$</td>
<td>tangential stress</td>
</tr>
<tr>
<td>$\sigma_{t,b}$</td>
<td>tangential stress at distance $b$</td>
</tr>
<tr>
<td>$\sigma_{t,p}$</td>
<td>tangential stress at the pore wall</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>vertical stress</td>
</tr>
<tr>
<td>$\bar{\sigma}_y$</td>
<td>average vertical stress</td>
</tr>
<tr>
<td>$\sigma_z$</td>
<td>longitudinal (axial) stress</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>initial total stress</td>
</tr>
<tr>
<td>$\sigma'_0$</td>
<td>initial (in situ) effective stress</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>total stress after swelling test</td>
</tr>
<tr>
<td>$\tau$</td>
<td>dimensionless time</td>
</tr>
<tr>
<td>$\phi$</td>
<td>porosity</td>
</tr>
<tr>
<td>$\phi_A$</td>
<td>anhydrite volume fraction</td>
</tr>
<tr>
<td>$\phi_{A0}$</td>
<td>initial anhydrite volume fraction</td>
</tr>
<tr>
<td>$\phi_{A0,\text{crit}}$</td>
<td>critical initial anhydrite volume fraction</td>
</tr>
<tr>
<td>$\phi_G$</td>
<td>gypsum volume fraction</td>
</tr>
<tr>
<td>$\phi_{G,A}$</td>
<td>volume fraction of gypsum grown on anhydrite particles</td>
</tr>
</tbody>
</table>
Notation

\( \phi_{G,G} \) volume fraction of gypsum grown on gypsum particles

\( \phi_{G,S} \) volume fraction of gypsum grown on inert solid particles

\( \phi_{G0} \) initial gypsum volume fraction

\( \phi_P \) volume fraction of particles consisting of inert solid and gypsum

\( \phi_S \) inert solid volume fraction

\( \phi_i \) volume fraction of the constituent \( i \)

\( \phi_w \) water volume fraction

\( \phi_{w0} \) initial water volume fraction

\( \Psi \) potential

\( \Psi_a \) adsorptive component of the matric potential

\( \Psi_{\pi} \) osmotic potential

\( \Psi_c \) capillary component of the matric potential

\( \Psi_{eq} \) potential at anhydrite-gypsum equilibrium

\( \Psi_m \) matric potential

\( \Psi_0 \) potential of pore water in situ

\( \Psi_l \) potential of pore water after swelling test
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213


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