Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Departement für Umwelt, Verkehr, Energie und Kommunikation UVEK
Département fédéral de l'environnement, des transports, de l'énergie et de la communication DETEC
Dipartimento federale dell'ambiente, dei trasporti, dell'energia e delle comunicazioni DATEC

Bundesamt für Strassen
Office fédéral des routes
Ufficio federale delle Strade

Swelling inhibitors for anhydritic claystones

Quellinhibitoren für anhydritführenden Tonsteinen

Inhibiteurs d'expansion pour des roches anhydritico-argileuse

ETH Zürich, Institut für Baustoffe
Prof. Dr. Robert J. Flatt
Dr. Timothy Wangler
Amir Shahab

Forschungsprojekt FGU 2012/001 auf Antrag der Arbeitsgruppe Tunnelforschung (AGT)

Dezember 2017 **1625**

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Departement für Umwelt, Verkehr, Energie und Kommunikation UVEK
Département fédéral de l'environnement, des transports, de l'énergie et de la communication DETEC
Dipartimento federale dell'ambiente, dei trasporti, dell'energia e delle comunicazioni DATEC

Bundesamt für Strassen
Office fédéral des routes
Ufficio federale delle Strade

Swelling inhibitors for anhydritic claystones

Quellinhibitoren für anhydritführenden Tonsteinen

Inhibiteurs d'expansion pour des roches anhydritico-argileuse

ETH Zürich, Institut für Baustoffe
Prof. Dr. Robert J. Flatt
Dr. Timothy Wangler
Amir Shahab

Forschungsprojekt FGU 2012/001 auf Antrag der Arbeitsgruppe Tunnelforschung (AGT)

Dezember 2017 **1625**

Imprint

Forschungsstelle und Projektteam

Projektleitung
Robert Flatt

Mitglieder
Timothy Wangler
Amir Shahab

Begleitkommission

Präsident
Prof. Dr. Georg Anagnostou

Mitglieder
Felix Amberg
Prof. Dr. Anton J. Schleiss
Dr. Benedikt Lindlar
Christian Amstad

Antragsteller

Arbeitsgruppe Tunnelforschung (AGT)

Bezugsquelle

Das Dokument kann kostenlos von http://www.mobilityplatform.ch heruntergeladen werden.

Table of Contents

Zusammenfassung

Die Problematik von Sohlhebungen verursacht durch sulfatische Tonsteine (in diesem Bericht gleichgesetzt mit Ausdruck “anhydrithaltige Tonsteine”) ist in Tunneln in der Gipskeuper-Formation der Schweiz und in Deutschland weit verbreitet. Diese wiederholten Sohlhebungen führten zu sehr teuren Sanierungen und Verkehrseinschränkungen, wie beispielsweise im Fall des Belchentunnels und des Chienbergtunnels. Es zeigt sich jedoch, dass diese kostenintensiven Sanierungen langfristig wirkungslos sind und nur temporäre Lösungen darstellen.

Aus diesem Grund befassen sich zahlreiche, zielorientierte Forschungsprojekte verschiedener Institutionen mit dieser Problematik. Dabei werden die zugrundeliegenden Prozesse vom hydrogeologischen Massstab bis hin zum Mikrobereich untersucht. Das Kernproblem stellt die Kopplung zweier sich oft ergänzenden Quellprozesse dar: das Tonquellen und die Umwandlung von Anhydrit zu Gips (nachfolgend als ATG bezeichnet); ein Prozess, welcher beachtlich hohe Kristallisationsdrücke ausübt. Ein fehlendes Element der bisherigen Forschung ist die Lösungsfindung auf der materialwissenschaftlichen Grundlage, was im Mittelpunkt dieses Forschungsprojekts des Instituts für Baustoffe an der ETH Zürich steht. In dieser Studie wird der Einsatz von Tonquell-Inhibitoren zur Beherrschung des Tonquellens, sowie von ATG-Inhibitoren zur Beherrschung der Probleme durch ATG untersucht. Hierbei werden bekannte Inhibitoren aus der Geotechnik (für Tone) und aus der Gipsplattenproduktion (für ATG) eingesetzt.

Ein limitierender Faktor dieses Forschungsvorhabens ist die Erforderlichkeit ausserordentlich zeitaufwändiger Versuche zur experimentellen Erforschung des Themas, wie die jüngsten Langzeitversuche – gestartet im Jahr 2006 und bis heute andauernd – zeigen (FGU 2006/001). Versuchszeiten über Jahre und Jahrzehnte eines komplexen gekoppelten Problems in einem sehr heterogenen Material erfordern Geduld und die Ergebnisse lassen sich oft nur schwer interpretieren. Da dies auch die Interpretation der Untersuchungen zur Wirksamkeit von Inhibitoren erschwert, konzentrierte sich das vorliegende Forschungsprojekt anfänglich auf die Entkopplung des Problems durch einen neuartigen „thermodynamischen Schalter“. Der sogenannte „Schalter“ ist die Anwendung des Phasenverhaltens bei der Löslichkeit der verschiedenen Calciumsulfatphasen: ab ungefähr 50°C überschreitet die Löslichkeit von Gips diejenige von Anhydrit, wodurch Anhydrit bei Kontakt mit Wasser die thermodynamisch stabilere Phase darstellt.

Die vorliegende Studie zeigt die Wirksamkeit dieses “thermodynamischen Schalters” in einem wässrigen System mit hohen Verhältnissen von flüssigen zu festen Substanzen, als auch in dichten Systemen mit tiefen Verhältnissen von flüssigen zu festen Substanzen, was den Bereich einer Tunnelsohle besser repräsentiert. Die ersten Untersuchungen in wässrigen Systemen mit reinen Phasen ermöglichten – nachdem der thermodynamische Schalter nachgewiesen wurde – die Bestätigung der Wirksamkeit des ATG-Inhibitors. Die Forschung in den wässrigen Systemen beinhaltete zudem die Messung der Adsorption verschiedener ATG-Inhibitoren an Anhydrit und Gips, als auch das Verfolgen der Entwicklung des Porenwassers. Dies ermöglichte es, den Wirkungsmechanismus der Inhibitoren zu definieren und zu zeigen, dass die beste Wirkungsweise erzielt wird, wenn sich die Inhibitoren in erster Linie auf die Anhydritphase auswirken und dadurch die Anhydritlösung hemmen, wobei die Hemmung der Nukleation und des Wachstums von Gips ebenfalls wirksam sein kann. Während diesen Untersuchungen konnte auch gezeigt werden, dass keine Interaktion zwischen den Ton- und AGT-Inhibitoren stattfand und dass das Vorhandensein von Ton ihre Wirksamkeit nicht beeinträchtigte.

Die bedeutendsten Experimente der gesamten Studie waren diejenigen Experimente, die in dichten Systemen unter Verwendung von Oedometern ausgeführt wurden. Durch die Verwendung von Gestein aus einem bestehenden Tunnel, welches gemahlen und zu einer sehr dichten, aber porösen Struktur wiederverdichtet wurde, konnten die Bedingungen einer Tunnelsohle am besten simuliert werden. Eine erste Serie von Oedometerexperimenten zeigte zum einen, dass eine korrekte Dosierung von ATG-Inhibitoren wichtig ist, vor allem aber, dass der Einsatz von Tonquell-Inhibitoren bei einer

vollkommen trockenen Sohle nicht ratsam ist. Tonquell-Inhibitoren funktionieren nach dem Prinzip der Substitution innerhalb der Tonzwischenschichten und erfordern deshalb eine anfängliche Quellung. Da Tonquell-Inhibitoren in der Praxis vor allem zur Beherrschung von längerfristigem osmotischen Quellen eingesetzt werden, ist ein langfristiger Einsatz nicht auszuschliessen, wenn osmotisches Quellen ein Problem darstellen kann.

Die zweite Serie von Oedometerversuchen zeigte zwei Hauptziele dieses Forschungsprojekts auf: das Prinzip der Entkopplung der Quellprozesse mithilfe des thermodynamischen Schalters und die Wirksamkeit der ATG-Inhibitoren. In dieser Versuchsserie wurden zwei Oedometer mit dem angeschlossenen Wasser in einen Ofen platziert, wodurch der ATG-Prozess „ausgeschaltet“ wurde und die Proben nur aufgrund des vorhandenen Tons quollen, bis ein konstanter Wert erreicht wurde. Durch das Entfernen eines Oedometers aus dem Ofen und dem Aufstellen bei Raumtemperatur, konnte die nachfolgende Quellung ausschliesslich auf ATG zurückgeführt werden. Der zweite Oedometer wurde ebenfalls aus dem Ofen entfernt, jedoch wurde die Flüssigkeit durch einen ATG-Inhibitor ersetzt und das Ausbleiben einer nachfolgenden Quellung zeigte, dass der ATG-Inhibitor wirksam war.

Eine letzte kombinierte experimentelle und numerische Modellierungsstudie zielte darauf hin, die Geometrie und den Einsatz der Tonquell-Inhibitoren für einen potenziellen Feldersuch zu definieren. Für diese Studie wurden für die Modellierung von quellfähigem, tonhaltigem Material massive Steinblöcke mit Bohrlöchern versehen, welche mit Wasser oder einer Inhibitor-Lösung gefüllt wurden. Einzelne Bohrlöcher als auch zwei sich beeinflussende Bohrlöcher wurden beispielhaft anhand eines Modells mit der Plaxis-Software zur Simulation des Quellverhaltens untersucht. Dieses wurde anschliessend validiert und erweitert, um einen Vorschlag für einen potenziellen Feldversuch zu liefern. Die wichtigsten belehrenden Erkenntnisse dieser Studie, mit dem Ziel Zeit und Geld für einen Feldversuch zu sparen, zeigten, dass es unerlässlich ist, die anfängliche Sättigung und Durchlässigkeit der Tunnelsohle ausreichend zu charakterisieren, damit die Bohrlochabstände zuverlässige und rasche Signale liefern. Eine weitere nützliche Erkenntnis war, die Reaktions-Diffusions-Front zu berücksichtigen, da der Inhibitor verbraucht wird, während die Lösung im Gestein fortschreitet. Diese Schlussfolgerung gilt sinngemäss auch für die Anwendung der ATG-Inhibitoren.

Zusammenfassend stellt das primäre Ergebnis dieses Forschungsprojektes die Nützlichkeit der Entkopplungstechnik für anhydrithaltige Tonsteine dar. Die Möglichkeit, Tonquellung von der ATG-Quellung zu entkoppeln, sollte in Zukunft effizientere experimentelle Vorgehensweisen ermöglichen und erlaubte es, die Wirksamkeit des ATG-Inhibitors in dieser Studie effizient zu untersuchen. Die Zweckmässigkeit des ATG-Inhibitors deutet darauf hin, dass er höchstwahrscheinlich für Tunnelbauten verwendet werden kann, vor allem als Zugabe in Bereichen wo Wasser eingesetzt wird, wie beispielsweise beim Bohren von Bohrlöchern. Weiter können sich - obwohl die anfängliche Tonquellung sehr schwierig zu bekämpfen ist - Tonquell-Inhibitoren als sehr nützlich erweisen für die langfristige Verringerung des osmotischen Quellens und der Wasseraktivität - beides Prozesse, die das ATG-Problem verschlimmern können.

Résumé

Les tunnels traversant la formation « Gipskeuper » en Suisse et en Allemagne souffrent depuis des décennies du problème de soulèvement des sols dû à des roches argileuses et sulfatiques (aussi décrites comme des marnes anhydrites dans ce rapport). Ces problèmes ont conduit à des réparations très coûteuses et à un impact important sur le trafic, notamment dans les tunnels de Belchen et de Chienberg. Bien que coûteuses, ces réparations se sont pourtant avérées inefficaces sur le long terme.

Ceci a conduit à de nombreux projets de recherche menés par différentes institutions, examinant les mécanismes à différentes échelles, de l'hydrogéologie jusqu'à l'échelle micro. De par son essence, ce problème est complexe, impliquant le couplage de deux phénomènes d'expansion souvent complémentaires : le gonflement des argiles et la conversion de l'anhydrite en gypse (ATG) qui peut générer des pressions de cristallisation très importantes. Toutefois, ces recherches ne se sont pas penchées sur les matériaux eux-mêmes. C'est l'objectif du présent travail, réalisé à l'Institut des Matériaux de Construction de l'ETHZ, que d'étudier cette question. En particulier, nous étudions l'utilisation d'inhibiteurs d'expansion sur le gonflement des argiles, ainsi que des retardateurs de l'hydratation du gypse pour l'ATG.

Une des barrières à ce type d'étude est la très longue durée requise par les expériences, comme celle initiée en 2006 (FGU 2006/001) et qui continue encore aujourd'hui. Des cycles expérimentaux s'étendant sur des années, voire des décennies, et traitant d'un problème complexe sur un matériau hétérogène, demandent de la patience et peuvent souvent produire des résultats délicats à interpréter. Ceci rendrait toute étude sur l'effet d'inhibiteurs aussi difficile à interpréter, raison pour laquelle nous avons focalisé notre attention sur la possibilité de découpler le problème grâce à un « interrupteur thermodynamique ». Celui-ci se base sur le diagramme de solubilité des phases de sulfate de calcium qui indique qu'au-dessus de 50°C l'anhydrite est la phase thermodynamiquement stable en présence d'eau.

Cette étude a validé le concept de cet « interrupteur thermodynamique » tant en régime dilué (pratique en laboratoire), qu'en régime concentré (plus représentatif de la réalité, mais moins pratique). Les premières études en systèmes dilués ont non seulement démontré la pertinence de l'interrupteur, mais aussi l'efficacité d'inhibiteurs pour l'ATG. Dans le même temps, nous avons fait des mesures d'adsorption de ces inhibiteurs sur l'ATG. Ces mesures étaient accompagnées de dosages des espèces en solution, ce qui a permis de conclure que l'action principale de ces additifs est d'inhiber la dissolution de l'anhydrite, même si on ne peut pas complètement exclure un effet sur la nucléation/croissance du gypse. Nous avons également montré que l'action de ces inhibiteurs n'est pas pénalisée par la présence d'argiles.

Les expériences centrales de cette étude ont été faites sur des systèmes dense en utilisant des oedomètres. Ici, en utilisant de la roche provenant de tunnels qui présentent ces problèmes, nous avons d'abord produit une poudre par broyage. Puis, par pressage nous avons produit des échantillons avec la bonne minéralogie, mais avec une porosité accrue. Ce faisant nous avons des échantillons permettant de simuler le comportement des roches ciblées, mais en des temps nettement plus courts. Une première série d'essais a montré qu'il est important d'utiliser le bon dosage d'inhibiteurs, mais surtout que l'utilisation d'inhibiteurs de gonflement d'argiles n'est pas conseillé dans des roches initialement sèches. Les inhibiteurs d'expansion d'argiles fonctionnent selon le principe de substitutions dans l'espace interfoliaire, ce qui ne se fait pas sans une certaine expansion initiale. Ces inhibiteurs ne peuvent donc pas empêcher des déformations telles que celles engendrées par l'expansion intercristalline. Par contre ils pourraient être intéressant pour des déformations plus larges, typiques d'un gonflement osmotique. Cette question ainsi que l'interaction avec l'ATG restent à étudier.

La deuxième expérience utilisant un oedomètre a démontré deux des principales hypothèses de cette étude : le principe du découplage utilisant l'interrupteur thermodynamique et l'efficacité d'inhibiteurs de d'ATG. Dans cette expérience, deux oedomètres ont été placés sous circulation d'eau dans une étuve à 60°C pour « éteindre » l'ATG. De ce fait la seule expansion possible était due au gonflement des argiles. Ensuite, un des oedomètres a été placé à température ambiante, rendant possible une expansion du fait du seul ATG. Plus tard, le second oedomètre a été retiré et placé à température ambiante, mais cette fois-ci la solution à laquelle il était exposé contenait l'inhibiteur ATG. Dans ce cas-ci, aucune expansion n'a été observée, ce qui confirme l'efficacité de l'inhibiteur.

Finalement, une étude expérimentale et de modélisation a été conduite pour déterminer la géométrie d'un possible essai d'application in-situ d'un inhibiteur d'expansion d'argiles. Dans cette étude, des blocs massifs d'une pierre contenant des argiles gonflantes ont été utilisés comme système modèle. Des trous y ont été percés, destinés à recevoir de l'eau ou une solution contenant l'inhibiteur. Des trous isolés ainsi que des paires de trous en interaction ont été étudiés, utilisant un modèle implémenté dans le logiciel Plaxis destiné à simuler l'expansion des argiles. En utilisant des résultats expérimentaux, ce code a été calibré et étendu afin de pouvoir fournir des conseils concernant une possible étude en site. Cette étude a montré qu'il est impératif de connaître l'état de saturation initial et la perméabilité de la roche afin d'optimiser l'espacement des forages pour obtenir des résultats rapides et fiables. Cette étude a aussi montré qu'il faut tenir compte du couplage réaction-diffusion alors que la solution se propage dans la roche. Cette conclusion s'applique aussi à l'utilisation d'inhibiteurs ATG.

En conclusion, le résultat principal de cette étude est la pertinence de "l'interrupteur thermodynamique" pour découpler les processus responsables de gonflements des marnes anhydriques. Il permet d'améliorer les procédures expérimentales pour étudier ce phénomène et a en particulier permis de démontrer l'efficacité potentielle des inhibiteurs ATG. L'utilité démontrée de ces produits implique qu'ils peuvent être considérés pour des essais dans des tunnels, dès lors qu'une opération impliquant l'utilisation d'eau est envisagée, en tant que fluide de forage mais aussi quand elle est utilisée pour contrôler la poussière. De plus, même s'il est difficile d'empêcher le gonflement initial des argiles par l'action d'inhibiteurs, l'action à long terme de ces produits sur le gonflement osmotique pourrait être bénéfique et devrait être approfondie.

Summary

The problem of floor heave due to sulfatic claystones (used interchangeably with the term “anhydritic claystone” in this report) has for decades plagued tunnels that go through the Gipskeuper formation in Switzerland and Germany. These repeated floor heaves have led to very expensive repairs and traffic impacts in highway tunnels such as the Belchen tunnel or the Chienberg tunnel. These repairs, while costly, have also proved to be ineffective on the longer term, making them just a bandaid solution.

This has led to many targeted research projects to address this problem at various institutions, examining the core processes on varying scales, from the hydrogeological all the way to the microscale. At its core, the problem is a difficult one, involving the coupling of two often complementary swelling processes: clay swelling and the conversion of anhydrite to gypsum (in the following referred to as ATG), a process that exerts considerable crystallization pressure. A missing element in the research has been to investigate solutions on the material scale, which is the focus of the research of this study undertaken at the Institute for Building Materials at ETH Zurich. In this study, we investigated the use of clay swelling inhibitors to control the clay swelling problem, and ATG inhibitors to control the ATG problem, taking inhibitors known from the geotechnical engineering (for clays) and from gypsum board production (for ATG).

One of the prohibiting factors in this research is that experimental research on the topic requires extraordinarily time-consuming experiments, such as the most recent long-term experiments initiated in 2006 (FGU 2006/001) and are still continuing today. Experimental cycle times spanning years and decades of a complex coupled problem in a very heterogeneous material require patience, and often results can be difficult to interpret. This would make any investigation of inhibitor effectiveness also difficult to interpret, and therefore this study first focused on decoupling the problem via a novel “thermodynamic switch”. This so-called “switch” was the use of the phase behavior in the solubility of various calcium sulfate phases: above approximately 50 °C, the solubility of gypsum exceeds that of anhydrite, making anhydrite more thermodynamically stable when exposed to water.

This study demonstrated the effectiveness of this “thermodynamic switch” in a dilute system, with high liquid to solid ratios, as well as in dense systems more representative of a tunnel invert, with low liquid to solid ratios. The first investigations in dilute systems with pure phases, following the confirmation of the thermodynamic switch, then allowed the confirmation of the effectiveness of the ATG inhibitor. Research in the dilute systems also involved the measurement of adsorption of various ATG inhibitors to anhydrite and gypsum while also following the pore solution evolution, helping to define their mechanism of action and demonstrating that acting upon primarily the anhydrite phase to inhibit dissolution seems to be the best mode of action, although inhibiting nucleation and growth of gypsum can also be effective. It was also demonstrated during these studies that there was no interaction between clay and ATG inhibitors, and clay presence did not decrease their effectiveness.

The experiments that defined the whole study were those in dense systems, using oedometers. Here, with actual tunnel rock that had been crushed and reconstituted into a highly dense but porous structure, the conditions that best simulate a tunnel invert could be met. A first round of oedometer experiments demonstrated that correct dosage of ATG iinhibitor is important, but more importantly that the use of clay swelling inhibitors might be inadvisable in completely dry inverts. Clay swelling inhibitors operate on the principle of substitution within the clay interlayers, thus requiring an initial amount of swelling. Therefore clay swelling inhibitors cannot counter swelling strains associated to intracrystalline swelling, but then may become useful for larger strains that develop with osmotic swelling. This question as well as interactions with ATG remains to be studied.

The second oedometer experiment demonstrated two of the primary goals of this study: the principle of decoupling the swelling processes using the thermodynamic switch, and the effectiveness of the ATG inhibitors. In this experiment, two oedometers were placed with water in an oven at 60°C to “turn off” ATG, and thus only swelled via clay swelling. By then removing one oedometer and placing it in ambient temperatures, its subsequent swelling could then be understood to be only ATG. Later, the second oedometer was removed and also place at ambient temperature, but this time its fluid was replaced by ATG inhibitor. For this case, the lack of subsequent swelling demonstrated that the ATG inhibitor was effective.

A final combined experimental and computational modeling study was aimed at defining a geometry for a potential field test application of the clay swelling inhibitor. In this study, massive stone blocks of a model clay-swelling geological material had boreholes drilled into them, and these boreholes were filled with water or inhibitor solution. Single boreholes and two interacting borehole examples were examined, with a model in Plaxis software to simulate swelling. Using experimental results, the code was then calibrated and the extended to give advice on a potential field study. The major cautionary findings from this study were that it is imperative to have the initial saturation and permeability of any tunnel invert well characterized in order to optimize borehole spacing to return a reliable and fast signal. Another useful finding was to consider the reaction-diffusion front as inhibitor is consumed while the solution proceeds through the rock. This is a conclusion that can apply also to ATG inhibitor application.

In conclusion, the primary finding of this study has to do with the usefulness of the decoupling technique for anhydritic claystones. The ability to decouple clay swelling from ATG swelling should create more efficient experimental protocols in the future, and greatly enabled the efficient study of ATG inhibitor effectiveness in this study. The usefulness of the ATG inhibitor means it is most likely ready for test use in tunnel operations, primarily in delivery wherever there is an operation involving water, such as drilling. Additionally, while controlling clay swelling initially is very difficult with clay swelling inhibitors, on the longer term clay swelling inhibitors could prove useful in reducing osmotic swelling and ought to be given further attention in the future.

1 Introduction

1.1 Context and objectives of the research

Swelling of anhydritic claystones remains a persistent problem for tunnels that go through the Gipskeuper, a type of formation that impacts a significant number of highway and rail tunnels in northwest Switzerland. The swelling can take place within short time scales, even during tunnel construction, or more usually over long time scales such as years to decades, leading to premature and very costly interventions and repairs. Therefore, a number of efforts have been undertaken to understand and combat this issue by various institutions within Switzerland, including the Group of Applied and Environmental Geology at University of Basel (Prof. Huggenberger, FGU 2008/004, FGU 2008/005, FGU 2012/004), the Chair of Underground Construction at ETH Zürich (Prof. Anagnostou, FGU 2006/001), and this study at the Chair of Physical Chemistry of Building Materials at ETH Zürich (Prof. Flatt, FGU 2012/001).

The research projects of the University of Basel focus primarily on large scale water hydrogeology, on the order of meters to kilometers. The Chair of Underground Construction at ETH Zurich's project is primarily focused on small to medium scale processes, on the order of micrometers to centimeters, but with an emphasis on the chemomechanical processes that lead to the observed damage. The project of the Chair of Physical Chemistry of Building Materials had its primary focus on the development of potential solutions to reduce swelling and swelling damage from these chemomechanical phenomena, and that is the focus of this report.

The primary objective of the research in this report is to investigate and demonstrate potential solutions to the issue of tunnel floor heave of anhydritic claystones, from a material level. These solutions are chemicals that can act to inhibit the swelling of the clay, and can inhibit the anhydrite-to-gypsum (ATG) transformation that leads to damaging crystallization pressures.

1.2 Outline of investigations

The investigations in this research consist primarily of two main topics: 1) decoupling of the two swelling phenomena (clay swelling and ATG crystallization pressure) and 2) investigating the efficacy of compounds known to inhibit swelling in clays as well as ATG transformation. Additionally, a large-scale experiment was performed on a model material to test the idea of using clay swelling inhibitors on larger scales. Each of these topics has also been subdivided into a number of smaller topics, detailed below:

Decoupling of clay swelling and ATG

The central experiment of this study revolved around what we term the "thermodynamic switch". One can observe in the phase diagram of the calcium sulfate and water that, above approximately 40-50 °C, the solubility of anhydrite becomes lower than that of gypsum, making it the more stable phase (see section 2.3). Therefore, running swelling experiments above this temperature should induce only clay swelling, allowing a full decoupling of the two phenomena.

The first step in the research was to ensure that no significant changes in clay swelling would occur at elevated temperatures. This step was taken using Villarlod molasse, a model material for clay swelling. Once this was confirmed, then the thermodynamic switch could then be confirmed: first it was confirmed on pure anhydrite, and then on Chienberg tunnel rock. These confirmation experiments were performed in dilute systems.

Oedometer experiments (dense systems) were then performed, with one ultimately confirming both the thermodynamic switch and the efficacy of ATG inhibitors, detailed next.

Efficacy of swelling inhibitors

Clay swelling inhibitors: inhibitors restricting clay swelling have been well known from borehole stability in oilwell drilling, as well as in cultural heritage. Their effectiveness is well known in situations where clays are exposed to wetting and drying cycles. ATG inhibitors, on the other hand, are known primarily from gypsum board production and scale prevention in desalination processes. Both were tested in this research.

ATG inhibitors were tested in dilute systems, similar to the way that the thermodynamic switch was confirmed, and their effectiveness was confirmed. Their working mechanism was investigated via the measurement of adsorption isotherms, as well as by following pore solution evolution in dilute systems. It was found that they function primarily by adsorbing both to anhydrite and gypsum, but the most effective inhibitors adsorbed more strongly to anhydrite, indicating dissolution control of anhydrite is the most important step to control. Inhibitors that seemed to form complexes with calcium, however, seemed primarily just to delay ATG rather than stop it completely.

These findings were extended to dense systems, in the form of oedometer tests. The first series of oedometer tests turned out to be unsuccessful for both ATG and clay swelling inhibitors. The ATG inhibitor was a problem of dosage, but it was confirmed that clay swelling inhibitors could not be so effective at restricting swelling in initially dehydrated clays, as these clays require some swelling to allow the inhibitor to enter the clay interlayers. This means that to prevent initial crystalline swelling, the clay swelling inhibitors, and indeed any inhibitors, will likely not be effective. For longer term swelling processes such as osmotic swelling, however, these inhibitors could prove useful.

The second oedometer experiment turned out to be the key experiment of the study. In this experiment, both the thermodynamic switch, and the efficacy of the ATG inhibitor, were both confirmed by running oedometer swelling experiments in elevated temperatures to allow first clay swelling. Then by changing conditions and replacing the fluid of the oedometer the ATG inhibition could be confirmed.

Model study of a field measurement case

The final experiment of this study involved the use of massive stone blocks to model a large scale field measurement campaign for the clay swelling inhibitors. A computer modeling software for swelling processes (Plaxis) was used first to inform the model swelling study on Villarlod molasse blocks, then to validate it. This was then extended to a potential field campaign, where a model geometry was proposed. The focus of this study was clay swelling, as these were readily available materials with a high degree of knowledge of them and the inhibitors, but learnings can be extended to the ATG system as well. The key findings of the study were that permeability and initial saturation degree will largely determine the speed at which information can be returned on the test, and therefore must be carefully determined in advance. Another key learning is that one must consider the advection-diffusion competition in terms of transport of these inhibitors – if advection is high compared to diffusion, then the treatment solution front will be depleted with respect to inhibitor and could lead to more swelling than anticipated.

1.3 Contributions to the project

Many people contributed their efforts to this project, and their contributions are detailed below.

Within the Institute for Building Materials at ETH Zurich, Heinz Richner provided critical technical and equipment support in all studies, particularly the model swelling study on massive stone blocks. Asel Maria Aguilar Sanchez and Gabriel Peschke provided all support on microscopic investigations. Dr. Marta Palacios was especially helpful in adsorption isotherm studies, and Dr. Francesco Caruso and Dr. Sara Mantelatto provided support for ICP-OES studies. Rolf Vonäsch and Danai Tsirantonaki were valuable student worker support in the early stages.

Cristina Hampel and Markus Mueller from Sika AG Schweiz graciously provided products for testing as ATG inhibitors.

From the Institute for Geotechnical Engineering at ETH Zurich, Dr. Erich Pimentel and Tara Huber-Wanninger both provided critical support and equipment in all tests related to oedometer measurements. Prof. Anagnostou, the head of the chair of Underground Construction, also provided useful information and insights.

Also from the Institute for Geotechnical Engineering at ETH Zurich, Dr. Michael Plötze and technicians Marion Rothaupt and Annette Röthlisberger provided equipment and technical support in characterization methods.

1.4 Scientific output

This project has most significantly resulted in an Invention Disclosure to ETH Transfer, and now a patent application which will be undertaken by Sika AG on behalf of ETHZ. Due to the publication restrictions because of patenting questions, much of the work remains unpublished. Significant parts of the research have been presented in various conferences, although none relating to the patent application. When publication will be possible, then one or two journal articles will be submitted, as detailed below.

Decoupling of ATG and clay swelling, and efficacy of swelling inhibitors

This is one of the key results of this entire study, with large implications for the community researching the problem of long term swelling in anhydritic claystones in Switzerland, Germany, Spain, and elsewhere. A persistent problem in this research field has been that the problem is coupled, and that it is difficult to distinguish the phenomenon of swelling clay from the phenomenon of ATG as they are occurring simultaneously. The proof of concept in this study of the ability to decouple the two phenomena to allow proper study opens up a new dimension of research in this field, potentially saving a lot of time in interpretation of confusing studies by allowing each phenomenon to be studied individually. This proof of concept can be published in a short communication or short journal article to propagate this information to this research community.

ATG mechanism on pure phases and geological materials

The results of the study of the ATG mechanism provided some insight into how various organics inhibit the conversion of anhydrite to gypsum. By measuring the adsorption isotherms and the pore solution evolution, the working mechanisms of these molecules have been brought more into the light with the pure phase studies, and interesting questions raised with respect to interaction of previously believed inert phases in the geological materials. The possibility to combine these results with molecular dynamics simulations within the Chair of Physical Chemistry of Building Materials still exists, which could provide a useful publication for various fields besides geotechnics.

2 State of Research

This section describes what is the state of the art at the commencement of the project with respect to materials research on this topic and the use of inhibitors in place of other prevention procedures.

2.1 Sulfatic claystones in tunnels

The problem of claystones containing anhydrite causing tunnel floor heave can be linked first to problems in two tunnels: the Belchen Tunnel in Switzerland, and the Wagenburg Tunnel in Germany. This issue was identified in a particular geological formation, the Gipskeuper, which often contained a large amount of finely divided anhydrite in a clay matrix [1]. An SEM micrograph illustrating the microstructure of an anhydritic claystone is seen in Figure 1.

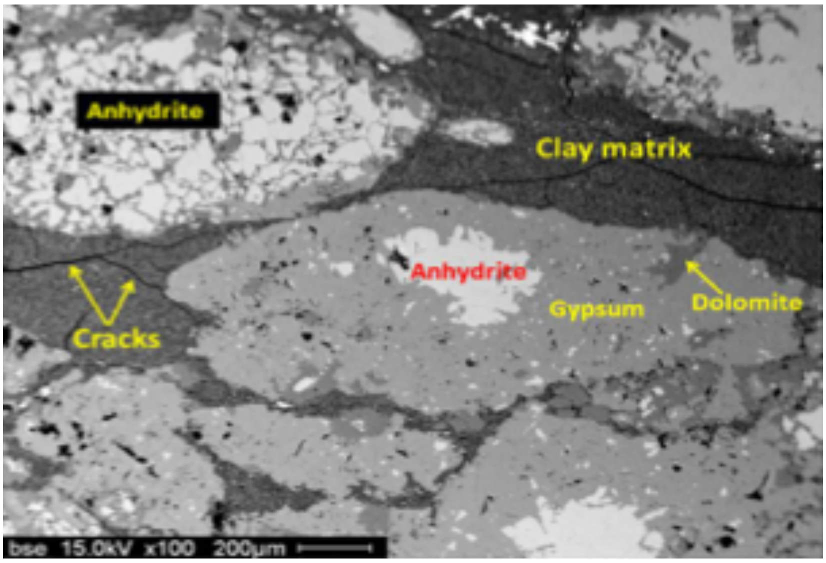

Fig. 1 *Anhydritic claystone backscattered SEM micrograph showing anhydrite and gypsum dispersed in a clay matrix. Cracks can be observed in the clay matrix.*

Clay swelling and inhibition

Water is at the source of the problem. Swelling clays are well known as an issue in geotechnical engineering for stabilization of slopes, foundational stability, and borehole stability. They are also a problem in cultural heritage of buildings with historical sandstones containing them in the matrix; repeated wet/dry cycles are often responsible for irreversible damage [2]. The source of swelling comes from hydration of counterbalancing cations that exist in the interlayer between sheets of the clay minerals; this hydration energy is very high and difficult to prevent initially by application of a counterpressure [3]. It leads to discrete increases in interlayer spacing and is known as crystalline swelling. After the entry of approximately 4 layers of water, it then proceeds into a regime known as osmotic swelling, related to the osmotic pressure formed between the concentration difference between clay layers and the pore solution [4]. The swelling in this regime is much easier to counter, with counterpressures of not more than a MPa or so required to completely suppress it [5]. It is this swelling that is most encountered in geotechnical engineering, and thus geotechnical engineering solutions can typically resolve the issue.

Inhibitors for swelling clays often simply replace the counterbalancing cations with a species that hydrates less, and also that can act as a “bridge” between opposing layers [6]. Some of the most effective of these are polyamines, or hydrocarbon chains of a few carbon groups with charged amine groups throughout. Amine groups have been found to be especially strongly bound within the clay interlayer and to suppress subsequent hydration much more than other cations. The simplest of these, the alkanediamines, have been well studied in the context of cultural heritage [7]. Other potential inhibitors could include potassium salts, which would be a cheaper alternative.

Anhydrite to gypsum (ATG) conversion and inhibition

The conversion of anhydrite to gypsum (ATG) takes place through solution, with anhydrite first dissolving and reaching its solubility limit (approximately 2.9 g/L). The solubility of gypsum is lower than that of anhydrite (2.0 g/L) and therefore it is thermodynamically favorable for gypsum to crystallize out of a solution that is saturated with respect to anhydrite. Damage arises due to crystallization pressure developing when the pore structure must resist the 60% volume increase of gypsum with respect to anhydrite. Crystallization pressure arises when, from a solution, crystals precipitate in porous media. It is directly related to the supersaturation, but it has been shown that for damaging stresses to occur, pores do not have to be filled if these are small enough [8-10]. Both conditions that are present in the anhydritic claystone. The crystallization pressure for gypsum would be at a maximum when the solution is in equilibrium with respect to anhydrite, and can be calculated via the following equation:

$$\sigma = \frac{RT}{V_G} \ln \frac{K_A a_{H2O}^2}{K_G} \quad (1)$$

Where σ is the crystallization pressure, R is the gas constant, T is the temperature, V_G is the molar volume of the gypsum crystal, K_A is the equilibrium constant of anhydrite, K_G is the equilibrium constant of gypsum, and a_{H2O} is the activity of water. The maximum crystallization pressure will be when the activity of water is one, and at a typical tunnel temperature of 10 °C, one can estimate the crystallization pressure to be 22 MPa.

Previously, with respect to this problem Einfalt et al. [11] tested highly concentrated salts, and Sahores [12] suggested to attack the problem by accelerating the ATG in the construction stage by use of a sulfate accelerator. From a surface chemistry standpoint, inhibition of ATG can be done either by inhibiting dissolution of anhydrite, or inhibiting nucleation and/or growth of gypsum. In both cases, organics that adsorb to anhydrite or gypsum surfaces would be of great use, and especially if they adsorb to high energy sites responsible for enhanced dissolution of anhydrite, nucleation sites for gypsum, or fast growth rate sites for gypsum. Whatever the function of these inhibitors, use of set retarders in the gypsum board industry could provide a starting point, as well as gypsum scale inhibitors from the desalination industry. These molecules, such as polyacrylic acid (PAA), typically feature carboxylic acid groups that adsorb strongly to calcium at the crystal surface.

Combined problem

The issue of tunnel floor heave due to anhydritic claystones is a combined problem, as could be seen in Figure 1. Clay swelling, although typically resolved by simply allowing heaves but resisting it in the more manageable osmotic range, is problematic in that it changes the microstructure of the rock and could allow more anhydrite surface to be exposed. The high crystallization pressure that can be generated during ATG, and the continuous supply of a solution supersaturated with respect to gypsum, ensures that ATG can be problematic for a very extended period of time. There is also the recent finding from FGU 2010/007 [13], in which it was demonstrated that anhydrite exists at relatively shallow depths in spite of its thermodynamic instability because the clays reduce the activity of water. This key finding, along with the microstructural considerations defined above, make decoupling the phenomena very important for study. Thus, a strategy to decouple the two phenomena is outlined in section 2.3, after a short description of the current mitigation strategies up to now.

2.2 Geotechnical solutions - attempts

Up to now, tunnel floor heave due to anhydritic claystone expansion has led to very expensive repairs and has had high impacts to traffic in road tunnels such as the Belchen tunnel and the Chienberg tunnel [14]. The primary method of resolving this has been through geotechnical engineering solutions, especially with the application of a counterpressure to the tunnel invert. This has been a very successful method in tunnels with swelling clays, where even allowing a little floor heave reduces the counterpressure requirement logarithmically. When dealing with the crystallization pressures induced by ATG, however, they have proved largely unsuccessful, and have functioned primarily as a bandaid until the next repair. This is in spite of rather ingenious engineering solutions of more recent times such as the yielding elements placed the Chienberg tunnel [15].

Alternative methods have sought to attack the problem by managing the water flow. These hydrological solutions have consisted of the construction of an adit (drainage tunnel) assisted by boreholes beneath the main tunnel in the case of the Belchen tunnel [16]. This experiment remains unsuccessful until now as well [1].

2.3 Research proposal

This research seeks to develop a solution for the problem of anhydritic claystones on the material level. This solution comes in the form of the swelling inhibitors detailed earlier. However, it is essential to decouple the two phenomena of clay swelling and ATG in order to better understand the effects of each inhibitor. Thus, we propose a novel idea based on the solubilities of calcium sulfate phases at variable temperatures, seen in Figure 2 below, the solubility curves of the respective calcium sulfate phases.

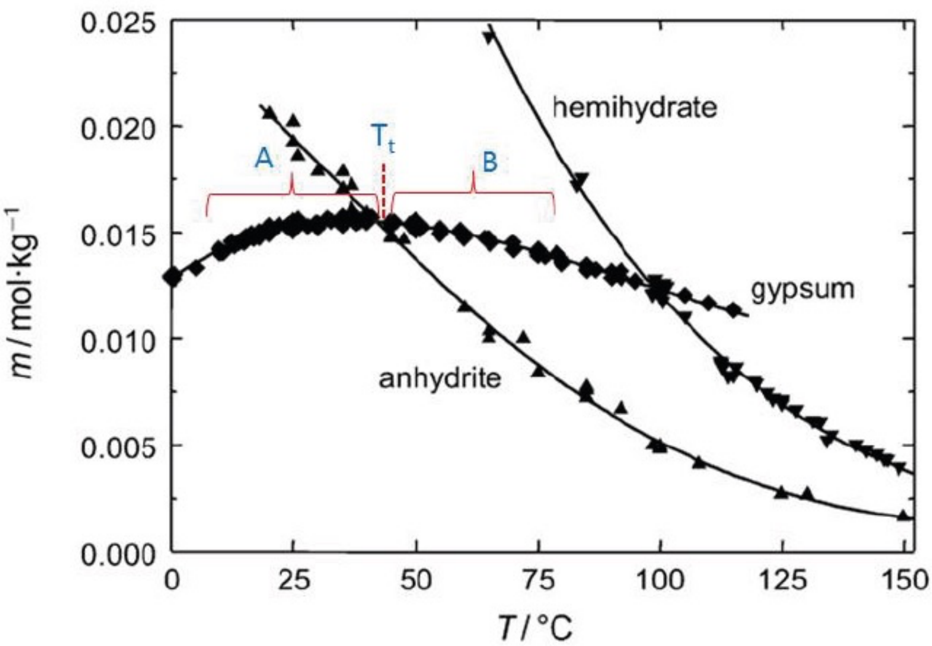

Fig. 2 *Solubility curves of various calcium sulfate phases. In region A, gypsum is the lowest solubility; in region B, anhydrite is the lowest solubility; the two curves cross at the transition temperature T_t. Plot from [17].*

In this diagram, it can be seen that the solubility of gypsum is the lowest solubility of all calcium sulfate phases at ambient temperatures, while the solubility of anhydrite is the lowest solubility at elevated temperatures. These two curves cross at a transition temperature, T_t. This temperature is typically cited in the literature to be about 40-60 °C, but centered primarily around 48-50 °C [17-20]. Thus, if one runs a swelling experiment on an anhydritic claystone above this temperature, one would expect to shut ATG off with this “thermodynamic switch”.

By performing swelling experiments at temperatures above this transition temperature, the effects of each inhibitor can be more accurately observed. Thus, the research carried out in this study centered on 1) confirmation that elevated temperatures do not affect clay swelling, 2) confirmation of the thermodynamic switch, first in pure phases and then in tunnel rock and lab scale, and 3) study of clay swelling and ATG inhibitors, first in pure phases then in tunnel rock at lab scale. A final model study was carried out on a clay swelling inhibitor in anticipation of a field scale test as well.

3 Materials and Methods

The following section defines the materials that were used in this study, and gives a brief description of the methods used to perform the study. Sample preparation techniques are also discussed in the respective experimental methods.

3.1 Materials

3.1.1 Villarlod molasse

Villarlod molasse a commonly used building sandstone from the Swiss plateau for monuments of significant cultural importance, is a subarkose clay-rich sandstone with a calcitic cement well known for its limited durability due to swelling and shrinking of clays within its matrix [21]. Swelling strains from 1.0 – 2.1 mm/m have been reported [21-22], with approximately 1.8-2.0 mm/m measured for the stones used in this study.

3.1.2 Tunnel rock

For the experiments with tunnel rock, two different types were used. One was obtained from a drilling campaign for ASTRA FGU 2006/001 [23] in the Chienberg Tunnel, and one was obtained for ASTRA FGU 2010/007 [13] from the Belchen Tunnel. Both rocks contained significant amounts of swelling clays and anhydrite, as detailed in each of those studies.

3.1.3 Powder raw materials

Pure phases were used to test adsorption of chemical inhibitors, as well as effectiveness of inhibitors in exposure tests. These pure phases included pure calcium sulfate as anhydrite (CAS 7778-18-9) and as gypsum (CAS 10101-41-4), obtained from Sigma Aldrich. Additionally, bentonite (CAS 1302-78-9) was obtained, also from Sigma Aldrich, as the swelling clay pure phase.

3.1.4 Swelling inhibitors

Clay swelling inhibitors

Clay swelling inhibitors used in this study included 1,4 diaminobutane dihydrochloride (CAS 333-93-7) for initial studies with Villarlod molasses, and 1,6 diaminohexane (CAS 124-09-4) for massive block studies. Both were obtained from Sigma Aldrich.

ATG Inhibitors

ATG inhibitors used in this study were four, all inspired by their use as either gypsum scale inhibitors from desalination processes, or their use in the gypsum board production industry as gypsum hydration retarders. The inhibitors included dietheylenetriaminepentacetic acid (DTPA) as pentasodic salt (CAS 140-01-2) obtained from Sigma Aldrich; polyacrylic acid (PAA) of MW ~5000 (product number 06519-250) obtained from Polysciences, Inc.; Retardan L obtained from Sika Schweiz AG; and Retardan 200L obtained from Sika Schweiz AG. Solid contents of each inhibitor (required to produce adsorption isotherms) were carried out using a Kern Moisture Analyzer MRS 120-3, in which the resulting mass after heating to 105 °C is measured automatically.

3.2 Experimental methods

3.2.1 Linear dilatation

Linear dilatation experiments to test the temperature dependence of Villarlod molasse clay swelling (section 4.1) were carried out by fixing a prism of Villarlod molasse, 10 cm in length, and 2 cm by 0.5 cm in cross section) in a metal frame. The frame was coupled to a linear variable differential transducer (LVDT) obtained from Tesa Instruments (Renens, Switzerland) with an accuracy of ±0.2 micron and a total range of 5 mm, with this LVDT coupled to the sample to measure the swelling. The entire frame was then immersed in water. The frame and the water for immersion was equilibrated at the respective temperatures to negate any thermal expansion effects. Temperatures of 20 °C and 60°C were tested.

3.2.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was carried out with a Quanta 600 SEM from FEI. Primarily secondary electron (SE) emission was used to obtain topographical information of pure phases and rock powder pre- and post-hydration. Backscattered electron (BSE) emission was used as well. Sometimes, an Environmental Scanning Electron Microscop (ESEM) was used for imaging (Quanta 200 3D), also from FEI.

3.2.3 Thermogravimetric analysis (TGA)

A commonly used experimental technique to probe the degree of hydration of calcium sulfate is thermogravimetric analysis, in which a small amount (approximately 20 mg) of powdered specimen is exposed to a steadily rising temperature, typically from room temperature up to 1000 °C. This small powder is attached to a sensitive balance which records the loss of mass as a function of temperature. In all experiments involving TGA, a Q50 Thermogravimetric Analyzer by TAInstruments was used.

3.2.4 Conductivity

Conductivity is a measure of the ion concentration of a solution via the measure of its ability to transfer electric current, and is reported in milliSiemens/cm (mS/cm). It correlates with the total number of ions in solution, and is a rapid estimation of ionic content, thus served useful in tests of pure phases in dilute systems. Conductivity measurements were performed with a SevenMulti pH meter from Mettler Toledo with a conductivity expansion unit.

3.2.5 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The accurate measurement of ionic content for various species, namely calcium and sulfur, was performed via inductively coupled plasma-optical emission spectroscopy. In this technique, samples of a diluted solution are put through an inductively coupled plasma to excite the atoms in solution, producing a distinct electromagnetic radiation at wavelengths characteristic of that particular element. In the experiments for this study, all were performed with an iCAP 6300 Dual view ICP-OES from Thermo Scientific. Samples were prepared for ICP-OES by dilution of filtered sample with a 2% nitric acid solution.

3.2.6 Total Organic Carbon (TOC)

Total organic carbon is a measurement technique in which the total carbon content in solution is measured by combusting all carbon containing species in a solution and detecting the resulting carbon dioxide with an IR analyzer, after reacting all inorganic carbon via sparging. This measurement is useful in the determination of adsorbed organic containing species for adsorption isotherms. All TOC analysis was performed on a

Shimadzu TOC Analyzer. Sample preparation for this technique required just centrifugation followed by 0.45 micron filtration of the solutions to be analyzed.

3.2.7 Nitrogen Adsorption (BET)

Nitrogen adsorption is a measurement technique in which a sample is exposed to varying partial pressures of nitrogen gas, and adsorbed amounts are measured. This information can be related, via BET analysis, to the surface area of the sample. In this study, BET analysis was used to determine the surface area of gypsum and anhydrite in order to measure adsorption isotherms. Powdered samples are taken and first dehydrated under a N_2 atmosphere at 40 °C for 18 hours [24] before analysis is carried out.

3.2.8 Adsorption isotherms

Adsorption isotherms were measured by TOC analysis of solution containing polymers, either standalone or exposed to a defined quantity of a gypsum, anhydrite, or clay powder. The adsorption amount was determined by the difference between the two.

Surface areas of all powders were obtained via BET Analysis to obtain adsorption isotherms against surface area. Gypsum powders required pre-grinding in a ball mill in order to increase the specific surface area to a measureable amount.

Adsorption experiments were performed by mixing some powder with the polymer solutions in a small beaker, and allowing the solution to equilibrate in an automatic shaker table-bath (OLS Aqua Pro) at 23 °C for some hours. The solutions are centrifuged and then put through a 0.45 micron syringe filter before analysis.

3.2.9 Dilute System Powder Tests

Dilute system powder tests consist of experiments where a powder of an anhydrite containing sample is exposed to deionized water for a period of time, and at varying times during the experiment duration, samples are pulled to analyze for degree of hydration via TGA and ion concentration via ICP-OES. The conductivity can be continuously monitored as well. Samples are continuously stirred through the experiment.

3.2.9.1 Pure phases

Pure phase experiments were carried out in two parts: 1) the confirmation of the thermodynamic switch and ATG retarder efficacy (section 4.2.1 and 4.3.1), and 2) the continuous monitoring of hydration and ATG efficacy (section 4.5.2).

Confirmation of thermodynamic switch

Dilute system powder tests were carried out with anhydrite powder. Approximately 100 mL of a 1:4 solid:liquid ratio was placed in constant stirring in a sealed bottle. The liquid was either pure water or a solution of ATG inhibitor, and the solid was always anhydrite. Bottles were placed at ambient temperature, or at 60 °C or 105 °C. After a defined period (usually approximately one week) the materials were centrifuged and the powders dried at ambient, before TGA analysis to determine degree of hydration.

Continuous monitoring of hydration and ATG efficacy

These experiments consisted of taking a powder and mixing with liquid, similar to above, but at 1:2 ratio. This mixture was placed under constant stirring and monitored continuously for conductivity. At predefined intervals, a sample was pulled from the agitated mixture by a syringe. This sample was then centrifuged, the supernatant was poured off and taken for analysis with ICP-OES, and then the powder remixed with isopropanol to stop hydration.

This was then again centrifuged and the powder dried at ambient before TGA analysis or microscopic analysis.

3.2.9.2 Tunnel rock powder

These experiments (results shown in section 4.5.5) were performed in a manner similar to the above, but instead with a 1:4 solid:liquid ratio. The protocol for preparation of the rock powder, however, was different. It required first a crushing by hand of the tunnel rock powder, then an additional milling in a ball mill to produce a very fine powder. This resultant powder was then used for the experiment in a similar way described above.

3.2.10 Dense system (oedometer) tests

Oedometer tests were performed as described in FGU 2010/007 [13], with significant sample preparation support and materials obtained from Prof. Anagnostou (IGT). An oedometer is depicted in Figure 3, in which a sample is exposed on the top and bottom to a liquid through porous steel plates, and is restricted in movement radially by a steel ring. The top plate is allowed movement along the vertical axis, and its displacement is measured by a dial gauge. Typically a counterpressure is applied, and in all experiments here the counterpressure was about 25 kPa, rendering the experiments more as a free swelling experiment.

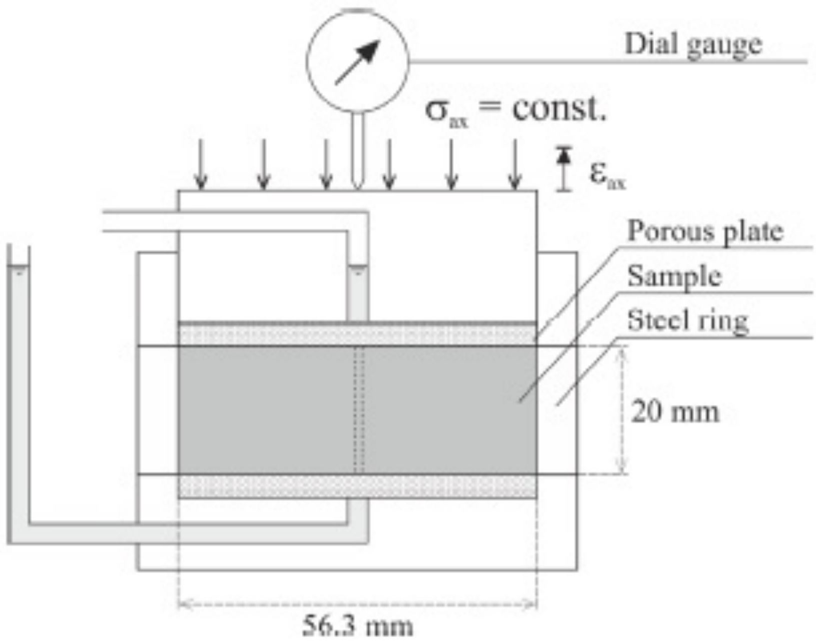

***Fig. 3** Cross section of oedometer cell used in studies. From [13].*

Samples of 20 mm height were prepared by taking crushed and milled tunnel rock powder, and subjecting it to a series of compressions within the oedometer steel ring up to 100 MPa, resulting in a density of approximately 2.0 g/cm^3.

A first series of oedometer tests was solely at ambient temperatures, and used 3 samples with 3 different fluids: calcium sulfate saturated fluid, a 0.1% Retardan L solution, and a 5 wt% diaminobutane dihydrochloride solution. Results are detailed in section 4.4.

The second series was performed with two oedometers. In this experiment, both oedometers were first placed in a 60 °C oven to allow clay swelling, then one oedometer was removed and placed in ambient to allow ATG conversion. As its ATG conversion proceeding and swelling continued, then second oedometer was then removed from the oven and placed at ambient temperature, but its fluid was replaced by an ATG inhibitor solution. Results are also detailed in section 4.4.

3.2.11 Massive block tests

A series of experiments were carried out in which massive blocks of Villarlod molasse were obtained to simulate a potential field test with clay swelling inhibitor. The obtained blocks from the Villarlod quarry were 0.5x0.5x0.5m and 0.5x0.5x1.0 m in size. The experiment consisted of drilling holes within the blocks, sealing the blocks to prevent evaporation, and then filling the holes with water or inhibitor (5 wt% diaminohexane dihydrochloride) solution. The deformation at varying points along the block was measured via LVDTs. The experimental procedure and results are described in more detail in section 4.6.

4 Results and Discussion

The following section gives the results of the tests described in Chapter 3. Within this section, the discussion of the results is included with the results.

4.1 Swelling clay dependence on temperature

The results of the experiment illustrating intracrystalline swelling strains at varying temperatures using Villarlod molasses are shown in Figure 4. In these experiments, it is clearly shown that temperature has a negligible effect on swelling strain of Villarlod molasse, regardless of treatment status with clay swelling inhibitor. This behavior is expected behavior for intracrystalline swelling, which generally shows small dependence on temperature [25]. This confirms that the later experiments of the thermodynamic switch should not see a large change in swelling strain at elevated temperatures.

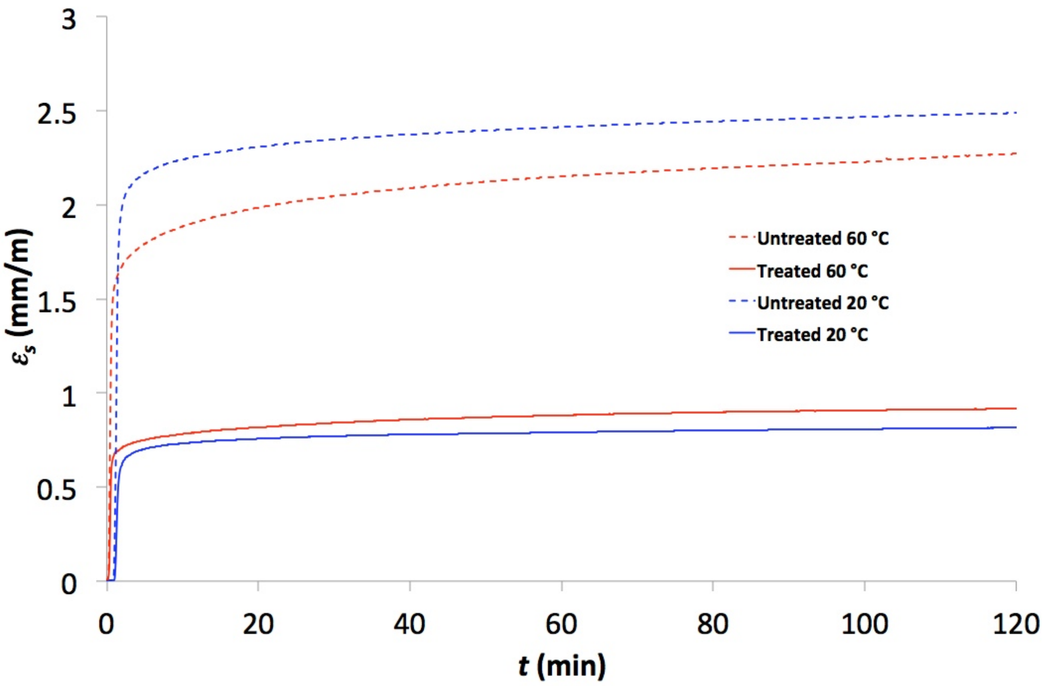

Fig. 4 *Swelling strain of treated and untreated Villarlod molasses samples at varying temperatures. Dashed lines show untreated samples, and red lines show samples at 60° C.*

4.2 Thermodynamic “Switch”

The tests to confirm the efficacy of the so-called thermodynamic “switch” are detailed in the following. First tests were performed on dilute systems with pure materials, followed by dilute systems with crushed tunnel rock, and finally performed on dense systems, i.e. ground and compressed tunnel rock.

4.2.1 Pure materials

Figure 5 shows the results of the TGA tests on pure anhydrite. With pure anhydrite powder exposed to water at 20 °C for a duration of one week, a clear water loss is observed in the range of 100-150 °C, which is the expected water loss for gypsum. The theoretical water loss for full conversion of gypsum is approximately 20%, so this indicates almost complete conversion.

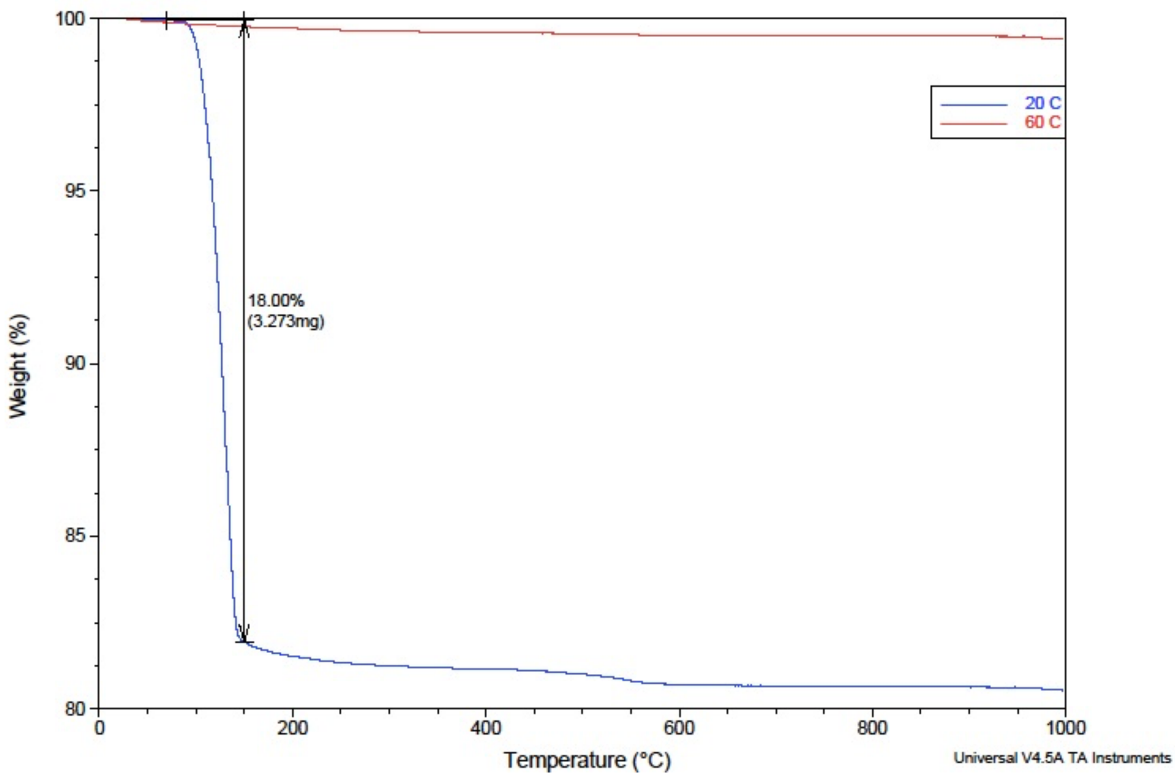

Fig. 5 *TGA curve of pure anhydrite samples exposed to water at 20 °C and 60 °C. Water loss of 20 °C sample indicates conversion to gypsum, while no water loss of 60 °C sample indicates no conversion.*

The results of this experiment demonstrate that the chosen temperature of 60 °C is adequate to hinder ATG conversion for pure anhydrite, and can thus be expected to hinder ATG conversion in geological samples.

4.2.2 Crushed tunnel rock

Figure 6 demonstrates the result of the test on crushed tunnel rock. The tunnel rock sample chosen was taken from the Chienberg tunnel, as indicated in section 3.2.9.2. Materials pulled from actual sites can have some native gypsum. Therefore, it is necessary to characterize also the initial state of the tunnel rock with respect to gypsum using TGA. TGA curves for the unwetted tunnel rock powder, and the rock powder exposed to water at 20 °C and 60 °C, are shown in the figure. It is clear to see that the powder exposed to 20 °C has additional water loss compared to the fresh tunnel rock powder. Additionally, it is clearly seen that the rock powder exposed to water at 60 °C shows no additional water, and thus no new gypsum has formed. This confirms that the thermodynamic switch functions as expected on geological samples.

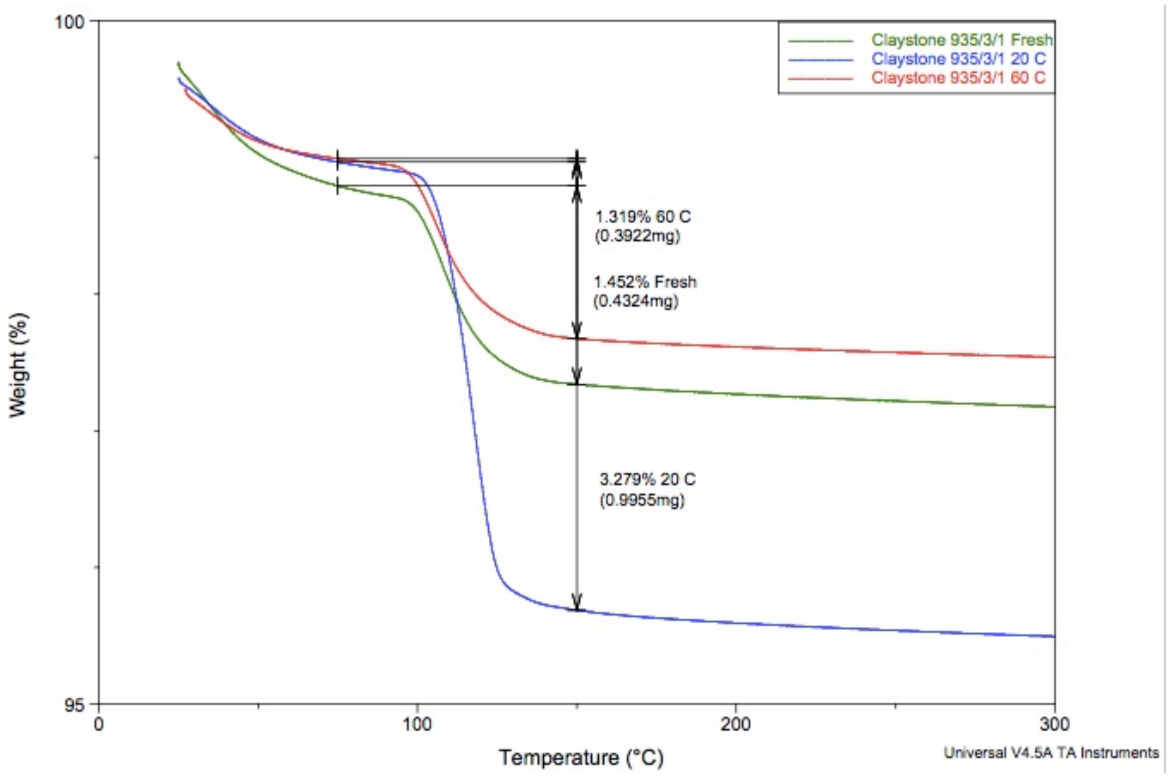

Fig. 6 *TGA curve of crushed tunnel rock powder in the fresh state, and exposed to water at 20 °C and 60 °C. Only 20 °C rock powder has additional mass loss, indicating ATG conversion.*

4.3 Anhydrite-to-Gypsum Inhibitors

As TGA is a proven method to indicate if ATG has taken place as seen in the previous results, the following results center on the use of TGA to indicate if ATG has taken place in samples treated with ATG inhibitors. These inhibitors are first tested on pure materials, then on crushed tunnel rock, in a similar strategy seen previously which used temperature to inhibit ATG.

4.3.1 Pure materials

Figure 7 shows the results of the test in which Retardan L and Retardan 200L from Sika are tested as chemical inhibitors of ATG in the pure anhydrite, compared to a control sample with no treatment. Inhibitor concentration was at 1%, and a solution/powder ratio of 5 was used. All samples were kept at 20 °C. It is clear that the inhibitors have functioned and have completely inhibited the ATG conversion, as evidenced by fact that no water loss indicative of gypsum formation is observed.

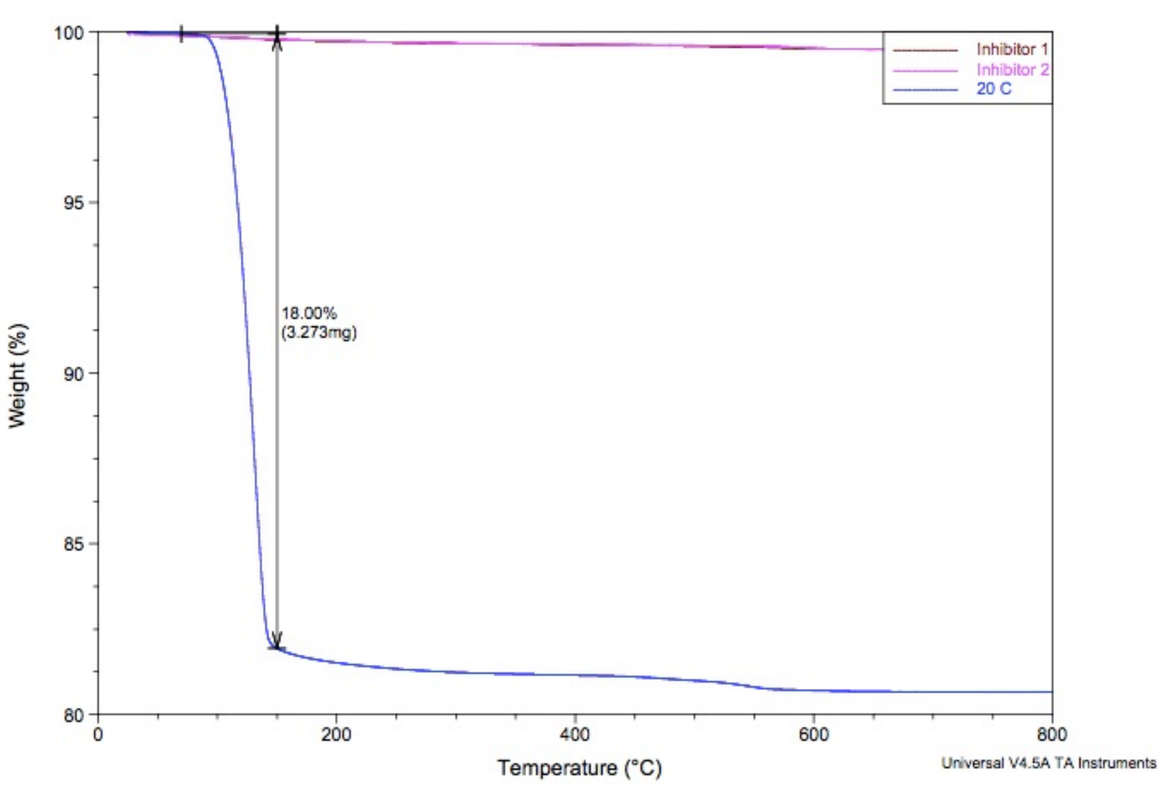

Fig. 7 *TGA Curves of control sample (20 °C) and Sika Retardan and Retardan 200 (indicated as Inhibitor 1 and Inhibitor 2, respectively). No gypsum formation is observed with inhibitor samples.*

4.3.2 Crushed tunnel rock

Figure 8 shows the result of a test in which crushed Chienberg tunnel rock powder was tested in a manner similar to the pure anhydrite powder of section 4.3.1. Only Retardan L was tested, as it was demonstrated that Retardan 200L functions similarly, and the dosage was similar to the pure anhydrite test, at 1% with a solution/powder ratio of 5. In the test, the TGA curves show no additional gypsum formation has occurred in the sample with Retardan L, indicating the efficacy of this retarder in the prevention of ATG conversion in geological samples.

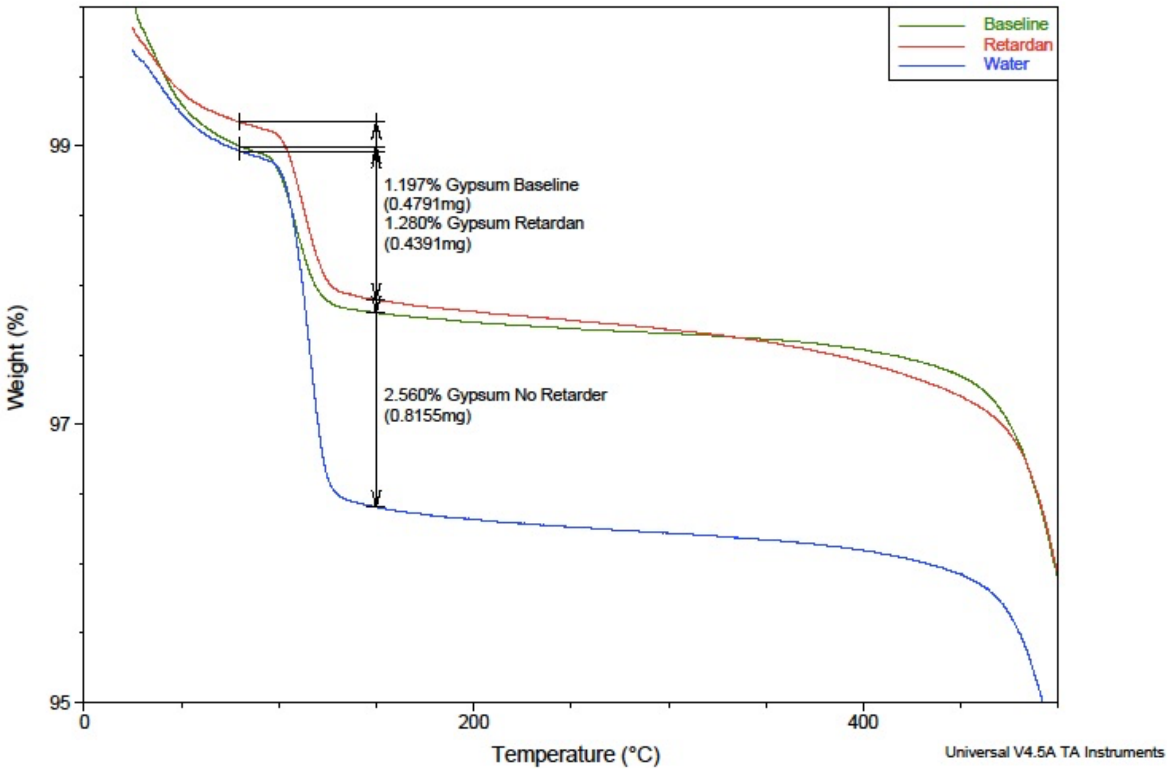

Fig. 8 *TGA Curves for crushed Chienberg tunnel rock samples, with baseline, control sample (20 °C) and Sika Retardan L. No new gypsum formation observed in sample inhibited with Sika Retardan L.*

4.4 Oedometer Tests

Two sets of oedometer tests were performed and are detailed below, each with the intent of demonstrating the efficacy of the swelling inhibitors. Both tests were performed with samples of pressed tunnel rock from the Belchen tunnel. The pressing procedure is described in section 3.2.10. The tunnel rock composition is seen in Table 1, taken from cores from FGU 2010/007 [13].

Tab. 1 *Belchen Tunnel Rock Rietveld Analysis*

Component	**Weight %**	**Error**
Anhydrite	43.1	1.0
Chlorite	4.5	0.5
Illite/Muscovite	6.5	0.7
Magnesite	11.6	0.6
K-feldspar	4.5	0.5
Pyritre	0.7	0.2
Quartz	5.1	0.3
Smectite/Corrensite	24.0	1.8
SUM	100	

Rock from the Belchen tunnel was used due to the lack of enough sample of the previous Chienberg tunnel samples. In addition, the Belchen tunnel samples had a higher anhydrite component and no native gypsum, which made the experimentation and subsequent analysis simpler.

Figure 9 shows the results of the first oedometer test. In this test, 3 oedometers were saturated at room temperature (20 °C): one with saturated calcium sulfate solution, one with clay swelling inhibitor (5% diaminobutane dihydrochloride), and one with ATG inhibitor (0.1% Sika Retardan L). The solution was more dilute than previous experiments due to experimental error. From this experiment, many things can be seen.

First, it is clear that the clay swelling inhibitor is ineffective in these relatively short term experiments. This can be explained based on the swelling inhibitor's known mechanism [6-7] which shows that the amine groups of the diamine exchange for the counterbalancing cations in the interlayer space and restrict swelling by holding the opposing layers together. This however requires a certain amount of intracrystalline swelling to take place, which can increase the initially dry clay layers (layer spacing 10 Å) by 6-7 Å, an increase in swelling of up to 70%. It is not clear, however, why the clay inhibitor sample actually swells *more* than the control sample. It is quite possible that the somewhat open conditions of the oedometer lead to conditions in which the diamine swelling inhibitor can crystallize and thus exert an additional crystallization pressure. Swelling with swelling inhibitor solution also tends to be a very rapid process, and the swelling dynamic change compared to swelling with water can lead to an alteration of the dissolution, nucleation, and growth process so important in ATG. This alteration could lead to higher swelling due to ATG. Whatever the source of the additional swelling, it is clear that the clay swelling inhibitor is not necessarily useful to impede initial swelling, as was proposed initially, because of intracrystalline swelling. Their demonstrated efficacy in impeding osmotic swelling [6-7,26], however, does not preclude their use to inhibit swelling in tunnels, however, as osmotic swelling is a noted problem in swelling in Swiss tunnels, particularly through clay-rich formations such as Opalinus clay [27]. Therefore, on the short term they could be damaging, but possibly a useful longer term solution.

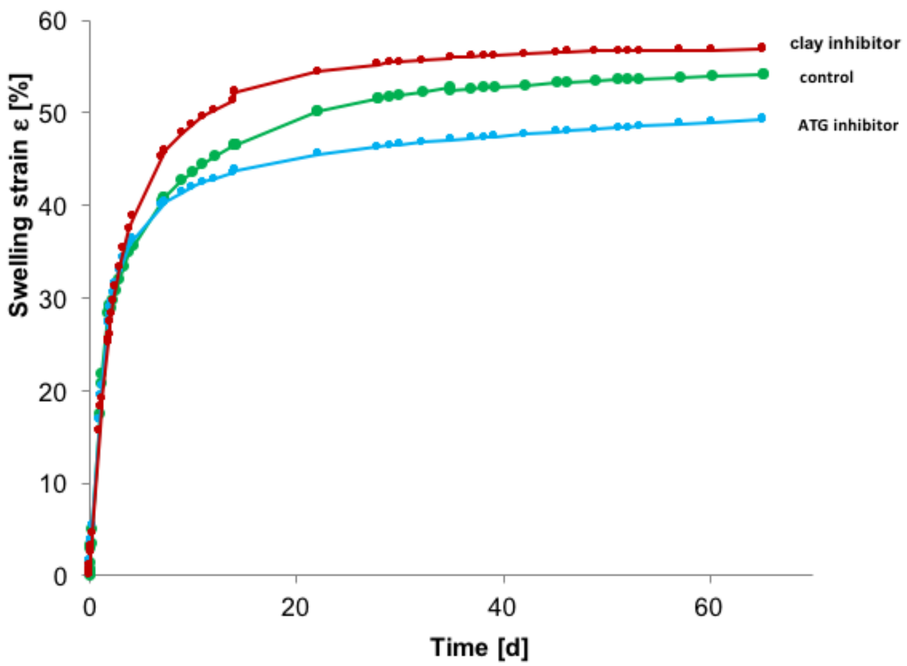

***Fig. 9** Result of 1st Oedometer test series. Results indicate inefficacy of clay swelling inhibitor, as well as inadequacy of dosage of ATG inhibitor (0.1% rather than 1%).*

The other important thing to note from this experiment is that while it appears that the ATG inhibitor was not functioning very well (only 10% reduction in swelling compared to control), TGA analysis shown in Figure 10 demonstrate that the ATG process was actually impeded by 50% after 60 days with this low dosage of inhibitor. Based on the Rietveld analysis of the Belchen tunnel rock, full ATG conversion would result in a 10% weight loss in TGA within the temperature range of 80-120 °C, which is observed in the calcium sulfate saturated sample. A similar drop is observed in the swelling clay retarder sample, demonstrating that nearly full conversion had taken place, and which also shows an additional drop at a temperature where the inhibitor pyrolizes. Indeed, this additional weight could be crystallized inhibitor (or crystallization of the exchanged salt), which was hypothesized earlier. The sample with Sika Retardan L, however, showed approximately half the weight loss of the saturated calcium sulfate solution sample.

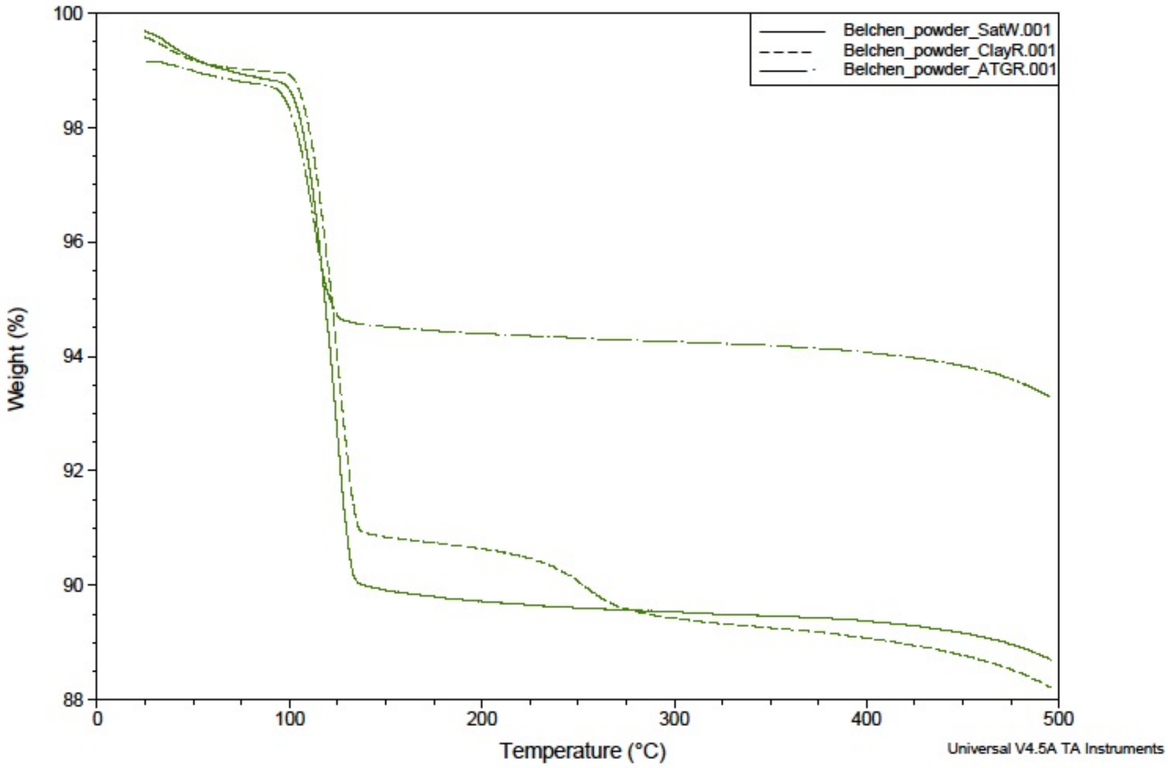

Fig. 10 *TGA analysis of the samples of the first oedometer experiment.*

After this experiment, an additional oedometer test was carried out and is pictured in Figure 11. This experiment is the key experiment of the entire study. In this experiment, crushed Belchen tunnel rock powder was pressed and placed in two oedometers with minimal (5 kPa) counterpressure, which were saturated and placed in an oven at 60 °C. An initial swelling to approximately 15% swelling strain is observed in both samples. Considering the results of section 4.1 and section 4.2, this can be reasonably assumed to be purely clay swelling. At the first point indicated in the figure, oedometer 1 was removed from the oven and placed in an environment with 20 °C. One would expect then that ATG takes place and that swelling can be observed, and this is indeed the case. Next, oedometer 2 was removed from the 60 °C environment and placed in a 20 °C environment, however its fluid was then replaced with 1% Sika Retardan solution instead of saturated calcium sulfate solution. It is clear that the ATG conversion is stopped by the solution of inhibitor, as no increase in the swelling is recorded. The experiment was ended before the first oedometer could reach full swelling potential (approximately 50% based on the first oedometer experiment) because of the need to reserve oedometers for other experiments. TGA analysis later confirmed that there was no conversion of ATG in oedometer 2 (with Sika Retardan L), but with >90% conversion in oedometer 1 (with no retarder).

The implications of this experiment are many. First, it is proof of the basis behind the entire research project, which is the decoupling of the clay- and ATG- swelling phenomena for further study. This strategy has been implemented in other projects [11] successfully as a result of this research and offers a new strategy for studying this persistent geotechnical engineering problem in Switzerland, Germany, Spain and other countries that have these geological formations. In the study of mitigation techniques on the material scale, this strategy should prove invaluable.

Another result of this study shows that clay swelling (at this counterpressure) reaches 15% for this particular claystone, or approximately one third of the total swelling potential. If one considers that based on Table 4, the rock samples are approximately 25% swelling clay, and that the clay layers in the completely dry state are 10 Å, one can come to the calculation that the clay layers are expanding by approximately 5-6 Å, or two water layers [3]. Based on this calculation, one can see why the clay swelling inhibitors in the initial oedometer experiment failed, as their intercalation is of the same order of magnitude. Therefore, it is not recommended to add these clay swelling inhibitors to completely dry claystone, although they could be useful on the longer term.

The most consequential result in the context of this study, however, is that the ATG inhibitors have been demonstrated unequivocally to function in their role of inhibiting the transformation of anhydrite to gypsum and the ensuing swelling from crystallization pressure. This means that provided they can be delivered to any affected material area, they will prevent swelling from this phenomenon.

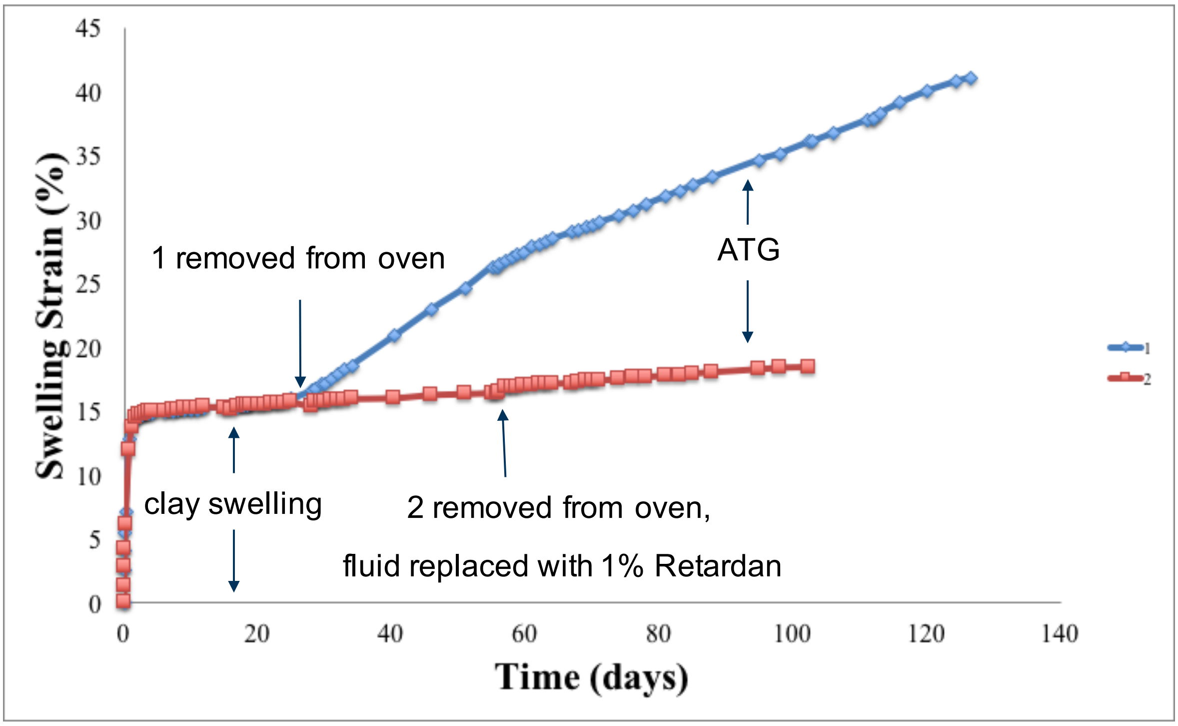

Fig. 11 *Result of 2nd Oedometer test series. Two oedometers were saturated and placed in a 60 °C oven to allow clay swelling. At indicated point, 1st oedometer was removed to 20 C environment, where immediately ATG conversion took place as seen. At second indicated point, 2nd oedometer was removed and placed in 20 °C environment, but fluid was replaced with 1% Sika Retardan solution. ATG clearly is stopped as can be seen compared to 1st oedometer.*

4.5 Anhydrite-to-Gypsum Inhibitors – working mechanism

The following section details more in depth the studies of the working mechanism of the ATG inhibitors, based on the results of a master thesis work [28]. The studies consist of the combination of adsorption isotherms and solution analysis via conductivity studies and inductively coupled plasma optical emission spectrometry (ICP-OES), as well as microscopy studies. The first study corresponded to adsorption isotherms coupled with ICP-OES, conductivity, and microscopy studies on pure materials [28] and the second study corresponded to the use of conductivity, ICP-OES, and microscopy studies combined with TGA analysis on the tunnel rock [29].

4.5.1 Pure phases: Adsorption

Adsorption studies were carried out with clay swelling inhibitors and ATG inhibitors on 3 surfaces: gypsum, anhydrite, and montmorillonite clay. In the case of clay inhibitors, their adsorption on clay surfaces is well known and is not detailed here. Additionally, the clay swelling inhibitors showed no affinity for the gypsum and anhydrite surfaces, and they are ignored from here on. The ATG inhibitors also showed no affinity for clay surfaces, which is also shown in the conductivity studies. Therefore, only ATG inhibitors and their affinity for calcium sulfate surfaces are shown.

As detailed in section 3.1.4, the ATG inhibitors tested were the Sika products Retardan and Retardan 200, polyacrylic acid (PAA), and diethylenetetraminepentaacetic acid (DTPA).

Adsorption was not carried out on geological samples, because with the variety of phases, it would not necessarily be understood which phase was being adsorbed onto.

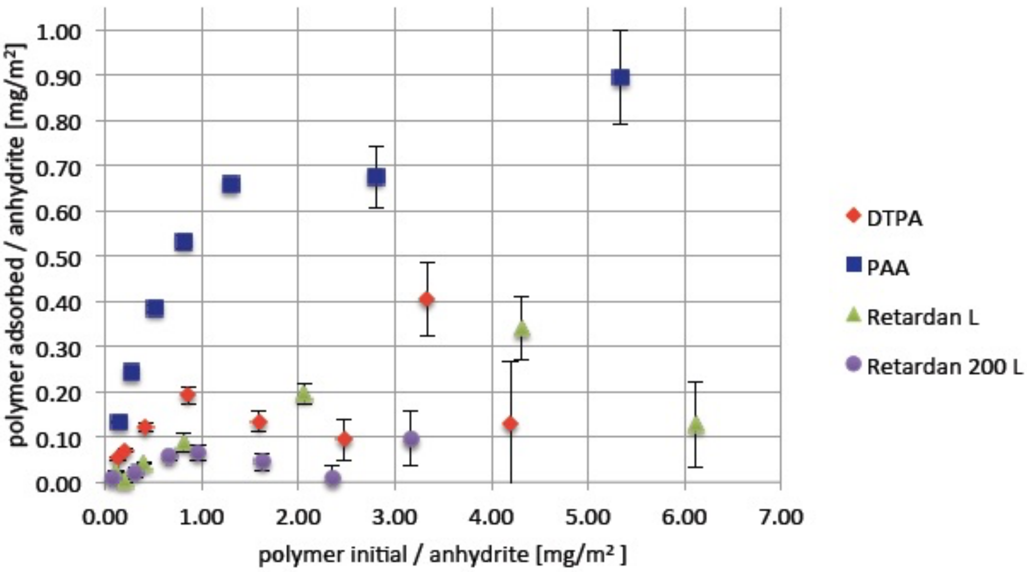

***Fig. 12** Adsorption isotherm of various adsorbates onto anhydrite.*

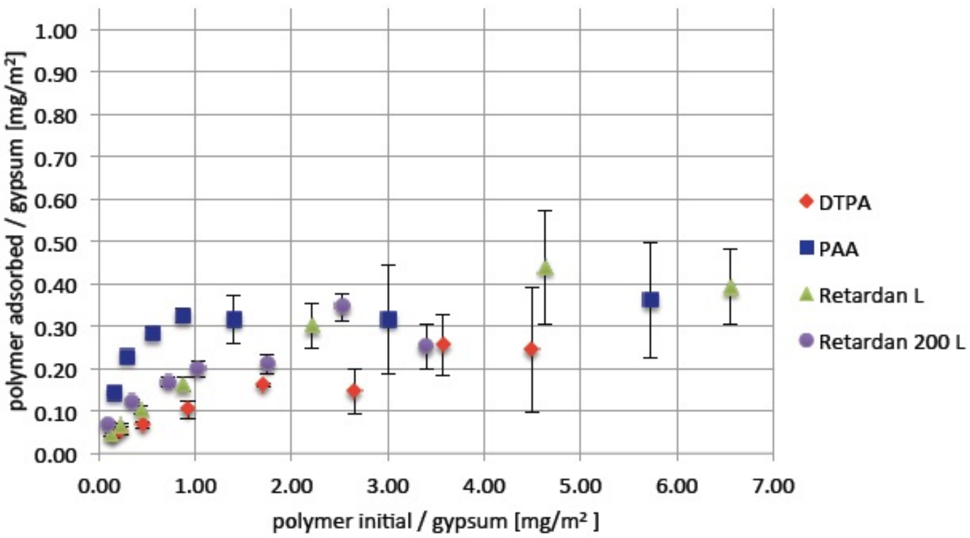

***Fig. 13** Adsorption isotherm of various adsorbates onto gypsum.*

Figures 12 and 13 show the results of the adsorption studies. Certain features can be noted. On a per mass basis, PAA adsorbs in much higher amounts to any calcium sulfate surface compared to the Sika products and DTPA.

4.5.2 Pure phases: Conductivity and ICP-OES results

The results of following the conductivity of ATG with anhydrite are seen in Figures 14 and 15 for pure anhydrite, and anhydrite with the various inhibitors. One can observe first that with pure anhydrite, the conductivity increases initially, and then slowly decreases with time before reaching a stable value. This conforms with the conversion of the anhydrite to gypsum, and is expected as the concentration (and thus the conductivity) of the solution would increase initially to solubility of anhydrite, and then slowly decrease to the solubility of gypsum.

The behavior of DTPA is markedly different from the other inhibitors and is seen in Figure 14. One observes that DTPA serves simply as a delay to the conversion of anhydrite to gypsum, and this delay increases with increasing DTPA concentration. The same general trend is observed in the conductivity as well, although the use of DTPA creates a higher conductivity due to the addition of DTPA as an ionic species in solution. The final thing to note is that while the addition of clay has a significant impact on the conductivity of the solution, it has no real impact on the conversion of anhydrite to gypsum. One can then reasonably assume that the clay has minimal interaction with DTPA as an ATG inhibitor.

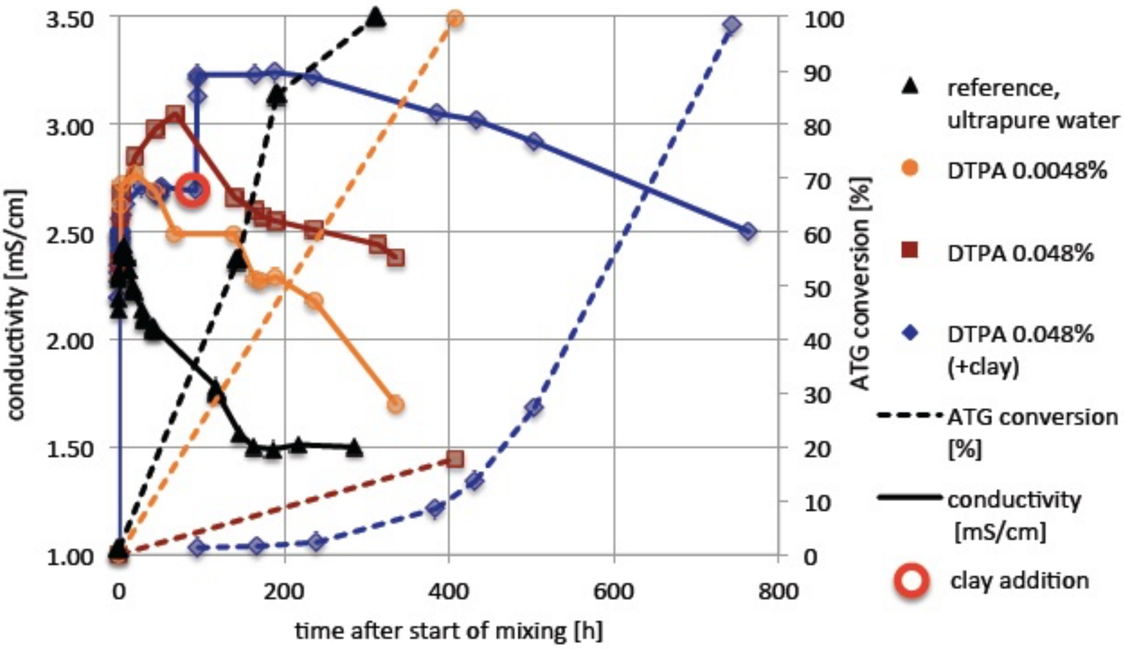

Fig. 14 *Conductivity vs. time of pure anhydrite, anhydrite with varying DTPA content, and with clay addition. Also plotted is ATG conversion. Clay added to 0.048% DTPA sample to observe if clay could consume DTPA.*

In Figure 15, one observes the behavior of PAA and the two Sika products as ATG inhibitors in terms of conductivity. This is also compared to the reference system with no inhibitor as in Figure 14. It is clear to see that for the duration of the experiment, all inhibitors are effective at retarding the ATG conversion. This does not change when clay additions are made (i.e., the ATG is still inhibited). While there is initially a spike in conductivity as well as a drift in the conductivity post clay addition, this is only related to the clay and ion exchange with the clay, and has no bearing on the ATG conversion.

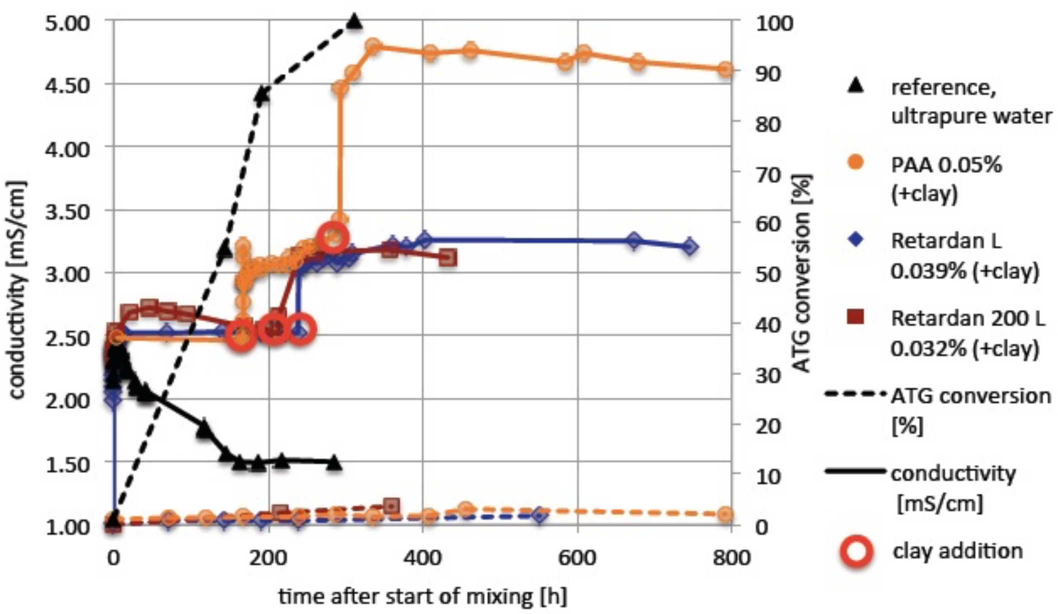

Fig. 15 *Conductivity vs. time of pure anhydrite, anhydrite with PAA, Retardan L, and Retardan 200L, and with clay additions. Also plotted is ATG conversion. Clay added to Retardan L and Retardan 200L samples to observe if consumption occurs.*

Figure 16 shows the calcium concentration with time after mixing as measured by ICP-OES. The calcium concentration decreases with time, as expected, for the case of the reference mixture. One would expect that it reaches a maximum at close to the solubility of anhydrite and decreases to the solubility of gypsum, each one respectively being about 25 mmol/L (1000 mg/L) and 15 mmol/L (600 mmol/L). One also observes a corresponding decrease in the concentration of Ca with the DTPA, that also coincides with an increase in the ATG conversion of Fig. 14.

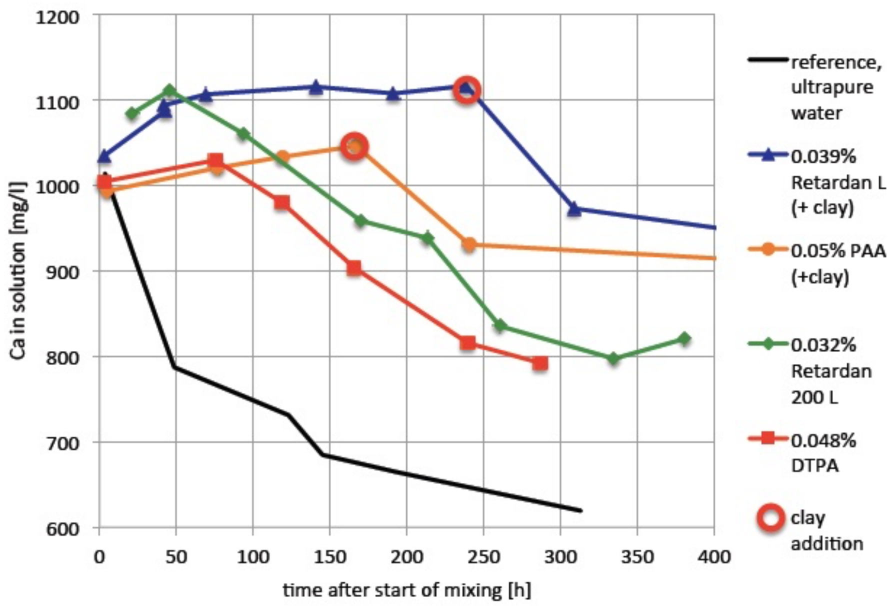

Fig. 16 *Ca concentration vs. time after mixing for all tests of Figs. 14 and 15. Ca concentration decreases over time when conversion occurs in the case of the reference or with DTPA, and decreases only due to ion exchange with the clay in the case of PAA, Retardan L and Retardan 200L.*

There are also drops in Ca concentration in the case of the effective ATG inhibitors. These are primarily related to ion exchange processes, as they clearly do not correspond to ATG conversion. PAA and Retardan L showed a drop in Ca concentration only after the addition of clay. This is understood to result from exchange of Ca into the clay interlayer, so that the decrease in the Ca content does not reflect any ATG conversion. In the case of Retardan 200L, there is a steady decrease in the Ca concentration, even without clay addition. The source of this decrease is not well understood, but most certainly does not correspond with the formation of gypsum. This could correspond to the formation of another calcium containing phase.

4.5.3 Pure phases: Microscopy results

The SEM results of the studies on pure phases are seen below. All images have been taken at 300x magnification to allow comparison across images. In a pure ATG system in Figure 17, the platy crystals of anhydrite convert to the familiar large needle morphology of gypsum.

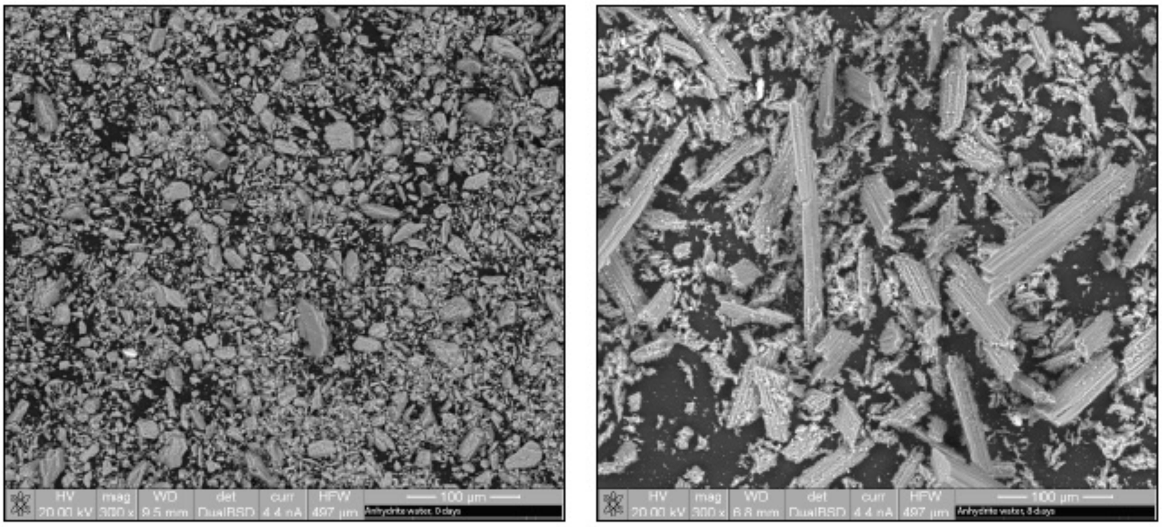

Fig. 17 *SEM micrographs of reference system of anhydrite exposed to water, (left) before exposure and (right) after 8 days exposure. Both images at 300x magnification.*

In Figure 18, one can see that anhydrite exposed to DTPA after 17 days alters the morphology significantly. As seen from TGA results, the ATG process is merely delayed for the duration of the experiment, rather than inhibited. This means that the Figure 18 depicts gypsum crystals, but with a much altered morphology as compared to Figure 17. DTPA allows the formation of many small gypsum crystals but none of the large needles seen in Figure 17.

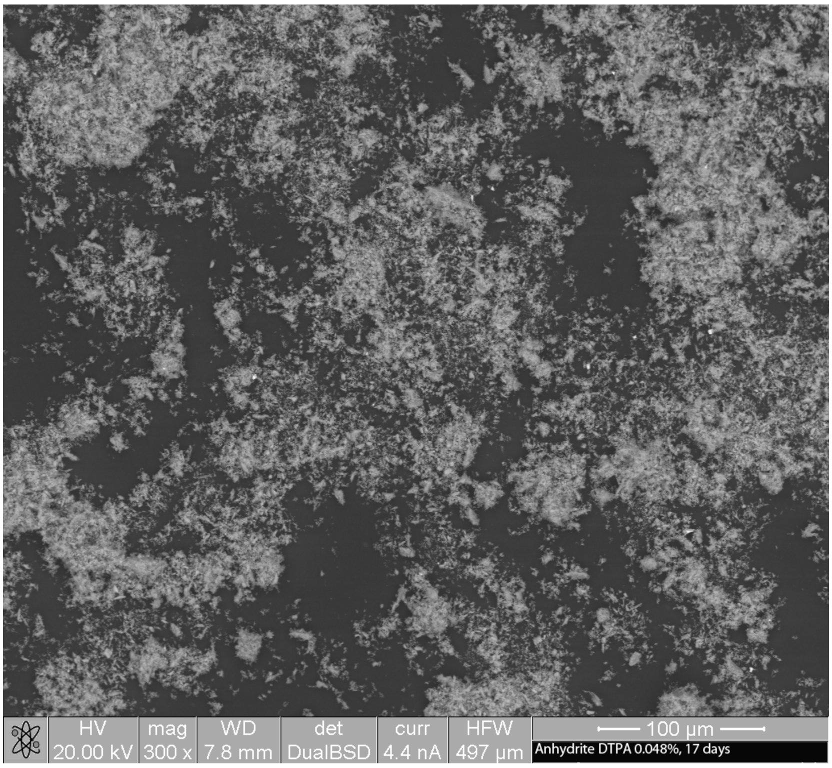

Fig. 18 *SEM micrograph of anhydrite exposed to DTPA 0.048% solution after 17 days, magnification of 300x.*

Figures 19 and 20 show the effect of PAA and Retardan L on the ATG process, respectively. TGA results indicated no formation of gypsum for the duration of the experiment. The morphology of the anhydrite crystals is not significantly altered from the initial platelike morphology, and the size is not changed very much, although in PAA it appears that some dissolution may have occurred.

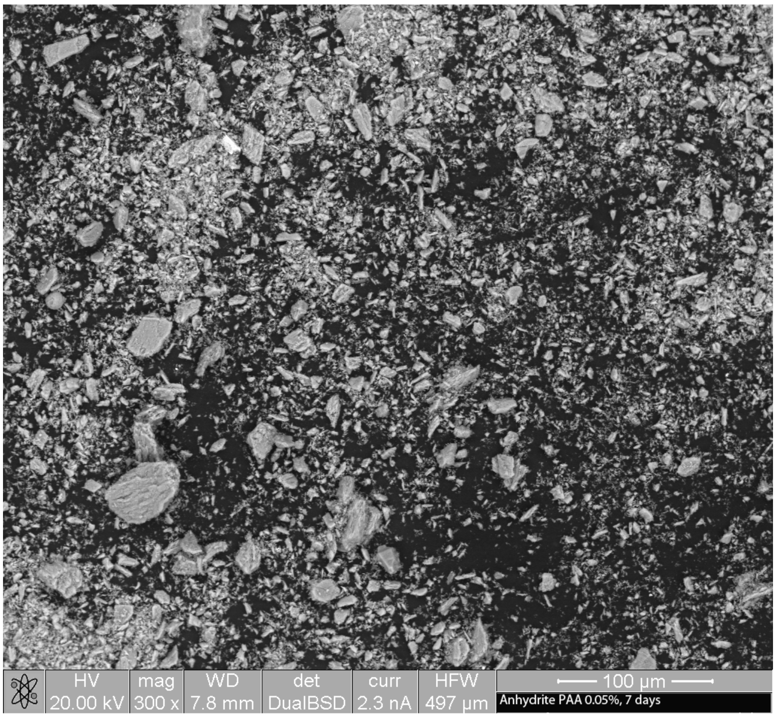

Fig. 19 *SEM micrograph of anhydrite exposed to PAA 0.05% solution after 7 days, magnification of 300x.*

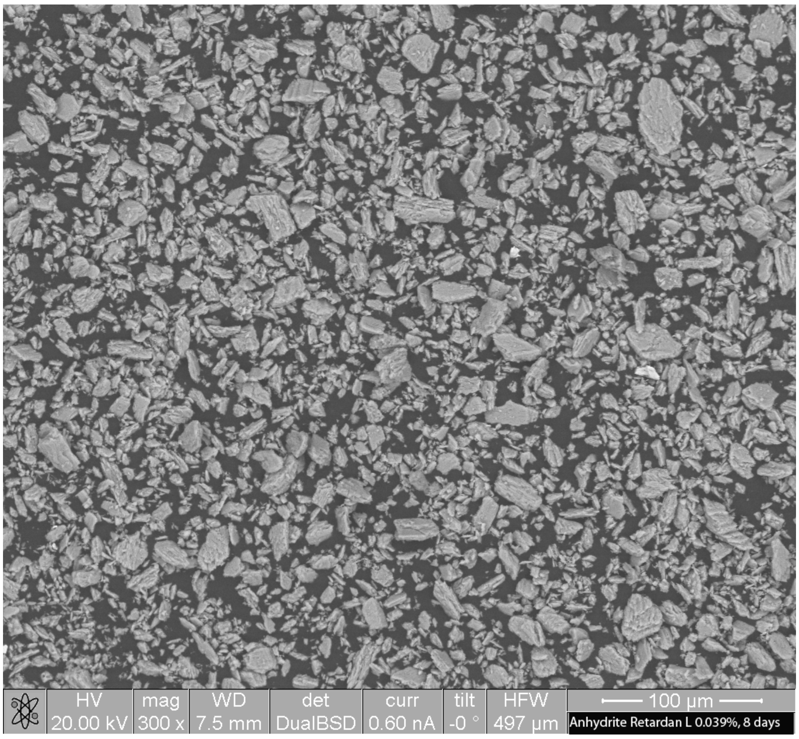

Fig. 20 *SEM micrograph of anhydrite exposed to Retardan L 0.039% solution after 8 days, magnification of 300x.*

Figure 21 shows the effect of Retardan 200L, which completely inhibited the formation of gypsum according to TGA results. The size of the crystals following the experiment, however, is significantly reduced. This inhibitor allowed the dissolution of anhydrite to occur to a certain degree.

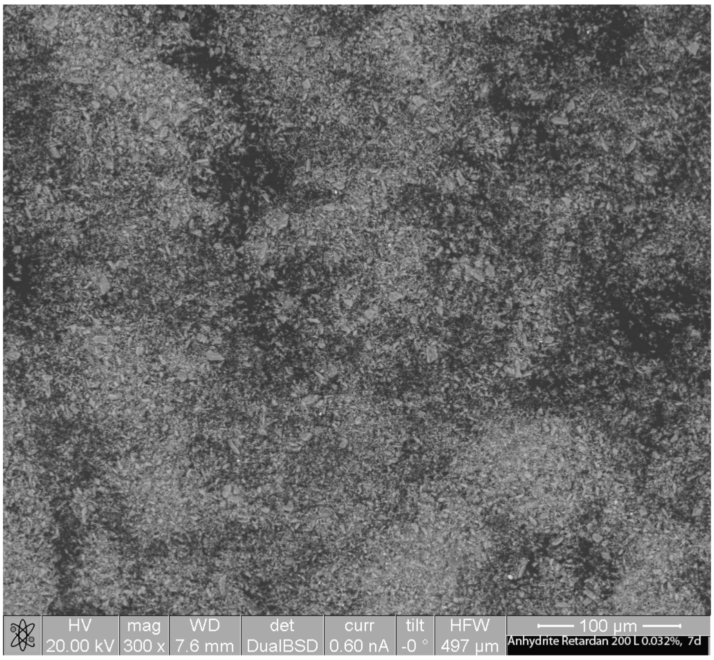

Fig. 21 *SEM micrograph of anhydrite exposed to Retardan 200L 0.032% solution after 17 days, magnification of 300x.*

4.5.4 Working mechanism of ATG Inhibitors

The results described in sections 4.5.1, 4.5.2, and 4.5.3 are interpreted so that these inhibitors have 3 primary mechanisms: 1) inhibition of both dissolution and growth and/or nucleation poisoning (PAA and Retardan L) through surface adsorption, 2) poisoning of nucleation and/or growth through surface adsorption (Retardan 200L), and 3) retardation of dissolution and growth primarily through complexation and/or surface adsorption (DTPA).

PAA and Retardan L: Both of these inhibitors showed adsorption to both gypsum and anhydrite in their adsorption isotherms, with PAA in particular showing a very strong adsorption compared to all other inhibitors. The unaltered morphology of the anhydrite crystallites suggests that dissolution is strongly inhibited via surface adsorption. The ICP results, however, show a very high content of calcium in solution: around 25-28 mmol/L, well above the saturation of gypsum. This suggests that these inhibitors are also poisoning gypsum nuclei or poisoning nucleation sites to inhibit gypsum precipitation.

Retardan 200L: This inhibitor showed adsorption to both gypsum and anhydrite as well, but the ensuing morphology of the anhydrite suggests that this inhibitor does very little to inhibit dissolution. The adsorption to gypsum in the case of this inhibitor was anyway much stronger than that to anhydrite, with a 5X difference in the plateau. What is very interesting and difficult to explain is the calcium content in solution. The calcium content decreases constantly through the experiment, from a concentration of 25 mmol/L down to 20 mmol/L. However, there is no gypsum formed at all, as confirmed by TGA. This final concentration is quite interesting as it is the saturation concentration of anhydrite, so it is quite possible that Retardan 200L allows the dissolution of the anhydrite initially, but supports the growth of other anhydrite morphologies. This would explain the removal of calcium from solution. It does not however preclude the formation of other calcium containing phases, such as calcium carbonate, which is a possibility as these solutions were not so well protected against the atmosphere. The presence of very fine particles and defective surfaces may also account for an initial dissolution that then stabilize when the fine particles have dissolved and the surfaces “annealed” in a process of surface energy minimization with analogies to Ostwald ripening.

DTPA: This inhibitor showed adsorption to both the gypsum and anhydrite phases, but TGA results and the final crystals seen by SEM showed that gypsum growth was merely delayed rather than inhibited. The final gypsum crystal morphology, however, was markedly different from the reference case, especially in terms of size. No large gypsum needles were seen, indicating that the gypsum growth was altered significantly by the inhibitor. Additionally, while the calcium in solution begins to decrease in conjunction with gypsum growth, the conductivity of the solution is very high. It is high initially, of course, as the DTPA is already a pentasodic salt, but it increases over the course of the experiment, suggesting that complexation of calcium is occurring. If the DTPA forms a more thermodynamically favorable complex with calcium over adsorption, this is a mechanism to remove DTPA from the surfaces of anhydrite and gypsum. As DTPA complexes calcium it increases the undersaturation of calcium, and increases dissolution, feeding the growth of gypsum.

4.5.5 Studies on geological materials

A master semester project was undertaken [29] using similar methods to the work on pure phases, but with actual tunnel rock from the Belchen tunnel. This work followed the ATG process on crushed tunnel rock powder using conductivity measurements, TGA and ICP analysis. SEM analysis was also performed. The inhibitor concentration was chosen at 1% by mass based upon the results of section 4.4.

The Rietveld XRD analysis is reported in Table 1.

TGA results of rock powder exposed to water is shown in Figure 22. Considering the composition of the rock is primarily anhydrite and clay, some things can be noted from the TGA curve of the unhydrated material, notably the absence of gypsum (confirming the Rietveld results) and the drop around 500 °C due to the dehydroxylation of clay. At a very early stage, the conversion is almost zero, but after 7 days the ATG conversion has commenced, and by 28 days is almost completely converted. A very interesting thing to observe is that there is a mass loss in the range of 750 – 900 °C appearing after 2 days. This is unexpected, possibly corresponding to the formation of a carbonatic phase such as calcite. The Rietveld analysis shows a magnesite ($MgCO_3$) phase up to 10%, and this variation in decomposition temperature could simply reflect the changing particle size with time of the carbonatic phase, or possibly the formation of calcium carbonate.

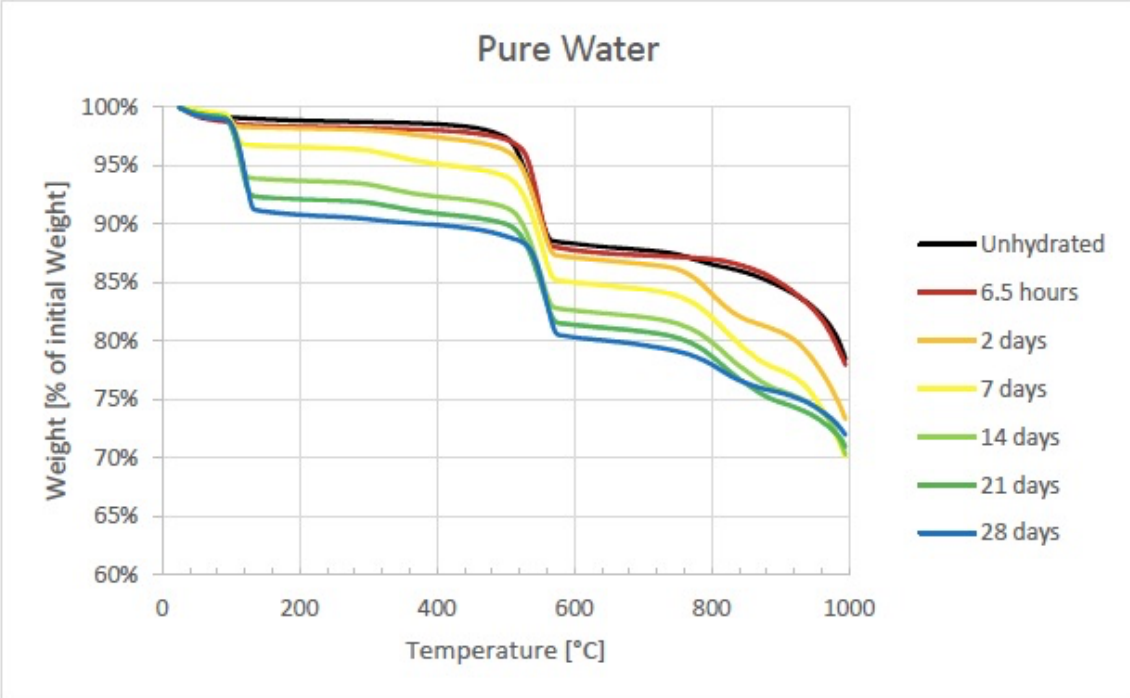

Fig. 22 *TGA results of pure water with Belchen tunnel rock powder. Up to 100% conversion after 28 days is observed. Decrease at 500 °C is due to clay dehydroxylation, and losses around 800 °C are due to calcination of carbonatic phases (most likely magnesite).*

In Figures 23-25, one sees the results of TGA with Retardan, PAA, and DTPA, respectively. In the range of temperatures for loss of water of gypsum, one observes no decrease, as expected. There is mass loss observed at around 300 °C for all, and similarly to the reference, at calcination temperatures.

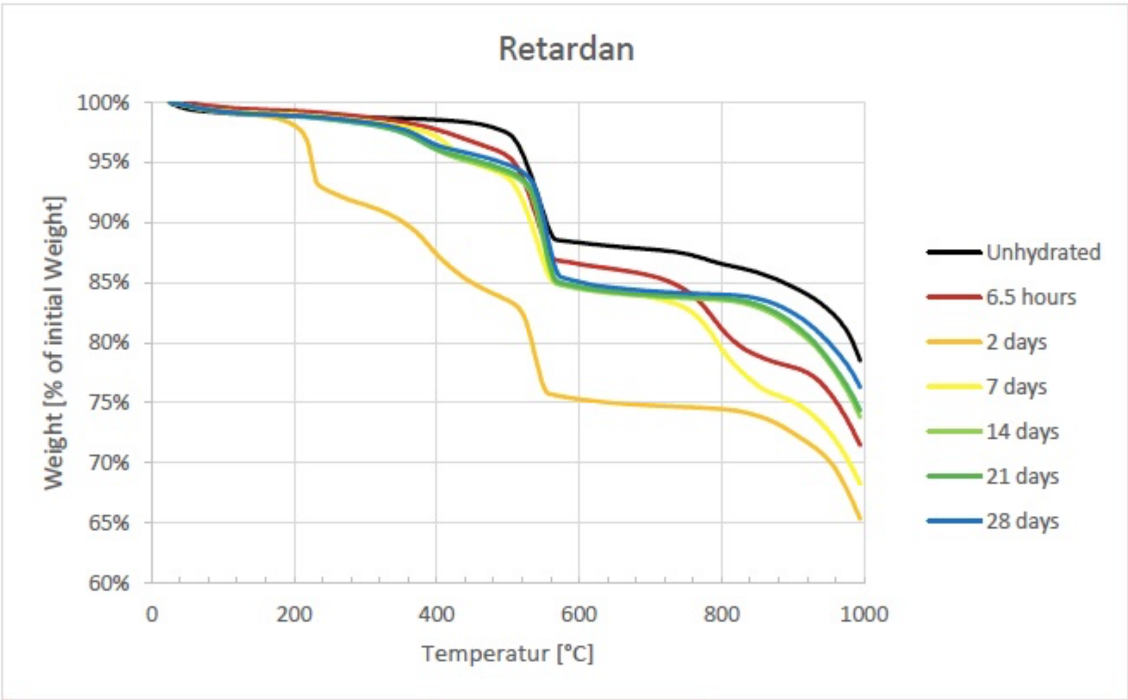

Fig. 23 *TGA results of Belchen tunnel rock powder exposed to 1% Retardan L solution. No gypsum formation observed.*

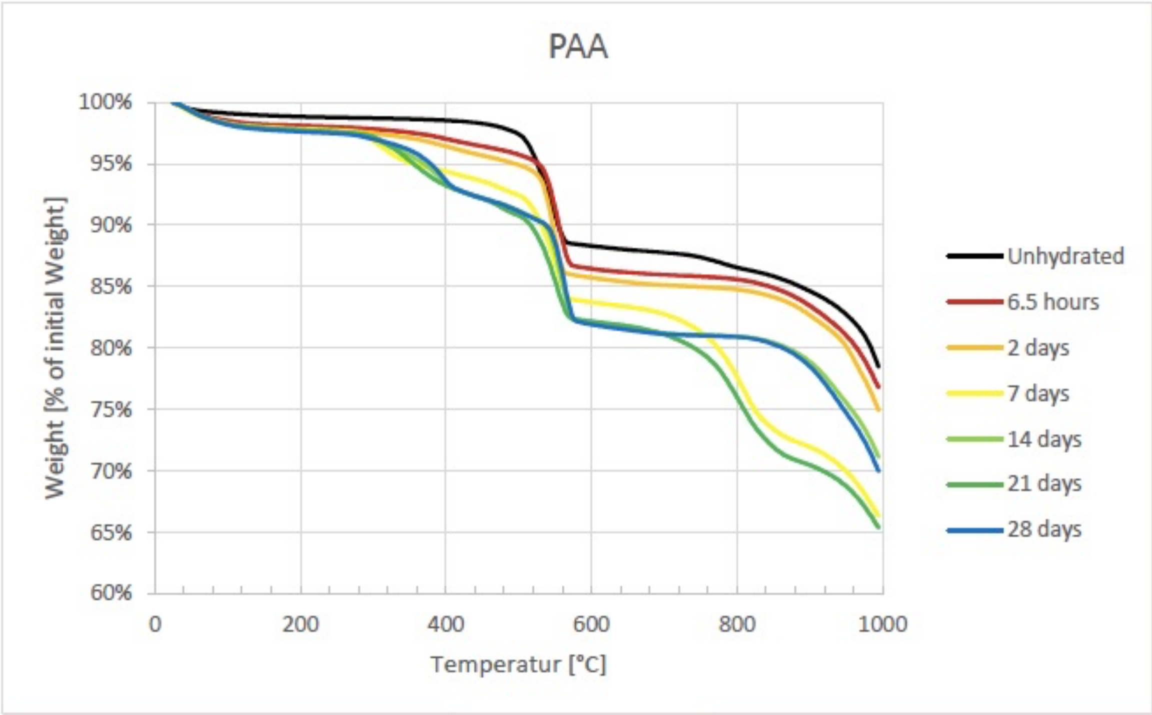

Fig. 24 *TGA results of Belchen tunnel rock powder exposed to 1% PAA solution. No gypsum formation observed.*

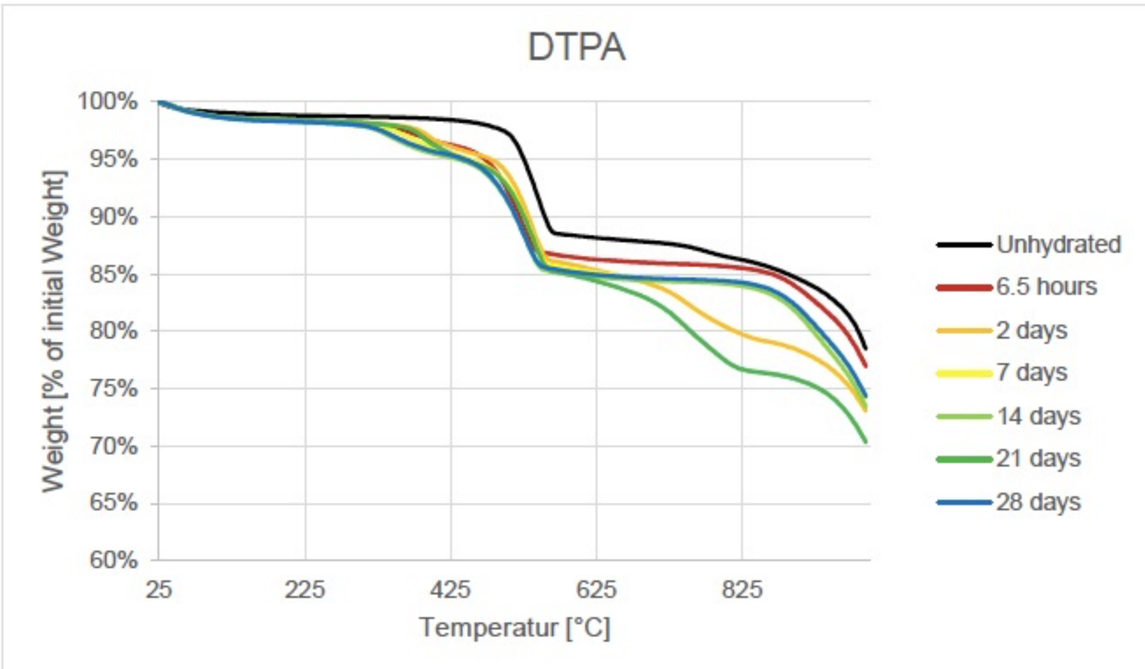

Fig. 25 *TGA results of Belchen tunnel rock powder exposed to 1% DTPA solution. No gypsum formation observed.*

The conductivity measurements are not shown in this report, as the main conclusion that can be drawn from them is that conductivity is not a useful tool to monitor ATG in geological samples. The signal to noise ratio as ATG progresses is too high to discern any meaning from the experiment.

In Figures 26-27, one sees the results of ICP analysis for the duration of the experiment for calcium and sulfate, respectively. One sees the expected decrease in calcium concentration in the reference sample with pure water, going from anhydrite to gypsum solubility, but a surprising result is the higher concentration of sulfate with respect to the calcium concentration for this particular sample. This can potentially be explained by the presence of other cations in solution due to exchange of calcium with the clay counterions. Another possibility is the formation of another calcium containing phase during the experiment, such as calcite.

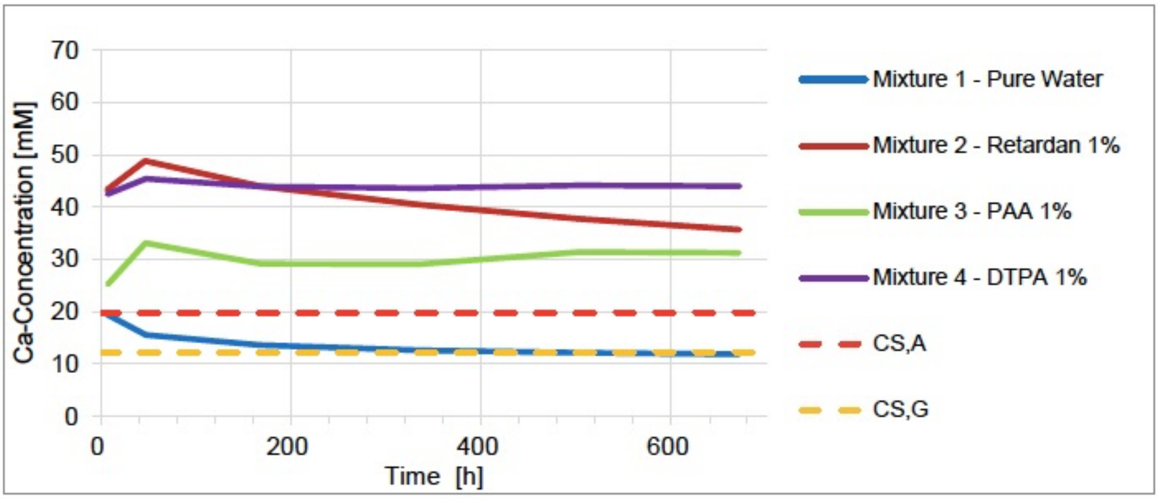

Fig. 26 *ICP results following calcium concentration over time. CS,A and CS,G mark the solubility of anhydrite and gypsum, respectively.*

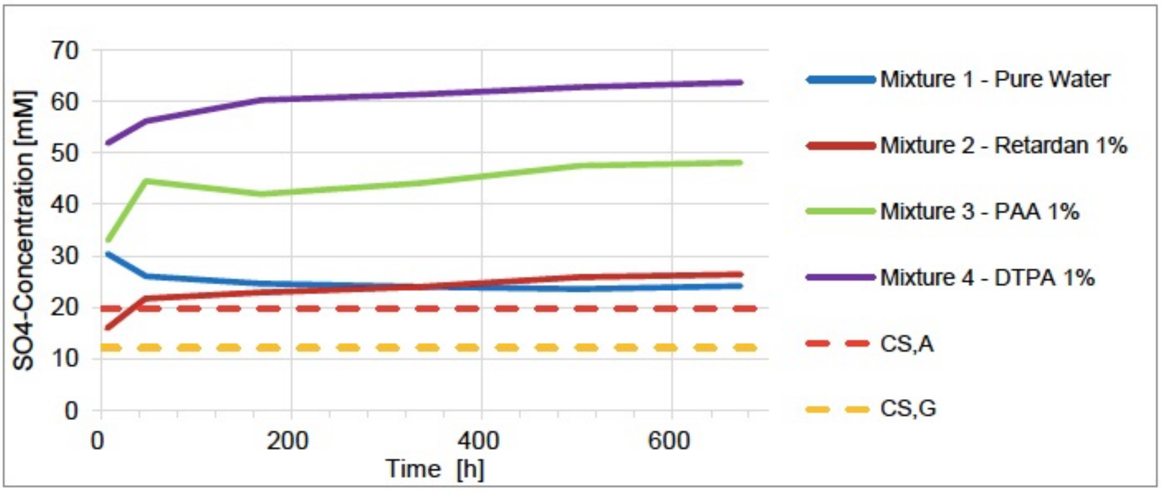

Fig. 27 *ICP results following sulfur concentration over time. CS,A and CS,G mark the solubility of anhydrite and gypsum, respectively. All sulfur is assumed to be in sulfate ion form.*

Retardan L in contact with the tunnel rock has an initially high calcium signal, which is expected thanks to the fact that calcium is included in the product. It decreases monotonically over the course of the experiment as well. This is in contrast to its behavior with the pure phases, where only Retardan 200L showed a decrease in calcium over time. In this case, however, as Retardan L is a calcium salt and in the tunnel rock there is a clay phase with exchangeable cations, which could explain the decrease. The decrease in calcium corresponds to an increase in sulfate as well, so anhydrite dissolution is continuing as calcium is being consumed.

Figure 28 shows the resulting morphology of the tunnel rock powder after all experiments. The only clear thing that can be seen is that the sample mixed with only water formed large gypsum needles, as expected. All other samples have similar morphology and particle size to the unhydrated sample, and confirm the TGA results which showed no gypsum formation.

In general, the experiments on tunnel rock powder demonstrate primarily that the retarders work well at these particular dosages. What is interesting is that the increased dosage of DTPA seemed also to inhibit gypsum formation over the course of this experiment,

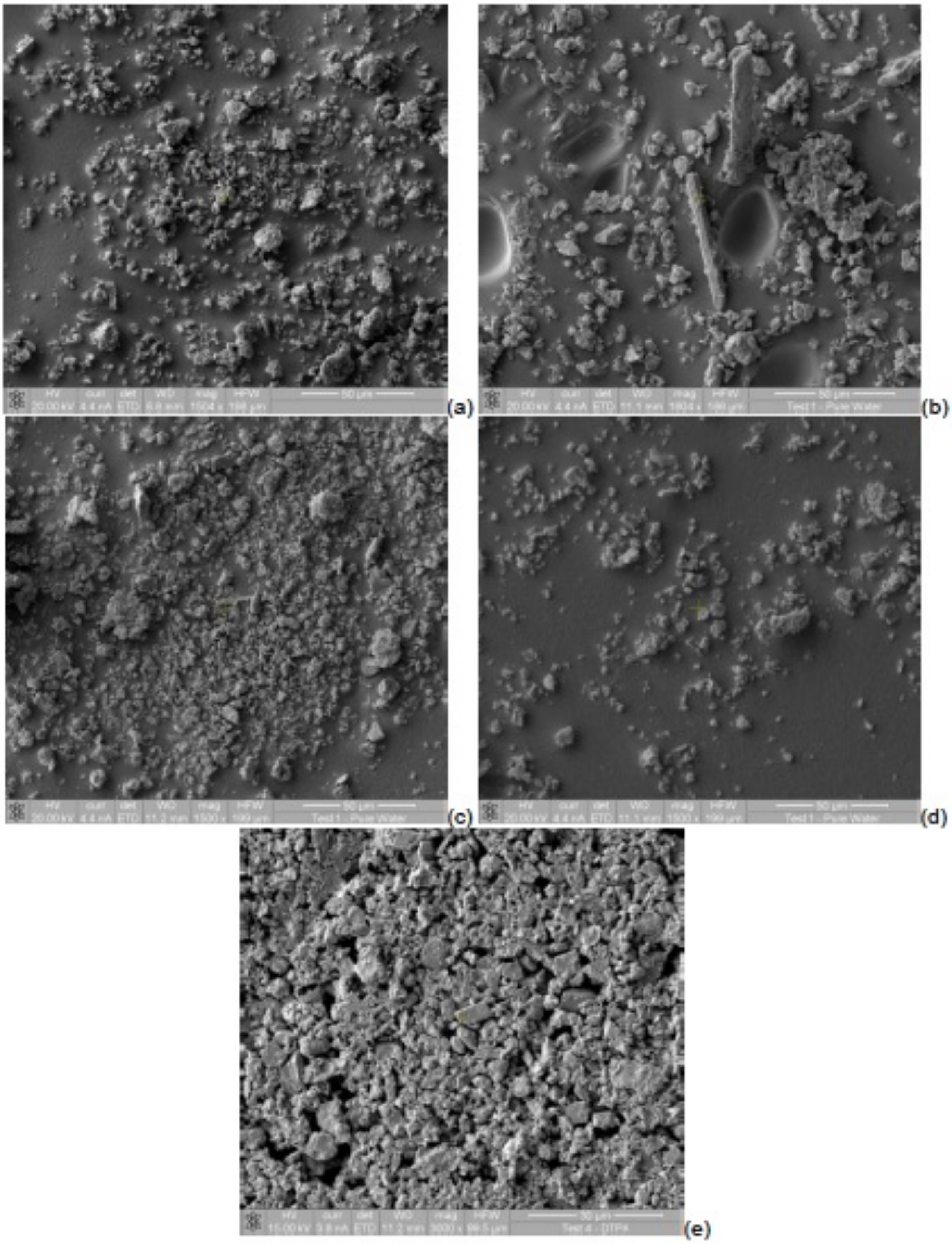

Fig. 28 *SEM micrographs of a)unhydrated Belchen tunnel rock powder, b) powder exposed to pure water, c) powder exposed to 1% Retardan L solution, d) powder exposed to 1% PAA solution, and e) powder exposed to 1% DTPA solution.*

4.6 Large scale model test of clay swelling inhibitors

This section details the testing of clay swelling inhibitors on large blocks of Villarlod molasse. The intent behind the study was to get some preliminary results that would 1) test the concept that a clay swelling inhibitor could still be useful and 2) develop some ideas on a potential field test concept. The study was performed under the purview of a Master thesis

[30] co-supervised by Prof. Anagnostou (ETHZ, IGT) and Prof. Flatt (ETHZ, IfB). The Villarlod molasse was chosen as a model material due to the level of knowledge obtained about it already within ETH, its swelling clay characteristic, and the high permeability allowing fast results to be obtained for a Master thesis.

The project consisted of first defining a measurement campaign concept that could be applied in the field, then developing a model study using the software Plaxis to define model setup geometries. This would then be implemented on the model massive stone blocks to validate, allowing a measurement campaign design for a field test.

4.6.1 Measurement campaign concepts

Two concepts were put forward as possibilities for a field test measurement campaign: 1) vertical boreholes in the tunnel invert filled with water and water plus inhibitor, and 2) horizontal boreholes in the tunnel invert bored from a trench, filled with water and water plus inhibitor. These can be seen in Figure 29.

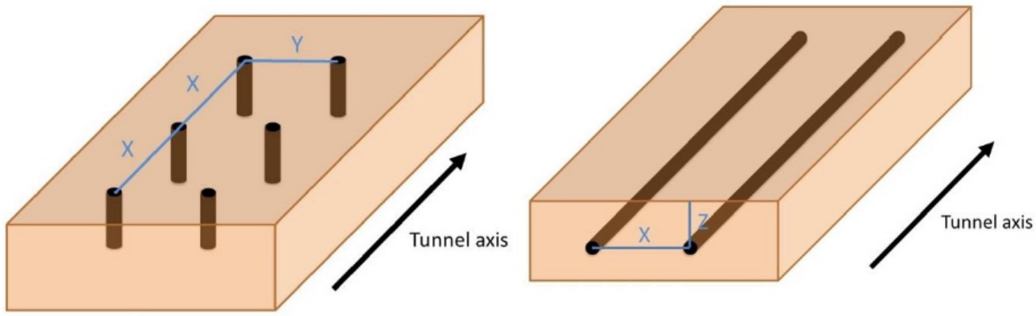

Fig. 29 *Two borehole field measurement campaign concepts.*

The selected concept was the vertical borehole design, primarily due to the difficulties that would be encountered in the drilling and filling of the boreholes in the horizontal design.

4.6.2 Modelling of massive stone blocks

Lab experiments then were designed for stone blocks of 0.5x0.5x0.5 m, and 0.5 x 0.5 x 1 m, obtained previously from the Villarlod Quarry. The blocks were modeled in Plaxis [31] using the geometry defined in Figure 30, with symmetry around the borehole, impermeability on the outside of the block, and a fixed bearing on the bottom and the horizontal axis of symmetry. Material isotropy was assumed in all properties except permeability, and only the dry E modulus was used as most stress changes occur in the dry states of the material. Three different models were used: a linear elastic model, linear elastic model with a Mohr-Coulomb failure criterion implemented, and the “Anagnostou model” [32], implemented into Plaxis by Prof. Thomas Benz of NTNU, which is based on elastic-perfectly plastic material behavior with Mohr-Coloumb failure criterion as well as the swelling law proposed by Anagnostou in [31]. Properties used for the models are found in appendix 3.

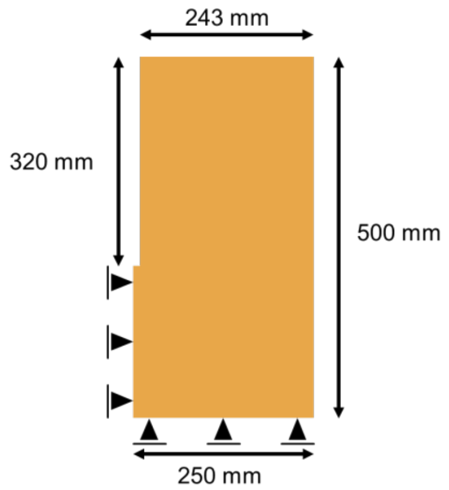

Fig. 30 *Geometry of simulation for stone block experiments, with mechanical boundary conditions. Moisture boundary conditions were impermeability throughout the whole block except along the borehole length and the symmetry axis.*

Water transport was modeled in Plaxis by using the van Genuchten equation [33] relating pore pressure to the degree of saturation, and relating also the degree of saturation to permeability. This allows the model to account for capillary pressure effects in the porous medium. The modelling was then performed by first initializing the system, and then adding water. Four measurement nodes on the top surface were selected at 2, 9, 16, and 23 cm away from the borehole.

Figure 31 shows the model results for the linear elastic model at t=0, 6 hours, and 4 days, showing the deformed mesh, the saturation level, and the vertical effective stress. The model implementing Mohr-Coulomb was identical, as the plastic failure criterion was never reached.

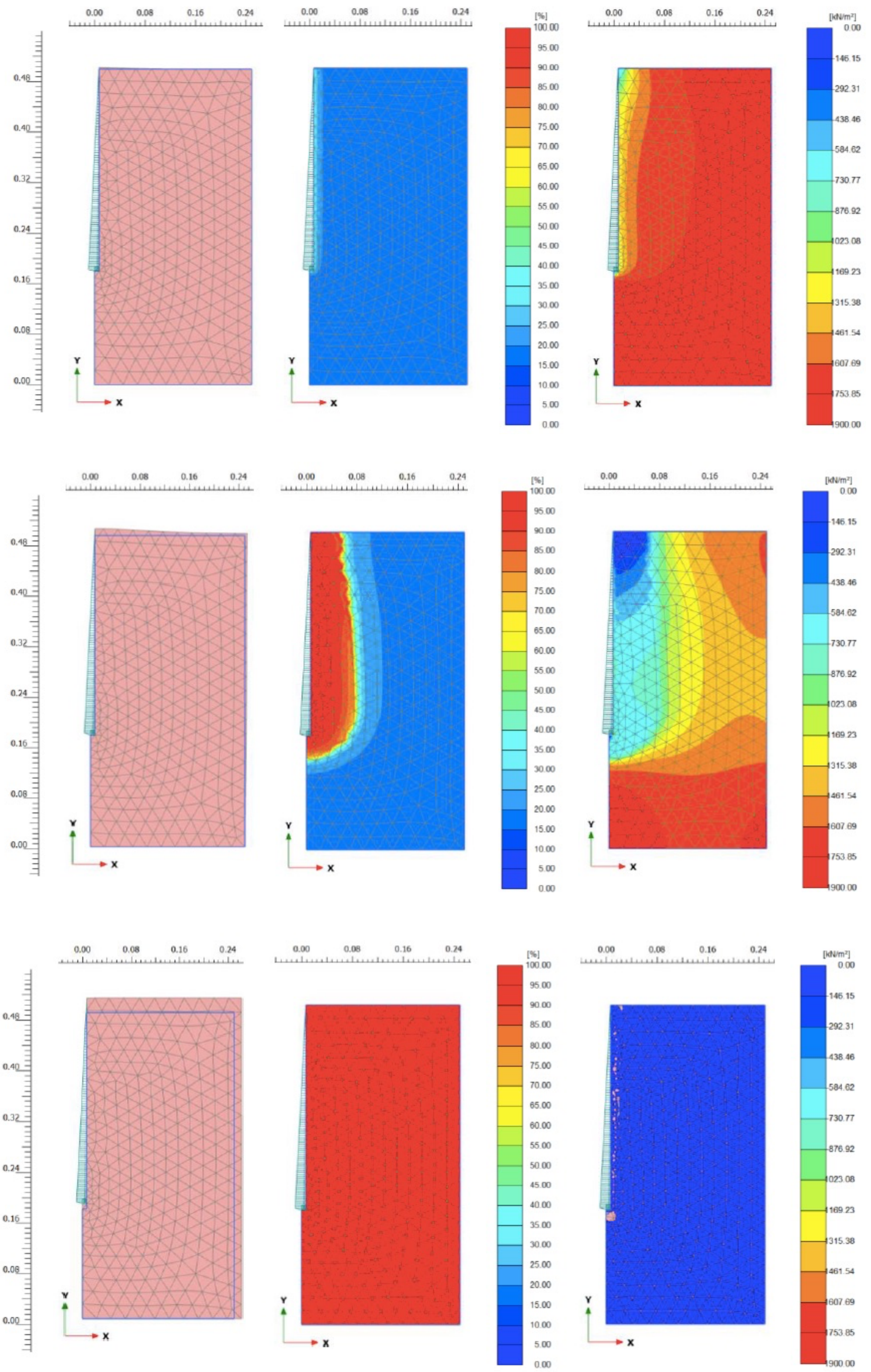

Fig. 31 *Simulation results at t=0 (top) t=6 hours (middle), and t=4 days (bottom). From left to right, the deformed mesh, the moisture content, and the effective vertical stress are shown.*

Figure 32 shows the evolution in time of vertical displacement at the four selected measurement notes for the linear elastic model. The results for the Anagnostou model are seen in Figure 33. A comparison of the two shows that the Anagnostou model has a slightly higher vertical displacement due to an additional swelling strain to the total strain.

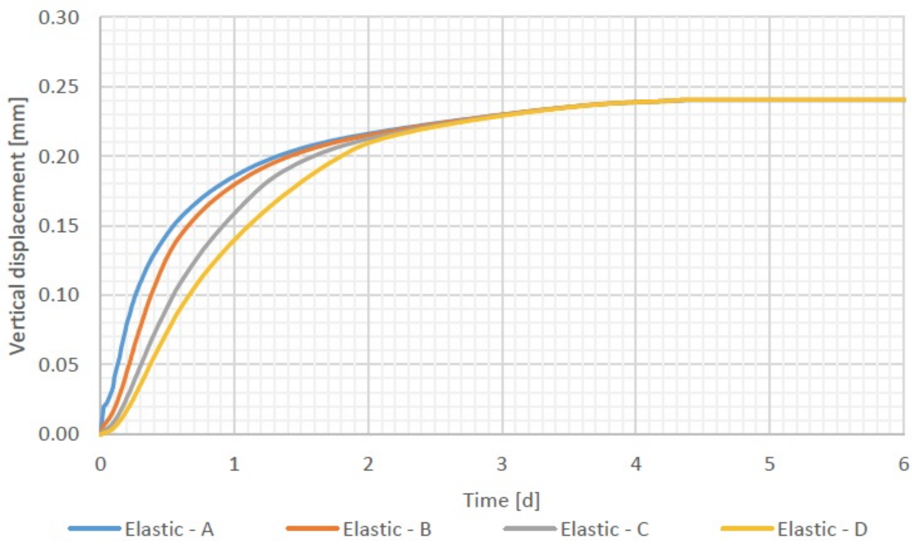

Fig. 32 *Vertical displacement at 4 surface nodes for linear elastic simulation. Same results applied to Mohr-Coulomb simulation as the plasticity limit was not reached.*

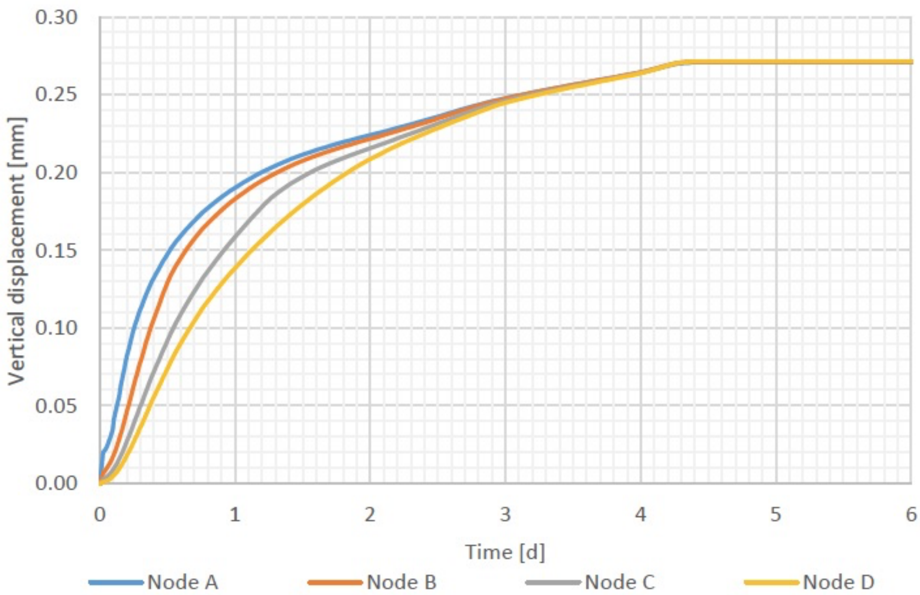

Fig. 33 *Vertical displacement of 4 surface nodes for Anagnostou model simulation. Similar results to the linear elastic model but with higher overall swelling observed.*

4.6.3 Massive stone block experiments

Massive Villarlod molasse stone blocks were obtained, with dimensions of 0.5x0.5x0.5 m and 0.5x0.5x1.0 m. Boreholes were drilled to depths of 32 cm at the nodes indicated in Figure 34. Two of the smaller blocks were used for comparison, one with water and one with a 0.3M hexane diamine dihydrochloride solution. In the larger block with two boreholes, one hole was filled with water and the other with the same 0.3M hexane diamine dihydrochloride solution. LVDTs were placed at the nodes indicated in the figure, and the stone was sealed to be made impermeable by the use of cellophane on the sides and plexiglass on the top surface, with holes drilled for the LVDTs.

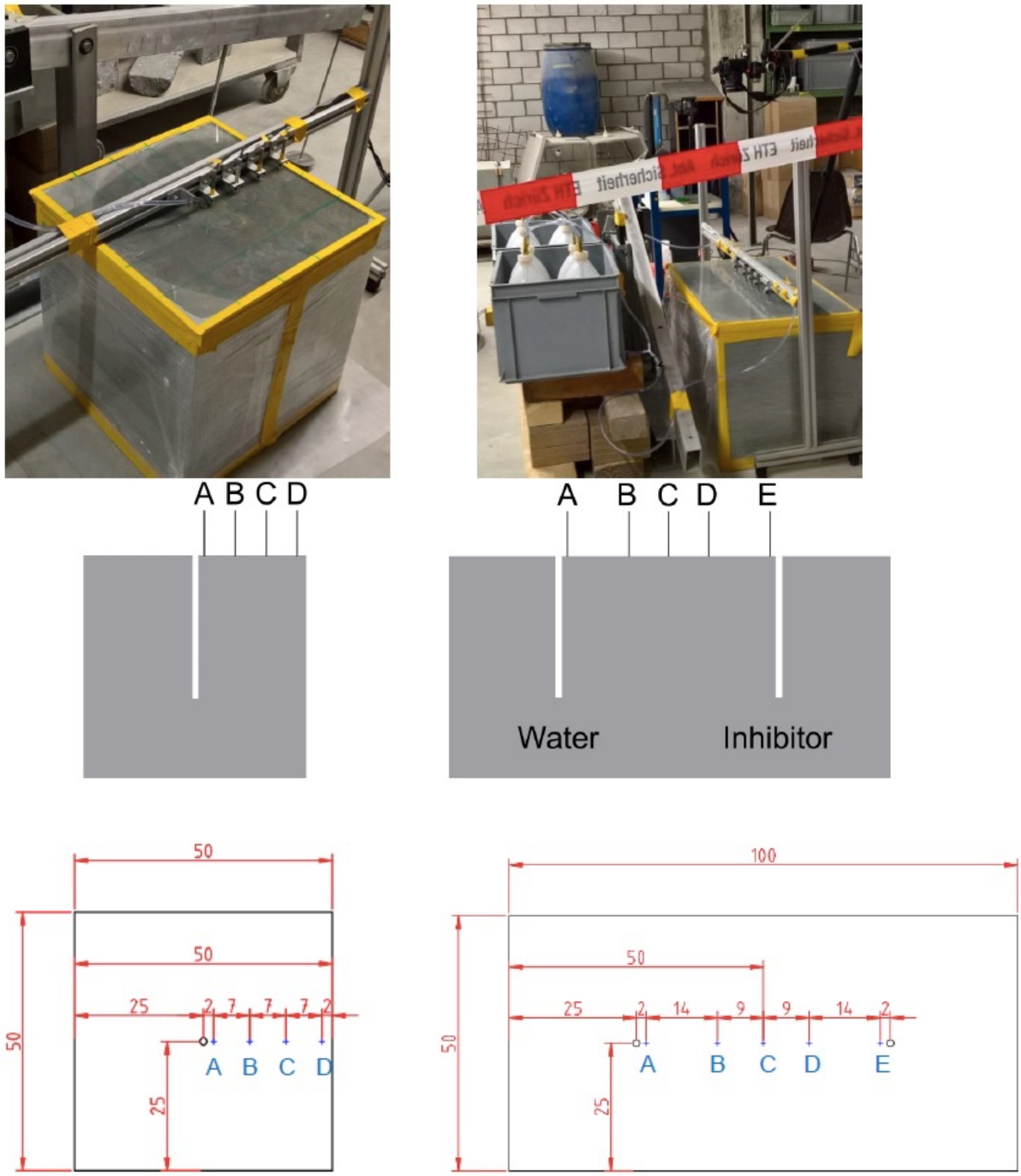

Fig. 34 *Images and geometry of small and large stone block experiments, with measurement nodes indicated.*

Figure 35 shows the results of the small stone block experiment, showing the deformation of each node with time for both a block with only water and one with inhibitor solution. The most noteworthy result is that the deformation of the block with inhibitor solution is much lower than that of the one with water, as expected.

Figure 36 shows the result of the large stone block, with water in one hole and inhibitor solution in the other. The nodes respond as expected, with higher swelling seen near the hole with water, and the lowest seen at the hole with inhibitor solution.

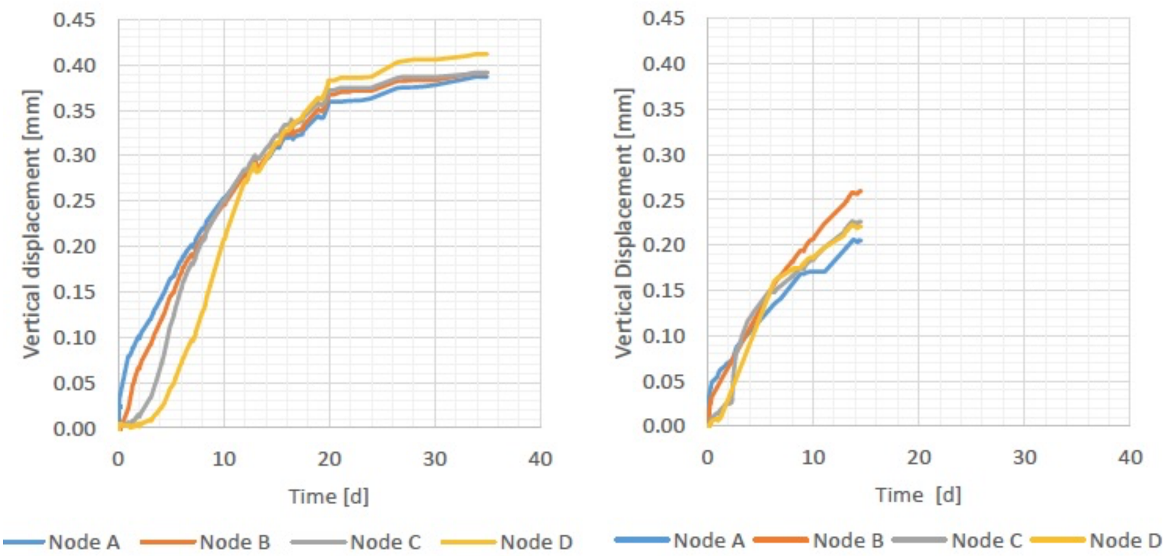

***Fig. 35** Resulting vertical displacements vs time of small stone block experiments. (Left) Stone block with only water, (right) stone block with inhibitor solution.*

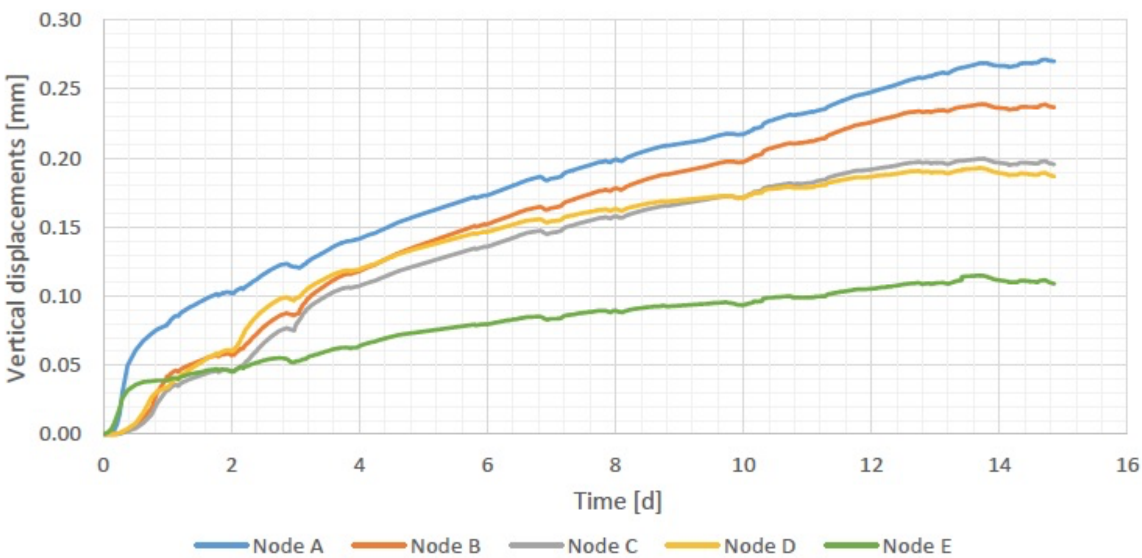

***Fig. 36** Resulting vertical displacements vs time of large stone block experiment.*

When compared to the modeling study, the experiment does not match up perfectly. For one, there is a large discrepancy in terms of the kinetics of the experiment, with the stone block showing a much longer time (33 days) to reach full swelling compared to the model study (4 days). This is probably partially explained by the uncertainty in the fitting parameters of the van Genuchten equation. Additionally, the modelling study was based on the assumption that swelling occurs the instant that water reaches a particular location in the stone block, which is most likely not a valid assumption, [34]. Additionally, one observes that the final deformation is much larger than expected. This deformation discrepancy can also be explained by the initial parameters input in the van Genuchten equation, where a very small change in the initial degree of saturation can lead to a large change in the final deformation. To make this estimation, a limited number of small samples were used due to equipment size limitations, and this is the source of much uncertainty in the model vs. experiment results.

One very important results can be seen in the experiment with the big block in Figure 35. In this experiment, node E, the closest to the inhibitor borehole, saw a rapid jump and fast leveling off of the swelling strain. Node D, the next node to be reached by the inhibitor solution, also sees a rapid increase, but it does not level off immediately, in fact it continues increasing for several days before it levels off. One would expect that the final deformations of each node would follow linearly between the boreholes as well, but node D is very similar in its final deformation to node D, meaning it swells more than expected in the end. This can be attributed to the consumption of inhibitor as it leaves the borehole. There is a reaction front propagating through the stone as the inhibitor solution spreads, and this leads to a depleted inhibitor solution as it travels through the stone. This has strong implications for any field application of any inhibitor solution, and has to do with the comparison between advective transport and diffusive transport, as well as the initial conditions before the treatment. If treating an initially dry stone, if the solution propagation front is fully depleted, then diffusive transport is required to get inhibitor to the saturated areas, and is a very slow process compared to advection. On the other hand, if the stone is already saturated, then diffusive transport is the only way to get the inhibitor to the affected areas. In this case, it might make sense to recommend the use of a smaller, more mobile solution such as potassium salt to reduce swelling.

4.6.4 Field campaign design

The results of the modeling and experiments led to the recommendations for a future measurement campaign in a tunnel invert. The recommended tunnel invert would be located in a high clay-containing formation such as the Opalinus clay formation that the Mont Terri tunnel laboratories go through [25]. This would be to avoid the coupled on site problems of both ATG and clay swelling. This does not preclude the use of a anhydritic claystone tunnel as well however, especially if the timing concerning such as study would be ideal.

The recommended geometry for such a field test would be seen in Figure 37. A borehole depth of 8 m with a diameter of 10 cm is recommended, although the diameter can be larger. The measurement of deformation should be done via sliding micrometers on boreholes between the fluid filled boreholes. Additionally, reflectors can be arranged as seen in the figure to measure surface deformation via tachymetry.

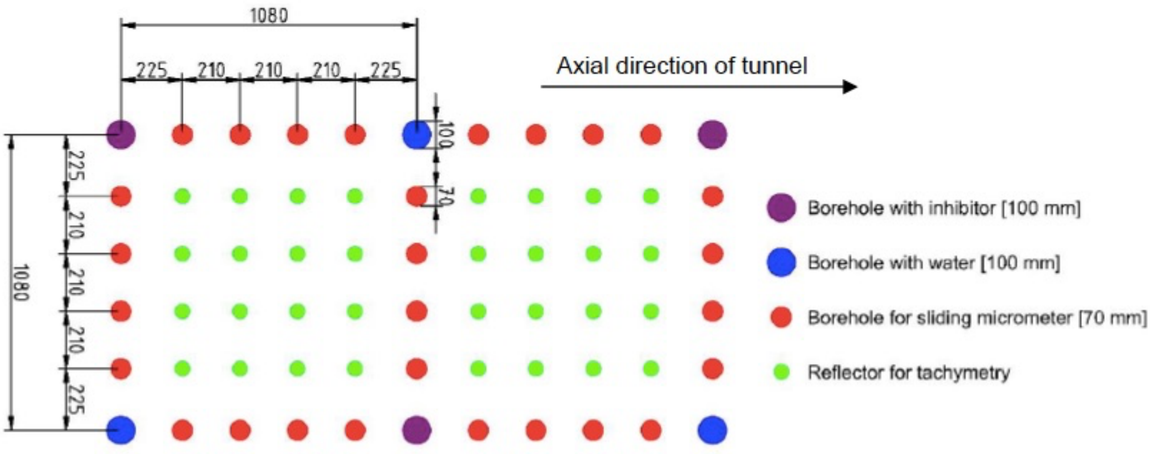

***Fig. 37** Recommended geometry for field measurement campaign in a tunnel invert.*

The greatest challenge has to do with the permeability of the tunnel invert. The primary goal will be to have the inhibitor move through the floor via advection to return faster results. This means a good estimation of the permeability and degree of saturation of the tunnel floor is critical before the borehole drilling can commence, and borehole spacing tuned in case of a highly impermeable and saturated invert.

5 Conclusions and Recommendations

To conclude, this project returned interesting and useful results with respect to the issue of swelling in tunnels through anhydritic claystone formations, primarily from a material perspective. The primary conclusions have to do with the use of the "thermodynamic switch" for the decoupling of ATG from clay swelling, and the success of ATG inhibition. Clay swelling inhibitors returned mixed results, and may depend primarily on the initial state of the tunnel and the treatment conditions.

5.1 "Thermodynamic switch"

The so-called "thermodynamic switch" turned out to be quite successful in decoupling the clay swelling from ATG phenomena, and has already been used at ETH by the group of Prof. Anagnostou (IGT). By the use of this technique, this study was able to unequivocally demonstrate the efficacy of ATG inhibitors. This efficacy was demonstrated, however, on crushed and reconstituted tunnel rock powder samples, which have an artificial homogeneity, and an artificially higher porosity and permeability than natural samples. The efficacy of ATG inhibitors should then be demonstrated on natural samples. This result, however, indicates already that this can probably be tested in the field, although a lab scale test of a natural sample would be more ideal. This has led to the filing of an invention disclosure form and a patent application.

Recommendations for further action on this are as follows:

- Demonstration of the efficacy of the ATG inhibitors on natural samples, either in lab scale or a field test.
- Field testing is ideal, as it would allow a better understanding of issues associated with delivery of the inhibitor.
- Submission of a publication to more broadly disseminate the use of the ATG/clay swelling decoupling technique in this research field.
- Use of this technique to better understand how the two phenomena are, in fact, coupled. For example, how swelling clay could accelerate the ATG process via allowing faster water access to anhydrite surfaces.
- Finally, it is necessary to understand what are the environmental risks associated with the use of these inhibitors.

5.2 ATG Inhibition Mechanism

The inhibition mechanism of the ATG inhibitor was studied with some detail, and provided important insights. The primary results showed that most likely, Sika Retardan L and PAA are the most effective inhibitors due to their strong interaction with the anhydrite phase and inhibition of the dissolution, coupled with their gypsum growth inhibition effect. It is also clear that clay does not interact negatively (i.e. through consumption via adsorption) with the ATG inhibitors, although it is possible that other phases within the tunnel rock may.

Recommendations for further action on this are as follows:

- More tests on other tunnel rock with varying phase assemblages (see below)
- More deep insight into the nature of the interaction between the ATG inhibitor and the anhydrite and gypsum surfaces, for example with molecular dynamics simulations.
- A deeper understanding on the interaction of other phases of tunnel rocks with the inhibitors, and indeed with the entire process of swelling.
  - While ATG inhibitors are not interacting with clay, it is possible that they could interact with other phases (i.e. magnesite in the case of the Belchen tunnel, or potentially dolomite in other tunnels)

- There is potential evidence that magnesite is participating in the process, as illustrated by the mismatching calcium and sulfate concentrations in experiments on tunnel rock. This mismatch could also be caused by interaction with the clays, i.e. exchange of calcium in the clay interlayer for another cation.

5.3 Clay Swelling Inhibitors

The work on clay swelling inhibitors for this problem returned mixed results. The inhibitors tested in this work are intended primarily for situations where there is either significant shrink/swell behavior due to wetting and drying cycles, or in situations where high osmotic swelling is expected and they can restrict this. Wet/dry cycles are not expected in a tunnel invert, where seepage flow is the primary concern, but osmotic swelling is a typical problem encountered in tunnels through ground with high swelling clay content. Typically, osmotic swelling is solved via geotechnical solutions in which a counterpressure is applied.

The swelling inhibitors did not show effective results on initially dry clay. This is due to the fact that the clays must swell in order to allow the exchange of this inhibitor to take place. This swelling has to be at least large enough to allow a solvated inhibitor entry into the clay interlayer, and previous experiments have demonstrated this to require a 70% increase in clay linear dimension. The exchange of the inhibitor, however, prevents the clay layers from expanding further into the osmotic range, which could be effective on the longer term.

The model study on swelling sandstones provided insight on what a potential field test of this inhibitor could entail, with conclusions that could be applied also to tests of ATG inhibition. The primary conclusion has to do with the permeability of the tested tunnel rock, and how to properly space any boreholes for tests. However, one must also consider the consumption of the inhibitor. In effect, this might mean that impermeability could play a useful role, as a less permeable rock would allow consumed inhibitor to be more effectively replaced via diffusion.

Recommendations for further action on this are as follows:

- A field test should be initiated to test the potential of clay swelling inhibitors. The first test should be done in a controlled environment where only clay swelling can be expected, such as the Opalinus clay formation in the Mont Terri tunnel complex. This would allow a better test of the idea that clay swelling inhibitor could be effective on the longer term by preventing osmotic swelling. Additionally, other inhibitors, potentially cheaper than the solutions tested here (potassium salts, for example) could also be tested.
- Any field test of any inhibitor, clay or ATG, will require first an understanding of the permeability and initial saturation state of where the test will take place.

Appendices

I Villarlod Molasse properties for simulation

I Appendix I: Villarlod Molasse properties for Simulations

Below is the table of modeling parameters for Villarlod Molasse in Plaxis, from section 4.6. Two values in column 3 indicate the anisotropic values; first value is normal to bedding planes, second is parallel to bedding planes.

Tab. A.1 *Beispieltabelle*

Parameter	Unit	Value
Young's modulus, Dry	GPa	1.87 / n/a
Young's modulus, Wet	GPa	0.667 / 1.23
Poisson's ratio	-	0.25 / 0.38
Permeability	m/s	3.3e-8 / 5.27e-8
Density, saturated	g/cm^3	2.385
Density, dry	g/cm^3	2.240
Void ratio	-	0.153
Friction angle	°	44.3
Cohesion, dry	MPa	9
Cohesion, wet	MPa	3.6
Dilatancy angle	°	30
Van Genuchten parameter ga	1/m	0.17
Van Genuchten parameter gn	-	1.349
Van Genuchten parameter gc	-	-0.259
Van Genuchten parameter gt	-	1
Swelling fit parameter A0	-	29.5
Swelling fit parameter Ael	-	0
Swelling fit parameter Apl	-	0
Max swell strain	%	0.244
Max swell stress	kPa	80
Swell coefficient	-	6.9e-5

References

[1] Anagnostou, G., Pimentel, E., and K. Serafeimidis. (2010) Swelling of sulphatic claystones – some fundamental questions and their practical relevance. Geomech. and Tunneling, 3 (5) 567-572.

[2] Jimenez-Gonzalez, I., Rodriguez-Navarro, C., and G.W. Scherer. (2008) Role of clay minerals in the physicomechanical deterioration of sandstone. Jour. Geophys. Res. Ear. Surf. 113 (F2).

[3] Madsen, F.T. and M. Müller-Vonmoos. (1989) The swelling behaviour of clays. Appl. Clay Sci. 4 (2) 143-156.

[4] Van Olphen, H. (1991) Clay Colloid Chemistry: for Clay Technologists, Geologists, and Soil Scientists. 2nd ed. New York, Wiley, 318 pp.

[5] Einstein, HH. (1996) Tunnelling in difficult ground – swelling behaviour and identification of swelling rocks. Rock Mech. And Rock Eng.29 (3) 113-124.

[6] Suter, JL., Coveney, PV, Anderson, RL, Greenwell, HC, and S. Cliffe. (2011) Rule based design of clay-swelling inhibitors. Ener. Env. Sci. 4 4572-4586.

[7] Wangler, T. and GW Scherer (2009) Clay swelling inhibitrion mechanism of a,w diaminoalkanes in Portland Brownstone. Jour. Mat. Res. 24 (5) 1646-1652.

[8] Scherer, GW. (1999) Crystallization in pores. Cem. Conc. Res. 29 (8) 1347-1358.

[9] Flatt, RJ. (2002) Salt damage in porous materials: how high supersaturations are generated. Jour. Crys. Growth 242 (3-4) 435-454.

[10] Scherer, GW. (2004) Stress from crystallization of salt. Cem. Conc. Res. 34 (9) 1613-1624.

[11] Einfalt, H.C., Fecker, E., and H.P. Götz. (1979) Das Dreiphasensystem Ton, Anhydrit, Gips und Dessen Zeitabhängiges Verhalten bei Zugabe von Wässrigen Lösungen (The three-phase-system clay-anhydrite-gypsum and its time-dependent behavior on saturation with water-based solutions). Proceedings of 4th International Society for Rock Mechanics and Rock Engineering, 2-8 September, Montreaux, Switzerland.

[12] Sahores, J. (1962) Contribution à l'étude des phénomènes mécaniques accompagnant l'hydratation de l'anhydrite (Contribution to the study of the mechanical phenomena accompanying the hydration of anhydrite). Doctoral thesis, Revue des matèriaux de construction.

[13] Anagnostou, G., Serafeimidis, K., Pimentel, E., Wanninger-Huber, T., and A. Vrakas. (2015) Modeling of anhydritic claystones. Research Project ASTRA / FGU2010/007.

[14] Butscher, C., Huggenberger, P., Zechner, E., and HH Einstein. (2011) Relation between hydrogeological setting and swelling potential of clay-sulfate rocks in tunneling. Eng. Geol. 122 (3-4) 204-214.

[15] Chiaverio, F. and A. Thut. Chienberg Tunnel: Rehabilitation using yielding elements of the section in Keuper sediments affected by heave. Geomech. and Tunneling 3 (5) 573-582.

[16] Amstad, C. and K. Kovari. (2001) Untertagbau in quellfähigen Fels (ETHZ Forschungsauftrag 52/94 auf Antrag des Bundesamtes für Strassen (ASTRA). IGT, ETH Zürich.

[17] Charola, AE, Pühringer, J., and M. Steiger. Gypsum: a review of its role in the deterioration of building materials. Env. Geol 52 (2) 339-352.

[18] Conley, RF, and WM Bundy. (1958) Mechanism of gypsification. Geochimica et Cosmochimica Acta 15 (1-2) 57-72.

[19] Knacke, O. and W. Gans. (1977) The Thermodynamics of the sytem CaSO4-H2O. Zeitschrift für Physikalische Chemie. 104 (1-3) 41-48.

[20] Freyer, D, and W. Voigt. (2003) Crystallization and phase stability of CaSO4 based salts. Monatshefte für Chemie. 134 (5) 693-719.

[21] Jimenez-Gonzalez, I. and GW Scherer. (2004) Effect of swelling inhibitors on the swelling and stress relaxation of clay bearing stones. Env. Geo. 46 (3-4) 364-377.

[22] Wangler, T. (2016) Swelling clay and its inhibition in Villarlod Molasse. In Science and Art: A Future for Stone, Proc. of 13th Int. Conf. on Deterioration and Conservation of Stone, Vol. 1. Paisley, University of the West of Scotland, 189-196.

[23] Pimentel, E., Anagnostou, G. (2010) Langzeitquellversuche an anhydritführenden Gesteinen Forschungsauftrag FGU 2006/001 auf Antrag des Bundesamtes für Strassen (ASTRA).

[24] Mantellato, S., M. Palacios and RJ Flatt. (2015) Reliable specific surface area measurements on anhydrous cements. Cem. Conc. Res. 67 286-291.

[25] Smith, DE, Wang, A., Chaturvedi, A., and HD Whitley. (2006) Molecular simulations of the pressure, temperature and chemical potential dependencies of clay swelling. Jour. Phys. Chem. B 110 (40) 20046-20054.

[26] Wangler, T. and GW Scherer. (2008) Clay swelling mechanism in clay-bearing sandstones. (2008) Env. Geo. 56 (3-4) 529-534.

[27] Bossart, P., Meier, PM, Moeri, A, Trick, T, and JC Mayor. (2002) Geological and hydraulic characterization of the excavation disturbed zone in the Opalinus Clay of the Mont Terri Rock Laboratory. Eng. Geo. 66 (1-2) 19-38.

[28] Aebersold, S. (2015) Chemical inhibitors for anhydritic claystones in Swiss tunnels. Master Thesis, Institute for Building Materials, ETH Zurich.

[29] Ottinger, D. (2016) Anhydrite to gypsum transformation inhibition in tunnels. Master Project, Institute for Building Materials, ETH Zurich.

[30] Ottinger, D. (2016) Model study for swelling and swelling inhibition in clay containing rocks. Master Thesis, Institute for Building Materials, ETH Zurich.

[31] Plaxis. https://www.plaxis.com/

[32] Anagnostou, G. (1993) A model for swelling rock in tunnelling. Rock Mech. And Rock Eng. 26 (4) 307-311.

[33] Van Genuchten, MT.. (1980) A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Sci. Soc. of America Jour. 44 (5) 892-898.

[34] Moonen, P. and T. Wangler. (2015) An analytical approach to the characterization of swelling in clay-bearing stone. Phil. Mag. 95 (28-30) 3103-3121.

Projektabschluss (Project closing)

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Departement für
Umwelt, Verkehr, Energie und Kommunikation UVEK
Bundesamt für Strassen ASTRA

FORSCHUNG IM STRASSENWESEN DES UVEK

Formular Nr. 3: Projektabschluss

Version vom 09.10.2013

erstellt / geändert am: 13.12.2017

Grunddaten

Projekt-Nr.:	FGU 2012/001
Projekttitel:	Quellinhibitoren fuer Anhydrit fuehrende Tonsteine / Swelling inhibitors for anhydritic claystones
Enddatum:	November 2017

Texte

Zusammenfassung der Projektresultate:

The problem of floor heave due to sulfatic claystones (used interchangeably with the term "anhydritic claystone" in this report) has for decades plagued tunnels that go through the Gipskeuper formation in Switzerland and Germany. These repeated floor heaves have led to very expensive repairs and traffic impacts in highway tunnels such as the Belchen tunnel or the Chienberg tunnel. These repairs, while costly, have also proved to be ineffective on the longer term, making them just a bandaid solution.

This has led to many targeted research projects to address this problem at various institutions, examining the core processes on varying scales, from the hydrogeological all the way to the microscale. At its core, the problem is a difficult one, involving the coupling of two often complementary swelling processes: clay swelling and the conversion of anhydrite to gypsum (in the following referred to as ATG), a process that exerts considerable crystallization pressure. A missing element in the research has been to investigate solutions on the material scale, which is the focus of the research of this study undertaken at the Institute for Building Materials at ETH Zurich. In this study, we investigated the use of clay swelling inhibitors to control the clay swelling problem, and ATG inhibitors to control the ATG problem, taking inhibitors known from the geotechnical engineering (for clays) and from gypsum board production (for ATG).

One of the prohibiting factors in this research is that experimental research on the topic requires extraordinarily time-consuming experiments, such as the most recent long-term experiments initiated in 2006 (FGU 2006/001) and are still continuing today. Experimental cycle times spanning years and decades of a complex coupled problem in a very heterogeneous material require patience, and often results can be difficult to interpret. This would make any investigation of inhibitor effectiveness also difficult to interpret, and therefore this study first focused on decoupling the problem via a novel "thermodynamic switch". This so-called "switch" was the use of the phase behavior in the solubility of various calcium sulfate phases: above approximately 50 °C, the solubility of gypsum exceeds that of anhydrite, making anhydrite more thermodynamically stable when exposed to water.

This study demonstrated the effectiveness of this "thermodynamic switch" in a dilute system, with high liquid to solid ratios, as well as in dense systems more representative of a tunnel invert, with low liquid to solid ratios. The first investigations in dilute systems with pure phases, following the confirmation of the thermodynamic switch, then allowed the confirmation of the effectiveness of the ATG inhibitor. Research in the dilute systems also involved the measurement of adsorption of various ATG inhibitors to anhydrite and gypsum while also following the pore solution evolution, helping to define their mechanism of action and demonstrating that acting upon primarily the anhydrite phase to inhibit dissolution seems to be the best mode of action, although inhibiting nucleation and growth of gypsum can also be effective. It was also demonstrated during these studies that there was no interaction between clay and ATG inhibitors, and clay presence did not decrease their effectiveness.

The experiments that defined the whole study were those in dense systems, using oedometers. Here, with actual tunnel rock that had been crushed and reconstituted into a highly dense but porous structure, the conditions that best simulate a tunnel invert could be met. A first round of oedometer experiments demonstrated that correct dosage of ATG iinhibitor is important, but more importantly that the use of clay swelling inhibitors might be inadvisable in completely dry inverts. Clay swelling inhibitors operate on the principle of substitution within the clay interlayers, thus requiring an initial amount of swelling. Therefore clay swelling inhibitors cannot counter swelling strains associated to intracrystalline swelling, but then may become useful for larger strains that develop with osmotic swelling. This question as well as interactions with ATG remains to be studied.

The second oedometer experiment demonstrated two of the primary goals of this study: the principle of decoupling the swelling processes using the thermodynamic switch, and the effectiveness of the ATG inhibitors. In this experiment, two oedometers were placed with water in an oven at 60°C to "turn off" ATG, and thus only swelled via clay swelling. By then removing one oedometer and placing it in ambient temperatures, its subsequent swelling could then be understood to be only ATG. Later, the second oedometer was removed and also place at ambient temperature, but this time its fluid was replaced by ATG inhibitor. For this case, the lack of subsequent swelling demonstrated that the ATG inhibitor was effective.

A final combined experimental and computational modeling study was aimed at defining a geometry for a potential field test application of the clay swelling inhibitor. In this study, massive stone blocks of a model clay-swelling geological material had boreholes drilled into them, and these boreholes were filled with water or inhibitor solution. Single boreholes and two interacting borehole examples were examined, with a model in Plaxis software to simulate swelling. Using experimental results, the code was then calibrated and the extended to give advice on a potential field study. The major cautionary findings from this study were that it is imperative to have the initial saturation and permeability of any tunnel invert well characterized in order to optimize borehole spacing to return a reliable and fast signal. Another useful finding was to consider the reaction-diffusion front as inhibitor is consumed while the solution proceeds through the rock. This is a conclusion that can apply also to ATG inhibitor application.

In conclusion, the primary finding of this study has to do with the usefulness of the decoupling technique for anhydritic claystones. The ability to decouple clay swelling from ATG swelling should create more efficient experimental protocols in the future, and greatly enabled the efficient study of ATG inhibitor effectiveness in this study. The usefulness of the ATG inhibitor means it is most likely ready for test use in tunnel operations, primarily in delivery wherever there is an operation involving water, such as drilling. Additionally, while controlling clay swelling initially is very difficult with clay swelling inhibitors, on the longer term clay swelling inhibitors could prove useful in reducing osmotic swelling and ought to be given further attention in the future.

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Departement für
Umwelt, Verkehr, Energie und Kommunikation UVEK
Bundesamt für Strassen ASTRA

Zielerreichung:

The primary target of this research was to investigate material solutions for inhibiting swelling in Swiss tunnels through anhydritic claystone, namely by including inhibitors in tunnel drilling fluid. This required first decoupling of the two swelling phenomena (clay swelling and anhydrite-to-gypsum, or ATG) through the use of a novel "thermodynamic switch". From this, a possible solution to apply in the field would be investigated.

Folgerungen und Empfehlungen:

The main conclusions of this work are as follows, and detailed more in the report:

1) The "thermodynamic switch" to decouple clay swelling from ATG was successfully implemented in this research, and enabled the confirmation that
2) ATG inhibitors are indeed effective at inhibiting ATG in tunnel rock samples, and appear to have no negative interaction with clay.
3) Clay swelling inhibitors are not effective on completely dry clays at inhibiting swelling, as they require some clay swelling in order to be effective, however, as these inhibitors can inhibit more long-range swelling usually observed with clays, they could find application on the longer term.
4) Field scale tests are highly impacted by tunnel rock permeability in returning fast results, and consumption of inhibitor also impacts performance.

Our recommendations are then as follows:

1) The results of the "thermodynamic switch" should be propagated to the research community to enable better systematic studies of this topic.
2) ATG inhibitors should be tested now on the field scale, and we would recommend their inclusion in drilling fluids based on these results.
3) Clay inhibitors could also be tested on a field scale, but we would not recommend their use as of now in a dry anhydritic claystone tunnel. We would recommend testing first in a tunnel with only swelling clay (through Opalinus clay for example) to determine the usefulness in inhibiting osmotic swelling. Additional testing in lab scale is probably also necessary to understand clay swelling inhibitor impact on ATG.
4) Before designing any field test in a tunnel invert, it is imperative to first fully understand the permeability and transport processes (reaction-diffusion) in order to best return fast results.

Publikationen:

Until now, only some conference presentations have been made on certain aspects of this work. The main part of this work has been unpublished, primarily because of a patent application that has now been undertaken by Sika AG on behalf of ETHZ for the use of their tested ATG inhibitors in tunnel drilling fluids. When this patent application has been filed, then two publications will be written:

1) a publication on the thermodynamic switch to decouple the phenomena of clay swelling from ATG. We expect this to be of great interest to the community studying this problem.
2) a publication on the working mechanism behind ATG inhibition.

Der Projektleiter/die Projektleiterin:

Name: Flatt   Vorname: Robert

Amt, Firma, Institut: ETH Zuerich, Institute fuer Baustoffe

Unterschrift des Projektleiters/der Projektleiterin:

Robert Flatt

Forschung im Strassenwesen des UVEK: Formular 3   Seite 2 / 3

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Departement für
Umwelt, Verkehr, Energie und Kommunikation UVEK
Bundesamt für Strassen ASTRA

FORSCHUNG IM STRASSENWESEN DES UVEK

Formular Nr. 3: Projektabschluss

Beurteilung der Begleitkommission:

Beurteilung:

Die Projektziele wurden indem erreicht, dass Additive gefunden wurden, die das Quellen anhydrit- und tonhaltiger Proben verhindern können. Durch die Zugabe solcher Additive dem Brauchwasser wären Arbeiten wie Nassbohren (für Sprenglöcher, Ankerungen oder Erkundungen) auch für Tunnels im anhydritführenen Gipskeuper möglich.

Umsetzung:

Die erzielten Ergebnisse sind zwar erfolgversprechend, vor einer Umsetzung in der Praxis jedoch sind weitere Untersuchungen erforderlich.

weitergehender Forschungsbedarf:

Die Begleitkommission ist mit den diesbezüglichen Empfehlungen der Forschungsstelle einverstanden. Vor der Durchführung eines Feldversuchs sollten allerdings Quellversuche an natürlichen anhydrithaltigen Tonsteinen durchgeführt werden. Ein Feldversuch könnte in Mont Terri oder im Drainagestollen des Belchentunnels stattfinden.

Einfluss auf Normenwerk:

Keiner.

Der Präsident/die Präsidentin der Begleitkommission:

Name: ANAGNOSTOU Vorname: GEORGIOS

Amt, Firma, Institut: ETH ZÜRICH, IGT

Unterschrift des Präsidenten/der Präsidentin der Begleitkommission:

Forschung im Strassenwesen des UVEK: Formular 3 Seite 3 / 3

Verzeichnis der Berichte der Forschung im Strassenwesen (List of Reports of Research in the Field of Road Traffic)

Das Verzeichnis der in der letzten Zeit publizierten Schlussberichte kann unter www.astra.admin.ch (*Forschung im Strassenwesen --> Downloads --> Formulare*) heruntergeladen werden.

The list of the most recent published Final Reports can be downloaded at www.astra.admin.ch (Research in road traffic → Downloads → Forms)