Applications of Chemical Modification of Smectite Clays in Geotechnical Problems

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Abstract

Soils containing clay minerals are sensitive to the compounds dissolved in the pore fluid, due to their large surface area and their mineralogy. In environmental geotechnics, this interaction is often regarded as a passive side effect due to leaching or ground-water pollution. However, there are chemicals in the pore fluid that influence the soil properties positively and can directly affect key geotechnical parameters, such as strength and hydraulic conductivity. In many geotechnical problems the water circulating in the porous ground is not only one of the main driving forces, its targeted modification is also often part of the solution, e.g., in the cases of slope stabilization by drainage or water-table lowering in construction pits. Using tailored chemicals to induce such changes enables the development of new techniques for designing innovative solutions.

This thesis is based on an extensive program of laboratory tests designed to explore the modification of clay soils due to treatment with guanidinium-salt solutions. This sort of treatment has been shown to lead to a significant increase in shear strength and a decrease in the swelling potential of clayey soils, both of which are highly desirable effects in the context of many geotechnical applications. In contrast to a number of other soil-improvement techniques, which reduce the permeability during treatment, our study has demonstrated that guanidinium can increase the hydraulic conductivity of both pure bentonites and quartz–bentonite mixtures by an order of magnitude. Based on the laboratory tests, the mechanisms causing this modification have been characterized and quantified on different scales.

Increased permeability may be used as a method for enhancing the delivery of other soil-improvement agents into the soil. A model was developed to describe the process of infiltrating or injecting the chemical into the soil, as a preparation for further treatment. The evolution of a growing zone containing improved soil with elevated permeability was modeled both analytically and numerically. A simplified analytical approach provides a means for quickly assessing the improvement using externally measurable quantities. It was validated against the one-dimensional propagation in soil columns observed in laboratory tests. In addition, the model is formulated and solved for a radial configuration, as encountered in applications where the treatment takes place around a bore hole.

In some geotechnical situations, however, increasing the soil permeability can be considered as a major soil improvement in its own right. To demonstrate the potential of such applications, the effect of chemical enhancement was investigated for two exemplary geotechnical problems. First, a well combined with chemically enhanced drainage was analyzed numerically, where the main purpose of the well operation is to lower the water table at a construction site to a target
value. The parametric study showed that the soil modification is most efficient when only a small area in the close vicinity of the well is treated. The chemical modification can lower the total cost of the dewatering system by lowering the operational cost for long-term wells with a one-time additional investment during the installation of the pump.

Second, the implementation of a chemical drain in a slope prone to failure was analyzed. This problem provides an example where chemically enhanced drainage can directly reduce the driving forces in a low-disturbance installation. A generic slope with a water table close to the surface was chosen as a representative example for slopes triggered by rainfall events. During the creation of the chemical drain, the factor of safety may decrease from 1.3 to 1.25, if the injection of the chemical coincides with high inflow rates, as is representative for a rainfall event. However, once the drain is formed, the water table downstream from the drainage section can be strongly reduced by the chemical drain, affording an increase in the global factor of safety from 1.3 to 1.5.

Moreover, the technique developed to address the phenomenon of locally increased hydraulic conductivity due to ions present in the pore water was applied to a third common geotechnical problem. A parametric study was carried out to assess the transport characteristics of a contaminant that crosses a hydraulic barrier perforated with steel piles. Laboratory experiments to quantify the parameters, as required for an analogous numerical implementation, were conducted for soils exposed to iron ions. A generic problem was numerically evaluated in order to predict the transport times of a contaminant through the barrier. The combined action of diffusion, corrosion and increased convection resulted in an overall increased transport rate and therefore in a significantly earlier arrival of the pollutant in the aquifer that was protected by a hydraulic barrier. The study showed conceptually that low-concentration pollutants may arrive in the aquifer up to four times earlier than expected based on the initially low hydraulic conductivity.

The investigations made as part of this thesis have shown that a targeted in situ soil improvement is feasible with guanidinium in smectite soil. The numerical simulations underline the high potential of the proposed technique in terms of efficiency and applicability to selected geotechnical-engineering problems. The tools developed to control the chemo-hydraulic coupling are also applicable to other problems caused by the interaction of pore-water chemistry with the soil matrix.
Kurzfassung


In einigen geotechnischen Situationen kann jedoch die Erhöhung der Durchlässigkeit für sich allein als Hauptbodenverbesserung betrachtet werden. Um das Potential dieser Anwendungsmöglichkeit zu zeigen, wurde die Wirkung der chemischen Verbesserung für zwei typische geotechnische Beispielprobleme untersucht.
Zunächst wurde ein chemisch verbesserter Brunnen numerisch untersucht, wobei der Hauptzweck des Brunnens eine Grundwasserabsenkung auf einer Baustelle sein soll. Die parametrische Untersuchung zeigte, dass die chemische Baugrundverbesserung am effizientesten ist, wenn nur eine kleine Zone unmittelbar um den Brunnen behandelt wird. Die chemische Modifizierung kann die Gesamtkosten der Baugrubenentwässerung reduzieren, wenn bei langfristiger Anwendung die Ersparnis durch die tieferen Betriebskosten die einmalig erhöhten Erstellungskosten übertrifft.


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Chapter 1: Introduction

1 Rationale of the thesis
Geotechnical engineering is a mature field, and yet there remain important problems to be solved, *e.g.*, how to stabilize a creeping landslide without cutting trenches for drainage or how to build pile foundations through hydraulic barriers without creating a preferential flow path for contaminant transport. The only way to find new effective solutions to these old problems is to search outside of the narrow box of soil mechanics and to venture into other fields, in particular, chemistry, biology and clay mineralogy. The thesis will be a step in such an interdisciplinary direction.

1.1 Main goal and objectives
Our ultimate long-term goal is to develop a fundamental understanding of the interaction of clay minerals with a broader range of environmentally acceptable chemicals. This will make it possible to further expand potential geotechnical applications of chemical soil improvement. The goal of the research described in this thesis is to investigate effects of different pore-fluid compositions on physical and mechanical properties of smectite clays, with the aim of enhancing drainage, reducing the swelling potential of clays, as well as assessing effects of steel-pile corrosion on creating conduits for contaminant transport along the piles. Element tests and physical-model experiments, together with numerical simulations, enable to quantify these phenomena and to develop recommendations for practical applications.

Towards this goal, the following significant objectives are pursued in the thesis:

Understanding and characterization of the interaction of clays with the pore fluid
For understanding and characterization of the interactions of clay minerals with pore fluids containing guanidine or iron ions, adsorption experiments are performed with different clay minerals and solution compositions. Based on the results of these measurements as main parameters, the adsorption/desorption affinity and kinetics as well as material influences are elucidated. As a result, chemo-mechanical interaction processes in the clay can be assessed for different pore-fluid compositions.

Chemically enhanced delivery: *in situ* formation of permeable zones in clayey soils
Permeability tests are performed with different pore-fluid chemistries to investigate their effects on the hydraulic conductivity of smectite clay. Based on the results of these element tests, the optimal pore-fluid chemistry is determined and the corresponding constitutive model for the coupled chemo-mechanical behaviour is developed. The constitutive model is incorporated into a
finite-element code and validated against experimental data. Numerical and analytical solutions are obtained to describe the permeability changes in one-directional and radial flow fields.

In order to illustrate possible practical applications of the soil-improvement technique, two geotechnical examples are analysed and evaluated numerically in parametric studies: the case of improved performance of a ground-water well and the stabilization of a slope by a chemically enhanced drainage.

Chemical interaction of foundation piles with hydraulic barriers

For the assessment of pile-corrosion effects on hydraulic barriers, permeability tests are performed with iron-rich pore fluid. Based on the results of these tests, the constitutive model for the coupled chemo-mechanical behaviour developed above is modified to account for a different pore-fluid chemistry. This constitutive model is then incorporated into a finite-element code, used to solve the problem of iron-cation diffusion originating from a corroding source, and applied to a virtual case study of pile foundations in a contaminated industrial site.

1.2 Literature review and gap of knowledge

1.2.1 Pore-fluid influences on the hydraulic conductivity of clays

The efficiency of a chemical or biological soil-improvement technology for clayey soils depends heavily on its ability to deliver agents to the problematic soil areas through fluid transport in porous media. Sometimes (e.g., Whiffin et al. 2007) the soil improvement resulting from chemical and biological reactions has a side effect of decreasing soil permeability, slowing down and even halting further delivery of agents. An acute need in practical methods capable of avoiding or, ideally, reversing these side effects inspires the search for chemicals that can increase soil permeability and enhance both their own transport and the transport of other soil-improving agents by first ‘opening’ the soil pores.

Numerous theoretical and experimental studies have emphasized the strong dependency of the soil permeability on the pore-fluid chemistry. Large increases in permeability can be observed when fine-grained soils are exposed to organic liquids or salt solutions. Major factors are the type of liquid (mainly through its dielectric constant; Fernandez and Quigley 1985, 1988, Bowders and Daniel, 1987), the type of dissolved salts and the ionic strength of the solutes (e.g., Madsen and Mitchell 1989; Lagaly et al. 2006). These studies were often carried out in the context of hydraulic-barrier design and containment of nuclear waste, where the increase was an unintended and dangerous effect caused by contaminants and leachates. Consequently, most of the organic
liquids and salt solutions, which were shown to increase soil permeability, were toxic and unsuitable for enhanced agent delivery for soil improvement.

This thesis investigates the suitability of guanidinium salts for the purpose of soil improvement combined with enhanced delivery of chemicals. Guanidinium ($C(NH_2)_3^+$) salts are readily dissolved in water and have been reported to be biodegraded by species occurring in natural surface water (Mitchell, 1987). Mineralogical investigations indicated that these strongly binding cations affect directly the interlayer distance of the stacked sheet-silicate structure of montmorillonite and stop its inner-crystalline swelling in water (Plötze and Kahr, 2008). The fact that this small molecule is not only strongly adsorbed but specifically intercalated in the smectite phase motivated its use as a chemical modifier in this study. As shown in this thesis, the effect leads to a significant increase in shear strength and decrease in the swelling potential of clayey soils, both of which are highly desirable results in the context of many geotechnical applications. Of particular importance for this study, however, is the ability of guanidinium — as demonstrated here — to increase soil permeability and to maintain this increased permeability under high confining stresses.

1.2.2 Modelling of the chemically modified soil properties via the pore fluid

The thesis attempts both to provide an understanding of the basic mechanisms behind the increased permeability and to quantify, experimentally and theoretically, the process of enhanced delivery of chemicals. Modelling of reactive advective flow with an evolving permeability field was initially performed with discrete interface-penetration models (Ravi and Jennings, 1990). Constitutive modelling of the processes for the increase of permeability on a micro-structural level of the pore system was proposed by Hueckel et al. (1997) and implemented in a coupled one-dimensional transport equation of the chemical (Kaczmarek et al. 1997). The problem of permeation that affects permeability is often encountered and modeled in the field of carbon-dioxide sequestration and transport of biocolloids (e.g., Xu et al. 2003; Keller and Auset 2007). The models developed in these contexts often focus on the slow processes (such as dissolution, precipitation or microbial growth) in multiscale approaches. However, the solutions obtained therein are not applicable for the case of soil improvement by enhanced delivery, as they are developed for dissolving rocks with initially low porosity (e.g., Wangen, 2013) or for soils with already-high flow rates (e.g., Ginn 2002). This thesis proposes a simple analytical enhanced delivery model and validates it against both experimental data on soil samples subjected to the flow
of guanidinium solution and a more sophisticated numerical analysis using the Comsol Multiphysics (2013) computing environment.

To summarize, one of the soil properties strongly influenced by chemicals in the pore solution is permeability. Large increases can be observed when fine-grained soil is permeated with organic liquids or salt solutions. This has so far been considered to be a negative effect on the performance of sealing clay liners and has not been adopted in a positive sense to transform soil locally into high-permeable zones acting as drainage conduits. This new approach requires an adequate quantification of the reaction, and new methods and numerical tools to model its implementations in geotechnical problems.

1.2.3 Effects of pile foundations on the performance of hydraulic barriers

Westcott et al. (2003) pointed out an increasing economic interest in construction on old landfills and waste deposits. They detected a lack of published research on the potential and actual contamination of ground water caused by the installation of pile foundations though these often soft and weak subsoils. Haymann et al. (1993) referred to three mechanisms for potential groundwater pollution due to the installation of pile through hydraulic barriers: direct transport during installation of the pile, wicking transport through the pile (mainly wooden piles) and conduit formation due to interface flow.

Achleitner et al. (2004) and Satyamurthy et al. (2008) showed that the direct transfer during installation is negligible and that during physical-modeling tests with dilute NaCl solution (0.24 M) no preferential flow along the pile was detectable. Kamon (2005) performed rigid-wall permeameter tests to study the influence of interface flow and considered it to be low under normally consolidated stress conditions. Both research groups, however, used non-swelling clays in their experiments and did not take into account the chemical interaction of the permeating fluid with the clay.

In contrast, Sridharan and Prakash (1999) have demonstrated that the clay mineralogy does have a great influence on the interaction with iron cations as well. Whereas iron will generate a dense structure in smectites, kaolinites tend to flocculate. The opposite behavior is observed when sodium ions are provided. In the context of nuclear-waste containment, the influence of corroding iron on bentonite properties became the subject of interdisciplinary research projects (Madsen and Kahr, 1991; Müller-Vonmoos et al., 1991). The results of a study by Carlson et al. (2007) emphasized the important influence of corrosion on the permeability and swelling potential of clays used as hydraulic barriers.
In summary, due to the low stiffness and strength of the barrier clay, foundations of structures on natural and artificial hydraulic barriers have often to be constructed using driven steel piles. The effects of the installation of such piles through these clay layers are controversially discussed, as they may impair the long-term performance of the hydraulic barrier. So far the effects of clay mineralogy and steel-pile corrosion on forming a preferential flow path along the pile foundation have not been considered and studied, even though some case studies suggest the existence of such a mechanism and call for its study, quantification and modeling.

1.3 Structure of the thesis

This thesis is structured into four main chapters (Chapters 2 to 5), each of them expected to make a valuable contribution towards the objectives laid out above.

After the introduction (Chapter 1), the interaction of the soil-improvement chemical is characterized thoroughly in an extensive experimental program both on a mineralogical and geotechnical level (Chapter 2). First, the general soil-improvement properties are assessed for standard geotechnical parameters. Second, the most important improvement effect of guanidinium — the increase in hydraulic conductivity — is investigated with a view to its potential for enhancing the delivery of pore fluids. Laboratory experiments on different scales were conducted to describe the mechanism of this process, both qualitatively and quantitatively.

Chapter 3 provides a detailed description of the constitutive relations governing the soil improvement and its propagation within porous media. Analytical and numerical solutions were obtained for the migration of the chemical and validated against the experimental data observed in the laboratory. In order to illustrate possible practical applications of the soil-improvement technique, two geotechnical examples are described in Chapter 4, both based on numerical simulations: the case of improved performance of a ground-water well and the stabilization of a slope by chemically enhanced drainage. A more exotic application of improved hydraulic conductivity is given in Appendix A, describing soil improvements by microbial cementation.

Chapter 5 extends the research to a wider scope by applying the newly developed numerical tools to a similar case of soil modification, but with a different chemical acting as the modifier. Effects of iron cations released due to corrosion of foundation piles are quantified experimentally in both chemical and geotechnical tests. A parametric study regarding the formation of vertical hydraulic conduits around a corroding steel pile demonstrates the practical consequences of the coupled hydro-chemical processes for aquifer contamination.

Finally, the conclusions and ideas for future research are summarized in Chapter 6.
Chapter 1: Introduction
Chapter 2: Characterization of the interaction of guanidinium with smectite soils

This chapter contains large portions of the first part of a journal publication (Minder et al., 2016), which were reorganized to fit into the structure of this thesis.

2.1 Introduction

This chapter describes an investigation of the suitability of guanidinium salts for the purpose of soil improvement combined with enhanced delivery of chemicals. Guanidinium ($C(NH_2)_3^+$) is readily dissolved in water and has been reported to be biodegraded by species occurring in natural surface water (Mitchell, 1987). Mineralogical investigations indicated that these strongly binding cations affect directly the interlayer distance of the stacked sheet-silicate structure of montmorillonite and stop its inner-crystalline swelling in water (Plötze and Kahr, 2008). The fact that this small molecule not only adsorbed strongly but specifically intercalated in the smectite phase motivated its use as a chemical modifier in this study. As shown below, this effect leads to a significant increase in shear strength and decrease in the swelling potential of clayey soils, both of which are highly desirable results in the context of many geotechnical applications. Of particular importance for this study is the ability of guanidinium to increase soil permeability and to maintain this increased permeability under high confining stresses.

By presenting the results of the laboratory testing, this chapter provides both a qualitative and quantitative interpretation of the fundamental processes underlying the proposed chemically enhanced delivery of soil-improvement agents.

2.2 Soil-improvement properties of guanidinium

In order to assess the soil improvement facilitated by guanidinium, laboratory tests were carried out on soil samples reconstituted using commercially available, standardised constituents. A commercial Ca-bentonite (Calcigel, Südchemie, Germany) with a total montmorillonite content of 65 wt.% was used as the fine-grain component. Other mineral phases present in this bentonite were quartz, feldspar, kaolinite, mica, and minor calcite. Where appropriate, the bentonite was mixed with rounded inert quartz grains (washed Perth sand, $d_{50} = 0.24$ mm, Cook Industrial Minerals, Australia).

The pore water of the reconstituted samples was prepared using a 0.01-mol/L CaCl$_2$ solution as standardised ground-water equivalent. Guanidinium concentrations were prepared from
analytical-grade guanidinium hydrochloride salt \((C(NH_2)_3Cl, \geq 99\%, \text{Fluka Analytical, Switzerland})\) and demineralised water.

2.2.1 *Shear strength*

The effects of the chemical modification on the strength parameters of the soil, in particular on the peak and residual shear resistance of bentonite samples, was assessed using a ring-shear apparatus. The samples were reconstituted before the tests from saturated, practically homo-ionic calcium bentonites with and without guanidinium, because in the ring-shear apparatus used in this study chemical modification of the soil within the sample cell was not possible. The residual shear resistance of the raw and modified pure bentonite was measured in a multi-stage procedure with a constant shear velocity and three different load steps for each sample. Figure 2.1 shows the residual shear stress after 30 to 40 mm of displacement for shear velocities of 0.2 mm/min and 0.01 mm/min. Moreover, the first load step was used to measure a first value for the peak-shear resistance (empty symbols in Figure 2.1). Assuming zero cohesion for these normally consolidated clay samples, the peak values were used to derive the peak friction angle for each material. Table 1 summarizes the results obtained for the friction angles from this data set. It shows that both peak and residual resistance are increased after chemical treatment.

![Figure 2.1](image_url)

*Figure 2.1: Results of multi-stage ring-shear tests on bentonite samples with shear velocities of 0.2 mm/min (left) and 0.01 mm/min (right). The empty symbols represent peak shear resistance of the initial failure during the first load step. The residual state (full symbols) was reached after 30 to 40 mm of displacement in each load step.*
### Table 1. Angle of internal friction (assuming zero cohesion) of bentonite samples in ring-shear tests.

<table>
<thead>
<tr>
<th></th>
<th>Raw material</th>
<th>Modified material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fast shearing</td>
<td>Slow shearing</td>
</tr>
<tr>
<td>Peak friction angle</td>
<td>24°</td>
<td>27°</td>
</tr>
<tr>
<td>Residual friction angle</td>
<td>7°</td>
<td>7°</td>
</tr>
</tbody>
</table>

#### 2.2.2 Swelling

The effects of the chemical modification on the swelling behavior were studied on reconstituted samples in oedometer cells. Initially dry powder samples of the raw calcium bentonite and the modified guanidinium bentonite were wetted with standardised artificial ground water (containing 0.01 mol/L CaCl₂) at low surcharge (12.5 kPa) and tested according to the sub-method B of the ASTM standard D 4546-03 (ASTM, 2003). This enabled assessing both the percentage of swelling at low stresses and the swelling pressure at zero volumetric strain. Figure 2.2 illustrates that both swelling parameters were drastically reduced due to the treatment with guanidinium.

![Swelling test graph](image)

**Figure 2.2: Swelling test: both the heave at low vertical stress (12.5 kPa) and the swelling pressure are reduced after treatment with guanidinium. The material tested was the same as in the ring-shear experiments (Figure 2.1).**

#### 2.3 Enhanced delivery potential of guanidinium

Whereas the soil-improvement ability of guanidinium is rather impressive, the most relevant guanidinium property in the context of this study is its suitability for chemically enhanced delivery. This implies an increase in hydraulic conductivity, which is quantified below based on oedometer and permeameter test results.
2.3.1 Oedometer tests

As a first step, the increase in permeability was measured based on the interpretation of time-settlement curves for pure bentonite samples. For this purpose, compacted samples of unmodified bentonite were reconstituted and mounted into a standard oedometer cell (sample height 20 mm, diameter 56.4 mm). The chemical agent was then delivered to the soil in the pore water by diffusion over 14 days from the top and the bottom filter plates. In order to increase the exchange rate, the liquid in the filter plates was replaced periodically in 48-h intervals with a fresh guanidinium solution of 2-mol/L concentration. A simple numerical evaluation of the diffusion process indicated that already after the third replacement 80% of the available adsorption sites were saturated. Hydraulic conductivities at different void ratios were derived based on subsequent incremental-loading experiments at pressures of up to 800 kPa. Untreated samples served as a reference.

Even for such a gentle treatment method, where the chemical is delivered diffusively via the sample boundaries, the oedometer tests showed a consistent improvement in hydraulic conductivity in pure Calcigel samples treated with guanidinium. The interpretation of the time-settlement curve based on the theory of one-dimensional consolidation yielded that — while the absolute permeability values decreased with increasing load — the relative improvement compared to the raw material of one order of magnitude was preserved (Figure 2.3). The aggregated clay minerals seemed to be able to keep the newly created flow paths open.

![Figure 2.3: Left: Decrease in hydraulic conductivity during incremental loading of pure bentonite samples (including log-linear regression). Right: Taking into account the individual void ratio of each sample, the parallel trend is well preserved. The relative improvement has not deteriorated during compaction.](image-url)
In real soils, however, the clay fraction — and the smectite content in particular — is in general much smaller than in pure bentonites. These soils consist mainly of quartz and feldspar grains, which do not react with the applied chemical but may form a stress-transferring skeleton structure. The relatively low content of clay is, however, still defining the total permeability as it fills the remaining space with its expandable high-water-content phases. Without fully representing natural soils, a step towards this more complex soil structure was taken by using sand/clay mixtures. Additional oedometer tests on compacted mixtures of bentonite (40%) and quartz sand (60%) were carried out to assess both the increase in permeability and the effects on stiffness due to the chemical treatment. Samples were reconstituted using either artificial ground water or guanidinium solutions and subsequently tested according to the procedure given in ASTM D2435-04 (ASTM, 2004). The evaluation of the time-settlement curves for three treated and three untreated samples provided hydraulic conductivities at different stress levels. Figure 2.4 shows clearly that even under vertical stresses of up to 800 kPa (corresponding to the smallest void ratios), the increased permeability has been maintained. These mixtures were also evaluated with respect to effects of guanidinium on potential changes in stiffness. The difference between unmodified and natural soil was small and in the order of the standard deviation for both initial loading and unloading/reloading (Table 2).

Figure 2.4: Left: Decrease of hydraulic conductivity during incremental loading of quartz/bentonite mixtures (including log-linear regression). Right: For identical void ratio the modified soil is consistently more permeable, by about one order of magnitude.
Table 2. Stiffness parameters averaged over three samples and three load steps each. Standard deviation is given in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Raw Material</th>
<th>Modified Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression index $C_c$</td>
<td>0.38 (0.04)</td>
<td>0.35 (0.02)</td>
</tr>
<tr>
<td>Swelling index $C_s$</td>
<td>0.09 (0.03)</td>
<td>0.11 (0.03)</td>
</tr>
</tbody>
</table>

### 2.3.2 Permeameter tests

Delivering a soil-improvement agent to the targeted area by mixing it with the soil or by diffusion are often not the optimal ways. Especially in deep-seated treatment zones, infiltration or injection of a chemical solution from bore holes provides a more efficient treatment technique. Treatment times for infiltration or injection of solutions are between those for the diffusive soaking as used above for pure clay samples in the first oedometer series and those for mechanical mixing as used above for quartz/bentonite mixtures in the second oedometer series. In order to evaluate the infiltration-delivery method, the same quartz-bentonite mixtures were used in constant-head permeameter tests, where the permeability was measured for both modified and unmodified soils. In a rigid-wall permeameter cell (sample height 40 mm, diameter 55 mm; Figure 2.5) the samples were subjected to a static vertical stress of 65 kPa and a hydraulic gradient of 100.

![Figure 2.5: Main components of the constant-head permeameter cell. The sample container shown in the center of the picture was a stainless steel cylinder of diameter 55 mm and accommodated samples of about 40 mm height. Vertical stress was applied with dead weights on top of the sample (far right).](image)

The effluent liquid was collected in a container on a precision balance. Reference values were obtained for modified and non-modified soils, and water was used as the permeation liquid. By mixing soils with guanidinium solutions an increase of the hydraulic conductivity by the factor of 30 was achieved (Figure 2.6). In addition, the temporal evolution of the permeability during flow-through treatment was recorded for a sample with initially unmodified soil and a guanidin-
um solution (concentration 500 mmol/L) as the permeation liquid. Even in this case, the average hydraulic conductivity increased over time by one order of magnitude (Figure 2.6).

![Figure 2.6: Evolution of hydraulic conductivity during flow-through treatment (dotted line) with guanidinium solution. For comparison the data for raw material (dashed line) and reconstituted modified soil samples (solid line) permeated with water are plotted.](image)

### 2.4 Mechanisms of enhanced delivery and drainage

Understanding the mechanisms of soil–guanidinium interaction requires experiments at different scales. Mineralogical analyses were carried out to quantify the reaction of the chemical with the clay phase. To investigate the changes in soil fabric and structure due to the cation exchange, a closer look on the resulting modifications at the particle and aggregate scales was taken.

#### 2.4.1 Exchange reaction at the mineralogical level

Sorption of guanidinium ions on clay surfaces was determined by batch-adsorption measurements. Soil samples were suspended in guanidinium solutions with different initial concentrations. Ion concentrations were measured in the supernatant after the reaction with the clay and compared with the initial concentration. The concentrations were determined using a fluorescent spectrometric method, after Conn and Davis (1959). The maximum adsorbed amount of guanidinium was compared with the cation-exchange capacity (CEC) of the clay measured with the copper-complex method (Meier and Kahr, 1999).

The hydration of the inner and outer crystalline clay surfaces was studied based on the static water-vapor adsorption from atmosphere, with controlled relative humidity ranging from 11% to 85% RH. Dry clay powder was thereby stored above saturated salt solutions in closed containers.
at constant temperature until the sample weight was stationary. Both adsorption and desorption paths of water were measured. All adsorption data are expressed relative to the dry weight of soil at 120 °C.

Guanidinium is adsorbed up to a saturation concentration (Figure 2.7). The well-fitting Langmuir sorption isotherm ($R^2=0.94$) indicates a limited amount of adsorption sites with the saturation constant of 6.2 mg/g. Based on the cation-exchange capacity of equivalently 7.4 mg/g, it can be concluded that more than 80% of the exchangeable cations in the clay phase are readily replaced by simple suspension in guanidinium solutions.

![Figure 2.7: Sorption of guanidinium ions. The dash dotted line indicates the theoretical maximum adsorption based on the cation-exchange capacity. The Langmuir sorption isotherm (solid line) with 95% confidence bands (dashed lines) is shown for the best-fit parameters.](image)

Smectite clays are generally capable of adsorbing large amount of water from humid air, due to interlayer hydration and capillary condensation. The measured curves for the unmodified bentonites — Calcigel and a sodium bentonite (MX-80, Amcol, USA) for comparison — are in good agreement with published data (e.g., Keren and Shainberg, 1975) and show the typical features such as the hysteresis during drying/wetting cycles and gradual (de-)hydration of cations. Modified bentonites however are much less sensitive to moisture and display reduced hysteresis during desorption (Figure 2.8).
2.4.2 Investigations on particle and pore scale

Homo-ionic bentonites were produced by saturation of Calcigel clay with 1.0-mol/L solutions of calcium and guanidinium, respectively. Images of the particles and aggregates were obtained using a scanning electron microscope. The grain-size distribution of the suspended material was measured with a laser-scattering analyser (Partica LA-950, Horiba, Retsch Technology, Germany).

After saturation, the modified soils were washed in suspension with demineralised water to remove excess ions and to avoid salt precipitation in the inter-particle pore space. Compacted samples were reconstituted from the washed material at water contents slightly above their liquid limit. Mercury-intrusion porosimetry (MIP, PASCAL 140/440, Porotec, Germany) on dry samples was used to quantify the alterations of the pore system due to guanidinium treatment. Crack-free pieces of the slowly dried clays were subjected to vacuum evacuation for 2 h prior to mercury intrusion.

During the preparation of modified bentonites sample, a granular, non-plastic behavior was observed. Images acquired with a scanning electron microscope (ESEM Quanta 600, FEI, Netherlands) in low-vacuum mode revealed that in suspension the clay fraction aggregated upon addition of guanidinium. Figure 2.9 shows the different aggregates observed after drying a drop of

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Figure 2.8: Influence of guanidinium modification on water adsorption of calcium bentonite (square) and sodium bentonite (triangle). Natural clays (dotted lines) show a high sensitivity to relative humidity and a pronounced hysteresis. Both phenomena are strongly reduced for the modified forms (solid lines).
the treated and untreated clay suspension, indicating a strong modification of the silt-sized grain fraction.

Figure 2.9: SEM images of dispersed bentonite after washing in suspension with demineralised water. The calcium form remains finely dispersed (left), whereas the exposure to guanidinium ions (right) leads to the formation of aggregates.

The measurement of the particle-size distribution supported this observation. Both calcium and guanidinium bentonites feature a bimodal distribution. However, the total volume fraction of the larger mode, containing the aggregates, has almost doubled for the guanidinium samples (42.4%), as compared to the calcium clay (22.4%), see Figure 2.10.

Figure 2.10: Bimodal particle-size distribution measured with laser diffraction. The volume fraction of the larger mode (aggregates) is significantly increased through the chemical modification.

Compacted samples were analysed using MIP, in order to examine whether these aggregates were rigid enough to maintain an open-pore structure. Considerable changes in the pore system
were detected. Even though the unmodified soil was prepared at a higher water content (\(w_{L,\text{Ca}} = 102\%\)) the modified bentonite (\(w_{L,\text{Gnd}} = 64\%\)) features a larger accessible pore volume (Figure 2.11). Whereas the reliability of the absolute values obtained by MIP is a subject of debate and strongly depends on the measurement procedure (Penumadu and Dean, 2000), the relative difference between the samples is apparent. The largest contribution to the additional pore volume stems from pores with an average radius of 2 µm. The total pore volume of these larger pores had increased; the volume of the smaller pore fraction (radius < 0.1 µm), however, was slightly reduced compared to the reference material.

![Figure 2.11: Cumulative pore-size distribution of two bentonite samples measured with mercury-intrusion porosimetry. The modified material features a significantly larger volume fraction for pores with a radius of about 2 µm.](image)

**2.5 Conclusion**

In this chapter, the concept of enhanced delivery of chemicals for soil-improvement applications based on clay treatment with guanidinium-salt solutions was explored. This treatment was shown to cause a significant increase in shear strength and decrease in the swelling potential of clayey soils, both of which are highly desirable in the context of many geotechnical applications. In contrast to a number of other soil-improvement techniques, which reduce permeability during treatment, the experiments reported here have shown that guanidinium can increase the hydraulic conductivity of both pure bentonites and quartz/bentonite mixtures by an order of magnitude.

Based on the experimental work on different length scales, the following conclusions could be drawn:
The origin of the increase in permeability due to guanidinium ions lies in its fixation to the inner and outer clay surfaces, due to a cation-exchange reaction. This fixation results in a strong inhibition of the water uptake into the interlayer space and an aggregation of the clay minerals.

The aggregated, non-swelling particles provide an open pore system with pores of about 2 μm. Upon wetting, these pores are no longer filled with an expanding clay phase but kept open. The pore water remains available for circulation and is not bound as immobile interlayer water. The compression tests have shown that the structure is stable also under stresses of up to 800 kPa.

Despite these drastic changes on the microstructural level, the stiffness is not significantly affected by chemical treatment. A negative influence on this particular mechanical property can therefore be excluded.
3 Modelling the evolution of the in-situ modification
This chapter builds on the second part of the paper (Minder et al.; 2016) but extends the analysis of the treatment process of soil with guanidinium solutions from a purely one-dimensional configuration to a radial configuration.

For the understanding of the hydro-chemical mechanisms underlying the enhanced delivery processes, analytical and numerical tools were adapted to the problem at hand, that is, a porous medium with chemically modifiable permeability. The transient, self-accelerating transport of the chemical by the pore fluid was modeled in a one-dimensional boundary-value problem using two methods. First, the simplified problem of discrete front propagation of the reactive fluid was solved analytically. Second, a more sophisticated approach of advective-diffusive transport of a reactive chemical was pursued, by modeling the processes using a commercial finite-element code for simulating coupled phenomena (Comsol Multiphysics, 2013). Both solutions were compared to the experimentally measured data for validation of the constitutive assumptions made in the derivation. Subsequently, the same two steps were repeated for a radial-symmetric boundary-value problem.

3.1 Hydro-chemical modelling of enhanced delivery in flow columns
3.1.1 Problem definition
In order to provide an analytical solution for the enhanced delivery process, the one-dimensional boundary-value problem for the advective propagation of a chemical front in a hydraulically modified porous medium is solved (see Figure 3.1). Field variables are the hydraulic head $h(x, t)$ (unit: m) and the chemical concentration in the pore fluid $c(x, t)$ (unit: mol/L).

The state of the current degree of treatment of the sample can be described by the normalized state parameter $x_f/L$, where $x_f$ stands for the position of the chemical front (unit: m). For all $x < x_f$ the concentration of guanidinium in the pore liquid is considered to be $c(x, t) > 0$. The experimental set-up is described by the parameters $L$ (sample length in m), $\Delta h$ (total pressure head in m) and $c_{in}$ (concentration of the chemical in the injection fluid in mol/L).
Figure 3.1: Formulation of the one-dimensional boundary-value problem. For a given chemical-front position $x_f(t)$, the hydraulic head $h(x, t)$ is a bilinear function. In the segment $x < x_f$, the chemical concentration in the pore fluid is equal to the inflow concentration and the adsorption sites on the solids are fully saturated. The increased hydraulic conductivity $k(x,t)$ is attributed to this segment. The untreated part ahead of the chemical front has the properties as the initial soil.

The hydraulic boundary conditions for a constant-head test are:

$$
\begin{align*}
    h(x = 0, t) &= \Delta h \\
    h(x = L, t) &= 0
\end{align*}
$$

(3.1)

The chemical concentration at the injection point is $c(x = 0) = c_{in}$ for $t > 0$. It is assumed that at the outlet at the sample end advection is the dominating effect that causes mass transport through the outflow boundary. The mass flux due to diffusion across the boundary is therefore assumed to be zero, in which case the boundary condition can be defined as $c''(x = L) = 0$ (e.g., Galeati and Gambolati 1989).

The initial conditions are taken from those of a stationary flow for a completely untreated sample:
Chapter 3: Modelling

\[ h(x, t = 0) = \Delta h \cdot \left(1 - \frac{x}{L}\right) \]
\[ c(x, t = 0) = 0 \]
\[ x_f(t = 0) = 0 \]  \hspace{1cm} (3.2)

3.1.2 Constitutive relations

The advective flow velocity \( v \) (m/s) in the porous media is considered to follow Darcy’s law:

\[ v = -\frac{dh}{dx} \cdot k(x, t) \]  \hspace{1cm} (3.3)

where \( k(x, t) \) is the local hydraulic conductivity of the soil (m/s).

The effective flow velocity \( u \) (m/s) in the pore system is

\[ u = \frac{v}{n_e} \]  \hspace{1cm} (3.4)

where \( n_e \) is the effective porosity contributing to the flow.

According to the batch experiments, adsorption of the chemical follows a Langmuir-type sorption isotherm (Figure 3.2, solid line), which links the adsorbed amount of chemical \( c_{ads} \) to the field variable \( c(x, t) \) (Langmuir, 1918). The analytical sorption function is designed for one-site adsorption processes and can be written as

\[ c_{ads}(x, t) = \frac{c_{max} \cdot K_L \cdot c(x, t)}{1 + K_L \cdot c(x, t)} \]  \hspace{1cm} (3.5)

where \( c_{ads} \) is the adsorbed mass of guanidinium per dry unit weight of soil (mg/g), \( c_{max} \) the maximum amount of guanidinium that can be adsorbed by the soil (mg/g), \( K_L \) the adsorption constant related to the binding energy (L/mol), and \( c(x, t) \) the concentration of guanidinium in the solution in equilibrium with the adsorbed substance (mol/L).
This relationship describes a gradual adsorption of the chemical depending on the available concentration in the liquid. In the simplified analytical model the soil will only feature two distinct states: untreated (with no chemical either in the fluid or adsorbed on the solids) and treated (with all substance provided through the pore fluid being fully adsorbed to the solid until saturation). The reaction is furthermore considered to be fast compared to the flow velocity and irreversible, since no guanidinium desorption was observed after intercalation into the interlayer. This simplified adsorption reaction is expressed by an irreversible saturation-type sorption isotherm

\[ c_{ads}(x, t) = \begin{cases} 0 & \text{for } c(x, t) = 0 \\ c_{max} & \text{for } c(x, t) > 0 \end{cases} \]  

(3.6)

This simplified isotherm is also illustrated in Figure 3.2 (dashed line). For the boundary-value problem formulated in Figure 3.1, the purely advective transport implies in non-adsorbing porous media a binary state for \( c(x, t) \), due to mass balance. \( c = c_{in} \) for \( c > 0 \). A porous medium with fully saturated sorption sites (\( c_{ads} = c_{max} \)) is, in terms of advective transport, equivalent to a non-adsorbing medium. The adsorption isotherm in (3.6) states that for \( c > 0 \), \( c_{ads} = c_{max} \), i.e., the porous media behind the front is fully saturated and behaves non-adsorbing for further transport. The binary state of the concentration on the solid given by the isotherm therefore implies a binary state for the concentration in the fluid as well, with

\[ c(x, t) = \begin{cases} c_{in} & \text{for } x \leq x_f \\ 0 & \text{for } x > x_f \end{cases} \]  

(3.7)
Where the reagent has adsorbed to the solid phase, the material is considered to feature locally the increased permeability. In the discrete model it is assumed that the increase is instantaneous and of constant magnitude once the sorption sites are fully saturated with the chemical. The hydraulic properties can therefore be directly coupled to the adsorbed concentration $c_{ads}$:

$$k(x, t) = f(c_{ads}) = \begin{cases} 
k_0 & \text{for } c_{ads} = 0 \\
\chi \cdot k_0 & \text{for } c_{ads} = c_{max}
\end{cases}$$  \hspace{1cm} (3.8)

where $k_0$ is the initial hydraulic conductivity (m/s); the dimensionless parameter $\chi$ describes the relative increase of the hydraulic conductivity due to the chemical modification of the soil. Since the definition of the front position states that for $x < x_f$ the concentration in the pore fluid is $c(x < x_f, t) > 0$, the coupling defined in (3.6) and (3.8) can be equivalently expressed as

$$k(x, t) = \begin{cases} 
k_0 & \text{for } x_f(t) < x < L \\
\chi \cdot k_0 & \text{for } 0 < x < x_f(t)
\end{cases}$$  \hspace{1cm} (3.9)

### 3.1.3 Derivation of transient solution for $t > 0$

#### A) Hydraulic field for a given front position

At a given time $t$, the front is located at $x_f(t)$ and the sample features two segments of constant hydraulic conductivity. In each segment the pressure drop is linear and can be expressed with the unknown pressure head at the front $h(x = x_f, t)$. The drop in pressure head along the two segments of the sample is

$$\Delta h_a = h(x = x_f, t) - h(x = 0, t)$$

$$\Delta h_b = h(x = L, t) - h(x = x_f, t)$$  \hspace{1cm} (3.10)

By assuming an incompressible fluid and no change in porosity, mass conservation of the fluid yields that the flow velocity in both segments $v_a$ and $v_b$ have to be identical. They both follow the constitutive relations (3.3) and (3.9):

$$v_a = -\frac{\Delta h_a}{x_f} \cdot \chi \cdot k_0 = -\frac{\Delta h_b}{(L - x_f)} \cdot k_0 = v_b$$  \hspace{1cm} (3.11)

Using the hydraulic boundary conditions (3.1), Equation (3.11) can be solved for the pressure head at the moving front $h(x = x_f, t)$:
h(x = x_f, t) = \Delta h \frac{(1 - \frac{x_f(t)}{L})}{1 + \frac{x_f(t)}{L} \left(\frac{1}{\chi} - 1\right)} \quad (3.12)

The flow velocity \( v(t) \) is constant along the entire sample and can be found by combining (3.10) and (3.12) with one side of the equilibrium of (3.11). In normalized form, this yields

\[
\frac{v(t)}{v_0} = \frac{1}{1 + \frac{x_f(t)}{L} \left(\frac{1}{\chi} - 1\right)}
\]

where \( v_0 = \frac{\Delta h}{L} k_0 \) is the initial stationary flow velocity (m/s). Based on this flow rate an indicator of enhanced delivery progress is defined by introducing the current average hydraulic conductivity \( k_m(t) \) (m/s). This parameter lumps the conductivity profile of the segmented sample into an equivalent homogeneous hydraulic conductivity of the entire sample as \( k_m = v \cdot L / \Delta h \). In normalized form, this yields with (3.13):

\[
\frac{k_m(t)}{k_0} = \frac{v(t) \cdot L}{\Delta h} = \frac{1}{1 + \frac{x_f(t)}{L} \left(\frac{1}{\chi} - 1\right)}
\]

B) Retardation due to adsorption

If the chemical substance reaches untreated material through the pore fluid, some part of it is adsorbed to the solid, and only after the solid is locally saturated, the remaining part of the chemical becomes available for further advective transport. The average propagation velocity of the chemical front is therefore smaller than the effective flow rate. This effect is in general described by introducing the retardation factor \( R \), as the ratio of the effective flow rate of the liquid and the average transport velocity of the chemical.

\[
R = \frac{\text{effective flow rate}}{\text{front velocity}} = \frac{u}{x_f} = \frac{v}{x_f \cdot n_e}
\]

Methods exist to define this value according to the adsorption isotherms (e.g., Zhu and Anderson, 2002). For instance, the retardation of transport of an adsorbing solute according to a Langmuir isotherm (3.5), without any hydraulic effects, is given as

\[
R = 1 + \frac{\rho_s}{n_e} \left(\frac{K_L \cdot c_{\text{max}}/n_{GND}}{(1 + K_L \cdot c)^2}\right)
\]

where \( \rho_s \) is the solid density (kg/m³) and \( n_{GND} \) is the molar mass of guanidinium (g/mol).
For the simplified isotherm (3.6), with assumed irreversible and saturating-type reaction of guanidinium to smectite, \( R \) can be calculated based on a mass balance of the substance. For all \( x < x_f \) the concentration of guanidinium in the pore liquid is considered to be equal to the concentration of the chemical in the injection fluid: \( c(x, t) = c_{in} \). In a time increment \( dt \), the volume of treated zone grows by \( \dot{x}_f \cdot dt \). The incremental amount of inflowing substance balances the substance in the pore fluid and on the solid phase of the additional volume, due to the propagated front (see also Figure 3.1):

\[
\text{amount inflow} = \text{amount in pore fluid} + \text{amount on solid} \\
(v \cdot c_{in})dt = (c_{in} \cdot n_e) \cdot \dot{x}_f dt + \left( (1 - n_e) \cdot \rho_s \cdot \frac{c_{\text{max}}}{n_{\text{Gnd}}} \right) \cdot \dot{x}_f dt
\]

Substituting \( q \) into the definition of \( R \) as given in (3.15), the retardation factor for irreversible limited adsorption then can be found as

\[
R = 1 + \frac{(1 - n_e) \cdot \rho_s \cdot c_{\text{max}}}{n_e \cdot c_{in} \cdot n_{\text{Gnd}}} 
\]

(3.18)

For a given soil (with properties \( n_e \), \( c_{\text{max}} \) and \( \rho_s \)) \( R \) will only depend on \( c_{in} \), i.e., on how much chemical is provided by the pore fluid relative to the adsorption sites in one unit volume:

\[
R = 1 + \frac{1}{\tilde{c}_{in}}
\]

(3.19)

with \( \tilde{c}_{in} = \frac{c_{in} \cdot n_e \cdot n_{\text{Gnd}}}{(1 - n_e) \cdot \rho_s \cdot c_{\text{max}}} \) being the normalized inflow concentration (%). 

C) Transient solution

The differential equation of the front position is found by substituting Equation (3.13) into (3.15):

\[
\dot{x}_f = \frac{dx_f}{dt} = \frac{v}{R \cdot n_e} = \frac{v_0}{R \cdot n_e} \cdot \frac{1}{1 + \frac{x_f}{L} \left( \frac{1}{\chi} - 1 \right)} 
\]

(3.20)

The transient solution is found by integrating this equation over time and using the initial conditions provided in (3.2):

\[
x_f^1 + \frac{x_f^2}{2L} \left( \frac{1}{\chi} - 1 \right) = \frac{v_0}{R \cdot n_e} t
\]

(3.21)
Without any change in soil permeability ($\chi = 1$) and without retardation ($R = 1$), Equation (3.21) provides the inert transition time $t_0$ (s) after which a non-reactive front will reach the end of the sample

$$t_0 = t(x_f = L) = \frac{n_e \cdot L}{q_0} = \frac{n_e \cdot L^2}{\Delta h \cdot k_0} \tag{3.22}$$

For $\chi > 1$ Equation (3.21) provides the transient solution for the relative front position $x_f/L$ (the other root of Equation (3.21) yields a physically impossible negative value of $x_f$):

$$\frac{x_f}{L}(t) = \sqrt{1 + 2\left(\frac{1}{\chi} - 1\right) \frac{v_0 \cdot t}{R \cdot n_e \cdot L} - 1} \tag{3.23}$$

By normalizing time as $T = \frac{t}{t_0}$ the dimensionless transient solution for the normalized front position $X_f = \frac{x_f}{L}$ is obtained as

$$X_f(T) = \sqrt{1 + 2\left(\frac{1}{\chi} - 1\right) \frac{T}{R} - 1} \tag{3.24}$$

This equation is only valid until the chemically retarded front reaches the end of the sample after the reactive transition time $T_{max}$. This limit can be found by equating (3.24) for $X_f = 1$

$$T_{max} = \frac{R}{2} \left(\frac{1}{\chi} + 1\right) \tag{3.25}$$

As shown in Figure 3.3, for a parametric study relevant for the geometry of the flow column experiment in Chapter 2.3.2, the front constantly accelerates during propagation due to improved hydraulic conductivity until it reaches the end of the sample. Once the chemical front has propagated through the entire sample, it is assumed that the front position remains at $x_f(T > T_{max}) = L$. Heavy retardation may increase the reactive transition time up to the inert transition time and even above (for $R > 2/\left[\frac{1}{\chi} + 1\right]$). This can be the case if the inflow concentration is low compared to the concentration required for full saturation (see Equation (3.19)).
Figure 3.3: Relative front position \( X_f = x_f / L \) vs normalized time \( t / t_0 \): (top) for different \( R \) and \( \chi = 13 \); (bottom) for different \( \chi \) and \( R = 2 \) (resp. \( \xi_{in} = 1 \)).

Substituting the obtained transient solution for the front position in (3.13) provides the solution for the current normalised flow rate \( Q(T) \) and the current average hydraulic conductivity of the entire sample over time.

\[
Q(T) = \frac{v}{v_0}(T) = \frac{k_m}{k_0}(T) = \left(1 + 2\left(\frac{1}{\chi} - 1\right) \frac{T}{R}\right)^{-0.5}
\]  

(3.26)

For times larger than the reactive transition time in Equation (3.25) the flow rate becomes constant and corresponds to stationary flow with increased permeability:

\[
Q(T) = \frac{v}{v_0}(T) = \frac{k_m}{k_0}(T) = \chi \quad \text{for} \ T > T_{max}
\]  

(3.27)
D) Cumulative flow volume

In the experimental setup the directly measured quantity for the flow is the cumulative flow volume, as recorded by the balance at the outlet. To account for sample size and geometry this fluid flow is commonly expressed as dimensionless pore volume $PV$, taking the ratio of the cumulative flow volume $V_{\text{Flow}}$ of the effluent pore fluid and the effective pore volume $V_{\text{Pore}}$ of the sample. For a comparison of the analytical model with experimental data, $PV(T)$ is derived based on the transient solution obtained above by integration over time for the flow rate given by (3.26) and (3.27):

$$PV(T) = \frac{V_{\text{Flow}}}{V_{\text{Pore}}} = \frac{\int v dt}{n_e L}$$

$$= \left\{ \begin{array}{ll}
\frac{R}{(1/\chi - 1)} \left( \sqrt{1 + 2(1/\chi - 1) \frac{T}{R} - 1} \right) & \text{for } T \leq T_{\text{max}} \\
R + \chi (T - T_{\text{max}}) & \text{for } T > T_{\text{max}}
\end{array} \right. \tag{3.28}$$

Figure 3.4 shows a parametric evaluation of Equation (3.28) for different retardation factors $R$ and different improvement factors $\chi$ for the geometry of the flow-column experiment described in Chapter 2.3.2. Initially, the cumulative flow for any $R$ or $\chi$ will not vary significantly. Calibration of the model parameters can be performed by fitting the final inclination (providing $\chi$) and the point with highest curvature (providing $R$).
Figure 3.4: Normalized cumulative flow vs dimensionless time: (top) for different $R$ and $\chi = 13$; (bottom) for different $\chi$ and $R = 2$ (resp. $\varepsilon_{\text{in}} = 1$).

3.2 Numerical evaluation of one dimensional propagation including diffusion

In order to validate the above analytical solution and to assess the influence of diffusion, a numerical analysis of the same boundary-value problem (coupled advective-diffusive transport of a hydraulically active chemical in the pore fluid) was carried out using a commercial finite-element code (Comsol Multiphysics). The standard modules for flow in porous media (“Darcy’s Law”) and advective-diffusive-reactive (ADR) transport of a dissolved chemical (“Species transport in Porous Media”) were used. The flow was described using Darcy’s Law as given in (3.33). Transport of the chemical included three components: (a) advective flux due to a flow velocity ($j_{\text{adv}} = -v \cdot c$), (b) diffusion flux according to Fick’s law due to a concentration gradient ($j_{\text{diff}} = -n_e \cdot D \cdot \nabla c$), where $D$ is the diffusion coefficient of the chemical in porous media (m²/s), and (c) reaction according to a Langmuir-isotherm as given in (3.5) due to adsorption.
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The first level of coupling was achieved by sharing the flow velocity $v$ among both the flow in porous media and the advective transport flux, which can be achieved using the implemented coupling settings of the software.

The implementation of the hydro-chemical coupling of improved hydraulic properties due to guanidinium adsorption was achieved by manually defining a time-dependent parameter field for the hydraulic conductivity for the whole domain. Hydraulic conductivity was directly coupled to the adsorbed amount of chemicals

$$k(x, t) = k_0 \cdot \left(1 + (\chi - 1) \frac{c_{ads}(x, t)}{c_{eq}}\right) \quad (3.29)$$

where $c_{eq}$ is the equilibrium concentration of adsorbed mass (mg/g) for a given inflow concentration.

$$c_{eq} = \frac{c_{max} \cdot K_L \cdot c_{in}}{1 + K_L \cdot c_{in}} \quad (3.30)$$

In contrast to the analytical model (see Equation (3.8)), local hydraulic conductivity increases linearly from $k_0$ for $c_{ads} = 0$ to $\chi \cdot k_0$ for $c_{ads} = c_{eq}$. The numerical code formulated mass conservation of fluid and chemical species over the problem domain and integrated over time with an implicit integration scheme to provide a transient solution. The geometry of the problem was chosen to fit the experimental sample dimensions of the flow-column tests. Table 3 gives a brief summary of the used parametric input to the simulation.

<table>
<thead>
<tr>
<th>Sample length</th>
<th>L</th>
<th>40 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>$n_e$</td>
<td>0.334</td>
</tr>
<tr>
<td>Solid density</td>
<td>$\rho_s$</td>
<td>2.65 kg/L</td>
</tr>
<tr>
<td>Hydraulic gradient</td>
<td>$i$</td>
<td>105</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>$k_0$</td>
<td>2.21e-9 m/s</td>
</tr>
<tr>
<td>Relative improvement factor</td>
<td>$\chi$</td>
<td>13</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$D$</td>
<td>1e-9 m$^2$/s</td>
</tr>
<tr>
<td>Inflow concentration</td>
<td>$c_{in}$</td>
<td>0.5 mol/L</td>
</tr>
<tr>
<td>Adsorption maximum</td>
<td>$c_{ads}$</td>
<td>6.2 mg/g</td>
</tr>
<tr>
<td>Langmuir parameter</td>
<td>$K_L$</td>
<td>55.6 L/mol</td>
</tr>
<tr>
<td>Molar mass of guanidinium</td>
<td>$n_{Gnd}$</td>
<td>60.08 g/mol</td>
</tr>
</tbody>
</table>

Table 3. Summary of the parameters used in the numerical model of the flow column test.
3.3 Comparison of the analytical and numerical model with laboratory data

The analytical model predicts for the observed experimental improvement $\chi = 13$ and a theoretical $R_{\text{Langmuir}} = 1.05$ (Equation (3.16)) that the chemical front would propagate through the entire sample by $T_{\text{max}}(R = 1.05; \chi = 13) = 0.57$. In other words, instead of reaching a breakthrough of a non-reactive chemical after $T_{\text{max}}(R = 1.0; \chi = 1) = 1$, a breakthrough of the adsorbing and hydraulically active chemical should be observed after $T = 0.57$. This is a direct result of the self-acceleration of the treatment in the constant-head delivery of the chemical. In contrast, using Equation (3.18) as an estimate for the retardation yields $R_{\text{mass balance}} = 2.09$, so that the retarded reactive transition time becomes $T_{\text{max}}(R = 2.09; \chi = 13) = 1.12$. (A hypothetical chemical that would adsorb as much as guanidinium but without affecting the hydraulic properties would travel the full length of the sample in $T_{\text{max}}(R = 2.09; \chi = 1) = 2.09$.)

In the top panel of Figure 3.5, the normalized cumulative flow PV predicted by the analytical model for these two retardation factors is compared with the numerical-model prediction. In spite of numerous simplifying assumptions made in the analytical model, the numerical model produces almost identical predictions for the cumulative flow as does the analytical one for the retardation factor, calculated assuming irreversible adsorption ($R = 2.09$). This result confirms the validity of Equation (3.18). Apart from a slightly earlier completion of the treatment, diffusive transport alone does not seem to significantly affect the enhanced delivery process.

Plotting the cumulative flow volume $PV$ observed in the experiment against the dimensionless time $T$ (bottom panel of Figure 3.5), together with the analytical predictions for the two cases of $R_{\text{Langmuir}} = 1.05$ and $R_{\text{mass balance}} = 2.09$, one can see a considerably better agreement for the mass-balance predictor. The best fit of the analytical model to the experimental data is, however, obtained with $R_{\text{best fit}} = 1.91$ and a corresponding $T_{\text{max}} = 1.03$, i.e., the observed enhanced delivery takes place 9% faster than theoretically predicted. A possible explanation for this acceleration is the formation of preferential flow paths. Indeed, the flow-through experiments show a higher increase in hydraulic conductivity than the permeability test in the oedometer cells. One possibility would be that during permeation erosion of fines occurs. But, as no fines were observed in the effluent and as the mix-treated samples featured higher permeability right from the beginning of the testing, this difference can more likely be attributed to the creation of preferential flow paths or the decreasing tortuosity/increasing connectivity of the pores. The results from mercury-intrusion porosimetry show a clearly dominating pore-radius size of 2 $\mu$m that completely defines the hydraulic conductivity and distribution of chemicals for flow-through conditions. Given that the models presented do not account for potential preferential flow paths, the
deviations of their predictions from measured data are hardly surprising. The measurements show an early rise in flow rate, as some high-permeability channels might have developed already over the entire sample length, whereas both the analytical and the numerical model still feature an untreated sample end that keeps the flow rate low. Possible approaches to capturing this phenomenon include taking into account different flow velocities for the channel flow and intra-aggregate flow, or modeling the dispersion of the front.

**Figure 3.5:** Normalized cumulative flow vs dimensionless time, analytical-model predictions for different retardation factors $R=1.05$, $1.91$ and $2.09$ compared with the predictions of the numerical model (top) and experimental data (bottom).
### 3.4 Analytical modeling of the radially propagating permeable zone

In this chapter, the analysis of the treatment process of soil with guanidinium solutions is extended from the purely one dimensional configuration in Cartesian coordinates to a radial configuration. The radial configuration is often encountered in applications where the substance is injected from a bore hole into the soil. The following derivations may seem in large parts repetitive, as they are developed analogously to Chapter 3.1. But they are given here in full, for the reader’s convenience, so that the chapters can be read individually.

#### 3.4.1 Problem definition for the radial problem

To provide an analytical solution for the enhanced delivery process around a bore hole, the axisymmetric boundary-value problem for an advective propagation of a chemical front in a hydraulically modified porous medium is solved below (Figure 3.6). Field variables are the hydraulic head \( h(r, t) \) (unit: m) and the chemical concentration in the pore fluid \( c(r, t) \) (mol/L).

\[
0 \quad r_{in} \quad r_f(t) \quad r_{out} \quad r
\]

\[
h_{in} = \Delta h \quad h_f(t) \quad h_{out} = 0
\]

\[
c_{in} \quad c \quad c = 0
\]

\[
\chi \cdot k_0 \quad k_0
\]

**Figure 3.6: Formulation of the radial boundary-value problem.** For a given chemical front position \( r_f(t) \), the hydraulic head \( h(r, t) \) follows two logarithmic curves. In the segment \( r < r_f \), the chemical concentration in the pore fluid is equal to the inflow concentration and the adsorption sites on the solids are fully saturated. The increased hydraulic conductivity \( k(r, t) \) is attributed to this segment. The untreated part ahead of the chemical front has the same properties as the initial soil.
The state of the degree of treatment of the sample can be described using the normalized state parameter \( R_f = (r_f - r_{in})/(r_{in} - r_{out}) \), where \( r_f \) stands for the position of the chemical front (m). For all \( r < r_f \), the concentration of guanidinium in the pore liquid is considered to be \( c(r, t) > 0 \). The experimental set-up is described by the parameters \( r_{in} \) (radius of the injection pipe in m), \( r_{out} \) (outer radius of the model in m), \( \Delta h \) (total pressure head in m) and \( c_{in} \) (concentration of the chemical in the injection fluid in mol/L).

The experimental set-up is described by the parameters \( r_{in} \) (radius of the injection pipe in m), \( r_{out} \) (outer radius of the model in m), \( \Delta h \) (total pressure head in m) and \( c_{in} \) (concentration of the chemical in the injection fluid in mol/L).

The hydraulic boundary conditions for a constant-head test are:

\[
\begin{align*}
  h(r = r_{in}, t) &= \Delta h \\
  h(r = r_{out}, t) &= 0
\end{align*}
\]

The chemical concentration at the injection point is \( c(r = r_{in}) = c_{in} \) for \( t > 0 \). As in the axial one-dimensional configuration, it is assumed that the advection is the dominating effect at the outlet at the sample that causes mass transport through the outflow boundary. The mass flux due to diffusion across the boundary is therefore assumed to be zero, in which case the boundary condition can be defined as \( c''(r = r_{out}) = 0 \).

The initial conditions are taken from those for a stationary flow for a completely untreated sample:

\[
\begin{align*}
  h(r, t = 0) &= \frac{\Delta h}{\ln\left(\frac{r_{out}}{r_{in}}\right)} \cdot \ln\left(\frac{r}{r_{in}}\right) \\
  c(r, t = 0) &= 0 \\
  r_f(t = 0) &= 0
\end{align*}
\]

### 3.4.2 Constitutive relations

The advective flow velocity \( v \) (m/s) in radial direction in the porous medium is considered to follow Darcy’s law:

\[
v = -\frac{dh}{dr} \cdot k(r, t)
\]

where \( k(r, t) \) is the local hydraulic conductivity of soil (m/s).

This implies an effective flow velocity \( u \) (m/s) and a total mass flux (i.e., flow rate) \( q \) (m²/s) in the pore system as
\[ u = \frac{v}{n_e} \]  
\[ q = v \cdot 2\pi r \]  
(3.34)  

where \( n_e \) is the effective porosity contributing to flow.

Mass conservation of the pore fluid yield for a homogeneous medium the following equations for \( h(r) \), \( q(r) \) and \( v(r) \). (See also the initial condition.)

\[ h(r) = \frac{\Delta h}{\ln \left( \frac{r_{out}}{r_{in}} \right)} \cdot \ln \left( \frac{r}{r_{in}} \right) \]  
(3.35)  

\[ q(r) = \frac{2\pi k_0 \cdot \Delta h}{\ln \left( \frac{r_{out}}{r_{in}} \right)} = q_0 = \text{const} \]  
(3.36)  

\[ v(r) = \frac{k_0 \cdot \Delta h}{\ln \left( \frac{r_{out}}{r_{in}} \right)} \cdot \frac{1}{r} \]  
(3.37)  

Different from the one-dimensional case, the flow velocity decreases hyperbolically and the hydraulic head varies according to a logarithmic function. The flow rate \( q \) however remains constant over the radial coordinate, due to continuity.

According to the batch experiments, adsorption of the chemical follows a Langmuir-type sorption isotherm (Figure 3.2, solid line), which links the adsorbed amount of chemical \( c_{ads} \) to the field variable \( c(r, t) \) (Langmuir, 1918). The analytical sorption function is designed for one-site adsorption processes and can be written as

\[ c_{ads}(r, t) = \frac{c_{max} \cdot K_L \cdot c(r, t)}{1 + K_L \cdot c(r, t)} \]  
(3.38)  

where \( c_{abs} \) is the adsorbed mass of guanidinium per dry unit weight of soil (mg/g), \( c_{max} \) the maximum amount of guanidinium that can be adsorbed by the soil (mg/g), \( K_L \) the adsorption constant related to the binding energy (L/mol), and \( c(r, t) \) the concentration of guanidinium in the solution in equilibrium with the adsorbed substance (mol/L).

This relationship describes a gradual adsorption of the chemical, depending on the available concentration in the liquid. In the simplified analytical model the soil will only feature two distinct states: \textit{untreated} (with no chemical either in the fluid or adsorbed on the solids) and \textit{treated} (with
all substance provided through the pore fluid being fully adsorbed to the solid until saturation).
The reaction is furthermore considered to be fast compared to the flow velocity and irreversible,
since no desorption of the guanidinium was observed after intercalation into the interlayer. This
simplified adsorption reaction can be expressed by an irreversible saturation-type sorption iso-
therm:

\[
c_{\text{ads}}(r, t) = \begin{cases} 
0 & \text{for } c(r, t) = 0 \\
c_{\text{max}} & \text{for } c(r, t) > 0 
\end{cases} 
\]  

(3.39)

Where the reagent has adsorbed to the solid phase, the material is considered to feature locally
the increased permeability. In the discrete model it is assumed that the increase is instantaneous
and of constant magnitude once the sorption sites are fully saturated with the chemical. The hy-
draulic properties can therefore be directly coupled to the adsorbed concentration \( c_{\text{ads}} \):

\[
k(r, t) = f(c_{\text{ads}}) = \begin{cases} 
k_0 & \text{for } c_{\text{ads}} = 0 \\
\chi \cdot k_0 & \text{for } c_{\text{ads}} = c_{\text{max}} 
\end{cases} 
\]  

(3.40)

where \( k_0 \) is the initial hydraulic conductivity (m/s); the dimensionless parameter \( \chi \) describes the
relative increase of the hydraulic conductivity due to the chemical modification of the soil. Since
the definition of the front position states that for \( r < r_f \) the concentration in the pore fluid is
\( c(r < r_f, t) > 0 \), the coupling defined in Equations (3.39) and (3.40) can be equivalently ex-
pressed as

\[
k(r, t) = \begin{cases} 
k_0 & \text{for } r_f(t) < r < r_{\text{out}} \\
\chi \cdot k_0 & \text{for } r_{\text{in}} < r < r_f(t) 
\end{cases} 
\]  

(3.41)

3.4.3 Derivation of transient solution for \( t > 0 \)

A) Hydraulic field for a given front position

At a given time \( t \), the front is located at \( r_f(t) \) and the sample features two segments of constant
hydraulic conductivity. In each segment the pressure drop is a logarithmic function and can be
expressed with the unknown pressure head at the front \( h(r = r_f, t) \). The drop in the pressure
head along the two segments of the sample is

\[
\Delta h_a = h(r = r_f, t) - h(r = r_{\text{in}}, t) \\
\Delta h_b = h(r = r_{\text{out}}, t) - h(r = r_f, t) 
\]  

(3.42)
By assuming an incompressible fluid and no change in porosity, mass conservation of the fluid yields an identical flux in both segments \( q_a \) and \( q_b \). They both follow the constitutive relations (3.34) and (3.41):

\[
q_a = -\frac{\Delta h_a}{\ln \left( \frac{r_f}{r_{in}} \right)} \cdot 2\pi \cdot k_0 = -\frac{\Delta h_b}{\ln \left( \frac{r_{out}}{r_f} \right)} \cdot 2\pi \cdot k_0 = q_b
\] (3.43)

Using the hydraulic boundary conditions (3.31), Equation (3.43) can be resolved for the pressure head at the moving front \( h(r = r_f, t) \) as

\[
h_f = h(r = r_f, t) = \Delta h \frac{\chi \cdot \ln \left( \frac{r_{out}}{r_f} \right)}{\chi \cdot \ln \left( \frac{r_{out}}{r_f} \right) + \ln \left( \frac{r_f}{r_{in}} \right)}
\] (3.44)

The flow rate \( q(r_f) \) is constant along the entire sample and can be found by combining (3.42) and (3.44) with one side of the equilibrium of (3.43). This yields

\[
q(r_f) = q_0 \frac{\chi \cdot \ln \left( \frac{r_{out}}{r_{in}} \right)}{\ln \left( \frac{r_{out}}{r_{in}} \right) + (1 - \chi) \cdot \ln (r_f)}
\] (3.45)

\[
= q_0 \frac{\chi (\ln (r_{out}) - \ln (r_{in}))}{\chi \ln (r_{out}) - \ln (r_{in}) + (1 - \chi) \cdot \ln (r_f)}
\]

where \( q_0 \) is the initial stationary flow rate \( (\text{m}^2/\text{s}) \) as defined in (3.36); \( \chi \) describes the relative increase of the hydraulic conductivity due to the chemical modification of the soil. Based on this flow rate, an indicator of enhanced delivery progress is defined by introducing the current average hydraulic conductivity \( k_m(t) \) \( (\text{m/s}) \). This parameter lumps the conductivity profile of the segmented sample into an equivalent homogeneous hydraulic conductivity of the entire sample as \( k_m = q \cdot \ln \left( \frac{r_{out}}{r_{in}} \right) / 2\pi \Delta h \). In normalized form, this yields with (3.45)

\[
\frac{k_m(t)}{k_0} = \frac{q(t) \cdot \ln \left( \frac{r_{out}}{r_{in}} \right)}{2\pi \Delta h \cdot k_0} = \frac{\chi (\ln (r_{out}) - \ln (r_{in}))}{\chi \ln (r_{out}) - \ln (r_{in}) + (1 - \chi) \cdot \ln (r_f)}
\] (3.46)

B) Retardation due to adsorption

If the chemical substance reaches untreated material through the pore fluid, some part of it is adsorbed to the solid, and only after the solid is locally saturated, the remaining part of the chem-
ical becomes available for further advective transport. The average propagation velocity of the chemical front is thus smaller than the effective flow rate. This effect is in general described by introducing the retardation factor \( R \), as the ratio of the effective flow velocity of the liquid and the average transport velocity of the chemical.

\[
R = \frac{\text{effective flow velocity}}{\text{front velocity}} = \frac{u}{\dot{r}_f} = \frac{v}{\dot{r}_f \cdot n_e} = \frac{q}{2\pi r_f \cdot \dot{r}_f \cdot n_e} = \tag{3.47}
\]

For the simplified isotherm (3.39), with assumed irreversible and saturating-type reaction of guanidinium to smectite, \( R \) can be calculated based on a mass balance of the substance. For all \( r < r_f \) the concentration of guanidinium in the pore liquid is considered to be equal to the concentration of the chemical in the injection fluid: \( c(r, t) = c_{in} \) (Figure 3.6). In a time increment \( dt \), the volume of the treated zone grows by \( \dot{r}_f \cdot dt \). The incremental amount of inflowing substance balances the substance in the pore fluid and on the solid phase of the additional volume, due to the propagated front (Figure 3.6):

\[
\text{amount inflow} = \text{amount in pore fluid} + \text{amount on solid} \quad (q \cdot c_{in})dt = (c_{in} \cdot n_e) \cdot 2\pi r_f \cdot \dot{r}_f dt + \left((1 - n_e) \cdot \rho_s \cdot c_{max}/n_{Gnd}\right) \cdot 2\pi r_f \cdot \dot{r}_f dt \tag{3.48}
\]

where \( \rho_s \) is the solid density (kg/m\(^3\)) and \( n_{Gnd} \) is the molar mass of guanidinium (g/mol).

Substituting \( q \) into the definition of \( R \) as given in (3.47), the retardation factor for irreversible limited adsorption then can be found as

\[
R = 1 + \frac{(1 - n_e) \cdot \rho_s \cdot c_{max}}{n_e \cdot c_{in} \cdot n_{Gnd}} \tag{3.49}
\]

For a given soil with properties \( n_e, c_{max} \) and \( \rho_s \), \( R \) will only depend on \( c_{in} \), i.e., how much chemical is provided by the pore fluid relative to the adsorption sites in one unit volume:

\[
R = 1 + \frac{1}{\tilde{c}_{in}} \tag{3.50}
\]

with \( \tilde{c}_{in} = \frac{c_{in} n_e n_{Gnd}}{(1 - n_e) \cdot \rho_s \cdot c_{max}} \) being the normalized inflow concentration (%).

According to the definition of the retardation factor (3.47), the chemical front propagates with a velocity proportional to the effective advective flow velocity \( u \) of the pore fluid:

\[
\dot{r}_f = \frac{u(r_f, t)}{R} = \frac{q(t)}{2\pi r_f(t) \cdot R \cdot n_e} \tag{3.51}
\]
C) Transient solution

The differential equation of the front position is found by substituting Equation (3.45) into (3.47):

\[
\dot{r}_f = \frac{dq}{d\tau} = \frac{q}{2\pi R \cdot n_e} \cdot r_f \cdot (\chi \ln(r_{out}) - \ln(r_{in}))
\]

(3.52)

The transient solution is found by separation of variables and integrating this equation using the initial conditions given in (3.32):

\[
\text{const.} + \left(\chi \ln(r_{out}) - \ln(r_{in}) - \frac{1}{4}(1 - \chi)\right) r_f^2 + \frac{1}{2}(1 - \chi) \cdot r_f^2 = \frac{q_0}{2\pi R \cdot n_e t} \cdot \chi \ln\left(\frac{r_{out}}{r_{in}}\right)
\]

(3.53)

This equation can be written in the form

\[
t = \alpha \cdot r_f^2 + \beta \cdot r_f^2 \cdot \ln(r_f) + \gamma
\]

(3.54)

with

\[
\alpha = \frac{2\pi R \cdot n_e}{q_0} \cdot \frac{1}{\chi \ln\left(\frac{r_{out}}{r_{in}}\right)} \cdot \frac{1}{2} \left[\chi \cdot \ln(r_{out}) - \ln(r_{in}) + \frac{1}{2}(\chi - 1)\right]
\]

(3.55)

\[
\beta = -\frac{2\pi R \cdot n_e}{q_0} \cdot \frac{1}{\chi \ln\left(\frac{r_{out}}{r_{in}}\right)} \cdot \frac{1}{2}(\chi - 1)
\]

(3.55)

\[
\gamma = -\frac{2\pi R \cdot n_e}{q_0} \cdot \frac{1}{\chi \ln\left(\frac{r_{out}}{r_{in}}\right)} \cdot \frac{1}{2} r_{in}^2 \left[\chi \cdot \ln\left(\frac{r_{out}}{r_{in}}\right) + \frac{1}{2}(\chi - 1)\right]
\]

(3.55)

Without any change in soil permeability (\(\chi = 1\)) and retardation (\(R = 1\)), Equation (3.54) provides the inert transition time \(t_0\) (s) after which a non-reactive front will reach the end of the sample.
\[ t_0 = t(r_f = r_{out}) = \frac{2\pi \cdot n_e \cdot 1}{q_0} \cdot \frac{1}{2} \left( r_{out}^2 - r_{in}^2 \right) \]  

(3.56)

This transition time is used to normalize the time \( T = t/t_0 \) in the dimensionless plots on the following pages. For \( \chi > 1 \), the positive root of Equation (3.54) yields the physically reasonable front position \( r_f \) for a given time \( t \)

\[ r_f(t) = \frac{2 \cdot (t - \gamma)}{\beta} \cdot \frac{1}{\sqrt{W_{-1} \left( \frac{2 \cdot (t - \gamma)}{\beta} \cdot \frac{2a}{e^a} \right)}} \]  

(3.57)

with \( W_{-1} \) being the second branch of the lambert W function.

This transient solution is only valid until the chemically retarded front reaches the end of the sample, after the reactive transition time \( t_{max} \). This limit can be found by solving (3.54) for \( r_f = r_{out} \)

\[ t_{max} = \frac{2\pi R \cdot n_e}{q_0} \cdot \frac{1}{\chi \ln \left( \frac{r_{out}}{r_{in}} \right)} \]

\[ \cdot \frac{1}{2} \left( r_{out} \left( \ln \left( \frac{r_{out}}{r_{in}} \right) + \frac{1}{2} (\chi - 1) \right) \right) \]

\[ - r_{in}^2 \left( \chi \cdot \ln \left( \frac{r_{out}}{r_{in}} \right) + \frac{1}{2} (\chi - 1) \right) \]  

(3.58)

\[ = \frac{2\pi R \cdot n_e}{q_0} \cdot \frac{1}{\chi \ln \left( \frac{r_{out}}{r_{in}} \right)} \]

\[ \cdot \frac{1}{2} \left( (r_{out}^2 - \chi r_{in}^2) \ln \left( \frac{r_{out}}{r_{in}} \right) + (r_{out}^2 - r_{in}^2) \cdot \frac{1}{2} (\chi - 1) \right) \]
Figure 3.7: Parametric evaluation of the front position (top, Equation (3.57)) and the front velocity (bottom, Equation (3.52)) for different improvement factors $\chi$ (left) and retardation factors $R$ (right).

The flow rate $q(t)$ can be expressed by inserting (3.57) into (3.45)

$$q(t) = q_0 \frac{\chi (\ln(r_{out}) - \ln(r_{in}))}{\chi \ln(r_{out}) - \ln(r_{in}) + (1 - \chi) \cdot \ln \left( \frac{2 \cdot (t - \gamma)}{\beta} \cdot \frac{1}{1 - \frac{2 \cdot (t - \gamma) \cdot 2 \alpha}{\beta} e^{\frac{2 \alpha}{\beta}}} \right)}$$

(3.59)

As in the one-dimensional case, the flow rate $q$ monotonously increases during treatment. However, as shown in Figure 3.7, the propagation of the front exhibits two phases. First, the front velocity decreases due to the radial spread and the strong reduction of the advective flow velocity of the fluid. For all $\chi > \ln \left( \frac{r_{out}}{r_{in}} \right)$ a second phase follows, where the increase in flow rate
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will eventually balance the geometric effect and the front velocity starts to increase again. For \( \chi > \frac{r_{out}}{r_{in}} \) the final front velocity will even be larger than the initial value.

D) Cumulative flow volume

In the experimental setup the directly measured quantity for flow is the cumulative flow volume as recorded by the balance at the outlet. To account for sample size and geometry, this fluid flow is commonly expressed as a dimensionless pore volume \( PV \), taking the ratio of the cumulative flow volume \( V_{Flow} \) of the effluent pore fluid and the effective pore volume \( V_{Pore} \) of the sample. For a comparison of the analytical model with experimental data, \( PV(t) \) is derived based on the transient solution obtained above by integration over time for the flow rate given by (3.59):

\[
PV(t) = \frac{V_{Flow}}{V_{Pore}} = \frac{\int q(t)dt}{\pi(r_{out}^2 - r_{in}^2) n_e} = \begin{cases} 
F(t) & \text{for } t \leq t_{max} \\
R + \frac{\chi q_0(t - t_{max})}{\pi(r_{out}^2 - r_{in}^2) n_e} & \text{for } t > t_{max}
\end{cases} 
\]

The function \( F(t) \) becomes difficult to handle if calculated using direct integration.

So far, all calculations were performed assuming a constant pressure at the injection radius. Using a different boundary condition \( (q_{in} = q = \text{const}) \) in Equation (3.52) leads to similar equations as above, but to a much simpler equation for the cumulative flow. For a constant injection rate the cumulative volume over time can easily be integrated and expressed in terms of the front position:

\[
V_{Flow}(t) = \int q(t)dt = \pi R n_e \cdot (r_f^2 - r_{in}^2)
\]

This equation is basically a mass balance for the pore fluid, linking the cumulative flow directly to the front position \( r_f \). It is therefore also valid for time-varying \( q \) and can be used for the constant pressure scenario as well. Combining (3.61) with the transient solution for the front position found in (3.57), we find for \( F(t) \)

\[
PV(t \leq t_{max}) = F(t) = R \frac{2 \cdot (t - \gamma) \cdot \frac{1}{\beta} \cdot W_{-1}\left(\frac{2 \cdot (t - \gamma) \cdot e^{\frac{2a}{\beta}}}{\beta}\right)}{r_{out}^2 - r_{in}^2} - r_{in}^2
\]

A parametric evaluation of this result is presented in Figure 3.8, together with the corresponding flow rate according to (3.59).
Figure 3.8: Parametric evaluation of the flow rate (top, Equation (3.59)), and the cumulative flow (bottom Equation (3.60)) for different improvement factors $\chi$ (left) and retardation factors $R$ (right). Initially the cumulative flow for any $R$ or $\chi$ will not vary significantly.

### 3.5 Numerical modelling of the propagating permeable zone

In order to validate the above analytical solution, a numerical analysis of the same boundary-value problem (coupled advective-diffusive transport of a hydraulically active chemical in the pore fluid) was carried out using a commercial finite-element code (Comsol Multiphysics). The standard modules for flow in porous media ("Darcy’s Law") and advective-diffusive-reactive (ADR) transport of a dissolved chemical ("Species transport in Porous Media") were used. The flow was described using Darcy Law as given in (3.33). Transport of the chemical included three components:

(a) advective flux due to a flow velocity $j_{\text{adv}} = -v \cdot c$,
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(b) diffusion flux according to Fick’s law due to a concentration gradient
\[ j_{\text{diff}} = -n_e \cdot (D + \alpha_D v) \cdot \nabla c \], where \( D \) is the diffusion coefficient of the chemical in porous media (m²/s) and \( \alpha_D \) the dispersivity (m), and

(c) reaction according to a Langmuir-isotherm as given in (3.38) due to adsorption.

The first level of coupling was achieved by sharing the flow velocity \( v \) among both the flow in porous media and the advective transport flux, which can be achieved using the implemented coupling settings of the software.

The implementation of the hydro-chemical coupling of improved hydraulic properties due to guanidinium adsorption was achieved by manually defining a time-dependent parameter field for the hydraulic conductivity for the entire domain. The hydraulic conductivity was directly coupled to the adsorbed amount of chemicals

\[ k(r, t) = k_0 \cdot \left( 1 + (\chi - 1) \frac{c_{\text{ads}}(r, t)}{c_{\text{eq}}} \right) \]  (3.63)

where \( c_{\text{eq}} \) is the equilibrium concentration of adsorbed mass (mg/g) for a given inflow concentration.

\[ c_{\text{eq}} = \frac{c_{\text{max}} \cdot K_L \cdot c_{\text{in}}}{1 + K_L \cdot c_{\text{in}}} \]  (3.64)

In the boundary-value problem, the concentration in the pore fluid never exceeds the inflow concentration \( c_{\text{in}} \), which leads to a maximum amount of adsorbed mass for \( c_{\text{eq}} \). The retardation in the numerical model will therefore be smaller than in the analytical model, where a larger amount of the substance is adsorbed to the solid.

\[ R_{\text{analytical}} = 1 + \frac{(1 - n_e) \cdot \rho_s \cdot c_{\text{max}}}{n_e \cdot c_{\text{in}} \cdot n_{\text{Gnd}}} \]

\[ R_{\text{numerical}} = 1 + \frac{(1 - n_e) \cdot \rho_s \cdot c_{\text{eq}}}{n_e \cdot c_{\text{in}} \cdot n_{\text{Gnd}}} \]  (3.65)

For the given parameters (see Table 4) \( R \) is reduced from \( R_{\text{analytical}} = 2.00 \) to \( R_{\text{numerical}} = 1.968 \), which is negligible.

In contrast to the situation in the analytical model, the local hydraulic conductivity increases linearly from \( k_0 \) for \( c_{\text{ads}} = 0 \) to \( \chi \cdot k_0 \) for \( c_{\text{ads}} = c_{\text{eq}} \).

Diffusion and dispersion was accounted for with two terms in the transport equation, first by introducing molecular diffusion \( j_{\text{diff}} = -n_e \cdot D \cdot \nabla c \) with a diffusion coefficient \( D \) and second
with a dispersion term \( j_{disp} = -n_e \cdot (\alpha_D \cdot \vec{v}) \cdot \nabla c \), where \( \alpha_D \) is the dispersivity. The diffusion coefficient \( D \) of the porous media was calculated using the single-phase diffusion coefficient \( D_e \) and the porosity \( n_e \) according the model proposed by Millington and Quirk (1961) to account for the tortuosity of the porous structure.

The numerical code formulated mass conservation of fluid and chemical species over the problem domain and integrated over time with an implicit integration scheme to provide a transient solution.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner radius ( r_{in} )</td>
<td>0.1 m</td>
</tr>
<tr>
<td>Outer radius ( r_{out} )</td>
<td>1.3 m</td>
</tr>
<tr>
<td>Porosity ( n_e )</td>
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</tr>
<tr>
<td>Solid density ( \rho_s )</td>
<td>2.65 kg/L</td>
</tr>
<tr>
<td>Total pressure head ( \Delta h )</td>
<td>4.2 m</td>
</tr>
<tr>
<td>Hydraulic conductivity ( k_0 )</td>
<td>2.21E-9 m/s</td>
</tr>
<tr>
<td>Relative improvement factor ( \chi )</td>
<td>13</td>
</tr>
<tr>
<td>Diffusion coefficient ( D_e )</td>
<td>1E-9 resp. 1E-8 m²/s</td>
</tr>
<tr>
<td>Dispersivity ( \alpha )</td>
<td>0.13 m</td>
</tr>
<tr>
<td>Inflow concentration ( c_{in} )</td>
<td>0.545 mol/L</td>
</tr>
<tr>
<td>Adsorption maximum ( c_{ads} )</td>
<td>6.2 mg/g</td>
</tr>
<tr>
<td>Langmuir parameter ( K_L )</td>
<td>55.6 L/mol</td>
</tr>
<tr>
<td>Molar mass of guanidinium ( n_{Gnd} )</td>
<td>60.08 g/mol</td>
</tr>
</tbody>
</table>

Table 4. Summary of the parameters used in the parametric study of the radial problem

The numerical model, including diffusive and dispersive fluxes, consistently predicts an earlier completion of the treatment, due to the additional flux term (Figure 3.9). It also shows increased flow rates at the early stages of treatment, as the diffusive flux at the very beginning of the treatment will contribute significantly to the transport rate for the chemical into the inner zone, close to the injection point. In contrast to the situation encountered for one-dimensional flow, this zone has a much higher influence on the total permeability of the model.
Figure 3.9: Influence of diffusion on flow in the radial configuration. The results for a diffuse front calculated for two diffusion coefficients are compared with the analytical solution for a sharp front. The diffusion will not only lead to an earlier completion of the treatment but also to a higher flow rate at the early stages of the treatment.

3.6 Summary and Conclusions

In this chapter, the concept of enhanced delivery of chemicals for soil-improvement applications based on clay treatment by guanidinium salt solutions was explored.

For a better understanding of the mechanisms underlying the process of enhanced delivery, a simple analytical hydro-chemical model has been developed and successfully validated against experimental data on soils samples subjected to the flow of guanidinium solutions and against a more sophisticated numerical analysis. Correct estimation of the retardation factors for the chemical front propagation appears to be the key element for an accurate prediction of the enhanced delivery effects in practical applications. It can be accomplished by simple mass-balance calculations or by fitting measured laboratory data.
This study provides a quantitative description of the fundamental processes underlying the proposed concept of chemically enhanced delivery of soil-improvement agents. Limitations of the results are that these fundamentals were obtained using generic model soils, where a significant effect was expected and where the conditions are reproducible. The influence of mineralogy, sample size and homogeneity will have to be addressed in a case-specific evaluation prior to an application in the field. In order to assess the temporal improvement in a practical implementation, the analytical model can serve as a first estimate, whereas a numerical model accounting for the specific boundary conditions will make it possible to predict the practical gain from chemically enhanced delivery.

For the geometry of one-dimensional axial flow columns, the diffusion did not strongly affect the results for a partial degree of treatment. Only towards the completion of the treatment a slightly earlier increase in the flow rate was observed, compared to the analytical solution. In order to correctly predict the evolution of the transient flow characteristics observed in laboratory experiments, it is more important to correctly assess the retardation than to measure the diffusion coefficient.

For the radial configuration, an analytical solution was found as well and verified against a numerical simulation that included diffusion. The results for the diffuse front were compared with the analytical solution for a sharp front. It was found that the diffusion has a significantly stronger influence in the radial configuration and will affect the flow rates already for partial degrees of treatment. This is due to the fact that for the radial configuration, the innermost zone of the model influences the average permeability of the sample more than in the axial configuration.
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## 3.7 Notation list

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c )</td>
<td>chemical concentration in pore fluid</td>
<td>mol/L</td>
</tr>
<tr>
<td>( c_{ads} )</td>
<td>adsorbed mass per dry weight of soil</td>
<td>mg/g</td>
</tr>
<tr>
<td>( c_{eq} )</td>
<td>adsorbed mass at equilibrium</td>
<td>mg/g</td>
</tr>
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<td>( c_{in} )</td>
<td>concentration at the injection point</td>
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<tr>
<td>( \tilde{c}_{in} )</td>
<td>normalized inflow concentration</td>
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<tr>
<td>( c_{max} )</td>
<td>adsorption maximum</td>
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<tr>
<td>( h )</td>
<td>hydraulic head</td>
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</tr>
<tr>
<td>( h_f )</td>
<td>hydraulic head at the front</td>
<td>m</td>
</tr>
<tr>
<td>( \Delta h )</td>
<td>total pressure head</td>
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</tr>
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<td>( j_i )</td>
<td>chemical flux component</td>
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<td>initial hydraulic conductivity</td>
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<td>( k_m )</td>
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<td>molar mass of guanidinium</td>
<td>g/mol</td>
</tr>
<tr>
<td>( q )</td>
<td>flow rate, total mass flux</td>
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</tr>
<tr>
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<td>m²/s</td>
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<td>( v )</td>
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<td>coefficient</td>
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</tr>
<tr>
<td>( \alpha_D )</td>
<td>dispersivity</td>
<td>m</td>
</tr>
<tr>
<td>( \beta )</td>
<td>coefficient</td>
<td>s/m²</td>
</tr>
</tbody>
</table>
\begin{align*}
\gamma & \quad \text{coefficient} \\ 
\rho_s & \quad \text{solid density} \quad \text{kg/m}^3 \\ 
\chi & \quad \text{relative increase of hydraulic conductivity} \quad (-) \\
D & \quad \text{diffusion coefficient} \quad \text{m}^2/\text{s} \\
D_e & \quad \text{Single-phase diffusion coefficient} \quad \text{m}^2/\text{s} \\
K_L & \quad \text{Langmuir adsorption constant} \quad \text{L/mol} \\
L & \quad \text{sample length} \quad \text{m} \\
PV & \quad \text{normalized cumulative flow volume} \quad (-) \\
Q & \quad \text{normalized flow rate} \quad (-) \\
R & \quad \text{retardation factor} \quad (-) \\
R_f & \quad \text{normalized front position} \quad (-) \\
T & \quad \text{normalized time} \quad (-) \\
T_{\text{max}} & \quad \text{normalized transition time} \quad (-) \\
V_{\text{Flow}} & \quad \text{cumulative flow volume} \quad \text{m}^3 \\
V_{\text{pore}} & \quad \text{effective pore volume} \quad \text{m}^3 \\
X_f & \quad \text{normalized front position} \quad (-)
\end{align*}
4 Examples of geotechnical applications with chemically enhanced drainage

In order to illustrate possible practical applications of the soil-improvement technique, two geotechnical examples are introduced in the following chapter. The case of improved performance of a ground-water well and the stabilization of a slope by a chemically enhanced drainage, both based on numerical simulations, are presented.

4.1 Example 1: Improvement of well efficiency

The efficiency of a well strongly depends on the hydraulic conductivity in the immediate vicinity of the well. The concentrated flow in this area produces in general high gradients in the homogeneous media and can be the limiting factor for the pumping rates that can be achieved. Traditionally, larger diameters for the well are used if insufficient flow rates are found in practical applications.

4.1.1 Model description and geometry

A parametric study is carried out for a small vertical well, which is operated to lower the phreatic surface reliably below the ground surface in a construction pit. A soil layer of 5 m is considered, with an impermeable base. The well reaches the base and is perforated only in the lower 3.5 m. Initially the soil is saturated up to 1.0 m below the ground surface. The detailed geometry is shown in Figure 4.1 and summarized in Table 5, together with the material parameters.

![Geometry of the well model. The blue line highlights the perforated section of the well, where lateral in- and outflow was allowed, depending on the pressure in the well.](image)

Figure 4.1: Geometry of the well model. The blue line highlights the perforated section of the well, where lateral in- and outflow was allowed, depending on the pressure in the well.
Chapter 4: Application examples

The numerical implementation was analogous to the radial configuration discussed in Chapter 3.5. The model was extended in the vertical direction (z-coordinate) and the flow was calculated with the extended Darcy’s flow model “Richard’s equation” that accounted for the free fluctuation of the water table. The permeability in the unsaturated zone \( h < 0 \) was reduced to 0 over a short range of 0.1 m with the standard Van Genouchnet-Retention Model implemented in Comsol. The phreatic surface fluctuated within the upper 1.5 m of the soil layer during the simulations, which made it possible to apply constant boundary conditions to the lower 3.5 m, which remained fully saturated throughout. Figure 4.2 shows a three-dimensional revolution of the model and depicts the hydraulic head during injection into the fully saturated zone.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of the well</td>
<td>( r_i ) 0.1 m</td>
</tr>
<tr>
<td>Outer radius of the model</td>
<td>( r_o ) 10 m</td>
</tr>
<tr>
<td>Perforated section of the well</td>
<td>( H_{Well} ) 3.5 m</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>( H_{Layer} ) 5.0 m</td>
</tr>
<tr>
<td>Coordinate of observation point</td>
<td>( r_x ) 5.0 m</td>
</tr>
<tr>
<td>Porosity</td>
<td>( n_e ) 0.5</td>
</tr>
<tr>
<td>Solid density</td>
<td>( \rho_s ) 2.65 kg/L</td>
</tr>
<tr>
<td>Hydraulic head at boundary</td>
<td>( H_{out} ) 4.0 m</td>
</tr>
<tr>
<td>Draw down at pump</td>
<td>( \Delta H_p ) +/- 0.5 m</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>( k_0 ) 1e-8 m/s</td>
</tr>
<tr>
<td>Relative improvement factor</td>
<td>( \chi ) 13</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>( D_e ) 1E-9 m²/s</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>( \alpha ) 0.0025 m</td>
</tr>
<tr>
<td>Inflow concentration</td>
<td>( c_{in} ) 0.5 mol/L</td>
</tr>
<tr>
<td>Adsorption maximum</td>
<td>( c_{ads} ) 6.2 mg/g</td>
</tr>
<tr>
<td>Langmuir parameter</td>
<td>( K_L ) 10 L/mol</td>
</tr>
<tr>
<td>Molar mass of guanidinium</td>
<td>( n_{Gnd} ) 60.08 g/mol</td>
</tr>
</tbody>
</table>

Table 5. Input parameters for the well model.
4.1.2 Results

Injection/treatment phase

First the treatment phase is presented, where the well is used to inject the chemical through the pore fluid into the soil in the immediate surrounding. The solution propagates into the modifiable aquifer and alters the pressure field, as shown in Figure 4.3 for different time intervals. The final pressure field for complete treatment of the model is identical to the initial field, except for the higher corresponding flow.

All radial coordinates were normalized relative to the outer radius of the model, $r_o$, where a constant head boundary $h(r) = H_{out}$ is assumed. Pore pressures are taken relative to the hydrostatic pressure of this outer boundary, $\Delta H(r) = h(r) - H_{out}$, and are normalized with respect to the applied pump pressure, $\Delta H_p$. 

Figure 4.2: Three-dimensional illustration of the hydraulic head in the fully saturated zone during injection.
Figure 4.3: Pore pressure along the normalized radial coordinate during injection of the chemical for different treatment durations. The dashed line indicates the initial and final pore-pressure distributions (which are identical).

The pore-pressure fields are analyzed based on two characteristic variables: The increase in pore pressure $\Delta H_x$ at coordinate $r_x$ relative to the pump pressure $\Delta H_p$ is calculated numerically and plotted against the treatment duration $t$ (Figure 4.4). The average increase in pore pressure in the inner zone, which extends to the coordinate $r_{av}$, is denoted as $\Delta H_{av}$. For all subsequent plots $r_x = r_{av} = \frac{r_0}{2}$ was chosen.

For a constant pump pressure $\Delta H_p$, the treated soil will yield to an increased flow rate $q(t)$. This flow field (or degree of treatment) can be characterized with an equivalent front position $r_f(t)$ of a discrete sharp front that would produce the same radial flow. The equation for the equivalent front position is found by solving Equation (3.45) — here relabeled as Equation (4.1) — with respect to $r_f$

$$q(t) = \frac{(2 \cdot \pi \cdot \Delta H_p \cdot k_0) \cdot \chi}{\chi \ln(r_0) - \ln(r_i) + (1 - \chi)\ln(r_f)} \tag{4.1}$$

This enables a calculation of an equivalent normalized front position $R_f$ for the simulations, with diffusion based on externally measured quantities $q(t)$ and $\Delta H_p$:

$$R_f = \frac{r_f(t)}{r_0} = \left(\frac{r_1}{r_0}\right)^{\frac{1}{1-\chi}} \cdot e^{\frac{2\pi \Delta H_p k_0 \chi}{(1-\chi)q(t)}} \tag{4.2}$$
Time was normalized to $t_0 = \frac{n_e \Delta t}{k_0 \Delta H_p} \cdot \frac{1}{2} \left( r_0^2 - r_i^2 \right)$, which is the time required for a non-reactive tracer to travel from $r_i$ to $r_o$ in the untreated soil. ($n_e$ being the effective porosity and $k_0$ the initial hydraulic conductivity.)

Figure 4.4: Development of the pore pressure during treatment. The solid line gives the increase in pore pressure at a point $r_x$ relative to the pump pressure and the dashed gives the average increase up to this point. The corresponding equivalent front position $R_f$ is plotted on the secondary axis. Full treatment ($R_f = 1$) is reached at $t/t_0 \approx 0.18$. 
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Pumping phase

After a given treatment duration \( t_t \) the injection phase is stopped and the well can be operated as a sink in order to lower the water table as planned. Due to the irreversible adsorption the front position is memorized in the soil structure and the modified zone can be characterized by \( r_f = r_f(t = t_t) \) for any time after the treatment. Further pumping will not reduce this modified zone. Figure 4.5 shows the normalized pressure field for different preceding treatment durations.

![Figure 4.5: Pore pressure during pumping for different preceding treatment durations \( t_t \) along the normalized radial coordinate. The dashed line shows the pore-pressure distribution for the untreated and the full treated soil body.](image)

Figure 4.6 shows the front position of the transient field during the pumping phase. The relative decrease in pore pressure \( \Delta H_x \) at coordinate \( r_x \) relative to the pump pressure \( \Delta H_p \) is calculated numerically and plotted against the front position \( R_f \). The average decrease in pore pressure in the inner zone up to the coordinate \( r_{av} \) is denoted as \( \Delta H_{av} \). When normalized with the pump pressure \( \Delta H_p \), these quantities are referred to as the relative draw down.
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Figure 4.6: Relative draw down (solid line) at the reference point \( r_x \) for different degrees of treatment (characterized by the front position) compared to the average draw down (dashed line) at the inner zone for \( r_i < r < r_{av} \).

### 4.1.3 Equivalent radius

The increase permeability in the zone around the well alters the characteristics of the hydraulic field in this zone. For practical purposes, the heterogeneous field can be represented by a hydraulically equivalent empty pipe in homogeneous soil (Figure 4.7). A hypothetical well with radius \( r^* \) would yield the same flow rate \( q \) for a given well pressure \( \Delta h \) as the original well in the heterogeneous field.

Figure 4.7: Sketch for the definition of the equivalent radius \( r^* \).
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The flow rate \( q \) in the assumed homogeneous field is given by

\[
q = \frac{2\pi k_0 \Delta h}{\ln\left(\frac{r_{out}}{r^*}\right)}
\]  
(4.3)

Equation (4.3) can be solved with respect to \( r^* \) and defines this characteristic variable by the measurable quantities \( q(t) \) and \( \Delta h \):

\[
r^* = r_{out} \cdot e^{-\frac{2\pi k_0 \Delta h}{q(t)}}
\]  
(4.4)

A fully treated sample is, regarding the radial flow, hydraulically equivalent to an empty pipe with radius \( r_{max}^* \)

\[
r_{max}^* = r_{out} \cdot e^{\frac{2\pi k_0 \Delta h}{q}} = r_{in} \cdot \left(\frac{r_{out}}{r_{in}}\right)^{\left(1-\frac{i}{\chi}\right)}
\]  
(4.5)

For the parameters given in Table 5 we find that \( r_{max}^* = 7.6 \cdot r_{in} = 0.84 \cdot r_{out} \), i.e., the chemically treated well performs as a conventional well with up to 7.6 times larger radius.

Equation (4.4) can also be used to represent the diffuse hydraulic field for boundary-value problems in numerical simulations and experimental tests, where \( \Delta h \) and \( q(t) \) are measured quantities with one simple variable similar to the relative front position \( R_f \).
4.1.4 Interpretation

Pump pressure required to achieve identical draw down in an untreated field.

The pump pressure for the numerical model defined by a constant boundary condition:

\[ h(r_i) = H_{\text{out}} + \Delta H_p \]  
(4.6)

This pressure produced a draw down \( \Delta H_x \) in the soil (Figure 4.6, above) for different degrees of treatment. The pump pressure required to achieve the same draw down in a homogeneous field \( \Delta H_{p,xnt} \) is expressed in (4.8): The radial pressure distribution untreated soil is given analytically in Equation (4.7) and can be evaluated directly to calculate the required pump pressure in an untreated field to achieve a draw down \( \Delta H_x \):

\[ \Delta H(r) = \Delta H_p \frac{\ln \left( \frac{r}{r_0} \right)}{\ln \left( \frac{r_i}{r_0} \right)} \]  
(4.7)

\[ \Delta H_{p,xnt} = \Delta H_x \frac{\ln \left( \frac{r_i}{r_0} \right)}{\ln \left( \frac{r_a}{r_0} \right)} \]  
(4.8)

In a homogeneous untreated field, the average draw down \( \Delta H_{av} \) in the volume between \( r_i < r < r_{av} \) for a pump pressure \( \Delta H_p \) can be found by calculating an average over this inner area for the function given in Equation (4.7).

\[
\Delta H_{av} = \frac{\iint_{r_i,0}^{r_{av}} \Delta H(r)r \, d\theta \, dr}{\iint_{r_i,0}^{r_{av}} r \, d\theta \, dr}
\]

\[
= \frac{1}{\pi \left(r_{av}^2 - r_i^2\right)} \int_{r_i}^{r_{av}} \frac{2 \pi \Delta H_p}{\ln \left( \frac{r}{r_0} \right)} \ln \left( \frac{r}{r_0} \right) \, r \, dr
\]

\[
\Delta H_{av} = \frac{1}{\pi \left(r_{av}^2 - r_i^2\right)} \frac{2 \pi \Delta H_p}{\ln \left( \frac{r_i}{r_0} \right)} \frac{1}{4} \left( r_{av}^2 \left( 2 \ln \left( \frac{r_i}{r_0} \right) - 1 \right) - r_i^2 \left( 2 \ln \left( \frac{r_i}{r_0} \right) - 1 \right) \right)
\]  
(4.9)

Solving (4.9) for the required pump pressure in an untreated field \( \Delta H_p = \Delta H_{p,av \, nt} \) to achieve a given average draw down \( \Delta H_{av} \) in the volume between \( r_i < r < r_{av} \), one finds
\[
\Delta H_{p,av,nt} = \Delta H_{av} \cdot \frac{2 \ln \left( \frac{r_i}{r_o} \right) \cdot (r_{av}^2 - r_i^2)}{r_{av}^2 \left( 2 \ln \left( \frac{r_{av}}{r_o} \right) - 1 \right) - r_i^2 \left( 2 \ln \left( \frac{r_i}{r_o} \right) - 1 \right)}
\]  
(4.10)

Figure 4.8 illustrates the required relative pumping pressure for a target draw down in the treated soil, obtained by evaluating Equations (4.8) and (4.10) for different \( \Delta H_x(r_f) \) and \( \Delta H_{av}(r_f) \). The required pumping pressure is reduced to 22%, depending on the size of the modified zone.

Figure 4.8: Comparison of the pumping pressure required in a treated soil to achieve the same draw down at a point (solid line) or in the inner area (dashed line) as in an untreated soil.

**Pumping power to achieve a target draw down**

The pump pressure for the untreated scenarios was chosen to produce the same draw down as the pumping in the treated soil (Figure 4.8, above). The corresponding increase in flow \( Q \) was taken into account for the calculation of the pumping power in the well. While increasing the permeability in the vicinity of the well facilitates the lowering of the water table in the modified zone, it also increases the total flow into the well and therefore elevates the operational effort to maintain the flow field.

The pumping power \( P_t \) required to maintain a prescribed draw down \( \Delta H_p \) in the well for the treated soil is calculated based on the numerically determined total inflow into the well \( Q \) as

\[
P_t(r_f) = Q(r_f) \rho g \Delta H_p
\]

(4.11)

In a homogeneous field (see Equation (3.36)) the total volume flow into a well is
\[ Q(\Delta H_p) = q(\Delta H_p) \cdot H_{Well} = \frac{2\pi k_0 H_{Well} \rho g}{\ln \left( \frac{r_0}{r_i} \right)} \Delta H_p \]  

(4.12)

With Equations (4.8) and (4.10) the corresponding pumping powers for untreated soil are:

\[
P_{x,nt} = Q(\Delta H_{p,x,nt}) \cdot \rho g \cdot \Delta H_{p,x,nt}
\]

\[
= \frac{2\pi k_0 H_{Layer} \rho g}{\ln \left( \frac{r_0}{r_i} \right)} \left( \frac{\ln \left( \frac{r_i}{r_o} \right)}{\ln \left( \frac{r_x}{r_o} \right)} \right)^2 \Delta H_x^2
\]

(4.13)

and

\[
P_{av,nt} = Q(\Delta H_{p,av,nt}) \cdot \rho g \cdot \Delta H_{p,av,nt}
\]

\[
= \frac{2\pi k_0 H_{Well} \rho g}{\ln \left( \frac{r_0}{r_i} \right)} \left( \frac{r_{av}^2}{2 \ln \left( \frac{r_{av}}{r_o} \right) - 1} - r_i^2 \left( 2 \ln \left( \frac{r_i}{r_o} \right) - 1 \right) \right)^2 \Delta H_{av}^2
\]

(4.14)

With \(P_{x,nt}\) being the pumping power required to produce a given draw down at point \(r_x\) in untreated soil and \(P_{av,nt}\) being the pumping power required to produce an average draw down in the inner zone in untreated soil.

For the following considerations, the power was normalized relative to the power implied by the initial conditions of the boundary value problem, \(P_0 = \frac{2\pi k_0 H_{Layer} \rho g}{\ln \left( \frac{r_0}{r_i} \right)} \Delta H_P^2\).

Figure 4.9 shows that for an increasing degree of treatment, the power required to maintain a constant draw down at the pump (\(\Delta H_p\)) constantly increases (dotted line). Simultaneously the relative draw down in the soil varies (see Figure 4.6, above) and the power to achieve the same lowering of the water table in an untreated soil varies accordingly (solid and dashed lines calculated using Equations (4.13) and (4.14)).
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Figure 4.9: Power requirement to achieve the same draw down at a point (solid line) or at the inner zone (dashed line) as obtained by numerical calculation (dotted line) for different degrees of treatment, characterized by the front position $R_f$.  

In a direct comparison of treated and untreated soil (Figure 4.10), the gain in efficiency relative to the required pumping power for a chemically enhanced well is evident.

![Diagram of normalized power vs front position](image)

Figure 4.10: Power required in the treated soil to produce a given draw down at a point (solid line) or in the inner zone (dashed line) relative to the power required in untreated soil.

For example, to achieve some average draw down in the inner zone, for a treated soil with $R_f = 0.3$ only 42% of the power needed for untreated soil is required. This front position is close to the optimum in terms of achievable power reduction for any average target draw down in the inner zone.
For a smaller degree of treatment \((R_f = 0.15)\), where only a small amount of substance is needed for treatment, the power consumption is already reduced by half of that for an identical well in untreated soil.

It is noteworthy that for very high degrees of treatment the model will predict a loss in efficiency, as the increased permeability leads to excessively high flow rates. This finding is only valid for the rigid assumptions of the model. The paradox originates from the limited size of the model and the corresponding unrealistically unlimited additional influx at the outer boundary for an increasing degree of treatment. In reality, the increased flow rate would continuously increase the range of effect \((r_F)\) of the well and thereby improve the well performance even more. For practical purposes, however, the largest gain in efficiency is at a low degree of treatment, where a short duration of treatment and small amounts of chemicals needed reduce the power consumption at the highest rate. For this degree of treatment, the range where the well is effective is unlikely to be affected.

### 4.1.5 Conclusion on wells

A well combined with chemically enhanced drainage was analyzed as a geotechnical example. The main purpose of operating the well is to lower the water table at a construction site to a target value.

The efficiency to fulfill this task of lowering the water table was quantified for different degrees of treatment in an axisymmetric boundary-value problem. The degree of treatment was characterized through the front position \(R_f\) of the modified zone and the measure of efficiency was the pumping power required at the well.

For a small degree of treatment \((R_f = 0.15)\), where only a small amount of substance is needed for treatment, the power consumption is already reduced by half, compared to an identical well in untreated soil. An optimum for the average draw down is reached when the soil had been treated up to \(R_f = 0.3\). In that case, a chemically enhanced well requires only 42% of the power needed for a conventional well to achieve the same average draw down in a zone up to 5 m around the well.

In summary, the parametric study showed that the method is most efficient when treating only a small area close to the well and that it can lower the total cost of the dewatering system by providing lower operational cost for long-term wells with a one-time additional investment during the installation of the pump.
4.2 Example 2: Slope stabilization with an integrated chemically enhanced drain

In this chapter it is shown how treating the soil around a sub-horizontal bore hole created by directional drilling can serve as a drainage system for instable slopes. Based on a virtual case study with a generic slope, the potential efficiency of such a system is demonstrated.

4.2.1 Slope properties

The slope features a permeable, potentially unstable layer with a clay content that defines the hydraulic conductivity and is sensitive to the chemical used for treatment. This sliding material is deposited on bedrock with low permeability and a distinct sliding surface at the interface. The slope has a constant inclination of $\beta = 15^\circ$ and is close to failure if the water table rises close to the surface. The slope is a finite step with horizontal terrain both at the top and at the bottom. The water table is defined by a constant influx $q_{in}$ at the top and eventually leads to slope-parallel flow in the lower part of the slope (Figure 4.11).

![Figure 4.11: Sketch of the model slope including the hydraulic features. A detail of the geometry in the drainage section is shown in Figure 4.13 below.](image)

The distinct sliding surface is chosen to provide a constant thickness of the sliding layer, $h_L = 10 \text{ m}$. It outcrops at the top with a constant inclination $\beta$. Towards the toe of the step, the sliding surface follows a circular curved line that is tangential to the bedrock and to the horizontal terrain of the valley (Figure 4.12).
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Figure 4.12: Geometry of the model slope including the sliding body (grey) and the x-coordinates for distinct points along the sliding surface.

**Detail of drainage implementation**

The drain is located close to the sliding layer, such that the water table can be sufficiently lowered without drilling too close to the sliding surface.

Figure 4.13: Detail of the drainage section and labels of the geometry.

For the present case study the location of the drain is chosen to be at $h_D/h_L = 0.2$. The initial conditions without drainage were calculated for a water table at $h_W/h_L = 0.7$. For this water table the factor of safety is $F_S = 1.3$. If the water level raises to the surface, an infinite slope with this inclination would fail.

For the out-of-plane extension of the slope the following assumptions were made:

a) Horizontal drains are drilled perpendicular to the two-dimensional cross-section of the slope (coordinate $z$).
b) Drainage collectors are periodically located in this drain (in shafts or access points for the directional drilling) at a distance \(2L_p\). These collectors can be equipped with a pump or with a conventional free-surface drainage pipe to transfer the drained water downslope.

c) The modeled section is between two collectors (at \(z=0\)) and the distance to the collector is \(L_p\). This section is the most critical section during draining and will provide a lower bound for the safety factor for the entire slope.

### 4.2.2 Numerical implementation in COMSOL

**Hydraulics and chemical transport**

The required upstream inflow for the chosen water level in the part with slope-parallel flow was applied as a constant-rate inflow boundary condition at the upstream boundary of the permeable layer. It was kept constant in all subsequent calculations. The downstream boundary condition was a constant-head boundary condition that provided a continuous inclined flow field. This downstream condition was applied to both the permeable upper layer as well as to the 100-times less permeable bedrock. The coupling of the permeability to the presence of the chemical was performed as in Chapter 3.2. During injection, a constantly high concentration of guanidinium was applied at the inner radius of the drain. The adsorbed chemical provided a durable increase in permeability in the zone around the initial injection pipe, also for the subsequent drainage when the concentration in the drain was reduced to zero.

The flow was calculated with the extended Darcy’s flow model “Richards equation” that accounted for the free fluctuation of the water table. The permeability in the unsaturated zone \((h < 0)\) was reduced to 0 over a short range of about 0.5 m with the standard Van Genuchten-Retention Model implemented in Comsol.

The transport of the drained water out-of-plane was not simulated in the FEM calculation but was accounted for by analytically integrating the flow into this drain over a series of coupled two-dimensional cross sections. The following procedure was applied:

a) Pressure in drain is \(h_d(z)\).

b) The draw down along the drain compared to the initial slope-parallel flow is defined as the pressure difference \(\Delta h_d(z) = h_{d0} - h_d(z)\) and will affect the outtake \(q_D\) for each two-dimensional section.

c) Based on the results of the numerical simulations we find that this outtake in each section is linearly proportional to the pressure difference \(\Delta h_d(z)\). Introducing \(q_{in}\) and \(\Delta h_{min}\) for the proportionality in Figure 4.16, the outtake can be written as
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\[ q_D = \Delta h_d \cdot q_{in}/\Delta h_{min} \]  \hspace{1cm} (4.15)

d) The flow along the chemical drain mainly takes place in the chemically improved zone with area \( A_D = \pi r_D^2 \) and hydraulic conductivity \( k_D \) according to Darcy’s law \((v \propto i)\).

e) The flow in the empty central bore hole follows a non-linear pipe flow equation \((v^2 \propto i)\). This contribution is neglected at this stage, given that the small directional-drilling hole can easily close over time, due to differential displacement.

f) Solving the flow in this drain analytically gives

\[ \Delta h_d(z) = \Delta h_{Pump} \cdot \frac{\cosh\left(\frac{z}{L_D}\right)}{\cosh\left(\frac{L_p}{L_D}\right)} \]  \hspace{1cm} (4.16)

with the characteristic drainage length \( L_D \), and \( \Delta h_{Pump} \) the draw down at the drainage collector

\[ L_D = \frac{k_D r_D^2 \pi}{\sqrt{q_{in}/\Delta h_{min}}} \]  \hspace{1cm} (4.17)

In the two-dimensional FEM model, the boundary condition applied in the critical section at \( z=0 \) for the drain is therefore

\[ \Delta h_d(z = 0) = \frac{\Delta h_{Pump}}{\cosh\left(\frac{L_p}{L_D}\right)} \]  \hspace{1cm} (4.18)

**Mechanical coupling**

Mechanical stresses and displacements were only calculated for the sliding soil body and its contact, through the sliding surface, to the rest of the model. The body was assumed to remain in the elastic range. A classical effective-stress concept was implemented manually. It took into account both the seepage forces and the changes in density due to the lower water content in the unsaturated zone. Three body-force components were applied to the sliding soil:

a) the gravimetric force due to the mass of the solids, \( f_{solid} \),
b) the gravimetric force to the liquid phase as a function of the saturation, \( f_{w+b} \) \((4.20)\), and
c) the seepage force due to the pore-water pressures exceeding hydrostatic pressures, \( f_{seepage} \) \((4.21)\).
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\[
f_{solids} = \begin{pmatrix} 0 \\ -1 \end{pmatrix} \cdot \gamma_{dry}
\]

(4.19)

\[
f_{w+b} = \begin{pmatrix} 0 \\ -w + 1 \end{pmatrix} \cdot \gamma_w \cdot Sat(x,y)
\]

(4.20)

\[
f_{seepage} = \begin{pmatrix} -\frac{\partial h_p}{\partial x} \\ -\frac{\partial h_p}{\partial y} - 1 \end{pmatrix} \cdot \gamma_w \cdot Sat(x,y)
\]

(4.21)

with \( h_p = \frac{\kappa}{\gamma_w} \) being the hydraulic pressure head (m) and \( Sat(x,y) \) standing for the local saturation condition. The use of the saturation condition in these body-force components lead to a suction-free soil above the ground-water table as used in classical effective-stress analysis.

The contact was formulated as a frictional contact with \( \varphi = 23.8^\circ \). In order to initialize this contact, a virtual spring foundation was introduced in a preliminary calculation step and its stiffness was subsequently reduced to zero. The input parameters for the simulation are listed in Table 6.

<table>
<thead>
<tr>
<th>Thickness of the sliding layer</th>
<th>( h_L )</th>
<th>10 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total height of the slope</td>
<td>( h_{\text{slope}} )</td>
<td>60 m</td>
</tr>
<tr>
<td>Inclination of the slope</td>
<td>( \beta )</td>
<td>15 (^\circ)</td>
</tr>
<tr>
<td>Location of the drain</td>
<td>( h_D )</td>
<td>2 m</td>
</tr>
<tr>
<td>Horizontal coord. of the drain</td>
<td>( x_{\text{Drain}} )</td>
<td>90 m</td>
</tr>
<tr>
<td>Porosity</td>
<td>( n_e )</td>
<td>0.37</td>
</tr>
<tr>
<td>Unit weight of solids</td>
<td>( \gamma_w )</td>
<td>16.3 kN/m(^3)</td>
</tr>
<tr>
<td>Unit weight of water</td>
<td>( \gamma_w )</td>
<td>10 kN/m(^3)</td>
</tr>
<tr>
<td>Angle of internal friction</td>
<td>( \varphi )</td>
<td>23.8 (^\circ)</td>
</tr>
<tr>
<td>Location of the water table</td>
<td>( h_w )</td>
<td>7 m</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>( k_0 )</td>
<td>1e-8 m/s</td>
</tr>
<tr>
<td>Relative improvement factor</td>
<td>( \chi )</td>
<td>13</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>( D_e )</td>
<td>1E-9 m(^2)/s</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>( \alpha )</td>
<td>0.0025 m</td>
</tr>
<tr>
<td>Inflow concentration</td>
<td>( c_{in} )</td>
<td>0.5 mol/L</td>
</tr>
<tr>
<td>Adsorption maximum</td>
<td>( c_{ads} )</td>
<td>6.2 mg/g</td>
</tr>
<tr>
<td>Langmuir parameter</td>
<td>( K_L )</td>
<td>55.6 L/mol</td>
</tr>
<tr>
<td>Molar mass of guanidinium</td>
<td>( n_{\text{Gnd}} )</td>
<td>60.08 g/mol</td>
</tr>
</tbody>
</table>

Table 6. Input parameters for the slope simulation
4.2.3 Results

The hydraulic conductivity is calculated based on the *in situ* saturation and the size of the chemical drain (Figure 4.14). There is a distinct unsaturated zone close to the surface of the slope. The inflow rate is small enough to avoid that the water table reaches the surface, which scenario would require additional boundary conditions. Having the water table always below the ground surface means that the hydraulics can be modeled with the Richards equation, assuming an impermeable ground surface.

![Figure 4.14: Hydraulic conductivity: Red color marks the area of the soil layer with high permeability, whereas blue color indicates low permeability, either due to a lack of saturation or an intrinsically low permeability of the rock. Grey: contours of hydraulic head.](image)

Figure 4.15 depicts the seepage component of the body force applied to the model and reveals that only a small area is directly affected by the increased seepage forces in the radial flow field around the drainage location.
Figure 4.15: Seepage force around the drainage location (color code for the seepage force, grey contours for the distinct levels between 1 and 1.5 kN/m$^3$).

A first parametric evaluation of the mass balance over the entire model shows that for different applied boundary conditions at the center of the drain, the local outtake of water is linearly proportional to the pressure (see Figure 4.16).

Figure 4.16: Measured outtake of water through the drain for a two-dimensional section and for a given pressure at the center of the drain.

Turning to the stress conditions along the sliding layer and the rock, continuous conditions for the effective normal stress were observed for each section of the slope (Figure 4.17).
Chapter 4: Application examples

Figure 4.17: Effective stress along the slip line for different draw-down values at the drain. The dashed lines mark: a) the start of the bedrock decline below the top layer, b) the location of the drain, c) the start of the curved slip line towards the toe.

The shear stresses only change marginally (since the changing seepage forces are one order of magnitude lower than the downslope component of the gravitational forces). The drainage is most effective downstream of the drain. The ‘crest’ part of the slope is not significantly affected by the drainage, as the upstream boundary condition is defined as a constant inflow rate.

The failure criterion for the slip surface is formulated in effective stresses, and neither the total gravimetric load inducing the vertical stress nor the shear force required for equilibrium does vary significantly. The main effect on the factor of safety arises from the change in pore pressure. The location of the water table is calculated based on the pore pressures along the slip line, by projecting the pressures according to a slope-parallell flow field (Figure 4.18). In this way the effect of the an active drainage can be illustrated both for the injection phase and for the drainage phase (Figure 4.19). The part downstream of the drain will essentially find a new equilibrium with an almost slope-parallel water table between the drainage location and the start of the curved slip line towards the toe.
Figure 4.18: Definition sketch for the calculation of the relative position of the water table for an arbitrary point P in the sliding body.

Relative position of the water table:

\[
\frac{h_w(x)}{h_L} = \frac{h_L - \Delta h_w(x)}{h_L}
\]

\[
\frac{h_w(x)}{h_L} = 1 - \frac{\text{surface}(x) - y \cdot \cos(\beta) - h_p(x)}{h_L}
\]

Figure 4.19: Water table along the slip line (where submerged): The dashed lines mark: a) the start of the bedrock decline below the top layer, b) the location of the drain, c) the start of the curved slip line towards the toe.

The locally mobilized friction was calculated along the slip line (Figure 4.20) and is later used in the interpretation when assessing the factor of safety.
Chapter 4: Application examples

Figure 4.20: Plotting the mobilized friction along the slip line emphasizes the sections of the slope that are most critical to fail. In the central part, the mobilized friction without drainage is close to the theoretical value for an infinite slope.

The central part of the slope (from the crest up to the start of the curved toe line) provides the main contribution to the mobilized friction. The fine dotted line in Figure 4.20 is the mobilized $\phi$ for a theoretical infinite slope with the initial water table. One can conclude that for the central part ‘infinite-slope’ conditions are obtained. Downstream of the pump, the effect of the drain provides a constant incremental improvement along the sliding surface.

4.2.4 Interpretation

At the drain location the total flux $q_{In}$ is reduced by the drainage outtake $q_d$. In the lower part a new slope-parallel water table, based on the remaining flux, is found. Figure 4.21 shows the effect of such a measure on the slope stability. The global factor of safety is calculated using the data shown in Figure 4.20, to obtain the ratio of the frictional resistance and the average mobilized friction angle along the entire slip surface, $F_S = \frac{\tan(\phi)}{\tan(\phi_{mob})_{average}}$. The dashed line shows the theoretical safety factor of an infinite slope with the reduced flow $q = q_{In} - q_d$ (i.e., approximates the slope-parallel portion downstream of the drain). One finds that the overall safety factor of the slope is larger than that of an infinite slope and slightly less sensitive as to changes in the water table.
Figure 4.21: Effect of implementing a drain on the factor of safety, owing to the reduction of the flow and therefore lowering of the water table within a finite slope. The dashed line is for an infinite slope and is shown for comparison.

By applying a hydraulic head $h_d$ at the drain above (+) or below (-) the stationary pressure for slope-parallel flow as an external boundary condition, we can assess the safety factor for each pressure. The pressure at the drain completely defines the downstream effective stresses and has therefore a large influence on the total stability. In the central part we observe full mobilization of shear resistance for injection pressures $\Delta h_d > 1$ m (Figure 4.22). The slope only remains stable due to its limited length and the mobilization of passive resistance at the lower boundary.

Figure 4.22: Influence of drainage pressure on the factor of safety. The pressure at the drain has a strong effect on the safety factor of the entire slope. The friction in the central part is fully mobilized during injection for $\Delta h_d > 1$ m and the slope only remains stable due to its limited length.
Chapter 4: Application examples

The radius of the drain has little influence on the slope stability, since the downstream flow is barely affected (Figure 4.23). Larger chemical drains only change the stresses in the immediate surrounding of the drain.

The analysis was performed in the critical section, far away from the drainage collector. This section is the most critical one when operating the pipe as drainage. It is noteworthy that during injection the section closest to the collector features the lowest factor of safety.

Whereas for a given pressure in the drain at the critical section the radius of the drain has no significant effect on the stresses in the 2D model, its influence on the feasible water-table reduction becomes evident when taking into account the flow from the drainage location out-of-plane along the drain to an outlet or pump, as described in Chapter 4.2.2.

In order to obtain a target draw down at the critical section $\Delta h_d(z = 0)$ the required pressure at the outlet easily exceeds any feasible pressure. The drain is located 5 m below the water table and suction cannot be applied as it would result in air flow in the unsaturated zone. The reduction in hydraulic head $\Delta h_d(z = L_p)$ at the drainage collector required to lower the water table in the critical section by 1.5 m exceeds 5 m for very small chemical drains and could not be applied to the outlet (Figure 4.24).

Figure 4.23: Influence of the effective drainage diameter (chemical or actual). Safety factors for different equivalent drain diameters are shown. Constant head prescribed at the drainage boundary ($\Delta h_d = -2.0\ m$). The influence of the drain radius on the factor of safety for a two-dimensional section is considerably less pronounced than the influence of the pressure at the drain.
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Figure 4.24: Pressures along the out-of-plane drainage pipe consisting of the injection tube and the modified soil featuring elevated hydraulic conductivity.

If the outlet is modeled as a free-surface discharge at the drainage collector with atmospheric pressure, the obtainable draw down $\Delta h_D (z = 0)$ in the critical section becomes highly dependent on the equivalent radius of the drain and the distance of the drainage collector (Figure 4.25).

Figure 4.25: Pressure along the drain from the critical section to the drainage collector for a constant collector pressure of $h_{Pump} = 0 \text{ m}$.

When operating an active drainage system with a pump at the collection point, the power consumption during a rainfall event becomes more important. Power consumption is defined analogously to the well example in Chapter 4.1. A larger radius of the drain due to the modification of
the soil by a chemical might decrease the required power at the drainage collector to less than 20% of the initial value (Figure 4.26).

![Figure 4.26: Gain in efficiency of the chemical drain for increasing size of the modified zone. Expanding the zone around the injection pipe will reduce the required power for a target safety factor.](image)

**4.2.5 Conclusions on slope stability**

The implementation of a chemical drain in a slope prone to failure was analyzed as an example for a practical geotechnical application of chemically enhanced drainage.

A generic slope with a water table close to the surface was chosen as a representative example for slopes triggered by rainfall events, where the factor of safety in general only drops below the required limits when the water table is raised due to increased ground-water inflow into the slope.

We found that for such a case the factor of safety can decrease from $F_S = 1.3$ to $F_S = 1.25$ during the creation of the chemical drain, if the injection of the chemical coincides with high inflow rates, representative for a rainfall event. The installation should therefore be planned during seasons with low probability of rainfall and supervised in order to take immediate action (e.g., lowering the injection pressure during rainfall events). However, once the drain is formed the water table downstream of the drainage section can be strongly reduced for quite moderate pressures at the center of the drain, thereby increasing the factor of safety from $F_S = 1.3$ to $F_S = 1.5$.

Whereas for a given pressure in the drain, the radius of the drain does not significantly affect the stresses in the two-dimensional model, its influence of the feasible reduction of the water table becomes evident when taking into account the flow from the drainage location out-of-plane along the drain to an outlet or pump. If the outlet is modeled as a free-surface discharge at the
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drainage collector with atmospheric pressure, then the obtainable draw down $\Delta h_D$ in the critical section becomes highly dependent on the equivalent radius of the drain and the distance of the drainage collector. The increased radius of the drain due to the modification of the soil by a chemical can decrease the required power at the drainage collector to less than 20% of the initial value. The chemical drain can thereby provide a flexible system that is compliant to deformation of the drainage, as the modified soil conduit will not fail as brittle as conventional drainage pipes.

4.3 Notation list

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$</td>
<td>body force</td>
<td>kN/m³</td>
</tr>
<tr>
<td>$h$</td>
<td>hydraulic head</td>
<td>m</td>
</tr>
<tr>
<td>$h_d$</td>
<td>hydraulic head in the drain</td>
<td>m</td>
</tr>
<tr>
<td>$h_D$</td>
<td>location of the drain</td>
<td>m</td>
</tr>
<tr>
<td>$h_L$</td>
<td>thickness of the sliding layer</td>
<td>m</td>
</tr>
<tr>
<td>$h_{stope}$</td>
<td>total height of the slope</td>
<td>m</td>
</tr>
<tr>
<td>$h_w$</td>
<td>location of the water table</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta h_d$</td>
<td>draw down at the drain</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta h_{min}$</td>
<td>proportionality factor</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta h_{Pump}$</td>
<td>draw down at the drainage collector</td>
<td>m</td>
</tr>
<tr>
<td>$k$</td>
<td>hydraulic conductivity</td>
<td>m/s</td>
</tr>
<tr>
<td>$k_0$</td>
<td>initial hydraulic conductivity</td>
<td>m/s</td>
</tr>
<tr>
<td>$l_{stope}$</td>
<td>length of the slope</td>
<td>m</td>
</tr>
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<td>$n_e$</td>
<td>effective porosity contribution to flow</td>
<td>(-)</td>
</tr>
<tr>
<td>$q$</td>
<td>flow rate in radial direction</td>
<td>m²/s</td>
</tr>
<tr>
<td>$q_{in}$</td>
<td>upstream inflow rate</td>
<td>m²/s</td>
</tr>
<tr>
<td>$q_D$</td>
<td>outtake at drain</td>
<td>m²/s</td>
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<tr>
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<td>equivalent radius of the drain</td>
<td>m</td>
</tr>
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<td>equivalent front position</td>
<td>m</td>
</tr>
<tr>
<td>$r_i$</td>
<td>radius of the well</td>
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</tr>
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<td>outer boundary of the model</td>
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<tr>
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<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
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</tr>
<tr>
<td>$r^*$</td>
<td>radius of the equivalent empty pipe</td>
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<td>time</td>
<td>s</td>
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<tr>
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<td>water content</td>
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</tr>
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<td>$x_{\text{Toe}}$</td>
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</tr>
<tr>
<td>$y$</td>
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<tr>
<td>$z$</td>
<td>coordinate out-of-plane</td>
<td>m</td>
</tr>
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<td>°</td>
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<td>kN/m$^3$</td>
</tr>
<tr>
<td>$\gamma_w$</td>
<td>unit weight of water</td>
<td>kN/m$^3$</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>angle of internal friction</td>
<td>°</td>
</tr>
<tr>
<td>$\chi$</td>
<td>relative increase of hydraulic conductivity</td>
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</tr>
<tr>
<td>$F_s$</td>
<td>factor of safety</td>
<td>(-)</td>
</tr>
<tr>
<td>$H_{\text{out}}$</td>
<td>hydraulic head at the outer boundary of the model</td>
<td>m</td>
</tr>
<tr>
<td>$H_{\text{Well}}$</td>
<td>perforated section of the well</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>draw down of the water table</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H_{av}$</td>
<td>draw down in the inner zone</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H_p$</td>
<td>draw down at the pump</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H_{p,\text{unt}}$</td>
<td>draw down at the pump for untreated soil</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H_{p,\text{av,unt}}$</td>
<td>draw down at the pump for untreated soil</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta H_x$</td>
<td>draw down at the observation point</td>
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</tr>
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<td>characteristic drainage length</td>
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</tr>
<tr>
<td>$L_p$</td>
<td>distance from drainage collector to critical section</td>
<td>m</td>
</tr>
<tr>
<td>$P$</td>
<td>pumping power</td>
<td>W</td>
</tr>
<tr>
<td>$P_{\text{nt}}$</td>
<td>corresponding pumping power for untreated soil</td>
<td>W</td>
</tr>
<tr>
<td>$R_f$</td>
<td>normalized equivalent front position</td>
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<tr>
<td>$Sat$</td>
<td>local saturation condition</td>
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</tr>
</tbody>
</table>
5 Corroding steel piles in hydraulic barriers

5.1 Introduction
The literature review in Chapter 1.2.3 showed that, due to the small stiffness and strength of the barrier clay, foundations of structures on natural and artificial hydraulic barriers often have to be built using driven steel piles. The effects of the installation of piles through these clay layers are controversially discussed, as they may impair the long-term performance of the hydraulic barrier. So far the effects of clay mineralogy and steel-pile corrosion on forming a preferential flow path along the pile foundation has never been considered and studied, even though some case studies suggest the existence of such a mechanism, calling for its study, quantification and modeling.

Element tests on clays with iron-rich pore fluid were performed for the assessment of pile corrosion effects on hydraulic barriers. Based on the results of these tests, the constitutive model for the coupled chemo-mechanical behavior developed in the previous chapters was modified to account for a different pore-fluid chemistry. This constitutive model was incorporated into a finite-element code, to solve the problem of iron diffusion originating from a corroding source in a case study on ground-water pollution.

5.2 Experimental results
The effect of Fe(II) ions on clayey soil was quantified with standard chemical and geotechnical laboratory tests to provide a solid foundation for the numerical modeling.

5.2.1 Chemical adsorption
Anaerobic corrosion of steel will release iron cations with two positive charges into the pore fluid of the surrounding soil. These cations can exchange the existing interlayer cation of the clay minerals and will thereby strongly affect the properties of the soil. This key reaction was quantified by assessing the adsorption isotherm in batch samples. Samples of 200 mg to 400 mg dry calcium-Bentonite (Calcigel, Südchemie) were suspended in a 50ml volumetric flask and exposed to a range of Fe(II) concentrations (0–20 mmol/L). The suspension was stirred for 30 minutes, then centrifuged and the remaining Fe(II) concentration was determined using a standard photometric method based on phenanthroline chloride, as described in Lange (1982). In order to avoid oxidation or adsorption of the iron cation, plastic laboratory ware was used and all liquids were de-aired with nitrogen. The difference between the initial concentration prior to addition of the bentonite and the equilibrium concentration after the exchange reaction allowed calculating the adsorbed amount on the solid. Figure 5.1 shows that already at very low concentrations the iron is readily adsorbed by the bentonite. However, a comparison with the cation-
exchange capacity reveals that in contrast to the reaction with guanidinium, the exchange is not complete. Nevertheless a Langmuir-type adsorption curve fits the data well and can be used for the numerical modeling.

![Figure 5.1: Fe(II)-Sorption curve on Calcigel bentonite. The dashes red line indicates the theoretical maximum adsorption, based on the cation-exchange capacity. The Langmuir sorption isotherm (solid line) with 95% confidence bands is shown for the best fit parameter.]

5.2.2 Element tests with iron solutions as pore fluid

For the geotechnical characterization of this phenomenon, two tests were carried out to quantify the processes. Element tests in a consolidometer with dissolved iron chlorides in the pore water of clay-sand mixtures (40% bentonite and 60% Quartz sand) were performed to assess the extent of increased permeability due to iron corrosion in clayey soils. The samples were mixed with the Fe(II) solutions during reconstitution under nitrogen atmosphere and directly mounted into the consolidometer device in order to avoid oxidation of the dissolved iron. The time-settlement curves of load increments up to 800 kPa were interpreted according to Terzaghi’s theory of one-dimensional consolidation. The deducted hydraulic conductivity of the samples with iron ions in the pore fluid was consistently higher than those measured in the control samples (Figure 5.2). These results bracket the range of relative increase in permeability in soils with moderate amount of smectite minerals.
5.2.3 Flow-column tests

In addition to the consolidometer tests, the process of the migration of iron ions into an unmodified soil was investigated in a one-dimensional flow. These flow-column tests were set up to provide evidence that the hydraulic conductivity is not only modified by iron during mixing but also during permeation. Samples of clay–sand mixtures (40% bentonite and 60% quartz sand) of 2.5 cm length were mounted into flow tubes of 1-cm$^2$ cross-sectional area and saturated with deaired water bottom up. Subsequently falling-head permeability tests with different Fe(II) solution were carried out. During the permeation the pore volume within the sample was replaced with the solution 12 times. The obtained average permeability over the entire sample at a given time was calculated over intervals of 24 hours and plotted against the relative amount of ions provided by the inflowing solution (Figure 5.3). A control sample permeated with water was tested in parallel to the other samples but showed no significant increase in permeability during the falling-head test.

The adsorption curve shows that only about 60% of the available cations in the clay are readily exchanged with Fe(II) ions. The results of the flow-column test are consistent with this finding, as the hydraulic conductivity was increased to its ‘saturation level’ after the amount of Fe(II) ions provided by the inflowing solution reached 60% of the exchangeable cations present in the soil. After this stage additional permeation did not further increase the hydraulic conductivity.
Figure 5.3: Fe(II)-solution lead to chemically enhanced delivery of pore fluids. Instead of guanidinium ions, iron ions were used in flow-through experiments and produced a similar, but less pronounced effect. The increase was completed when the inflowing solution provided 60% of all available exchangeable ions in the soil.

5.3 Parametric study on an example problem

In order to illustrate the effect of the observed phenomenon, a parametric study was performed. It is loosely based on a case of ground-water pollution by a dissolvable chemical due to the operation of an industrial plant on an aquifer close to a river. The aquifer is sealed to the plant by a clay layer with low permeability. For the foundation of the buildings, however, steel piles are driven through this natural barrier into the underlying sandy aquifer. On average a downward gradient is present and leads to some convective transport, in addition to the diffusive flux.

5.3.1 Model description

Size and soil profile

An axisymmetric model is built around a single pile. The pile measures 0.1 m in radius, the whole model extends to \( r_{\text{max}} = 0.4 \) m (Figure 5.4). The soil profile consists of three layers. The first layer directly below the plant is a clay with low plasticity and a hydraulic conductivity of \( k_1 = 10^{-7} \) m/s. This layer extends down to a depth of 15 m and is polluted by the chemicals leaching from the plant. At time \( t = 0 \) the concentration of the pollutant in this layer is constant over depth and referred to as \( c = c_{\text{top}} \). The aquitard extending from 15 m to 30 m is a clay with high plasticity and a hydraulic conductivity of \( k_2 = k_1/10 \). The concentration of the pollutant in this layer is initially assumed to be zero. Below the aquitard the pile extends 4 m into a sandy aquifer with a hydraulic conductivity of \( k_3 = k_1 \times 100 \). The concentration at the interface be-
between the aquifer and the aquitard is recorded as key output of the simulation, as it is responsible for the onset of pollution of ground water. The pile itself is modeled as being impermeable and as not contributing to the vertical flow.

![Figure 5.4: Depiction of the axisymmetric boundary-value problem. Left: initial hydraulic conductivity of the clay layers. Right: Detail of the model plot, showing the modified field of hydraulic conductivity around the pile at the end of the simulation. Note that the model is calculated in two dimensions and that the presentation in three dimensions is for illustration only.](image)

**Reactions and coupling**

At the interface between the pile and the clay layer an Fe(II) source is incorporated to account for anerobic corrosion. The release of the iron is assumed to be constant over time and was chosen based on literature values obtained for iron surfaces exposed to clay soil. Fe(II) is transported to some extend along the pile advectively, due to the hydraulic gradient, but it will for the most part propagate diffusively in radial direction into the surrounding soil. Both clay layers will adsorb Fe(II) ions according to a Langmuir adsorption curve and feature increased permeability proportional to the adsorbed amount. When 60% of the available cations are exchanged the increased hydraulic conductivity is capped at $k(z,r) = \chi \cdot k_{initial}$. The hydro-chemical coupling was achieved in the same way as described previously for the guanidinium simulations; the detailed description can be found there (Chapter 3.5). The pollutant however is modeled as a non-adsorbing tracer (i.e., the most mobile kind of pollutant is analyzed in this worst-case scenario) and will be subjected to both advective and diffusive/dispersive flow.
Chapter 5: Pile corrosion

Hydraulic and chemical boundary conditions

The seasonal fluctuations of the ground-water level in both the upper clay layer as well in the aquifer were neglected and a constant downstream gradient was applied through fixed hydraulic heads at the top and the bottom of the model. The gradient was chosen to be $i_2 = 1/5$ in the aquitard, as the ground-water table of the aquifer was on average 3m below the ground-water table measured in the upper clay layer. The hydraulic initial conditions were calculated in an initial stationary step. The vertical boundaries were modeled as hydraulically impermeable, given that no global horizontal flow was considered. For the pollutant a constant inflow concentration at the surface of $c_{in}(t) = c_{top}$ is incorporated. The horizontal system boundary in the aquifer is an open-boundary outflow condition. The vertical model boundaries are considered to be impermeable for both Fe(II) and the pollutant. This is justifiable as, for the time scales of this simulation, the iron will not reach this outer boundary (Figure 5.4, right).

Discretization

The model was meshed with rectangular elements with uniform size of 0.025 m x 0.025 m. Both the pressure and the concentration variables were discretized within the elements with quadratic shape functions. Time steps of the solver using a backward differential formula (BDF) were adaptive in order to account for the changing hydraulic flow. The maximal time step was limited to 1/800 of the total transition time in order to keep the initial Courant number below 1. This ensured stability for both the advective and the diffusive parts of the transport equation. Local change in pressure gradients due to chemical reaction was in this numerical simulation less pronounced as both the upstream and the downstream boundary condition were both applied as fixed-hydraulic-head conditions and the propagation of the modified zone was perpendicular to advection.

The parameters for the case study are summarized in Table 7. The following results were obtained in a parametric study for variable chemical-increase factor $\chi$. 

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### Table 7: Summary of the material parameters and the discretization

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>Diffusion of iron</td>
<td>$D_{FE}$</td>
<td>$1.00E-09 \text{ m}^2/\text{s}$</td>
</tr>
<tr>
<td>Diffusion of pollutant</td>
<td>$D_{poll}$</td>
<td>$1.00E-09 \text{ m}^2/\text{s}$</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>$\alpha$</td>
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</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>$k_2$</td>
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</tr>
<tr>
<td>Porosity of the clay layers</td>
<td>$n_1 = n_2$</td>
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</tr>
<tr>
<td>Chemical increase factor</td>
<td>$\chi$</td>
<td>1 to 20</td>
</tr>
<tr>
<td>Hydraulic gradient in aquitard</td>
<td>$i_2$</td>
<td>$1/5$</td>
</tr>
<tr>
<td>Convective time to pass aquitard</td>
<td>$t_0$</td>
<td>140.3 years</td>
</tr>
<tr>
<td>Mesh size</td>
<td>$\Delta z = \Delta r$</td>
<td>0.025 m</td>
</tr>
<tr>
<td>Maximum time increment</td>
<td>$\Delta t_{max}$</td>
<td>$T_{conv}/800$</td>
</tr>
</tbody>
</table>

### 5.3.2 Results

Adsorption of the Fe(II)-ions released by corrosion and the simultaneous modification of the soil

Data from a point at $r = 0.1 \text{ m}$ in the center of the aquitard ($z = -22.5 \text{ m}$) was used to illustrate the temporal evolution of the chemical modification close to the pile (Figure 5.5, left). As the Fe(II) concentration in the pore fluid (blue line) increases over time, some fraction is adsorbed by the soil. According to the experimentally determined adsorption isotherm, Fe(II) will adsorb up to 60% of cation-exchange capacity. In Figure 5.5, the adsorbed amount is expressed relative to the cation-exchange capacity (red line). The linear coupling between the adsorbed amount and the relative increase of hydraulic conductivity will then lead to a modification of the local permeability. This degree of transformation ($\kappa$, green line) is expressed relative to the maximum increase, according to Equation 5.1, and thus ranging from 0% to 100%.

$$
\kappa = \frac{k(c_{Fe})}{k_{initial}} - 1 \quad \frac{\chi - 1}{k_{initial}}
$$

with $k(c_{Fe})$ being the local hydraulic permeability affected by the iron exchange, $k_{initial}$ the initial hydraulic conductivity of the soil layer and $\chi$ the increase factor due to reaction with Fe(II).
Chapter 5: Pile corrosion

Figure 5.5: Evolution of the iron release and the degree of modification of the local permeability. The graph in the left panel is for a point on the interface to the pile, that in the right panel for a point at $r = 0.2$ m. The increase of iron in the pore fluid (blue, left axis) leads to an exchange of the cations up to 60% of the cation-exchange capacity (red, right axis) and a simultaneous transformation of the soil (green, right axis).

Close to the pile the full improvement is reached already after $t/t_0 = 0.2$ i.e., after 28 years. The second plot in Figure 5.5 shows the same data for a point at $r = 0.2$ m at some distance away from the pile. Even though the iron concentration in the pore fluid will remain significantly lower, the degree of transformation will exceed 99% at the end of the time considered in the simulation.

Radial growth of the modified zone due to Fe(II) and total increase in convective flow

Analyzing the degree of modification between $r = r_{pile}$ to $r = r_{max}$ at intervals of 14 years shows that the modified zone grows continuously in a quite diffuse front, but without reaching the outer boundary of the model during the simulation (Figure 5.6). Even though a small amount of Fe(II) is also transported convectively along the pile, the radial growth is uniform over depth within reasonable precision.
Figure 5.6: Degree of local modification along the radial coordinate for time intervals of 14 years. The modified zone grows radially with high degree of modification close to the pile and unmodified soil at the outer boundary of the model.

Depending on the absolute chemical increase factor $\chi$, the convective flow in the modified zone will increases by up to 20 times of its initial value and thereby increase the total convective flow through the model (Figure 5.7). Despite the radial geometry and the non-linearity introduced by the adsorption isotherm, the increase over time is almost linear.

![Figure 5.6: Degree of local modification along the radial coordinate for time intervals of 14 years.](image)

![Figure 5.7: Comparison of the total convective flux through the model normalized relative to the initial flux for different increase factors $\chi$.](image)

Figure 5.7: Comparison of the total convective flux through the model normalized relative to the initial flux for different increase factors $\chi$. The ongoing modification of the soil leads to a continuous (almost linear) increase of the total convective flux, thereby increasing the transport rate of the pollutant into the aquifer.

Processes contributing to pollutant migration through the aquitard

This front propagation is driven by two main processes: convection and diffusion. When differentiating between these processes during the passage of the front through the center of the aquitard we find for this cross-section that the convective component exceeds the diffusive compo-
Chapter 5: Pile corrosion

nent (Figure 5.8). Once the front has passed the measurement point, the diffusive component will reduce gradually to zero, whereas the convective component will increase according to the ongoing modification of the soil.

![Figure 5.8: Temporal evolution of the total contaminant transport through a cross-section at the center of the aquitard ($z = -22.5 \, \text{m}$) for each transport process. Advection is the dominating process and becomes orders of magnitudes larger once the front ($c = 0.5 \, c_i$) has passed.](image)

However the convective transport is not uniform over the radius. The transport quantities originating from the different processes are plotted in Figure 5.9 for $\chi = 5$ at different time intervals along the radial coordinate. The local diffusive vertical flux drops after the second interval below $10^{-11}$ mol/m$^2$s and is negligible compared to the convective flux.

![Figure 5.9: Differentiation of the transport quantities over radius for intervals of 20 years (same color for same time). The convective flux (solid lines) is significantly larger than the diffusive flux (dashed lines) in vertical direction and mainly concentrated around the pile.](image)

Diffusive fluxes will mainly contribute to evening out the concentration in radial direction, whereas the transport into the aquifer is mainly driven by convection in the modified zone.
around the pile. Due to this slenderness of the model and the equilibrating diffusive flux in radial direction, the concentration of the pollutant at a given time does not significantly vary in radial direction. Figure 5.10 illustrates this for the central part of the aquitard \( z = -22.5 \text{ m} \). The concentration close to the pile is almost undetectably higher than at the outer boundary.

![Concentration profiles along radial coordinate in the center of the aquitard at intervals of 7 years. Due to the horizontal diffusion the concentration is almost constant over the radius, representing a moving front perpendicular to the pile direction.](image)

5.3.3 **Interpretation**

The key result of the parametric case study is the time of arrival of the pollutant in the aquifer. The purely convective transport in unmodified soil would indicate that the breakthrough of the front would occur after 140 years. In a combined diffusive advective transport the front position is defined at a concentration of \( c = 0.5 c_{in} \); there are low concentrations of the transported pollutant ahead of this front. The front however still requires 140 years to travel through the aquitard. Figure 5.11 shows the concentration profiles along the pile for the migration of the front through the unmodified soil. As found in the previous chapter, the concentration along the pile is a good conservative estimate for the almost perpendicular front for soils with modified hydraulic gradients. Figure 5.12 shows for the same time intervals and an increased factor of \( \chi = 5 \) the front migration in a faster but similar pattern to the unmodified soil.
Chapter 5: Pile corrosion

Figure 5.11: Concentration profile along the pile at time intervals of 10 years for unmodified soil and non-corroding piles. Low concentrations of the pollutant arrive at the aquifer long before the breakthrough of the main plume.

Figure 5.12: Concentration profile along the pile at time intervals of 10 years for an increase factor of $\chi = 5$. The front arrives significantly earlier at the aquifer.

Breakthrough curves were recorded at the interface between the aquitard and the aquifer in order to illustrate the influence of the increased hydraulic conductivity (increase factor $\chi$) on the arrival of low concentrations as well as the breakthrough time for $c = 0.5 \ c_{in}$ (Figure 5.13).
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Figure 5.13: Breakthrough curves for different increase factors $\chi$. The contaminant plume will arrive at the aquifer during the operation lifetime of the industrial plant, if accounting for the effects caused by the corrosion of the pile foundation.

When looking at the arrival time of low concentrations of the contaminant, orders of magnitudes lower than in the highly contaminated upper clay layer (i.e. $c_{in}/c_{aq} > 100$), pollutants are found in the aquifer may be as early as 30 years after the installation of the piles (Figure 5.14). Such low concentrations may already be harmful if they reach drinking-water wells.

Figure 5.14: Absolute arrival time of the pollutant in the aquifer. The influence of the increased factor $\chi$ on the transport duration for small critical concentrations of the contaminant is evident.

The combined action of diffusion, corrosion and increased convection will result in an overall increased transport rate and therefore a significantly earlier arrival of critical concentrations of the pollutant in the aquifer that was initially protected by a hydraulic barrier. Once this barrier is perforated with countless foundation piles subjected to corrosion, small concentrations can arrive...
in the aquifer up to four times earlier than implied by the initially low hydraulic conductivity (Figure 5.15).

Figure 5.15: Effect of diffusion, corrosion and increased convection on the arrival time of the pollutant in the aquifer expressed relative to the purely convective transport.

5.4 Conclusion

The developed tools to model alterations of hydraulic conductivity in soil due to chemical reactions were applied in a third geotechnical problem where the modification in fact was a side effect of a standard foundation solution. Laboratory tests were carried out to adapt the constitutive relations for iron cations originating from the corrosion of steel piles. A parametric numerical study was carried out to assess the transport characteristics of a contaminant through a hydraulic barrier perforated with steel piles. The purely convective transport in unmodified soil would indicate that the breakthrough of the front would occur after 140 years. In a combined diffusive advective transport the front position is defined at a concentration of $c = 0.5 \, c_{in}$ and there are low concentrations of the pollutant transported ahead of this front. The front however still requires 140 years to travel through the aquitard. When looking at the arrival time of low concentrations, orders of magnitudes lower than in the highly contaminated upper clay layer (i.e. $c_{in}/c_{aq} > 100$), the study showed that pollutants can reach the aquifer as early as 30 years after the installation of the piles. Such low concentrations may already be harmful if they reach drinking-water wells.

The combined action of diffusion, corrosion and increased convection will result in an overall increased transport rate and therefore a significantly earlier arrival of critical concentrations of the pollutant in the aquifer that was initially protected by a hydraulic barrier.
## 5.5 Notation list

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>contaminant concentration in pore fluid</td>
<td>mol/L</td>
</tr>
<tr>
<td>$c_{ads}$</td>
<td>concentration of Fe(II) ions on solids</td>
<td>mol/g</td>
</tr>
<tr>
<td>$c_{aq}$</td>
<td>contaminant concentration at interface to aquifer</td>
<td>mol/L</td>
</tr>
<tr>
<td>$c_{Fe}$</td>
<td>concentration of Fe(II) ions in solution</td>
<td>mol/L</td>
</tr>
<tr>
<td>$c_{in}$</td>
<td>inflow concentration of contaminant</td>
<td>mol/L</td>
</tr>
<tr>
<td>$c_{top}$</td>
<td>initial concentration in top layer</td>
<td>mol/L</td>
</tr>
<tr>
<td>$i$</td>
<td>initial hydraulic gradient</td>
<td>(-)</td>
</tr>
<tr>
<td>$r$</td>
<td>radial coordinate</td>
<td>m</td>
</tr>
<tr>
<td>$r_{max}$</td>
<td>outer radius of the model</td>
<td>m</td>
</tr>
<tr>
<td>$r_{pile}$</td>
<td>pile radius</td>
<td>m</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$t_0$</td>
<td>convective breakthrough time</td>
<td>s</td>
</tr>
<tr>
<td>$z$</td>
<td>vertical coordinate</td>
<td>m</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>degree of modification</td>
<td>(-)</td>
</tr>
<tr>
<td>$\chi$</td>
<td>relative increase factor of hydraulic conductivity</td>
<td>(-)</td>
</tr>
<tr>
<td>$CEC$</td>
<td>cation-exchange capacity</td>
<td>mol/g</td>
</tr>
<tr>
<td>$H_{Layer}$</td>
<td>layer thickness</td>
<td>m</td>
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<tr>
<td>$T$</td>
<td>normalized time</td>
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</table>
6 Conclusions and Outlook

6.1 Problem statement
Clay soils react strongly with the compounds dissolved in the pore fluid, due to their large surface area and their mineralogy. In environmental geotechnics this interaction is often regarded as a passive side effect due to leaching or ground-water pollution. However, some chemicals in the pore fluid influence the soil properties and can directly affect key geotechnical parameters, such as strength and hydraulic conductivity. In many geotechnical problems the water circulating in the porous ground is not only one of the main driving forces, its targeted alternation is also often part of the solution, i.e., in the case of slope stabilization by drainage or of lowering the water table in construction pits. Using tailored chemicals to induce such changes enables the development of new techniques to design innovative solutions.

6.2 Main results
In an extensive program of laboratory tests, the modification of clay soils based on the treatment with guanidinium-salt solutions was explored. This treatment has shown to cause a significant increase in shear strength and decrease in the swelling potential of clayey soils, both of which are highly desirable in a wide range of geotechnical applications. It has been demonstrated that guanidinium can increase hydraulic conductivity of both pure bentonites and quartz/bentonite mixtures by an order of magnitude, in contrast to a number other soil-improvement techniques that reduce permeability during treatment. Based on the experimental work on different length scales the following conclusions could be drawn on how this specific compound causes changes:

- The origin of the increase in permeability due to guanidinium ions is in its fixation to the inner and outer clay surfaces due to a cation-exchange reaction. This fixation results in a strong inhibition of the water uptake into the interlayer space and an aggregation of the clay minerals.
- The aggregated, non-swelling particles provide an open-pore system with pores of about 2-µm size. Upon wetting these pores are no longer filled with an expanding clay phase but kept open. The pore water remains available for circulation and is not bound as immobile interlayer water. The compression tests have shown that the structure is stable also under stresses up to 800 kPa.
- Despite these drastic changes on the microstructural level, the stiffness is not significantly affected by chemical treatment. A negative influence on this particular mechanical property can therefore be excluded. Limitations of the results are that these fundamentals were obtained on generic model soils, where a significant effect was to be
Chapter 6: Conclusions

expected and where conditions are reproducible. The influence of mineralogy, sample
size and homogeneity will have to be addressed in a case-specific evaluation prior to
application in the field.

Furthermore, for a better understanding of the mechanisms behind the process of enhanced
delivery, a simple analytical hydro-chemical model has been developed and successfully
validated against experimental data on soils samples subjected to the flow of guanidinium
solution and against a more sophisticated numerical analysis. Correct estimation of the
retardation factors for the chemical front propagation appeared to be the key element for an
accurate prediction of enhanced delivery effects in practical applications. It can be done by
simple mass-balance calculations or by fitting measured adsorption data. The combination of the
experimental results and the constitutive relations provided a quantitative description of the
fundamental processes behind the proposed concept of chemically enhanced delivery of soil
improvement agents. For the assessment of the temporal improvement in a practical
implementation, the analytical model can serve as a first estimate, whereas a numerical model
accounting for the specific boundary conditions will make it possible to predict the practical gain
from chemically enhanced delivery.

In some geotechnical applications, however, the local increase in soil permeability is in its own
right a highly desirable result. This aspect was investigated based on geotechnical examples,
where the chemical was used to create zones of enhanced permeability in situ as a part of drain-
age systems:

a) A vertical well combined with chemically enhanced drainage was analyzed as a geotech-
nical example where the main purpose of well operation was to lower the water table at a
construction site to a target value. The efficiency of such a system was quantified for dif-
ferent degrees of treatment in an axisymmetric boundary-value problem. The degree of
treatment was characterized with the relative front position \( R_f \) of the modified zone and
the measure of efficiency was the pumping power required at the well to achieve a given
draw down.

In summary, this parametric study showed that the method is most efficient when treating
only a small area around the well with \( R_f < 30\% \). The power consumption could be re-
duced to less than half compared to chemically unmodified wells. Treating the soil with
the chemical during construction of the well can lower the total cost of the dewatering
system by providing lower operational cost for long-term wells with a one-time addition-
al investment during the installation.
b) The implementation of a chemical drain in a slope prone to failure was analyzed as an example where chemically enhanced drainage would directly reduce the driving forces and provide a low-disturbance installation. A generic slope with a water table close to the surface was chosen as a representative example for slopes triggered by rainfall events, where the factor of safety in general only drops below the required limits when the water table is raised due to increased ground-water inflow into the slope.

The analysis showed that for such a case the factor of safety may decrease from 1.3 to 1.25 during the creation of the chemical drain, if the injection of the chemical coincides with high inflow rates, representative for a rainfall event. The installation has therefore to be planned during seasons with low probability of rainfall and supervised in order to take immediate action (e.g., lowering the injection pressure during rainfall events). However, once the drain is formed, the water table downstream of the drainage section can be strongly reduced for quite moderate pressures at the center of the drain and thereby increasing the factor of safety up to 1.5.

If the outlet of the drain is modeled as a drainage collector with atmospheric pressure, the obtainable pressures reduction in the critical section become highly dependent on the equivalent radius of the drain and the distance of the drainage collector. The increased radius of the drain due to the modification of the soil by a chemical may decrease the required power at the drainage collector to less than 20% of the initial. The chemical drain can thereby provide a flexible system that is compliant to deformation of the drainage as the modified soil conduit will not fail as brittle as conventional drainage pipes.

Finally, the tools developed to model alterations of hydraulic conductivity in soil due to chemical reaction were applied in a third geotechnical problem, where the modification in fact was a negative side effect of a standard foundation solution. Laboratory test were carried out to adapt the constitutive relations to iron cations originating from the corrosion of steel piles. A parametric numerical study was carried out to assess the transport characteristics of a contaminant through a hydraulic barrier perforated with steel piles. The purely convective transport in unmodified soil would indicate that the breakthrough of the front would occur after 140 years. In a combined diffusive advective transport the front position of the contaminant plume is defined at a concentration of $c = 0.5 \ c_{in}$ and there are low concentrations of the pollutant transported ahead of this front. The front, however, still requires 140 years to travel through the aquitard. When looking at the arrival time of low concentrations of pollutants, orders of magnitudes lower than in the highly contaminated upper clay layer (i.e., $c_{in}/c_{aquifer} > 100$), the study showed that the occur-
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The occurrence of pollutants in the aquifer may be as early as 30 years after the installation of the piles. Such low concentrations may already be harmful if they reach drinking water wells.

The combined action of diffusion, corrosion and increased convection will result in an overall increased transport rate and therefore a significantly earlier arrival of critical concentrations of the pollutant in the aquifer that was initially protected by a hydraulic barrier. Once this barrier is perforated with countless foundation piles subjected to corrosion, small concentrations can arrive in the aquifer up to four times earlier than implied by the initially low hydraulic conductivity.

6.3 Further research

The study shows that a targeted modification was feasible with guanidinium in smectite soil. The numerical simulations indicate a high potential of the proposed technique in terms of efficiency and applicability to selected geotechnical engineering problems.

The strategic direction of further research should focus on (a) the choice of the chemical for a given soil, (b) the influences of scalability and field conditions, and (c) possible combination with other soil improvement techniques.

a) The mechanism found in the mineralogical analyses indicates that smectite soils with high cation-exchange capacity are most sensitive to the treatment with guanidinium. For soils, where the main clay minerals responsible for initially low permeability are kaolinite or illite minerals, guanidinium is less likely to be as efficient as in soils with smectite minerals. A search for other environmentally compatible chemical components that are applicable to a wider range of soils is highly recommended.

b) The experimental results were mostly obtained in small-scale laboratory tests and standard geotechnical tests. Further research including full-scale tests in a controlled laboratory environment and field tests would be of significant value and are a prerequisite for commercially implementing the proposed technique in geotechnical-engineering praxis.

c) The increased hydraulic conductivity has a high potential for facilitating other soil-treatment techniques such as bio-mineralization or bio-decontamination. The combination of chemically enhanced delivery with other methods for soil improvement has a high potential for broadening the range of application and should therefore be investigated further.
References


Comsol (2013). "COMSOL Multiphysics Version 4.3.2.189", by COMSOL Ltd, Hertfordshire UK.


7 Appendix A: Combining biomineralization with chemically enhanced drainage
This chapter was published in a conference proceeding on coupled phenomena in environmental geotechnics (Minder and Puzrin 2013).

7.1 Abstract
This work focuses on the potential combination of microbial soil improvement methods with chemically enhanced drainage in fine grained soil. The efficiency of carbonate precipitation with *Bacillus pasteurii* cultures was evaluated on laboratory scale soil samples containing clay minerals. Microbial carbonate precipitation successfully increased uniaxial compression strength even in fine-grained soils with a minimum hydraulic conductivity of 5E-9 m/s. During treatment, permeability is reduced by one order of magnitude and can decline below the required limit. In order to avoid falling below the threshold it is proposed to improve in advance hydraulic properties of the soil by using a technique of chemically enhanced drainage. In this study permeability increase of more than one order of magnitude was achieved for soils containing smectite clay minerals. Combination of the two methods allows expanding the possible range of applicability of biomineralization toward less permeable soils.

7.2 Introduction
Artificial cementation of soils by addition of chemicals is widely used (e.g., in road construction for hydraulic stabilization of the deck). These methods usually require mechanical mixing of the treated soil, yield highly alkaline soil chemistry and are limited to close surface application. (Hammes and Verstraete, 2002)

Microbially induced precipitation of calcite (CaCO₃) provides cementation of soil particles under flow-through conditions. Hammes and Verstraete (2002) have shown that calcite precipitation is governed by four key parameters. The formation of calcite depends on

- the concentration of calcium in the solute,
- the available carbonate,
- the pH of the environment and
- the availability of nucleation sites.

Microorganisms can locally influence these parameters by their metabolism, so that calcite precipitation occurs distributedly and not locally at the injection point of calcium solutions. A homogeneous distribution of an active bacteria culture can therefore provide homogeneous cementation of soil under flow-through treatment.
Bacillus pasteurii bacteria are especially appropriate to provide a controlled precipitation of calcite. They produce large amounts of the urease enzyme that enables them to use urea \((\text{CO(NH}_2\text{)}_2)\) as energy and nitrogen source. The decomposition of urea simultaneously increases the pH in the vicinity of the bacteria and releases carbonate (after Whiffin et al., 2007). The bacteria surface itself can serve as nucleation site (DeJong et al., 2006).

In sands with high hydraulic conductivity homogeneous cementation was obtained and correlation between calcite content and shear strength could be assessed (Harkes et al., 2008).

In this project the method of biomineralization is evaluated with respect to its application in less permeable soil.

7.3 Materials and methods

7.3.1 Conceptual design

On a conceptual level, this study assesses the potential of combining microbial methods to increase shear strength with chemical methods to increase permeability of soils. The former requires a sufficient hydraulic accessibility of the open pore space in order to place and feed microorganisms in soil. This is naturally not given in fine-grained soil, where already a small percentage of clay can reduce the fluid flow drastically.

The first step in this study consists of the placement of bacteria and inducing precipitation of carbonate in a soil with large aggregated clay minerals (Figure 7.1). The goal of this step was to investigate, whether in the presence of clay minerals an increase in shear resistance can be achieved by biomineralization. In order to keep the cultivation of the bacteria unaffected by any chemical treatment, the soil used in this step was a quartz illite mixture, where large illite clay particles are chosen to represent an aggregated smectite phase.

![Figure 7.1: Cementation of clay particles by microbial induced precipitation of carbonates.](image)

In a second step, it is then investigated whether the hydraulic conductivity allowing for successful biomineralization can be produced by means of a permanent chemical modification of the sealing smectite clay phase (Figure 7.2).
Many of the chemically enhanced drainage methods proposed in the literature are not compatible with the use of microorganisms, e.g., one of the most efficient methods to increase permeability by several orders of magnitude (Fernandez and Quigley, 1985) uses liquid hydrocarbons, which are toxic to the microorganisms established in biomineralization methods and in general classified as environmental pollutants. Based on its specific interaction with the clay surface (Plötze and Kahr, 2008) the organic salt guanidinium was chosen as chemical agent to increase permeability. It is soluble in water and reacts with the clay at low concentrations. Biodegradation of guanidinium is reported for species occurring in natural surface water (Mitchell, 1987). Different mixtures of smectite clay (Calcigel, Süd-Chemie AG, Germany) with quartz grains (sand <0.3 mm, Cook Industrial Minerals Pty.Ltd, Perth, Australia and silty sand, Millisil B1, Sihelco AG, Birsfelden, Switzerland) were subjected to standard oedometer test both in their natural and their modified form. The analysis of the time-settlement curve was used to investigate the efficiency of the chemical improvement. Additionally its effectiveness under flow-through conditions was tested in one set of permeameter tests.

Both steps are addressed individually in this study and finally evaluated on their potential combination.

### 7.3.2 Experimental setup for biomineralization

Biomineralization experiments were operated with microorganisms of the species *Bacillus Pasteurii* (also classified as *Sporosarcina Pasteurii*). Cultivation was conducted under aerobic batch condition in a medium containing 20 g/l urea and 8 g/l nutrient broth. Inoculation of the samples was performed by transferring 5 volume percent of a freshly grown culture to new nutrient solution. Sterile handling techniques were applied to keep the cultures pure and guarantee reproducibility.

The feasibility of biomineralization in clay was evaluated by performing flow-through experiments with bacteria suspensions and nutrient media in soil columns. The soil was inoculated
Appendix A

with *B. Pasteurii* by mixing the soil with bacteria suspension prior to sample reconstitution. Supply of nutrient and calcium was provided by flushing the soil with an optimized pore water solution as proposed by DeJong *et al.*, (2006). Adjustment of nutrient solution to a pH 6.5 with sterilized HCl provided stable solutions without calcite precipitates prior to bacteria exposure. The increase in shear strength due to cementation was subsequently assessed by uniaxial testing of biomineralized and natural control samples. Since exposure to air of the clay rich samples would lead to drying and negative pore water pressures the uniaxial tests were performed in an oil bath.

The sample cell for the biomineralization experiments was based on an oedometer cell extended by two half tubes (Figure 7.3), which were removable to provide a laterally unsupported sample for uniaxial testing.

![Figure 7.3: Disassembled sample cell with the two removable sidewalls for uniaxial testing.](image)

Two biomineralization samples of an illite-quartz soil were operated with different pumping schemes. As active *B. Pasteurii* cultures raise the pH of the pore fluid permanently, the change in pH of influent and effluent medium was taken as rough indication for bacteria activity. In both samples the effluent pH exceeded 9.5 after the second day of treatment with nutrient solution.

Intermitting pumping led to growth of the bacteria into the tubing and eventually to failure to supply the nutrient into the soil. Constant flushing resulted in less premature precipitation in the supply tubing. Nevertheless high backpressure was generated after two days of feeding. The peristaltic pump was not able to maintain the flow rate. Therefore the feeding technique was changed to injection of media directly into the soil with two needles. The injection point was moved by 1 cm per day. After a feeding time of nine additional days the sample was sheared at a displacement rate of 10 mm/h. An untreated control sample was tested at the same shear rate.
7.4 Results

7.4.1 Biomineralization in soils with low permeability

The local injection of solution into the soil with needles allowed supplying the nutrient to the microorganisms homogeneously. This finally led to the expected cementation of the soil particles throughout the sample. During undrained uniaxial loading a higher failure load was detected compared to the sample without biomineralization (Figure 7.4) and the failure occurred more brittle. The presence of clay minerals did not impair the cementing effect of microbial calcite precipitation.

![Figure 7.4: Uniaxial shear behavior of a microbially improved soil sample and an unmodified control sample for comparison. The shear strength is improved and the failure occurs more brittle.](image)

On the way to this result several additional qualitative and quantitative observations were made. A considerable decrease in permeability was observed for all biomineralization samples. The average permeability of the soil decreased from 4.8E-8 m/s before the experiment to 3.1E-9 m/s after biomineralization. These average values were obtained with constant head experiments and are – due to the heterogeneity of the biomineralized samples – only very rough estimates for the local decrease.

The reduced hydraulic conductivity led to a significant reduction of fluid flow and a localization of the calcite precipitation in the vicinity of the inlet. Without moving the injection point, the development of a high backpressure and the growth of the bacteria into the tubing would eventu-
ally lead to termination of the treatment. Once the hydraulic conductivity declined below $5 \times 10^{-9}$ m/s, it was no longer feasible to feed the bacteria homogeneously with nutrients.

In order to provide an adequate flow rate under such conditions, it is required to use either high hydraulic gradients or long treatment time with low-activity bacteria. Both adaptations will result in unsatisfying side effects in the field.

In practical applications increasing the hydraulic gradient to achieve sufficient flow rates will result in locally very high pore-water pressures close to the injection points. For the treated soil layer the factor of safety for slope stability can therefore be reduced significantly during the injection phase. Since the slopes requiring soil improvements are mostly already close to failure this additional exposure during treatment is generally not acceptable. High injection pressures additionally bear the potential to produce hydraulic fractures, which will lead to pronounced preferential flow and eventually to failure to homogeneously mineralize the soil layer.

Conversely, accepting low pressures only will require a fundamental adjustment of the used nutrients and microorganisms. Feeding abundant nitrogen reducing soil bacteria (e.g., *Castellaniella denitrificans*, van Paassen *et al.*, 2008) - instead of injecting new microorganisms - together with low concentrated nutrients is theoretically an option, but the prolonged duration of treatment will conflict with economical and temporal requirements for soil improvement methods.

In conclusion, the experiment have shown, that biomineralization is possible for fine-grained soil with a sufficiently high permeability. There is however a risk that during treatment the permeability will fall below the required limit. The most promising solution to overcome this obstacle is to increase the hydraulic conductivity in advance, so that – once the process has started – fluid flow will not drop below the required minimum. In the next step we therefore investigate the potential of chemically enhanced drainage.

### 7.4.2 Increase of permeability in smectite/quartz mixtures

The analysis of the time-settlement curves revealed that permeability was increased for all samples with the chemically modified clay compared to the unmodified samples. In mixtures with sand the permeability was increased to such an extent, that the data could not be evaluated as the settlement occurred almost immediately. Hence, only the data of silty sand mixed with clay is presented, where both sample sets showed the expected time dependent settlement according to the 1-dimensional consolidation theory.
Figure 7.5 shows the derived permeability at different stress levels for a clay content of 10%. The initial difference between modified and unmodified samples at low stresses is almost perfectly maintained during loading. For close to surface applications (effective vertical stress < 100 kPa) the increase is one order of magnitude and the permeability is elevated to the targeted range of 1E-8 m/s. The relative improvement slightly drops during compaction of the sample by higher stresses.

In the case of a higher clay content a more pronounced decrease during loading is observed for both the absolute permeability and the relative improvement (Figure 7.6). Here it is informative to compare the permeability at a given void ratio (Figure 7.7) as well. An initially more than 50 times higher permeability is observed prior to compaction at a void ratio of 0.68. The modified soil structure features thus more effective flow paths for circulation than the raw material at the same void ratio. Due to the large plastic deformations, this difference reduces significantly upon compaction.

![Figure 7.5: Hydraulic conductivities during oedometric loading for 10% clay content. The permeability of the chemically modified soil is increased over the whole range compared to the unmodified raw material.](image-url)
Figure 7.6: Hydraulic conductivities during oedometric loading for 20% clay content. During compaction the difference between modified and raw material is reduced.

Also under flow-through conditions the chemical enhanced drainage maintained is effectiveness. Figure 7.8 compares the different treatment methods and shows that even the structurally undisturbing delivery of the chemical via the pore fluid lead to the targeted increase above $10^{-8} \text{ m/s}$.

The improvement achieved by chemically enhanced drainage methods reached values above $10^{-8} \text{ m/s}$ for both types of addition (mixing and flushing). Only after significant mechanical straining, the newly formed structure is destroyed. The flow rate feasible at this elevated perme-
ability should be sufficient in order to supply the microorganisms with nutrients for carbonate precipitation.

![Graph](image)

Figure 7.8: Hydraulic conductivity over time during permeameter testing. The sample flushed with the guanidinium solution features a gradual increase of permeability in the course of the treatment.

### 7.5 Conclusion

The qualitative and quantitative findings of the performed experiments allow drawing four main conclusions about biomineralization with respect to its application in fine-grained soils.

Firstly, microbial carbonate precipitation successfully increases shear strength above a certain limiting permeability even in fine-grained soils. In this study the minimum hydraulic conductivity was 5E-9 m/s. It could be shown that the presence of clay minerals did not impair the strength improvement.

Secondly, during the process of biomineralization the precipitated calcite reduces the hydraulic conductivity. The experimental data indicated a decrease of one order of magnitude. If during this process the permeability declines below the limiting threshold, incomplete and heterogeneous soil improvement will be the result.

Thirdly, a measure to expand the application of the microbial method to less permeable soils is to increase the hydraulic conductivity in advance by one order of magnitude, so that during treatment the required fluid flow can be maintained with reasonable pore-water pressures.

Finally, it could be shown, that with the chemical enhanced drainage technique an efficient method to increase hydraulic conductivity exists. Increase in hydraulic conductivity of more than one order of magnitude was achieved for soils containing smectite clay minerals.
There is a reasonable likelihood that the chemical method works in soil with other clays minerals as well. Further research is recommended in order to assess the optimum range of applicability of the combined bio-chemical method with respect to initial hydraulic conductivity, soil composition and microorganism.

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References: Appendix A


8 Appendix B: Materials and Devices

This appendix lists the specific chemicals and soil materials used in this thesis. A short description detailing the sample procedures used for each device/testing apparatus is given as well.

8.1 Materials

Analytical grade chemicals:

Guanidinium hydrochloride, C(NH$_2$)$_3$Cl, ≥99%, CAS 50-01-1, Sigma-Aldrich, Switzerland

Guanidinium carbonate, C(NH$_2$)$_3$HCO$_3$, ≥97%, CAS 593-85-1, Sigma-Aldrich, Germany

Calcium chloride dihydrate, CaCl$_2$ ⋅ 2H$_2$O, ≥99%, CAS 10035-04-8, Sigma-Aldrich, Germany

Iron(II)-chloride tetrahydrate, FeCl$_2$ ⋅ 4H$_2$O, ≥99%, CAS 13478-10-9, Sigma-Aldrich, Germany

Clays and soils:

Calcium-bentonite, CALCIGEL, Südchemie, Germany

Sodium-bentonite, MX-80, Amcol, USA

Quartz sand, washed Perth sand, $d_{50} = 0.24$ mm, Cook Industrial Minerals, Australia

The soil components were used as delivered (no additional drying, milling or fractioning) and their mineralogical composition had been determined by the Claylab. The cation exchange capacity was determined for this thesis using the Copper (II) - triethylenetetramine method after Meier and Kahr (1999).
8.2 Sample preparation and devices

All aqueous solutions were prepared by using demineralized water (resistivity at 25 °C: 18.2 MΩcm, Milli-Q Gradient, Millipore, France) and the chemicals indicated above. A standardized ground-water equivalent was used by preparing a solution of 0.01 mol/L CaCl₂.

8.2.1 Homo-ionic bentonites

The bentonites were saturated in solutions of 1 mol/L of CaCl₂ and GndCl respectively for 2 hours. The supernatant solutions were replaced once with new solutions of the same concentrations and the soil resuspended for 24 hours. Subsequently the soil was washed 4 times with demineralized water, by centrifugal settlement and supernatant removal. The dried samples were homogenized by milling in a hand mortar.

8.2.2 Densities

The specific density (or absolute density) ρₛ was determined from samples of the homo-ionic bentonites dried at 105 °C for 2 days until no further weight change was observed. The sample weights were about 5 g. The pycnometer was a helium pycnometer (AccuPyc 1330, Micromeritics, Germany). The sample volume is calculated from the observed pressure change the helium undergoes when it expands from one chamber containing the sample into another chamber without sample (Webb and Orr, 1997).

8.2.3 Ring-shear apparatus

The samples for the ring-shear apparatus were reconstituted from the homo-ionic Calcigel powder (after Gnd- and Ca- saturation) in separate consolidation cells with standardized ground water. The ring shaped samples were cut from these containers after consolidation to 100 kPa vertical stress and transferred to the ring shear apparatus (designed by the institute for Geotechnical Engineering, ETH Zurich, e.g., Puzrin and Schmid, 2011). The samples were tested in a multi-stage procedure with constant shear velocity and three different load steps (100 kPa, 150 kPa, and 200 kPa) for each sample. Two separate sets of samples were tested at shearing velocities of 0.2 mm/min and 0.01 mm/min respectively.
8.2.4 Oedometer tests

A standard oedometer frame (Strassentest AG, Switzerland) with samples of 20 mm height and 56.4 mm diameter was loaded incrementally with increasing load steps from 12.5 kPa to 3'200 kPa according to the procedure given in the ASTM D2435-04 (ASTM, 2004).

The pure bentonites were tested on unmodified samples reconstituted with standardised ground water and subsequent addition of guanidinium solutions via diffusion from the top and bottom ends of the samples over the course of 14 days (see chapter 2.3.1). The 2 mol/L solution was periodically replaced every 48 h in order to increase the exchange rate. The exchange reaction in took place in the consolidometer cell at vertical stresses of 12.5 kPa.

The effect of accompanying inert material and different kind of modifying chemicals was studied by adding up to 60 weight percent of quartz sand to dry bentonite and supplying the pore water (standardized ground water, guanidinium chloride or iron-chloride solutions) during reconstitution of the samples, (i.e., mix-treatment). The concentration of the modifying chemicals in the pore solution was chosen to amount to 100% of the available adsorption sites indicated by the cation exchange capacity of the bentonite fraction.

The evaluation of the time-settlement curves for each load step was performed based one-dimensional consolidation theory. The derived parameters (stiffness and hydraulic conductivity) were obtained with an automated procedure by fitting the theoretical response with a least square-fit to the measured data on a logarithmic time scale. The compliance of each frame was measured with dummy samples of solid brass and taken into account for the calculation of the stiffness of the sample.

8.2.5 Swell potential

The effects of the chemical modification on the swelling behavior were studied on reconstituted samples of homo-ionic bentonite in oedometer cells. Initially dry powder samples of the raw calcium bentonite and the guanidinium saturated bentonite were wetted with standardised ground water (with 0.01 mol/L \( \text{CaCl}_2 \)) at low surcharge (12.5 kPa) and tested according to the sub-method B of the ASTM standard D 4546-03 (ASTM, 2003). Both powder samples were compacted to the same density prior to wetting with the pore water.
8.2.6 Permeameter tests

The permeameter tests were conducted in a self-assembled flow column (Figure B.1), where compacted samples were subjected to a static vertical stress of 65 kPa and a hydraulic gradient of 100. The samples were reconstituted from unmodified bentonite and standardised ground water or guanidinium solutions as pore water directly into the permeameter cell. The concentration of guanidinium ions in the pore solutions of these samples amounted to 100% of the available adsorption sites indicated by the cation exchange capacity of the bentonite. In some tests (see section 2.3.2) the guanidinium solutions was provided later during testing, permeating an initially unmodified sample with guanidinium solutions \(c(Gn\text{dCl}) = 0.5 \text{ mol/L}\).

Figure B.1: Main components of the constant head permeameter cell. The sample container in the center of the picture was a corrosion-less steel cylinder with diameter 55 mm and allowed for sample heights of about 40 mm. Vertical stress was applied with dead weights on top of the sample (far right).

8.2.7 Porosimetry

Mercury intrusion porosimetry (MIP, PASCAL 140/440, Porotec, Germany) on dry samples was used to quantify the alterations of the pores system due to guanidinium treatment. Mercury as a non-wetting fluid enters the pores of a sample only when forced under pressure. With slowly increasing pressure, mercury intrudes into progressively smaller pores. The mercury intrusion porosimetry only determines the percentage of open Hg-accessible meso- and macropores (2 nm – 100 µm). Pores connected to the external surface by narrow openings will not be intruded up to the point where sufficient pressure is applied to intrude those entrances. The entire volume of such pores will be allocated to the threshold radius class of the most restricted part of the entry-way. The pore volume can be derived from the quantity of intruded mercury and the pore size distribution according to the Washburn equation, which gives a relationship between pressure and pore size.
(Washburn, 1921) for circular pores:

\[ r = -\frac{2\gamma \cos \Theta}{p} \]

\( r = \) pore radius, \( p = \) pressure, \( \gamma = \) surface tension of mercury = 0.48 N/m, \( \Theta = \) wetting angle of mercury (139°, Diamond, 1970).

Crack-free pieces of the slowly dried samples were subjected to vacuum evacuation for 2 h prior to mercury intrusion. The sample material was obtained from consolidometer samples, after measuring the effects of guanidinium on hydraulic conductivity.

8.2.8 Laser diffractometry

The particle size distribution of both the homo-ionic bentonite powders as well as parts of the oedometer samples that were mix-treated with guanidinium was measured with a laser particle sizer (Partica LA-950, Horiba, Retsch Technology, Germany). Demineralized water without any dispersion agent was used as suspension fluid during testing. Both modified and unmodified samples were exerted to an identical amount of ultra-sonic agitation (3x5min) until no further aggregate breakdown was observed. This ultra-sonic agitation allowed breaking the macro-aggregates that were formed during drying of the clay and measuring the chemically and mechanically stable particle-aggregates instead.

References: Appendix B


