Experimental investigations for the modelling of chemo-mechanical processes in anhydritic rock

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Abstract

Swelling anhydritic rock can cause severe damage to tunnels. Even though this phenomenon was first observed more than a century ago, many knowledge gaps persist concerning the swelling mechanisms caused by the transformation from anhydrite to gypsum. One of these gaps is the relationship between swelling pressure and swelling strain. This paper presents experimental research results concerning the stress dependency of the swelling caused by anhydrite to gypsum transformation.

1. Introduction

When anhydritic rock comes into contact with water, the anhydrite dissolves and gypsum precipitates as a result of oversaturation of the sulphate and calcium ions in the water. This anhydrite to gypsum transformation (AGT) leads to an increase in solid volume of roughly 61% and possibly also in pore volume, thus resulting in macroscopic swelling. In tunnelling, swelling rock can cause massive damage, since it can exert high pressures on the lining or result in significant heave of the tunnel floor. Even though this phenomenon was first observed more than a century ago, the swelling behaviour of anhydritic rock still includes many knowledge gaps [1, 2].
One particularly important knowledge gap concerns the coupled chemo-mechanical processes, i.e. the development of stresses and strains during AGT [3]. An understanding of this relationship is highly important for the conceptual design of tunnels through anhydritic rock. The establishment of a chemo-mechanical model which can take account of anhydrite dissolution, gypsum precipitation (i.e. the chemical reaction $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot \text{H}_2\text{O}$) and also stresses and strains is therefore of interest. Only few approaches for a chemo-mechanical model are to be found in the literature, one example is that of Ramon [4].

A general formulation for the chemo-mechanical model is given by Equation (1), which connects the effective stress increments with the elastic strain increments. The latter is defined as the difference between the total strain increments and the strain increments due to plasticity and due to chemical reactions (see Equation 2).

$$\sigma_{ij}^* = D_{ijkl} \cdot \varepsilon_{ijkl}^{EL}$$  \hspace{1cm} (1)

$$\varepsilon_{ijkl}^{EL} = \varepsilon_{ijkl} - \varepsilon_{ijkl}^{PL} - \varepsilon_{ijkl}^{CH}$$  \hspace{1cm} (2)

The chemical strains due to AGT depend on changes in the masses of anhydrite and gypsum. For the sake of simplicity we assume that all dissolved calcium and sulphate ions from the anhydrite are used for gypsum precipitation (the rate of anhydrite dissolution is slower than that of gypsum precipitation [5]) and that the ions are not transported by water. The chemically induced strains can therefore be expressed via the change in the mass of anhydrite and a single unknown material-specific tensor $\zeta_{kl}$:

$$\varepsilon_{ijkl}^{CH} = \frac{\zeta_{kl}}{\rho_m} \cdot m_A.$$  \hspace{1cm} (3)

The chosen strategy for establishing $\zeta_{kl}$ is to perform multiple series of laboratory tests under various radial symmetric conditions. In this paper we focus specifically on the results from oedometer tests, where radial strains are prohibited and an axial load is applied and held constant while the axial deformation, which develops during water uptake, is measured (see Fig. 1). By formulating Equations (1) – (3) for these boundary conditions, while...
assuming that no plastic strains occur, the pore water pressure remains constant and equal to atmospheric pressure during each test and by using Hooke’s linear elastic law to determine the elasticity tensor, Equations (4) and (5) are obtained for the rate of swelling strain in the axial direction and the rate of total stress in the radial direction. These equations allow the factors $\chi_{ax}$ and $\chi_{rad}$ to be obtained separately based on the experimentally determined rates for axial strain, radial stress and anhydrite mass. However, as it has not yet been possible to measure the radial stresses in an oedometer cell, $\chi_{ax}$ and $\chi_{rad}$ are combined to a single unknown factor $\chi$ on the right-hand side of Equation (4).

$$\frac{\partial \varepsilon_{ax}}{\partial t} = \frac{1}{\rho_{ax}} \frac{\partial m_{ax}}{\partial t} \left( \chi_{ax} + \frac{2\nu}{1-\nu} \chi_{rad} \right) = \chi \frac{1}{\rho_{ax}} \frac{\partial m_{ax}}{\partial t}$$  \hspace{1cm} (4)

$$\frac{\partial \sigma_{rad}}{\partial t} = -\chi_{rad} \frac{E}{(1-\nu) \rho_{ax}} \frac{1}{\rho_{ax}} \frac{\partial m_{ax}}{\partial t}$$  \hspace{1cm} (5)

In order to reduce uncertainties caused by the inhomogeneous compositions and structures of natural rock samples and to distinguish chemical swelling from the swelling of clay, experiments at the present stage of this research are performed on artificially created and thus reproducible samples consisting of anhydrite and practically inert minerals (see Chapter 2.1).

In the first series of oedometer tests (Chapter 2.2), we aim to determine the influence of axial stress on the maximal strain. This is accomplished by measuring the swelling strain of samples under various constant axial stresses until they reach their final swelling strain, i.e. until a steady state is observed. The experimentally obtained relationship between the axial stress and the final swelling strain is presented in Chapter 3.1.

Next, we aim to establish the relationship between the swelling strain and the mass of anhydrite in the samples over time (i.e. the unknown factor $\chi$). For this purpose, two further series of oedometer tests are performed, where the samples are subjected to a specific axial stress and then extracted after different test durations, before the swelling reaches a steady state (see Chapter 3.2).

For the evaluation of the above mentioned results, it was necessary to determine the amount of anhydrite remaining in each sample post test. This was accomplished via thermogravimetric analysis (TGA) and X-ray diffraction analysis (XRD), cf. Chapter 2.3.
2. Experimental procedures

2.1. Samples

The samples are mixtures of 40 g of commercial anhydrite from Sigma-Aldrich and 60 g of kaolin (Polwhite E China Clay, a high quality medium particle size kaolin produced from deposits in the south west of England [6, 7]).

Kaolin was chosen, because it has a very low swelling potential compared to other so-called swelling clays. On the one hand, kaolinite has no significant negative structural charge, so that little or no water is adsorbed in the lattice (the cation exchange capacity is 1 - 10 meq/100 g [8] as opposed to, e.g., 70 - 120 meq/100 g in the case of montmorillonite, a swelling clay [9]). On the other hand, kaolinite has a small specific surface in contact with the water compared to swelling clays, i.e. the adsorption of water molecules due to electric load concentration is negligible (the specific surface of kaolinite is 10 - 30 m²/g while that of montmorillonite amounts to 750 - 820 m²/g; cf., e.g., [10, 11]). It should be noted however, that kaolin, like any fine powdered and compacted dry material, can swell upon saturation due to reduction of suction pressure (cf., e.g., Thom et al [12]). However, this swelling mechanism is much faster than the swelling caused by AGT and thus the two swelling mechanisms can be distinguished from one another.

The particle size distribution of the used anhydrite (determined via laserdiffraction in isopropanol) ranges from \(d_{10} = 5\ \mu m\) to \(d_{90} = 16\ \mu m\), similar to that of the Polwhite E China Clay (determined via laserdiffraction in distilled water), which ranges from \(d_{10} = 4\ \mu m\) to \(d_{90} = 18\ \mu m\). The density of the anhydrite is assumed to be 2.96 g/cm³ (cf., e.g., [13]) and the density of the kaolin is 2.6 g/cm³ [6, 7]. Rietveld analysis (XRD, see Chapter 2.3) revealed the following average mineralogical composition of the kaolin: 69% kaolinite, 15% orthoclase, 10% illite and muscovite, 3% quartz and 2% plagioclase.

The two powders are weighed and mixed together while adding about 10% - 15% of pure ethanol in order to reduce formation of dust during compaction and to bind the powder, thus ensuring that the compacted samples do not crumble before they are used for testing. The mixed material is then inserted in a steel (oedometer-) ring and compacted by cyclical loading with increasing axial pressure up to 100 MPa. The samples are air-dried so that nearly all of the ethanol evaporates. In order to accelerate wetting of the samples during the following oedometer tests, a small hole with a diameter of 1.1 mm is bored through the centre of each sample. Via this sample preparation procedure, intact discs are created with dimensions as given in Fig. 1. The dry density of the samples was 1.8 - 1.9 g/cm³ and the porosity amounted to 0.29 - 0.35, determined via back-calculation from the masses of the powders and the measured volume. The accuracy of these calculated values was verified via porosimetry on a reference sample.

2.2. Oedometer tests

The compacted samples were inserted in a conventional oedometer apparatus (see Fig. 1) and loaded axially. The axial load was then held constant during the entire duration of each test. After loading, when the settlement steadied, the samples were wetted from the bottom, thus beginning the actual swelling test (time \(t = 0\)). The water was originally demineralized water which was saturated with respect to gypsum for the experiments (approximately 2 g/l CaSO₄). The axial deformation was measured via a digital dial gauge (Fig. 1) either by manual readings or by computer-based data-logging. At the end of each test, the water supply was cut off and the axial load was reduced. The samples were extracted from the oedometer rings, weighed, dried in an oven (at 40° - 65°C) and weighed again in order to determine the mass of water bound in the sample.

In the first series of oedometer tests the following axial stresses were applied: 3 kPa, 20 kPa, 200 kPa, 400 kPa, 800 kPa, 1600 kPa, 2200 kPa and 3200 kPa. For each axial load at least one oedometer test was conducted until the swelling strain seemed to have reached a steady state and thus the final strain was measured. For the second and third series of oedometer tests, the experiments were repeated at 3 kPa and 800 kPa and the samples were extracted before the swelling strain reached a steady state.

Two additional oedometer tests were performed at 3 kPa and 400 kPa on samples containing 100% kaolin in order to ensure that, apart from a rapid initial heave due to reduction of suction pressure, no swelling other than
chemical swelling occurs during the main oedometer tests with samples containing a mixture of anhydrite and kaolin.

2.3. Investigations regarding sample composition

Each sample was investigated via TGA after the oedometer tests, where a small representative specimen (about 17-20 mg) is heated (10°C per minute) and the change in weight is measured [14]. At about 90°-130°C a drop in the weight can be observed, which is attributable to the reverse reaction as in Chapter 1: the gypsum dehydrates (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \)) and the now free water evaporates. By considering the molar masses of water and gypsum it is then possible to calculate the mass of gypsum in each oedometer sample post test and to determine (via back-calculation) the corresponding amount of dissolved anhydrite, as well as the mass of remaining anhydrite in the sample. Finally XRD analysis was performed on three oedometer-samples as well as on a reference specimen containing solely the used kaolin.

3. Results

3.1. Stress-strain dependency

The results from the first series of oedometer tests are presented in Fig. 2, which shows the measured swelling strain over time until a steady state was reached for all the axial stresses investigated. At an axial stress of 3200 kPa no swelling strain could be observed over the entire duration of the test. At 3 kPa and at 800 kPa multiple tests were repeated and some scatter in the results was observed (e.g. the final swelling strain at 800 kPa varied from 6% to 10%). The dot-dashed curves in Fig. 2 indicate the swelling behaviour of the samples containing only kaolin. These samples also exhibited a rapid initial strain during the first couple of hours due to wetting of the sample and reduction of the negative pore pressure (similar to the other curves). However, no further swelling strain occurred after that, thus the strain which develops after the initial heave of the other samples is due to AGT. This initial rapid strain is significant especially for low axial stresses and can lead to an overestimation of the chemical swelling strain, if it is not taken into account in the evaluation of the experimental results.

![Fig. 2. Results of oedometer tests up to a steady state (note: the dashed line indicates a longer period of time where the axial deformation was not measured).](image-url)
Fig. 3 shows the final strain that was reached at each test versus the corresponding axial stress in a semi-logarithmic diagram. These results indicate a linear relationship between the final strains and the logarithm of the axial stress for this type of sample. Should such a swelling strain – swelling stress behaviour be verified for anhydritic rock as well, tunnel design reliability would be improved considerably [1, 2].

In all samples, the anhydrite appeared to have dissolved nearly entirely with one exception: the sample that was loaded with 3200 kPa and did not swell at all (but even settled slightly) contained almost no gypsum according to the TGA results. This is shown in Fig. 4, where the masses of anhydrite prior and post test, as well as the mass of gypsum post test (per unit volume), are mapped against the applied axial stresses for each sample.

3.2. Relationship between swelling strain and mass of anhydrite

Fig. 5 shows the swelling strain over time for the oedometer tests which were repeated at 3 kPa and 800 kPa and where the samples were extracted prior to reaching a steady state. The points of extraction are indicated by an “x”. The amount of anhydrite in each sample post test, versus the reached swelling strain at the point of extraction, is shown in Fig. 6.
Fig. 5. Results of oedometer tests up to various swelling strains. a: results from tests with an axial stress of 3 kPa; b: 800 kPa. (Note: black lines indicate samples that reached steady state, while grey lines represent samples that were extracted prior to reaching the final swelling strain and dashed lines indicate a longer period of time where the axial deformation was not measured).

A correlation clearly exists between the change in the mass of anhydrite and the swelling strain. It seems that the relationship (denoted by $\chi$ in Equation 4) is linear during the first stages of swelling, i.e. until about half the anhydrite is dissolved (cf. Fig. 6). The swelling strain then stagnates while further anhydrite dissolves and gypsum precipitates. One possible explanation is that after a first expansion of the sample the gypsum precipitates mainly in its pores. However, further experiments are necessary to draw definite conclusions for the case when $m_{\text{an,d}} < 0.4 \text{ g/cm}^3$.

The values for $m_\chi$ in Fig. 6 are back-calculated based on the results from TGA. In order to verify the reliability of the TGA results, XRD analysis was performed on three of the tested samples (1_XRD, 2_XRD, 3a_XRD and 3b_XRD) as well as on a reference specimen containing only the used kaolin (4_XRD). The results are shown in Fig. 7, where the mineralogical compositions of the specimens according to the XRD analysis are compared to the back-calculated results from TGA performed on specimens of the same oedometer-samples (e.g. comparison of

Fig. 6. Swelling strain vs. anhydrite mass of each sample for the second series of oedometer tests (extraction of samples at various swelling strains). a: 3 kPa axial stress, b: 800 kPa axial stress. (Note: black diamonds indicate samples that reached max. swelling strain, grey diamonds represent samples that were extracted prior to reaching max. swelling strain).
Fig. 7. Composition of three samples post oedometer test (comparison between results from X-ray diffraction analysis and thermogravimetric analysis) and mineralogical composition of the kaolin based on X-ray diffraction analysis (pillar on the far right).

“1_XRD” to “1_TGA”). Obviously, it is not possible to distinguish between the different minerals in the kaolin via TGA (as opposed to XRD, where each mineral is shown in a different grey tone in Fig. 7), which is why the kaolin is shown as one component in the results from TGA (hatched pillars in Fig. 7).

One observation that can be made is that the analysis via TGA delivered generally higher anhydrite contents compared to the XRD analysis. This discrepancy was probably due to faulty specimen preparation (further gypsum may have precipitated during air-drying of specimens 1_XRD, 2_XRD and 3a_XRD at room temperature and humidity) because almost the same result was achieved as via TGA upon repetition of one of the specimens (3b_XRD, which was dried in an oven at 40°C). Furthermore, repetition of TGA on that same sample showed that the TGA results are very consistent concerning reproducibility (i.e. 3a_TGA vs. 3b_TGA). Evidently, the TGA results can be considered reliable and sufficiently accurate for the analysis of the oedometer tests.

4. Closing remarks

The oedometer tests revealed that there is a correlation between the swelling strains and the change in the mass of anhydrite, while at an axial stress of 3200 kPa no swelling occurred at all and nearly no gypsum was precipitated. Furthermore, it can be seen from the first series of tests that a semi-logarithmic relationship seems to exist between the axial strains and the axial stresses for this type of sample. Knowledge of such a relationship is needed for structural design when tunnelling through anhydritic rock.

The relationship between the chemical and mechanical processes needs to be determined in greater detail, also by considering various boundary conditions and determining the influence of the sample composition and structure. In ongoing experiments, the same types of samples are investigated under other boundary conditions. On the one hand, samples are held under complete constraint in steel rings, while the axial pressure occurring due to AGT is measured. First results show that the stress which this type of artificial sample produces under full constraint is about 3 MPa, which correlates well with the results from the oedometer test performed with an axial stress of 3.2 MPa, where no swelling was observed (Chapter 3.1). This appears to be the confining pressure of these samples, which inhibits swelling due to AGT. However, based on the model for the determination of macroscopic swelling pressure by Serafeimidis et al. [15], the confining pressure should be at least twice as high and thus needs to be investigated more closely. Furthermore, experiments are performed in a special set of (“flexible”) oedometers, where some radial deformation develops and the occurring radial stresses can be determined in order to distinguish between the relationship \( \chi \) in the axial direction from the one in the radial direction.
Furthermore, the influence of the chosen sample material needs to be established, e.g. by performing oedometer tests as described in this paper but with mixtures of quartz powder and anhydrite. It will also be necessary to perform experiments on mixtures with swelling clays or on natural rock, and attempt to incorporate the findings based on artificial samples into the observed behaviour of natural rock.

Additionally, the change in structure of the samples due to AGT (e.g. change of pore volume or aperture of cracks as well as the distribution and shape of the growing gypsum crystals) is under investigation, also on some of the samples from the oedometer tests described in this paper. For example, the first results from a thin-section analysis of a sample that swelled until a steady state was reached (at 800 kPa axial stress) showed more gypsum than the sample that did not swell at all (at 3200 kPa). Also, images from scanning electron microscopy revealed clear “nests” of gypsum needles in the cracks and pores of some samples.

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