Two-Phase Reactive Mass Transfer of an Oil-Soluble Chemical in Porous Media: A CT-Scan Study
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# Table of Contents

1. Introduction ............................................................................................................. 1  
   1.1. The oil production lifecycle .............................................................................. 1  
   1.2. Water production in the oilfield ....................................................................... 1  
   1.3. Water control .................................................................................................... 3  
      1.3.1. Mechanical water control .......................................................................... 3  
      1.3.2. Chemical water control ............................................................................ 4  
      1.3.3. The need for ‘smart’ water control ............................................................ 5  
   1.4. Scope and organization of the thesis ................................................................. 6  
   1.5. References ....................................................................................................... 7  

2. The chemistry of alkoxysilanes ................................................................................. 9  
   2.1. Alkoxysilanes in water ...................................................................................... 9  
      2.1.1. Reactions .................................................................................................... 9  
      2.1.2. Effect of parameters .................................................................................. 10  
   2.2. Two phase systems in bulk .............................................................................. 12  
   2.3. TMOS in porous media ...................................................................................... 13  
      2.3.1. Micromodel studies ................................................................................... 13  
      2.3.2. Porous media studies ................................................................................ 14  
   2.4. References ....................................................................................................... 14  

3. Coupled mass-transfer and reaction in water of TMOS ....................................... 17  
   3.1. Introduction ..................................................................................................... 17  
   3.2. Experimental ................................................................................................... 18  
      3.2.1. Experimental setup and materials .............................................................. 18  
      3.2.2. Principles of X-ray CT ............................................................................. 20  
      3.2.3. Data processing ......................................................................................... 22  
   3.3. Results and discussion ................................................................................... 25  
      3.3.1. Oil and water calibrations .......................................................................... 25  
      3.3.2. Mass transfer out of the oil phase .............................................................. 31  
      3.3.3. Coupled mass-transfer and gelation in water ........................................... 35  
   3.4. Conclusions .................................................................................................... 39  
   3.5. References ....................................................................................................... 40  

4. Porous media experiments ...................................................................................... 43  
   4.1. Experiments .................................................................................................... 43  
      4.1.1. High temperature experiments .................................................................. 44  
      4.1.2. X-ray CT scan monitored experiments ...................................................... 44  
      4.1.3. Experiments with effluent monitoring ...................................................... 44
4.2. Materials ........................................................................................................... 45
  4.2.1. Fluids........................................................................................................... 45
  4.2.2. Rock samples ............................................................................................... 45
4.3. Experimental set-up ......................................................................................... 46
4.4. Experimental procedure ................................................................................... 48
4.5. X-ray CT monitoring of flow .......................................................................... 50
4.6. Single-phase flow .............................................................................................. 51
4.7. Oil-water relative permeabilities ...................................................................... 54
  4.7.1. Drainage ........................................................................................................ 54
  4.7.2. Imbibition ..................................................................................................... 55
  4.7.3. Ratio between water and oil relative permeability ......................................... 56
4.8. Discussion and conclusions ............................................................................. 57
4.9. References .......................................................................................................... 58
5. Dynamics of TMOS in porous media ................................................................. 61
  5.1. Introduction ...................................................................................................... 61
  5.2. Experimental results ....................................................................................... 63
    5.2.1. TMOS placement at high temperatures ....................................................... 63
    5.2.2. TMOS placement at room temperature ...................................................... 65
    5.2.3. TMOS placement and analysis of effluents ............................................... 67
  5.3. Stages of reactive transport ............................................................................ 68
  5.4. The effect of the physical parameters ............................................................ 71
    5.4.1. Effect of injection rate ................................................................................ 71
    5.4.2. Influence of lithology .................................................................................. 73
  5.5. Conclusions ...................................................................................................... 74
  5.6. References ........................................................................................................ 75
6. TMOS gelation in porous media .......................................................................... 77
  6.1. Introduction ...................................................................................................... 77
  6.2. Results .............................................................................................................. 78
    6.2.1. Brine back-flush ......................................................................................... 80
    6.2.2. Oil back-flush in homogeneous porous media ............................................ 82
    6.2.3. Layered cores ............................................................................................ 86
  6.3. Discussion ......................................................................................................... 88
  6.4. Conclusions ..................................................................................................... 91
  6.5. References ........................................................................................................ 91
7. General conclusions .............................................................................................. 93
  7.1. TMOS as a water shutoff chemical ................................................................. 93
  7.2. Coupled mass-transfer and reaction in water of TMOS .................................. 93
  7.3. Porous media experiments ............................................................................. 94
7.4. Dynamics of TMOS in porous media ............................................. 94
7.5. TMOS gelation in porous media.................................................. 96
Summary.............................................................................................. 97
Samenvatting..................................................................................... 101
Appendices........................................................................................ 105
  Appendix A: TMOS placement at high temperatures...................... 107
  Appendix B: TMOS placement at room temperature with effluents
  analysis............................................................................................ 115
Acknowledgments ........................................................................... 125
About the Author ............................................................................. 127
1. Introduction

1.1. The oil production lifecycle

Oil recovery can be divided into three stages: primary recovery, secondary recovery and tertiary or enhanced oil recovery. Primary recovery is the stage in which the initial pressure in the reservoir is sufficient to generate and sustain production. In many reservoirs the initial pressure is not sufficiently high to allow for primary recovery. Secondary recovery is the stage during which the reservoir pressure is so low that it needs to be maintained artificially to aid hydrocarbon recovery. This is typically accomplished by injecting either water or gas – depending on reservoir type, geometry and other parameters – to maintain a reservoir pressure sufficient to drive fluids to surface. Tertiary or enhanced oil recovery (EOR) represents the final stage of oil recovery, when oil production is stimulated using injection systems such as polymer, surfactants and miscible gas such as CO₂.

1.2. Water production in the oilfield

Water production during oil and gas recovery has been a growing concern for several decades. It is an unavoidable part of hydrocarbon recovery. Poor management of produced water can have a huge impact on the economics of oil recovery and is a potential environmental hazard. Many oil and gas fields in the main oil provinces are maturing, and consequently hydrocarbon productivity declines. Nearly 98% of the waste produced during oil and natural gas exploration and production consists of produced water; estimates on the amount of produced water in the United States range between 7 barrels of water produced for each barrel of oil to as much as 9.5 barrels [1]. Khatib and Verbeek [2] report an average of 3 barrels of water to each barrel of oil worldwide. The amount of water being produced along with hydrocarbons is increasing [1].
Formation water is often toxic and can adversely impact terrestrial and marine ecosystems. Most formation waters are saline. Often they also contain dispersed hydrocarbons (in the form of small droplets), partially soluble hydrocarbons (C6 to C15), organic acids, polycyclic aromatic hydrocarbons, phenols and volatiles. The soluble components present a particularly serious challenge to produced water treatment. Some formation waters may even contain naturally occurring radioactive materials such as radium-226 and radium-228, uranium and thorium [1]. Also metals such as zinc, lead, manganese, iron and barium can occur naturally in formation water.

Chemicals that are introduced into the reservoir will affect the chemistry of formation water and often resurface [3]. Common chemicals used during the production lifecycle of a well include biocides, scale inhibitors, emulsion breakers and corrosion inhibitors.

The easiest way to dispose of produced water is to discharge the water directly, but because of the polluting agents that can be present in produced water government regulations in many hydrocarbon-producing countries impose strict limits on the amount of pollutants that may be present in the discharge. If the composition of produced water is such that local regulations prohibit direct discharge, additional efforts are needed to decontaminate the produced water prior to disposal in the environment, thus increasing the costs related to the hydrocarbon recovery.

Re-injection of produced water can present a solution, especially in cases where water injection is necessary to maintain reservoir pressure or when a deep aquifer is available that is not used for drinking water. However, produced water re-injection can also introduce new problems. For example, the presence of particles in suspension in produced water used for re-injection purposes may cause well impairment [4, 5].

Inevitably formation water finds its way to a production well. The main mechanisms through which water reaches oil and gas wells are water coning, cusping, cresting and channeling through high-permeability zones (including fractures and faults) that are in contact either with aquifers or directly with injection wells meant to pressurize the reservoir. Water coning refers to a hydrodynamic process in which the oil-water contact is locally drawn upwards towards the perforated interval of the well. In horizontal wells the oil-water interface forms a characteristic crest, hence the name water cresting. This effect is
a result of the mobility ratio between oil and water typically favoring water flow over oil flow and is very difficult to avoid and even more difficult to remediate once it leads to water breakthrough.

The second manner in which water can reach a production well is through a high permeability connection between either an aquifer or a water injection well (in case of secondary recovery) to the production well. This high permeability connection between the well and a water source can lead to early water breakthrough at the production well, leaving significant amounts of oil in place, mostly in the low permeability zones. Hypothetically water production from a well as a result of channeling can be remedied by blocking the high permeability zone, thus stimulating production from the zones still containing hydrocarbons. This process is greatly aided when the high permeability zone that needs to be blocked is isolated from other layers, for example, by an impermeable shale barrier. In case the high and low permeability zones are connected, e.g. in the absence of shale barriers between layers, water will eventually find its way from the blocked zones into the well.

1.3. Water control

1.3.1. Mechanical water control

Treatments aiming to reduce water production are typically referred to as water control or conformance control treatments. If excessive water production can be attributed to a specific zone within the reservoir, and this zone is isolated from overlying and/or underlying reservoir intervals by impermeable barriers such as shale layers, blocking flow from this zone could contribute significantly to reducing water influx and thus increase the lifespan of a well.

If water production is principally in the lower reaches of the reservoir, and only the upper parts are still producing, a bridge plug can be set to close off the lower regions of the well. If water comes from an intermediate interval that is not too thick a straddle packer or a casing patch can be used to seal a specific interval off without losing connections with the over- and underlying intervals.
Cement is often used for mechanical water control. Cement squeezes are the most common water control system. A cement squeeze is a remedial procedure in which cement is injected into a certain well interval to plug leaks in casings or to block perforations. When performed at the interval in the well that is producing water this will have beneficial effects on the overall production by closing off the perforations responsible for water production. A drawback of the application of cement for water control is that the relatively large particles of cement will not easily penetrate the formation, thus it is difficult to achieve a good seal in the perforations located in the treated interval. Furthermore, this treatment requires that the interval that is to be treated is known, as the interval must be isolated so as not to damage oil-producing zones.

Although cheap and proven, the above solutions have limitations and drawbacks: one major drawback is that they require very specific knowledge of the location of the problem area, and that the borehole is affected over a limited area only. A bridge plug is effective only when water is coming from the lowermost regions of the borehole, while a straddle packer or a tubing patch only covers a limited area of the borehole casing. While cement is somewhat more flexible, mechanical water control has the advantage of providing relatively cheap and easy to apply solutions for water control but is not always feasible. It may be that the zone to be treated is too large, the exact level unknown, or the well too constricted or complex (e.g. highly deviated wells, horizontal wells) to perform mechanical isolation.

1.3.2. Chemical water control

Besides the mechanical water control options mentioned above, it is also possible to treat excessive water production with chemicals. Two main categories of chemical water control are distinguished. The first is chemical water shutoff, which fully blocks flow in the areas in which it is injected. The second category of chemical water control is the relative permeability modifier (RPM). RPM’s are chemicals which reduce the permeability of water more than that of hydrocarbons in the zone in which they are introduced. Typically RPM’s are polymers that adsorb to the formation, leaving flow paths open, but constricting the flow of water. The advantage of using chemicals is that they invade deeper into the
formation thus treating the near wellbore, something that cannot be accomplished with a
cement squeeze. Extensive research has been performed on the mechanisms behind relative
permeability modification [6-11], but thus far no consensus is reached, mainly because the
pore scale mechanisms responsible for the relative permeability modification are difficult to
investigate.

The chemical water shutoff and RPM systems used at present are typically hydrophilic
chemicals. They are placed in the formation as an aqueous solution. Placement can occur in
two different ways. The most targeted placement is injection through coiled tubing with
zonal isolation. In this case, the zone that needs to be treated is isolated from the rest of the
formation using mechanical packers, and the chemicals are pumped only into that part of
the formation that is between the packers.

The alternative to targeted injection using coiled tubing and packers is to “bullhead” the
chemicals. Bullheading is the process by which fluids are injected from surface without any
isolation using packers or otherwise. This is easier and cheaper than targeted injection, but
it is also much more difficult to control where fluids will invade when bullheading. If the
injected water control chemicals do not enter the right formation the treatment could be less
effective, or in the worst case hydrocarbon productivity could be negatively affected.

When using chemicals for water control zonal isolation is often crucial to avoid damage of
the overall oil production. Zonal isolation – especially in complex reservoirs – can be
difficult to achieve, so the ideal water shutoff treatment is one that can be injected without
performing zonal isolation, i.e. a treatment that can be ‘bullheaded’ into the well.

1.3.3. The need for ‘smart’ water control

The suite of water control methods presently available to the industry is large, but extensive
research is still being carried out to find more efficient methods and improve on existing
systems. Water control methods are not very well known and the mechanisms behind the
effects that relative permeability modifiers have on porous media are poorly understood.
The main challenge in most water shutoff treatment is the complexity of the reservoirs, or
the lack of knowledge of reservoir architecture and heterogeneity. Often the exact problem
area within the well is not well localized, making targeted treatment impossible. This can
lead to decreased performance of the water shutoff chemicals or even formation damage resulting in a reduction of hydrocarbon production.

The need exists to improve water control processes, and our knowledge thereof. An important characteristic of the currently available chemical water control methods is that they are based on hydrophilic polymers and gels. These are injected into the near-wellbore region as an aqueous solution. This increases the water saturation and reduces the relative permeability of oil in the near-well zone. If the chemical invades the oil-bearing zones along with – or even instead of – water-bearing zones, it may lead to a severe reduction of oil productivity. The idea of using ‘smart’ chemicals for water control emerged in the late 1990s [12] as a way to broaden the scope of application of water control treatments to wells where zonal isolation is not feasible. The ‘smart water control’ concept is based on the use of chemicals that are soluble and chemically inert in oil but form a gel in presence of water, a so-called saturation based treatment.

Tetra-Methyl-Orthosilicate (TMOS) could act as a ‘smart’ water control system. It is an alkoxy silane that reacts with water in two steps: it first hydrolyzes to form silicic acid, which then condensates to form a silica gel network. TMOS is soluble and inert in oil, but will transfer to water once the oil it is dissolved in is brought into contact with water. This makes TMOS a potential saturation-based treatment: TMOS will only form a gel when the rock it enters contains significant amounts of water. If the rock contains oil, no gel will form and the rock properties will remain unchanged. Fluid distributions are however more complicated in real reservoir situations: even oil-saturated reservoir intervals contain minor amounts of water (known as connate or irreducible water saturation), indicating that even in rock that contains mainly oil there is a risk of gel formation. No studies have been performed to investigate how connate water saturation affects the gelation process when using TMOS dissolved in oil for water shutoff purposes.

1.4. Scope and organization of the thesis

This thesis concerns the investigation of the Tetra-Methyl-Orthosilicate or TMOS as a prototype of ‘smart’ oil soluble chemicals. This work focuses on how TMOS behaves when
injected into a porous medium, and how it modifies the properties of that porous medium (porosity, permeability, etc.) when TMOS dissolved in oil is transferred into water and forms a gel in-situ. The emphasis is on the influence of TMOS gelation on natural sandstone cores commonly used as analogues for oil and gas reservoir rocks. The study of the coupled mass-transfer and reaction of TMOS in water in bulk and in porous media relies on X-ray Computed Tomography (XRCT) for imaging and quantifying not only the phases but also their chemical composition. In a closely related project, Castelijns [13] used NMR to study the coupled mass-transfer and reaction in bulk and in porous media by focusing on the physical chemical aspects. We will see that the XRCT technique is more advantageous when working with large natural rock samples containing TMOS in a two phase fluid system.

The thesis is organized as follows: Chapter 2 provides a short overview of the chemistry of alkoxysilanes, of which TMOS is the simplest example. Chapter 3 reports on the experimental investigation of TMOS behavior in two-phase bulk systems: TMOS is dissolved in oil and then brought into contact with water to investigate the mass transfer reaction behavior. Chapter 4 details the experimental procedure used in the core flooding experiments and the two-phase flow prior to the introduction of TMOS. Chapter 5 examines the mass transfer reaction behavior observed during the core-flow experiments, while chapter 6 discusses the results of gelation of TMOS in the cores. Chapter 7 provides a general discussion of the findings of this work as well as their implications.

1.5. References

2. The chemistry of alkoxy silanes

2.1. Alkoxy silanes in water

Alkoxy silanes are molecules that have up to four alkoxyl groups bound to a silicon atom. They exist in a wide range of compositions from very simple (i.e. tetramethyl orthosilicate, TMOS) to extremely complex with highly branched alkoxyl groups. When the alkoxy silanes come into contact with water they react to form an alcohol and silicic acid \[ \text{1-3} \]:

\[
\text{SiOR}_4 + 2 \text{H}_2\text{O} \xrightarrow{\text{catalysis}} 2 \cdot \text{ROH} + \text{Si(OH)}_4,
\]

where \(R\) represents an alkyl group. The alkoxy silanes have been studied extensively because they are used to manufacture high quality glass products such as fiberglass, thin films and ceramics with varying mechanical properties. Obtaining such properties depends on the conditions imposed on the reaction.

Kay and Assink [4-6] have shown that a full description of alkoxy silane reaction is complex due to the large amount of subspecies that can form during the reaction process. However, using simplified statistical reaction modeling they were able to reduce this number to the three main rate coefficients representing hydrolysis, water-catalyzed and alcohol-catalyzed condensation.

2.1.1. Reactions

The first step is hydrolysis in which water reacts with an alkoxy silane to form an alcohol and silicic acid. During hydrolysis a nucleophylic attack of the oxygen in a water molecule occurs on the silicon atom and an alkyl group breaks off and forms an alcohol and a silicic acid group according to the following reaction equation:
The degree of hydrolysis is defined as the number of alkyl groups that are substituted from the alkoxyysilane. At full hydrolysis, all four alkyl groups are displaced by hydroxyl groups and react to form alcohol, but lesser degrees of substitution are possible (with one to three groups being replaced).

Even though hydrolysis is often regarded as an irreversible process the reverse is also possible: hydroxyl groups being replaced with alkoxy groups [3]. When an alcoholic solvent is used a variation on this reverse hydrolysis is trans-esterification where the alkoxy groups that initially form part of the silane can be replaced by the alcoholic solvent [3].

During condensation a silica network is formed. The structure of this silica network is strongly dependent on the degree of hydrolysis of alkoxyysilane compounds. When the hydrolysis is extensive (three to all four silicon bonds have been hydrolyzed) the silica will form a dense and branching network, whereas lower degrees of hydrolysis will lead to more linear silica networks. Two different types of condensation reaction can be discerned, both of which form silica bonds:

\[
\equiv Si - OH + H_2O \equiv Si - OH + ROH 
\]

\[
\equiv Si - OR + HO Si \equiv Si - OH + Si \equiv +H_2O 
\]

\[
\equiv Si - OR + HO Si \equiv Si - OH + Si \equiv +ROH 
\]

Eq. 2.3 depicts the water-catalyzed condensation reaction in which both active groups are hydrolyzed sites on the silicon atom; Eq. 2.4 shows the alcohol-catalyzed condensation where only one of the involved groups is hydrolyzed.

### 2.1.2. Effect of parameters

For alkoxyysilanes the hydrolysis rate tends to decrease with increasing complexity of the alkoxy groups [3, 7 and 8]. This is attributed to the steric effect of the alkoxy groups. The
steric effect hampers hydrolysis. Larger alkoxyl groups will cause a larger steric effect on the molecule as a whole.

The most basic parameter affecting alkoxy silane chemistry is the water to silane molar ratio. If full hydrolysis is to occur, four moles of water need to be present for each mole of alkoxy silane. Schmidt et al. [1] pointed out that the molar ratio determines the degree of polymerization for molar ratios below four. Colby et al. [9] and Anglaret et al. [10] showed that the time required to form a gel is also affected, with gel times increasing at under-stoichiometric values. Above stoichiometric values the gel time is fairly constant. Brinker [3] indicated that alcohol catalyzed condensation is preferred at under-stoichiometric water to silane ratios.

The solubility of alkoxy silanes in unreacted form in water is limited [11 and 12] and as such the hydrolysis rate is also low [12]. To increase the solubility, alcohol can be added to the water/silane mixture. Trans-esterification can take place once an alcohol is present in the mixture [2]. Kamiya and Yoko [11] also showed that hydrochloric acid (HCl) could act as a solvent.

Fig. 2.1 shows the effect pH has on alkoxy silane reactions. Acids and bases are often used in sol-gel chemistry as catalysts for the hydrolysis and condensation [13]. The hydrolysis rate is minimal at neutral pH and increases with both high and low pH. Condensation on the other hand is promoted at high pH values. The condensation rate is minimal at the isoelectric point (for silica the isoelectric point is situated at a pH of approximately 2), and maximizes at neutral pH. At higher pH the degree of hydrolysis also increases, and the silica networks become more branched. At lower pH values linear polymerization will dominate.
2.2. Two phase systems in bulk

A reservoir typically contains two to three different phases (water, oil, and gas), the distribution of which depends on the history of the reservoir and the present-day conditions. Since silanes are proposed as oil-soluble treatment chemicals all experimental work reported in literature focuses on two-phase systems consisting of oil and water. Most investigations focus on the use of TMOS and TEOS. Both are inert in oil (whether crude or refined), but TMOS is slower to react and form a gel than TEOS. TEOS however tends to flocculate in heavier brines [16].

Figure 2.1: Hydrolysis (dotted line), condensation (dashed line) and de-polymerization (solid line) rate behavior of TMOS as a function of pH [3].
Some shrinkage of the water phase is reported as gelation sets in. Gel time is shortened with increasing temperature, increasing initial silane concentration in the oil phase and initial oil to water ratio. Thompson and Fogler [17] also investigated application of TMOS catalyzed by ammonium hydroxide and an alcoholic solvent. Reaction rates of this combination are much higher than TMOS by itself.

2.3. TMOS in porous media

The application of silanes in porous media was initially proposed by Plazanet and Thomere [18], who patented the use of TMOS for downhole sand stabilization. The concept of applying TMOS for well conformance by selectively blocking water-bearing zones was first proposed by Thompson and Fogler [17, 19].

The work that has been done provides a broad basis: bulk experiments [16, 20] were performed with two phase systems in test tubes to investigate mass transfer and gelation behavior. Two phase flow experiments in etched glass micromodels [16, 17, 19-21] showed phase behavior and gel distribution, and flow experiments in porous media demonstrated placement and blocking behavior [16, 17, 19-22].

2.3.1. Micromodel studies

Etched glass plates that have porous medium-like geometries can be used to bridge the gap between bulk behavior and actual pore scale experiments. Although the pore size is typically still large in comparison with porous media, micromodels allow visualization that can lead to new insights.

Most authors [16, 17, 19-21] report micromodel studies that contribute to the understanding of silica gel placement in porous media. These studies indicate that oil pathways tend to remain intact during gel placement, although mass transfer tends to shrink the oil volume proportionally to the volume of TMOS present. An important observation made on the basis of micromodels is that wettability of the micromodel changes to more hydrophobic as a result of treatment, especially when the gel is allowed to age [20, 21].
2.3.2. Porous media studies

The closest approximation to field application in experimental investigation is formed by coreflooding, and several authors have already applied TMOS in porous media. Thompson and Fogler [17] were the first to apply TMOS in porous media and they report significant flow alteration. They report both water and oil permeability are adversely affected by TMOS placement and propose the concept of using a backflush: when the core is flushed with water after OSC placement the permeability is damaged more than when the core is flushed with oil. This concept is carried through by Thompson and Fogler [19] and Zitha [16]. The former also suggest TMOS gel placement works better as a water shutoff treatment than a relative permeability modifier.

An important observation made in micromodel experiments is that the wettability of the porous media is altered by TMOS treatment. Zitha [16] reports a shift from water-wet to mixed wet, and Lakatos et al. [22] report hydrophobization strong enough that spontaneous imbibition was no longer possible after treatments, even though the media were initially strongly water-wet.

2.4. References


3. Coupled mass-transfer and reaction in water of TMOS

3.1. Introduction

In the previous chapters we explained that alkoxy silane compounds such as tetramethyl orthosilicate (TMOS) are soluble in oil without chemical reaction. When a solution of TMOS in oil is brought in contact with water, the chemical is transferred from the oil phase into the water phase. In the water phase TMOS reacts to form a silica gel according to a two-step process [1-4]. The first step consists of the hydrolysis of TMOS and produces silicic acid and methanol according to the following reaction,

\[
\text{Si}\left(OCH_3\right)_4 + nH_2O \rightarrow nCH_3OH + \text{Si}\left(OCH_3\right)_{4-n}\left(OH\right)_n
\]  

(3.1)

Hydrolysis leads to the formation of a large amount of subspecies of silica-methyl-hydroxyl groups of the form shown in Eq. 3.1 [5]. The degree of hydrolysis depends on the pH and salinity of the water phase; however Eq. 3.1 is an acceptable representation of the overall hydrolysis process under typical pH and salinity [4]. Note that TMOS is poorly soluble in water but the solubility increases by the presence of alcohols such as methanol. The mass transfer of TMOS from oil into water is thus promoted by the appearance and increasing concentration of methanol resulting from the hydrolysis [6].

The silicic acid undergoes condensation (or polymerization) according to the following overall reaction:

\[
n\text{Si}\left(OH\right)_4 \rightarrow n\text{SiO}_2 + 2nH_2O
\]  

(3.2)
leading to the formation of a macromolecular silica gel network in the water phase. The above combination of mass-transfer from an oil phase into the water phase and the subsequent chemical reaction in water is an ingenious way to deliver the alkoxy silane into the water phase and allow it to form a gel in a controlled way. This process has many potential applications including sand stabilization [7] and water control [8-10] during oil and gas recovery.

Grattoni et al. [11] and Karmakar et al. [12] showed that coupled mass transfer and gelation of TMOS can modify the flow behavior of fluids in porous media and quasi-2D etched-glass micro-flow models. Elewaut and Zitha [13] revealed the changes in porosity (void fraction) and permeability of granular porous media caused by the coupled mass transfer and gelation using X-ray Computed Tomography. Castelijns et al. [14] have investigated two-phase reactive systems with TMOS dissolved in the oil phase using NMR.

This chapter reports the investigation of the physical-chemical aspects involved in the coupled mass-transfer and gelation process of TMOS under controlled experimental conditions. For this work X-ray Computed Tomography is used as a chemical analysis tool.

3.2. Experimental

3.2.1. Experimental setup and materials

The experiments were done under isothermal conditions and the initial conditions that were varied are initial water-to-oil ratios, initial concentration of TMOS in the oil phase and salinity and pH of the water phase. The geometry of the samples is shown in Fig. 3.1. TMOS was initially present only in the oil phase. Oil is the lighter phase and floats on top of the water phase. The experiments were carried out with 50 mL batches in which the compositions of oil and water/oil volume ratios were varied. The different settings for the batches are given in Table 3.1. TMOS has an appreciably higher density (1.023 g/mL) than oil (commercially available diesel with a density of 0.826 g/mL) and a slightly higher density than water (1.017 g/mL).
To be able to interpret the measurements, several assumptions need to be made. The system consists of two phases that can be identified separately using the X-ray CT scanner. Initially TMOS is only present in the oil phase. When the oil containing TMOS is brought in contact with the water phase, mass transfer is assumed to begin instantaneously. During mass transfer the total volume of the oil phase decreases by the volume of TMOS that transfers to the water phase (i.e. it is assumed that there is no swelling or shrinkage as a result of mass transfer or reaction). As a result of mass transfer of TMOS the density of the oil phase decreases while the water phase density increases slightly. One of the reaction products is methanol, which remains entirely in the water phase.

The assumption that the system consists of two physically separable phases is reasonable since oil and water will not mix easily, especially in a static system (no stirring or shaking is applied to accomplish mixing). However, during the hydrolysis reaction methanol is formed in the water phase, which could have an impact on the interaction between the two phases.
phases. Furthermore a third phase is introduced once gelation sets in. The gel forms a separate phase from the water phase.

Table 3.1: The properties of the oil- and water phase of all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial TMOS concentration in the oil phase (vol%)</th>
<th>Water phase</th>
<th>Initial water to oil ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>20</td>
<td>Distilled water</td>
<td>1:1</td>
</tr>
<tr>
<td>A-2</td>
<td>10</td>
<td>Distilled water</td>
<td>1:1</td>
</tr>
<tr>
<td>B-1</td>
<td>50</td>
<td>Distilled water</td>
<td>1:1</td>
</tr>
<tr>
<td>B-2</td>
<td>30</td>
<td>Distilled water</td>
<td>1:1</td>
</tr>
<tr>
<td>C-1</td>
<td>20</td>
<td>WELGEL brine</td>
<td>1:1</td>
</tr>
<tr>
<td>C-2</td>
<td>40</td>
<td>Distilled water</td>
<td>1:1</td>
</tr>
<tr>
<td>D-1</td>
<td>20</td>
<td>Distilled water</td>
<td>3:1</td>
</tr>
<tr>
<td>D-2</td>
<td>20</td>
<td>HCl brine (pH=2)</td>
<td>1:1</td>
</tr>
<tr>
<td>E-2</td>
<td>20</td>
<td>NaOH brine (pH=12)</td>
<td>1:1</td>
</tr>
<tr>
<td>F-2</td>
<td>20</td>
<td>Distilled water</td>
<td>2:1</td>
</tr>
<tr>
<td>F-2</td>
<td>20</td>
<td>Distilled water</td>
<td>4:1</td>
</tr>
<tr>
<td>H-2</td>
<td>20</td>
<td>Distilled water</td>
<td>1:4</td>
</tr>
</tbody>
</table>

3.2.2. Principles of X-ray CT

An X-ray CT apparatus reconstructs maps of the attenuation coefficients of an object from multidirectional X-ray transmission data obtained by rotating X-ray source and detector around the subject. The technique is of particular use to reveal flow phenomena in porous media [15-18]. The attenuation coefficient \( \mu \) of a pure substance is given by

\[
\mu = \rho \frac{N_a Z}{M} \left( a + b \frac{Z^{3.8}}{E^{3.2}} \right),
\]

(3.3)

where \( \rho \) [kg/m\(^3\)] is the density of the material, \( N_a \) [1/mole] the number of Avogadro, \( Z \) the atomic number, \( M \) [kg/mole] the molecular weight and \( E[J] \) the X-ray photon energy; \( a \) [m\(^2\)] is the Klein-Nishina cross-section and \( b \) is a constant (\( a = 9.8 \times 10^{-28} \) m\(^2\)/electron for \( E \) in keV). The two terms in Eq. 3.3 account for Compton scattering and photoelectric absorption which are predominant at respectively high and low energies (\( E >> 100 \) keV and \( E << 100 \) keV).

In the range investigated (80-120 keV) both contributions are significant. Due to losses, the actual energy of the X-ray beam is significantly lower than the nominal value [19]. Eq. 3.3
holds for compounds and mixtures of compounds by replacing $\rho$, $Z$ and $M$ by effective quantities. The effective atomic number $Z$ is given by, 

$$Z = \left( \sum_i g_i Z_i^{3.8} \right)^{1/3.8},$$

where $g_i$ and $Z_i$ are respectively the electron fraction and atomic number of the $i$-th atomic species.

The attenuations used in these experiments are normalized to the attenuation of water as:

$$CT = 1000 \left( \frac{\mu_w - \mu}{\mu_w} \right),$$

where these normalized attenuations (also known as CT numbers) are expressed in Hounsfield units (HU).

The concentration of TMOS dissolved in oil as a function of time, $\phi_o^T(t)$, can be determined from the measurement of the CT numbers of the mixture of oil and TMOS during the experiment, $CT_{O/T}(t)$, pure oil, $CT_O$, and pure TMOS, $CT_T$:

$$\phi_o^T(t) = \frac{CT_{O/T}(t) - CT_O}{CT_T - CT_O}$$

Eq. 3.5 assumes a linear relation between the TMOS concentration and the oil phase response. To verify this, a calibration was performed with samples of oil containing varying concentrations of TMOS. The calibration samples were scanned at two energies: 80 $kV$ and 120 $kV$.

For the water phase a calibration similar to that of the oil phase was not possible. In contact with water TMOS hydrolyses to form methanol and silicic acid. These compounds undergo a condensation process reacting into various subcomponents, and ultimately silica. The kinetics are complex and time-dependent making calibration of the possible components difficult.

As a first approach the reaction in the water phase can be omitted: TMOS that transfers from the oil phase into the water phase does not react and the same linear mixing that is used for the oil phase can be used for the water phase. The concentration of TMOS in the
water phase can be derived from the change in volume of TMOS in the oil phase and the initial volume of the water phase Eq. 3.6:

\[ \phi_{WT}^e(t) = \frac{\Delta V_T(t)}{V_w + \Delta V_T(t)} \]  \hspace{1cm} (3.6)

The total volume of the system is assumed constant throughout the experiment, and the initial volumes both of the oil and water phase and the volume fraction of TMOS in the oil phase are known so the amount of TMOS that transfers to the water phase can be derived from these parameters. Using Eq. 3.6 and the calibration values for water and TMOS a prediction can be made of the attenuation of the water phase as a function of the concentration of TMOS,

\[ CT_{WT}(t) = \phi_{WT}^e(t)CT_T + (1 - \phi_{WT}^e(t))CT_w \]  \hspace{1cm} (3.7)

In this study, the experiments were done using a Siemens Somatom Volume Zoom X-ray CT scanner. The machine was set to 80 kV and to optimize signal to noise the current was 250 mAs. The resolution of the images is 300×300 micron and each slice has a thickness of 2 mm. The total acquisition time for each scan (containing multiple samples) is one minute and two seconds yielding a total of 54 images per scan, with each sample being captured in 12 to 13 slices. As the CT scanner requires manual operation the acquisition times vary during the experiments.

### 3.2.3. Data processing

Two main approaches were used to analyze the CT scan data, the first relying on geometrical analysis of X-ray CT images, and the second on quantitative CT measurements converted to phase density. The first method is based on interface tracking, developed by Castelijns et al. [20]. Fig. 3.2 shows three vertical profiles through the samples. The profiles show two distinct zones, an upper and lower zone, separated by a sharp transition. The upper zone is characterized by lower CT numbers than the lower zone. The upper zone
represents the oil phase, while the lower is the water phase. The sharp transition is the interface between the two phases. This interface can be localized by fitting a hyperbolic tangent through the profiles obtained using the X-ray CT scanner and localizing the inflection point. The change in height of the interface is proportional to the change in volume between the two phases, and assuming there are no volume changes as a result of mixing of TMOS with the water phase, these volume changes are fully attributable to mass transfer of TMOS from the oil phase into the water phase. Since the radius and the initial volumes are known it is possible to use this interfacial height data to derive the volume change.

The second approach used to gain information on mass transfer and reaction behavior from the CT scan measurements is based on the assumption that the two phases can be separated based on their density, and that the change in density of the phases is a direct result of mass changes.
transfer of TMOS from the oil phase into the water phase. If we assume that mixing is instantaneous, the variation in density within a given phase is minor and the measured density should be a direct result of the phase composition. By converting the CT scan data into histograms and fitting the oil and water peak with a Gaussian function we find the mean phase density of each phase (Fig. 3.3). The histograms are made by binning all values in whole number intervals. The pixels that represent air (-1000 HU) are not included in these histograms.

Figure 3.3: CT scan image histogram at the beginning of experiment A-1, showing two peaks. The peak on the left represents pixels belonging to the oil phase while the peak to the right is made up of pixels belonging to the water phase. By fitting Gaussian curves through the peaks (black line) the mean value of each phase is found.
3.3. Results and discussion

3.3.1. Oil and water calibrations

The profiles in Fig. 3.2 show that the CT number of the oil phase decreases as a function of time, while the CT number of the water phase increases, although the amount of change is significantly greater for oil than it is for water. This change in CT number is accompanied by a rise of the interface between the two fluids. Fig. 3.2 also shows that there is no clear concentration gradient away from the interface in either of the two phases indicating that the vertical distribution of TMOS within a phase is nearly independent of location. Hence, the concentration of TMOS can be assumed to be homogeneous because of the relatively small geometry of the vessels used in these experiments. The concentration gradients observed near the upper and lower interface in Figs. 3.1 and 3.2 are most likely due to beam hardening. Beam hardening is an effect of the image reconstruction process which causes the edges of an object to seem brighter (i.e., seem to have a higher attenuation) due to partial absorption of the X-ray beam energy spectrum [21]. The histogram in Fig. 3.3 also shows the influence of beam hardening. Each of the two peaks is slightly skewed to the right, where the peak has values greater than the theoretical Gaussian curve. In the peak representing oil (the left-hand peak) this discrepancy is in part due to the plastic container (which has values close to but slightly higher than the value of the oil phase) and in part due to beam hardening.

As gelation sets in, another peak can appear on the right-hand side of the water peak, which represents the formation of gel. Because of the higher attenuation of the gel phase in relation to the water phase, this peak is clearly distinguishable to the right of the water phase peak.

To determine the relation between density, X-ray attenuation and TMOS concentration seven samples were scanned, each at a different concentration. The TMOS in oil concentrations were 0%, 5%, 10%, 25%, 50%, 75% and 100%. Fig. 3.4 shows the bulk density of the oil/TMOS mixture as a function of volumetric concentration determined from these calibration samples; the bulk density of the oil phase increases linearly with the concentration (volume fraction) of TMOS. This can also be seen in Fig. 3.5, which shows
the relation between CT number and TMOS concentration of the oil phase for the calibration samples.

Figure 3.4: Measured density of the oil phase as a function of the volumetric TMOS concentration. The samples used for these experiments have a TMOS in oil concentration of 0%, 5%, 10%, 25%, 50%, 75% and 100%.

Both settings show a linear relation between CT number and TMOS concentration. At 80 kV the absolute difference between the samples was larger than at 120 kV, while the differences in noise levels were not much different. Therefore all experiments were done using 80 kV. Using the measurements from Fig. 3.5 a linear function for the relation between CT number and TMOS concentration was derived.

Fig. 3.6 shows a histogram at the beginning of the experiment in the left-hand graph. Only two peaks are visible because only two phases are present: oil and water. The difference in attenuation is initially small because the presence of TMOS in the oil phase increases the total attenuation. Once mass transfer begins the attenuation of the oil phase will decrease until it reaches the attenuation of “pure” oil (not containing any TMOS), while the
attenuation of the water phase will increase as a result of the addition of TMOS. The histogram in the right-hand graph of Fig. 3.6 shows a histogram of the final CT scan images. The two peaks representing oil and water have moved apart as a result of mass transfer and a third peak is present to the right of the water phase peak. This peak is the result of gel formation and could be seen as representative of a new phase that has formed: the gel phase.

![Histograms showing initial and final CT scan images](image)

Figure 3.6: The initial (left) and final (right) histograms for sample B-1.

The attenuation in the water phase can be predicted based on the amount of TMOS transferred out of the oil-phase (Eq. 3.6 and 3.7). For simplicity linear mixing is assumed, as is the case in the oil phase (Fig. 3.5). This prediction can then be compared to the measured attenuation of the water phase (Fig. 3.7).
From the data shown in Fig. 3.7 – which compares the attenuation of the water phase calculated using Eq. 3.6 and 3.7 with the measurements – it is clear that the prediction underestimates the attenuation of the water phase. The discrepancy between prediction and measurements increases as the amount of TMOS that has transferred increases. This higher-than-expected attenuation of the water-TMOS mixture is probably due to the chemical reactions, i.e. due to hydrolysis and condensation taking place in the water.

The total X-ray attenuation of chemical compounds is a result of the contribution of their elements [22, 23]. It is affected by the chemical state and environment of the atoms (i.e., the adjacent atoms in the compound and the mode of bonding).

---

**Figure 3.7**: The water phase behavior of sample A-1 as calculated from the oil phase behavior and as measured directly in the water phase.
Although quantitative data for silicon in various compounds is not yet available in literature, it is reasonable to assume that the same principle applies. In the oil phase only one component containing silicon is present, namely TMOS. In the water phase, on the other hand, at any time three main species containing silicon are present: unreacted TMOS, hydrolyzed TMOS and condensed TMOS.

Fig. 3.8 shows the measured CT values of the water phase plotted against the predicted value based on linear mixing of TMOS and the water phase (Eq. 3.7). The relation between the two is linear, but the plot indicates that the calculated attenuation is typically 30 percent lower than the measured values. This 30% offset can be used for calibration of the water phase attenuation.

Sample A-2, which has a water to oil ratio of 1:1 and an initial concentration of TMOS in the oil phase of 10%, deviates from the linear trend in Fig. 3.8. Compared to other samples, the change in CT number is relatively small as a result of the low initial concentration. This could be the cause of the weak correlation observed in Fig. 3.8.

Fig. 3.8 shows that the data for this sample follows a different trend than the data for the other initial concentrations. The difference with other samples is also that the change in CT number is small. This is probably why there is a weak correlation.

In Fig. 3.9 the measured CT response and the shifted expected response are plotted against time for the sample with 40% TMOS. After 15 hours the measured data begin to deviate from the calculated CT number in that the values are subsequently lower than they should be.
The reason becomes apparent in the images acquired at the time that the data diverges from the prediction. At this time bright spots form indicating local increase in density. This indicates local accumulation of silica, showing that gelation is occurring. The onset of divergence is thus an indication for the gel time.

Figure 3.8: The calculated attenuation of the water phase plotted against the measured attenuation. There is a linear relation between measured and predicted, where predicted underestimates measured by 30 percent.
3.3.2. Mass transfer out of the oil phase

By fitting the oil-water interface at different time intervals, we can monitor the volume changes of the two phases and hence the evolution of the TMOS content in the phases as a function of time.

Fig. 3.10 shows a semi-log plot of the normalized volume of TMOS in the oil phase as a function of time derived using the above method for different initial TMOS concentrations, with the same initial water to oil ratio of 1:1. Up to about 20 hours all lines fall on the same straight trend line, indicating that TMOS content in oil decreases exponentially with time, in agreement with the NMR imaging studies of Castelijns et al. [14]. Accordingly we can express the TMOS concentration as

\[
\phi_o^T(t) = \phi_o^T(0) \exp(-\alpha_s t) \quad (3.8)
\]
Figure 3.10: TMOS concentration (mol/L) in the oil phase normalized to the initial concentration of TMOS in the oil phase as a function of time. The initial water to oil ratio of all tests is 1:1, the initial concentration is varied.

where \( \alpha_r \) is the mass transfer rate coefficient in \( s^{-1} \). The above equation corresponds to a simple physical model, where mass transfer is much slower than the hydrolysis process and hence the coupled mass-transfer and hydrolysis process is controlled by the mass transfer. This suggests that the concentration of TMOS in the water phase is always negligible compared to that in the oil phase. The mass transfer coefficients for the different experimental runs are listed in Table 3.2 and Table 3.3.

Table 3.2: Mass transfer coefficients derived using an exponential fit for samples in which the initial TMOS in oil concentration was varied, while the initial water to oil ratio for all tests is the same: 1:1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial TMOS concentration in the oil phase (vol%)</th>
<th>Mass transfer coefficient (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-2</td>
<td>10</td>
<td>2.55x10(^{-5})</td>
</tr>
<tr>
<td>A-1</td>
<td>20</td>
<td>2.50x10(^{-5})</td>
</tr>
<tr>
<td>B-2</td>
<td>30</td>
<td>2.48x10(^{-5})</td>
</tr>
<tr>
<td>C-2</td>
<td>40</td>
<td>2.45x10(^{-5})</td>
</tr>
<tr>
<td>B-1</td>
<td>50</td>
<td>2.52x10(^{-5})</td>
</tr>
</tbody>
</table>
Table 3.3: Mass transfer coefficients derived using an exponential fit for samples in which the water to oil volume was varied. The initial TMOS concentration is 20% for all samples. The final column shows the mass transfer multiplied by the fraction of oil of the total volume.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial water to oil ratio</th>
<th>Mass transfer coefficient (s(^{-1}))</th>
<th>Mass transfer per parts water to oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-2</td>
<td>1:4</td>
<td>1.60x10(^{-5})</td>
<td>1.28x10(^{-5})</td>
</tr>
<tr>
<td>A-1</td>
<td>1:1</td>
<td>2.50x10(^{-5})</td>
<td>1.23x10(^{-5})</td>
</tr>
<tr>
<td>F-1</td>
<td>2:1</td>
<td>3.56x10(^{-5})</td>
<td>1.19x10(^{-5})</td>
</tr>
<tr>
<td>D-1</td>
<td>3:1</td>
<td>5.93x10(^{-5})</td>
<td>1.48x10(^{-5})</td>
</tr>
</tbody>
</table>

These mass transfer coefficients have been determined for points derived less than 20 hours after the beginning of the experiments, as the measurements tend to become erratic after approximately 20 hours as shown in Fig. 3.10. The mass transfer coefficients for the samples with a different initial TMOS in oil concentration are very similar, indicating that the mass transfer rate is not significantly affected by initial concentration. When the water
to oil phase ratios are varied (at a constant initial TMOS in oil concentration of 20 percent) the mass transfer rate seems to increase as the water to oil ratio increases as shown in Table 3.3. When the mass transfer rates for these experiments are multiplied by the fraction of the total volume that is made up by the oil phase the mass transfer rates become more consistent.

Fig. 3.11 shows the TMOS concentration in oil volume as a function of time for different initial water to oil volume ratios. The slopes of the curves increase significantly with increasing water to oil ratio unlike the experiments with varying initial TMOS concentration. This indicates that the mass transfer rate increases as the water-to-oil ratio increases, as reflected by the mass transfer coefficients shown in Table 3.2. This can be attributed to the limited solubility of TMOS in water: when more water is present, more TMOS can be dissolved.

Fig. 3.12 shows the effect of salinity on mass transfer out of the oil phase. The decrease in concentration seems to be slightly slower when the salinity of the water phase is higher, although the difference is not very profound. Fig. 3.13 shows the effect of pH in the water phase on the coupled mass-transfer and hydrolysis. Under basic conditions the mass transfer does not deviate significantly from mass transfer for a neutral water phase. When the water phase is acidic the transfer rate is significantly faster. The pH is lowered by adding HCl to the water phase. As Kamiya and Yoko [24] have shown, HCl acts as a solvent for TMOS in water. The increased solubility of TMOS in the water phase containing HCl leads to a faster mass transfer.
Sample A-1 illustrates the processes observed during the mass transfer reaction process. The water to oil ratio is initially 1:1, the oil phase initially contains 20% in volume of TMOS and the water phase consists of distilled water.

Fig. 3.10 shows the evolution of the TMOS concentration in the oil phase as derived from the X-ray attenuation. As mass transfer of TMOS occurs the total volume of oil phase decreases. The volume has been normalized to the initial volume of TMOS and is plotted on a semi-logarithmic scale. The volume-derived and the attenuation-derived data are in agreement within the experimental accuracy. The graphs in the figure show that at least during the first 15 hours of the mass transfer process the volume decrease is exponential. After 15 hours the behavior deviates from the exponential and begins to flatten off, probably because gelation begins to hamper the mass transfer process.

3.3.3. Coupled mass-transfer and gelation in water

Sample A-1 illustrates the processes observed during the mass transfer reaction process. The water to oil ratio is initially 1:1, the oil phase initially contains 20% in volume of TMOS and the water phase consists of distilled water.

Fig. 3.10 shows the evolution of the TMOS concentration in the oil phase as derived from the X-ray attenuation. As mass transfer of TMOS occurs the total volume of oil phase decreases. The volume has been normalized to the initial volume of TMOS and is plotted on a semi-logarithmic scale. The volume-derived and the attenuation-derived data are in agreement within the experimental accuracy. The graphs in the figure show that at least during the first 15 hours of the mass transfer process the volume decrease is exponential. After 15 hours the behavior deviates from the exponential and begins to flatten off, probably because gelation begins to hamper the mass transfer process.
The behavior of the water phase during mass transfer and reaction is depicted in Fig. 3.14. The gelation time as indicated by the deviation of the measured data from the expected data becomes shorter as the initial concentration increases. The only exception to this behavior is sample A-2 where deviation occurs relatively quickly. This is a result of the relatively small (in comparison with the measured range) change in attenuation of the water phase when the TMOS transfers.

The 30 percent offset observed in Fig. 3.9 between measured and predicted values does not hold for the samples with a variable initial water to oil ratio. With the exception of samples A-1 and H-2 (respectively an initial water to oil ratio of 1:1 and 1:4) all samples have a low total TMOS content which results in a low total transferred amount into the water phase. Fig. 3.9 shows that low amounts of transfer (as is the case with the sample containing ten
volume percent of TMOS in the oil phase initially) cause a greater inaccuracy in the measurement.

![Graph](image)

Figure 3.15: The CT response of the water phase calculated from the oil phase behavior plotted against the measured response. The salinity is increased in this sample which shortens the gel time. The squares (distilled water) represent sample A-1, the triangles (brine) sample C-1.

The effect of salinity on the oil phase behavior is not very significant indicating that the coupled mass-transfer hydrolysis is only mildly sensitive to the salt content. Fig. 3.15 shows the effect that dissolved salts have on the behavior of TMOS in the water phase compared to the behavior of TMOS in distilled water. However, the water phase is strongly affected, with gelation setting in much faster (ten hours for the synthetic sea water against approximately 20 hours for distilled water). The absolute amount of variation is also greater. When salts are present gelation seems to leach more TMOS out of the overall water phase causing a greater deviation from the predicted values than is the case in distilled water. A similar behavior was reported by Martin and Odinek [25], who observed that
adding salt to the water phase leads to a higher rate of gelation. The authors argued that the addition of small amounts of salt screens the negative charge of silicic acid groups and facilitates the condensation reaction. Fig. 3.16 shows the water-phase behavior under varying pH.

Figure 3.16: TMOS concentration (mol/L) in the oil phase as a function of time. In these three samples the pH of the water phase is varied. Mass transfer samples with a water phase that has a basic or neutral pH are very similar, at acidic pH the mass transfer is significantly faster. Sample D-2 has a low pH (squares), sample A-2 has a neutral pH (triangles), and sample E-2 has a high pH.

It is clear that gelation occurs much faster at higher pH than under neutral conditions. When the water phase is acidic gelation begins to occur around 5 hours, while under basic conditions gelation is seemingly even faster. This is supported by the fact that for the sample with a high pH white fibrous material appears at the interface immediately after placing the solution of TMOS in oil on the water phase, indicating an almost instantaneous polymerization. The amount of TMOS leached from the water phase to form a gel is also
much greater at high pH than at low or neutral pH as is evident from the large difference between measured and expected CT response. Faster condensation with increasing pH is also reported in literature [2, 26].

3.4. Conclusions

We have studied the coupled mass-transfer and reaction behavior of TMOS in an oil-water system using X-ray Computed Tomography analysis. Upon bringing solutions of TMOS in oil into contact with water the TMOS is transferred into the water phase. TMOS then undergoes hydrolysis resulting in silicic acid and methanol; the silicic acid condensates and ultimately forms a gel.

Mass transfer rates at different volume fractions of TMOS in oil do not differ significantly indicating that the initial volume fraction is not significant for the process. Varying the ratios has a much greater effect, where mass transfer tends to be quicker as the water to oil ratio is increased.

Salinity of the water phase does not have a significant effect on mass transfer. However, it is clear that at high pH, the mass transfer is not significantly different from mass transfer at neutral pH, while at low pH the mass transfer is significantly faster.

The CT response of the oil phase is linearly related to the TMOS concentration in the oil phase, which makes it possible to interpret the CT response of the oil phase in terms of TMOS concentration and change in concentration as a function of time. The CT response of the water phase cannot be derived directly from the oil phase, as would be expected in a closed system where mass and volume are conserved. In fact, the measured values of the water phase are higher than expected. This is because the attenuations of the reaction products of TMOS (especially silicic acid) are higher than that of unreacted TMOS.

The main factor that seems to affect the mass transfer of TMOS out of the oil phase is the solubility of TMOS in the water phase. When the solubility is increased by adding a solvent (e.g. an alcohol) or the total water phase volume is increased (thus increasing the total volume of TMOS that can be dissolved) the mass transfer rate increases.

As a first approximation the attenuation of the water phase can be derived using linear mixing of TMOS and water. This calculation however has an offset of approximately 30%
with respect to the measured attenuation of the water phase. This is because TMOS reacts in the water phase and forms new compounds (silicic acid and ultimately silica). Variations in attenuation between chemical compounds containing the same components (i.e. the silicon in TMOS, silicic acid and silica) are not uncommon and are the result of differences in interaction between the atoms in the different compounds.

After correcting for this shift the fit is initially good, until the predicted values begin to underestimate the measured values. At this point the images show that gelation sets in, indicating that the gel time can be derived from the water phase response. For all samples where the total volume of TMOS is less than ten percent of the total volume of the two phases together the measured difference in the water phase becomes erratic and cannot be fitted using the described procedures.

The gel time decreases with increasing concentration. Due to the small difference in attenuation in the samples where the ratios are varied the gel times for these samples are not determined. An increased salinity shortens the gel time and both high and low pH also shortens the gel time.

3.5. References

4. Porous media experiments

4.1. Experiments

Three sets of experiments were performed to investigate the effect of TMOS on porous media. All of these experiments followed the same procedure as described in section 4.4 of this thesis. First the pre-TMOS placement behavior was investigated, after which TMOS was injected and the placement behavior monitored, followed by the post-TMOS placement. All experiments are listed in Table 4.1. The first series of experiments (experiments 1 to 11) were done at elevated temperatures, ranging between 70 and 90 degrees Celsius. The next series of experiments (12 to 21) was performed using X-ray computed tomography to investigate the effect of TMOS placement on rock porosity, and in the remaining experiments (22 to 26) the effluent oil phase during the TMOS injection stage was sampled and analyzed to investigate further the behavior of TMOS during placement.

Table 4.1: Overview Sample properties and experimental parameters. The absolute permeability reflects the permeability to single phase flow. The relative permeabilities are the measured phase permeability at end point normalized to the absolute permeability.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Rock Type</th>
<th>Core length x diameter (mm)</th>
<th>Oil Type</th>
<th>Porosity (%)</th>
<th>Absolute Permeability (mD)</th>
<th>Oil relative permeability</th>
<th>Water relative permeability</th>
<th>Ko/Kw</th>
<th>TMOS injection rate (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>IsoparH</td>
<td>N/A</td>
<td>190 ± 22</td>
<td>0.84</td>
<td>0.22</td>
<td>3.90</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>IsoparH</td>
<td>N/A</td>
<td>114 ± 15</td>
<td>1.21</td>
<td>0.33</td>
<td>3.63</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>IsoparH</td>
<td>N/A</td>
<td>170 ± 20</td>
<td>1.02</td>
<td>0.13</td>
<td>7.91</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>183 ± 21</td>
<td>1.02</td>
<td>0.37</td>
<td>2.74</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>127 ± 10</td>
<td>1.05</td>
<td>0.34</td>
<td>3.09</td>
<td>0.2</td>
</tr>
<tr>
<td>6</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>152 ± 33</td>
<td>0.69</td>
<td>0.18</td>
<td>3.75</td>
<td>0.2</td>
</tr>
<tr>
<td>7</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>141 ± 11</td>
<td>0.63</td>
<td>0.32</td>
<td>1.98</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>260 ± 33</td>
<td>0.60</td>
<td>0.19</td>
<td>3.14</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>220 ± 24</td>
<td>0.56</td>
<td>0.15</td>
<td>3.65</td>
<td>6/2*</td>
</tr>
<tr>
<td>10</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>224 ± 17</td>
<td>0.64</td>
<td>0.25</td>
<td>2.51</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>Berea</td>
<td>90x40 ± 1</td>
<td>Tellus22</td>
<td>N/A</td>
<td>271 ± 47</td>
<td>0.63</td>
<td>0.23</td>
<td>2.80</td>
<td>6</td>
</tr>
<tr>
<td>12</td>
<td>Bentheim</td>
<td>150x40 ± 1</td>
<td>Diesel</td>
<td>0.18</td>
<td>1070 ± 55</td>
<td>0.84</td>
<td>0.33</td>
<td>2.53</td>
<td>6</td>
</tr>
<tr>
<td>13</td>
<td>Bentheim</td>
<td>78x40 ± 1</td>
<td>Diesel</td>
<td>0.22</td>
<td>1189 ± 57</td>
<td>0.68</td>
<td>0.30</td>
<td>2.28</td>
<td>5</td>
</tr>
<tr>
<td>14</td>
<td>Bentheim</td>
<td>78x40 ± 1</td>
<td>Diesel</td>
<td>0.22</td>
<td>764 ± 90</td>
<td>0.73</td>
<td>0.25</td>
<td>2.87</td>
<td>6</td>
</tr>
<tr>
<td>15</td>
<td>Velsen</td>
<td>89x40 ± 1</td>
<td>Diesel</td>
<td>0.18</td>
<td>2.80 ± 0.41</td>
<td>0.94</td>
<td>0.20</td>
<td>4.68</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>Bentheim</td>
<td>88x40 ± 1</td>
<td>Diesel</td>
<td>0.25</td>
<td>687 ± 311</td>
<td>0.83</td>
<td>0.27</td>
<td>3.08</td>
<td>1</td>
</tr>
<tr>
<td>17</td>
<td>Velsen</td>
<td>89x40 ± 1</td>
<td>Diesel</td>
<td>N/A</td>
<td>2.34 ± 0.05</td>
<td>0.68</td>
<td>0.13</td>
<td>5.27</td>
<td>N/A</td>
</tr>
<tr>
<td>18</td>
<td>Bentheim</td>
<td>92x40 ± 1</td>
<td>IsoparH</td>
<td>0.21</td>
<td>1066 ± 30</td>
<td>0.62</td>
<td>0.28</td>
<td>2.23</td>
<td>1</td>
</tr>
<tr>
<td>19</td>
<td>Velsen</td>
<td>89x40 ± 1</td>
<td>IsoparH</td>
<td>0.18</td>
<td>115 ± 3</td>
<td>0.85</td>
<td>0.06</td>
<td>13.42</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>Berea</td>
<td>89x40 ± 1</td>
<td>IsoparH</td>
<td>0.16</td>
<td>121 ± 10</td>
<td>0.99</td>
<td>0.08</td>
<td>12.00</td>
<td>8</td>
</tr>
<tr>
<td>21</td>
<td>Bentheim</td>
<td>89x40 ± 1</td>
<td>IsoparH</td>
<td>0.19</td>
<td>715 ± 264</td>
<td>1.20</td>
<td>0.31</td>
<td>3.90</td>
<td>5</td>
</tr>
<tr>
<td>22</td>
<td>Bentheim</td>
<td>289x37 ± 1</td>
<td>IsoparH</td>
<td>0.22</td>
<td>1349 ± 150</td>
<td>0.35</td>
<td>0.10</td>
<td>3.55</td>
<td>4</td>
</tr>
<tr>
<td>23</td>
<td>Bentheim</td>
<td>295x37 ± 1</td>
<td>IsoparH</td>
<td>0.22</td>
<td>1084 ± 66</td>
<td>0.59</td>
<td>0.12</td>
<td>5.11</td>
<td>1</td>
</tr>
<tr>
<td>24</td>
<td>Bentheim</td>
<td>291x37 ± 1</td>
<td>IsoparH</td>
<td>0.22</td>
<td>1053 ± 28</td>
<td>0.44</td>
<td>0.13</td>
<td>3.36</td>
<td>2</td>
</tr>
<tr>
<td>25</td>
<td>Bentheim</td>
<td>296x37 ± 1</td>
<td>IsoparH</td>
<td>0.22</td>
<td>1114 ± 151</td>
<td>0.47</td>
<td>0.14</td>
<td>3.45</td>
<td>2</td>
</tr>
<tr>
<td>26</td>
<td>Bentheim</td>
<td>127x37 ± 1</td>
<td>IsoparH</td>
<td>0.21</td>
<td>1173 ± 136</td>
<td>0.65</td>
<td>0.12</td>
<td>5.27</td>
<td>5</td>
</tr>
</tbody>
</table>

* The first TMOS injection of 2 PV at 6 mL/min did not cause a significant permeability reduction, so the core was re-used, and 4 PV of TMOS were injected at 2 mL/min.
4.1.1. **High temperature experiments**

Details on the experimental procedures and results are listed in Appendix A. All experiments were performed with Berea sandstone cores. In experiments 1 to 3 TMOS was dissolved in IsoparH oil, a low viscosity oil, whereas Tellus22 (a high viscosity oil) was used in experiments 4 to 11. In experiment 9 TMOS was two pore volumes of TMOS were initially injected at 6 mL/min. This did not result in a significant reduction in permeability so the core was re-used and 4 pore volumes of TMOS were injected at 2 mL/min.

4.1.2. **X-ray CT scan monitored experiments**

Experiments 12 to 22 were performed using the same experimental procedure while using X-ray computed tomography to monitor pre- and post gelation porosity and fluid saturations. In total 10 experiments were performed while monitoring with the CT scanner. The method of acquiring data during these experiments using X-ray CT is described in section 4.5. Pre-TMOS flow behavior in these experiments is detailed in this chapter, placement behavior is detailed in Chapter 5, and the effect of gelation on porous media is discussed in Chapter 6.

The experiments were conducted with three different types of sandstone: Bentheim, Berea and Velsen sandstone. In these experiments the injection rate of TMOS was also varied and part of the experiments was carried out with diesel oil, while others were done with IsoparH (Table 4.1).

During experiment 15 (carried out with a Velsen sandstone), the differential pressure during water injected reached such a high level that the core fractured. This fracture however did not noticeably affect the multiphase flow behavior, so the core was still subjected to TMOS injection.

4.1.3. **Experiments with effluent monitoring**

In this final series of experiments (22-26) the effluent was collected during TMOS injection using a fraction collector. Of this effluent the oil phase was separated immediately to terminate the mass transfer process. These samples were analyzed to determine the amount of TMOS that had transferred during its migration through the core per effluent sample
gathered. Details on these experiments can be found in Appendix B. All experiments were performed with Bentheim sandstone cores with IsoparH as oil phase.

4.2. Materials

4.2.1. Fluids

During the core flow experiments brine and oil were injected in the core. The brine used in the experiments was a synthetic brine, hereafter denoted as WELGEL brine. Its composition is shown in Table 4.2. Three types of oil were used: Tellus22, Isopar H and Diesel oil. The densities and viscosities of the fluids used at room temperature are listed in Table 4.3.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>24.05</td>
</tr>
<tr>
<td>MgCl2·6H2O</td>
<td>10.77</td>
</tr>
<tr>
<td>CaCl2·2H2O</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Table 4.3: Fluid viscosities at room temperature.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity (cP)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WELGEL brine</td>
<td>1.01</td>
<td>1.017</td>
</tr>
<tr>
<td>Diesel</td>
<td>2.86</td>
<td>0.826</td>
</tr>
<tr>
<td>IsoparH</td>
<td>1.15</td>
<td>0.729</td>
</tr>
<tr>
<td>Tellus22</td>
<td>34.5</td>
<td>0.865</td>
</tr>
<tr>
<td>TMOS</td>
<td>1.69</td>
<td>1.023</td>
</tr>
</tbody>
</table>

4.2.2. Rock samples

Three types of cores were used in the experiments: Bentheim sandstone, Velsen sandstone and layered Berea. The three rock types have different properties: Bentheim sandstone is of Late Cretaceous age. It has excellent sorting and well-rounded grains consisting almost entirely of quartz. The main cement is quartz from pressure solution. The porosity is typically around 20 percent and the absolute permeability ranges between 700 and 1500 mD. Table 4.1 shows which rock types were used in the experiments and their petrophysical properties.
The Velsen sandstone is a continental sandstone of Triassic age. It is a lithic sandstone containing significant amounts of K-Feldspar and clays. The porosity of the cores is respectively 16% and 20%. The permeabilities are however extremely low compared to the Bentheim samples, ranging between 2 and 3 mD; as with the Bentheim sandstone samples, no layering is discernable in the samples. In experiment 15 the core was fractured during the pre-gelation stage of the experiment as a result of very high. This did not result in significant alteration of flow properties. It did however have an impact on the effects of gel placement, as will be illustrated in chapter 6.

The Berea sandstone samples are regularly laminated on a millimeter scale, the laminae being visible as an alternation of darker and lighter layers. The porosity is 16-18% and the permeability of the samples varies between 100 and 300 mD.

For the high temperature experiments (experiments 1 to 11) all experiments were performed with Berea sandstone. For the experiments in which the effluent was collected (experiments 22-26) all samples were Bentheim sandstone. No layering was visible either to the naked eye or with the CT scanner in any of the Bentheim or Velsen sandstone samples.

### 4.3. Experimental set-up

The setup described here was especially designed for studying flow processes in porous media with the aid of X-ray Computed Tomography (experiments 12 to 22). All experiments discussed in the next chapters were done using the set-up shown schematically in Fig. 4.1, or setups very similar to it.

Fluid was circulated using two double-effect piston displacement pumps (Pharmacia P-500), one for brine and the other for oil or the oil/TMOS mixture. The pumps allow very stable flow rates ranging from 1 to 499 ml/h and can produce a maximum line pressure of 40 Bar.

The cores had a diameter of 40 ± 1 mm and a length of 90 ± 1 mm, except in experiment 12 where the length was 150 ± 1 mm. The cores were mounted in a holder made of polyether etherketone (PEEK). This material combines good mechanical strength and thermal resistance with a low X-ray attenuation. Before they were fitted inside the core-holder, the
cores were cast in a thin layer of low X-ray attenuation Araldite (CW 2215) superglue with CIBA HY 5160 Araldite (CW 2215) as hardener to eliminate possible boundary flow effects. After the superglue set, the ends were sawed off to allow fluid flow at both sides of the core. The high viscosity of the superglue mixture ensures limited penetration of the core (less than 1.0 mm).

Five pressure transducers were integrated into the setup: one mounted at the core inlet, one at the outlet and three mounted along the core length. The three pressure transducers along the core length were not used since it was found that gelation tended to make these measurements unreliable. In addition, two differential pressure transducers (one with a range of 0-3 Bar, the other with a range of 0-40 Bar) recorded the differential pressure over the core. The injection rate was registered, as was the effluent mass.

Fig. 4.1: Schematic of the experimental setup. The pumps and key valves are controlled remotely via the data acquisition system.

During the experiments, the entire setup was placed on the couch of the CT scanner (Fig. 4.2), with the instrumentation behind the core-holder. The core was mounted at the leading
edge of the couch (visible on the right in Fig. 4.2) so that only the core in its coreholder was scanned during the experiment. Depending on the desired core orientation (vertical or horizontal), the core was mounted using a polymethyl methacrylate (PMMA) stand or a stainless steel bracket that could be mounted on the end of the couch. The experiments were conducted in a room at constant temperature of $20 \pm 1 ^\circ C$.

To avoid gelation in the tubing, valves, back-pressure regulator or other parts of the setup a bypass was also built into the setup that allowed flow through most of the setup, but circumvented the coreholder itself.

4.4. Experimental procedure

The experimental procedure consists of four steps: 1) initial saturation, during which the core was filled with brine until the entire pore space was filled, 2) multiphase flow, during which oil and brine were alternately injected into the core, 3) TMOS placement into the core and finally 4) post-TMOS placement flow characterization. Steps 3) and 4) have been
repeated in a number of experiments to investigate the multiphase flow behavior after TMOS placement.

Before the initial saturation with brine, the core was flushed with CO₂ gas until it was fully saturated with CO₂. Then the CO₂ was displaced with degassed brine at a back pressure of at least 10 Bar until the core was 100% water-saturated. Any gas that was not displaced by the brine would be dissolved in the brine as a result of the elevated back pressure and the fact that the brine was degassed prior to injection. The saturation was considered complete once the water phase behind the back pressure valve (where the pressure declines to atmospheric) no longer contained dissolved gas and the differential pressure over the core was stabilized. CT scan imaging also revealed whether the entire core had been saturated, or whether some parts still remained gas-filled. Once the core was fully saturated, brine was injected at different flow rates to determine the permeability of the core using Darcy’s law for single phase flow.

All core samples used in the experiments were assumed to be water-wet. Therefore drainage refers to oil injection and brine injection will be referred to as imbibition. Two-phase flow is investigated by alternating oil and brine injection to displace each other. The first time oil is injected in the fully water saturated core is referred to as primary drainage, all later drainage and imbibition is secondary. Drainage and imbibition were performed at constant flow rate, until the differential pressure becomes constant. At this point the end point relative permeability was determined by varying the flow rate and registering the effect this had on the differential pressure, using the same principle as is used to determine the single phase permeability. The number of imbibition and drainage cycles performed varies from experiment to experiment.

Once the two-phase flow behavior was characterized TMOS was placed in the core by injecting an oil/TMOS mixture at a constant flow rate. The rate and total volume injected was varied in the different experiments (Table 4.1). After placement the setup was flushed over the bypass to avoid gelation occurring in the setup itself. Depending on the experimental run the core was shut- in (i.e. closed at both ends and not subjected to flow) for a period of time, or flow re-initiated right after placement. Either water or oil was then injected, depending on the situation.
4.5.  X-ray CT monitoring of flow

The X-ray CT scanner used in this study is a SOMATOM Volume Zoom quad-slice, manufactured by Siemens. In this third-generation apparatus, the X-ray source-detector system rotates continuously during object examinations and acquires data using the traversing slice method [5]. The imaging system uses the Somaris software to reconstruct the images of the subject, from multidirectional transmission data. Standalone image processing software reads the absorption data of CT slices stored in a binary form into 512 by 512 image matrices with a 16 bit data depth. The initial porosity of the cores is determined by the difference between the CT scan attenuation values (in Hounsfield units) for dry and a fully water-saturated core with respect to the absolute difference in attenuation between brine and air.

Since gelation is likely to immobilize all brine present in the core, the system is expected to be reduced to a single-phase oil saturated medium after gelation has taken place. This is an opportunity to investigate the porosity. It can be done by doping the oil phase, in this case by adding iodated benzene. The difference between the sample saturated with doped oil and non-doped oil divided by the absolute difference between oil and doped oil yields the post-gelation porosity. After the post-gelation flow of oil is stabilized, oil with 2% iodated benzene (contrast enhancement agent) is injected to determine the new porosity. This porosity consists only of the segments of the core through which fluid flow is still possible. Where pore spaces have become too constricted to allow flow, the effective porosity calculated with this method is reduced to zero. Porosity and saturation calculations are performed using standard techniques [6].
4.6. Single-phase flow

Prior to TMOS placement in each core the two phase flow behavior was characterized using standard methods [1-3]. This was necessary to provide the flow properties that serve as a reference for describing the effects of TMOS placement in the porous media (Chapter 6). Initially a dry core was flushed with CO\textsubscript{2} and saturated with brine by simple displacement of the gas. Dissolution of CO\textsubscript{2} ensured 100% brine saturation, as can be seen from the saturation maps shown in Fig. 4.3.

The CT scan images show three distinct zones: the dry zone (blue) containing only CO\textsubscript{2} gas, a fully water-saturated zone (red), and a mixing zone (yellow). The mixing zone is irregular, possibly due to fingering which is interpreted to be the result of the difference in mobility between gas and water.

Figure 4.3: Saturation maps during initial saturation. Water is injected from left to right, displacing the CO\textsubscript{2} present in the core.
The initial saturation shown in Fig. 4.3 is displayed in the form of one-dimensional profiles in Fig. 4.4 along the core axis showing how the water saturation evolves during the experiment. Since brine was injected from left to right, the front is seen moving in the same direction, with low (initially zero) water saturation in front, and high saturation behind. Displacement was not piston-like. Judging only from the one-dimensional data, diffusion could be argued as at least part of the reason why the fluid front was disperse, but from the images in Fig. 4.3 it appears that the mixing zone (yellow zone) was the main reason the front was irregular along the core axis. The initial saturation lines also exceed a water saturation of 100% ($S_w=1$), which seems unlikely. Higher CT values of the water phase when dissolved CO$_2$ is present could be responsible for this, particularly because the effect was not noticed in later profile lines, which show a uniform water saturation of 100% along the entire core axis. However, the consistency with which the anomalously high water saturations are present (four time steps) and the apparent repeatability (the shape of the curves overlaps very well) suggest that some systematic effect is responsible for this. Since

Figure 4.4: Water saturation profiles along the core axis. These profiles represent the same dataset as Fig. 4.3.
the water saturation calculations are based on X-ray attenuation and this attenuation is mainly a function of density it seems likely that either a change in gas or water phase density is responsible. Since the effect is transient and water saturation returns to unity once the gas has been displaced, it is likely that the CO₂ gas is responsible in that it increases the density of water as it is dissolved into the water phase.

Fig. 4.5 shows the evolution of the differential pressure divided by the injection rate during the same initial core saturation. In the first pore volume water with a higher viscosity displaced the gas with a much lower viscosity and the differential pressure increased accordingly.

![Figure 4.5: Differential pressure corrected for injection rate during initial stages of initial saturation in experiment 15. The data are plotted against injected pore volumes.](image)

The increase in differential pressure during initial saturation was not linear. This indicates that displacement was not fully piston-like and residual gas was left behind, establishing a two phase flow regime. At the same time, CO₂ was dissolved into the injected degassed brine, and therefore the residual gas saturation was not a constant. In fact, the remaining CO₂ that accounted for the residual gas saturation was reduced to zero prior to the next
phases of the experiment. Fig. 4.5 shows that the differential pressure stabilized in less than two pore volumes of degassed brine injection.

4.7. Oil-water relative permeabilities

After the initial saturation with brine, the oil- and water flow behavior was investigated. The two-phase flow experiments started with oil injection, referred to as primary drainage and all later drainage and imbibition cycles are referred to as secondary. Drainage reduced the cores to residual water saturation and the governing permeability was the oil permeability at residual water saturation. Conversely, imbibition increased water saturation to its maximum \((1-S_{or})\) and the permeability governing flow was the water permeability at \(1-S_{or}\).

4.7.1. Drainage

Drainage is the process by which a non-wetting fluid is displacing a wetting fluid in a porous medium. Since all samples used in these experiments were water-wet, drainage was always accomplished by injecting oil. Fig. 4.6 shows the differential pressure development during primary drainage in experiment 17. The differential pressure peaked in less than one pore volume. This peak represents the moment when oil first reached the end of the core. At this point in time a continuous network of oil is present from the beginning to the end of the core, facilitating the flow of oil. This occurred in less than one pore volume because part of the pore space was occupied by water. Since the cores are all water-wet, the water phase always had a continuous pathway and even after five pore volumes of oil had been injected the differential pressure was not fully stable. Prior to the TMOS injection in each experiment the core was drained as much as possible by injecting oil at a higher flow rate than the rate used to place the oil/TMOS mixture (see Chapter 5).
4.7.2. Imbibition

Imbibition is the opposite of drainage, the process by which a wetting fluid (in this case water) displaces a non-wetting fluid (in this case oil) from a porous sample [1]. When imbibition is complete, the oil saturation is reduced to residual oil saturation. Fig. 4.7 shows a typical differential pressure development during imbibition of water into a water-wet, oil-saturated core. Again, the main change in differential pressure occurred in less than one pore volume. In the case of experiment 17 the Velsen sandstone used has a high residual water and residual oil saturation, making the total volume available to the mobile phases (1-$S_{or}$-$S_{wc}$) small. As a result, water breakthrough occurred after less than half a pore volume had been injected; after this the differential pressure stabilized.

Figure 4.6: Differential pressure normalized to injection rate during primary drainage in experiment 17. The data are plotted against injected pore volumes.
4.7.3. Ratio between water and oil relative permeability

The ratio between the end point oil and water permeabilities is listed in Table 4.1. By normalizing the permeabilities to the single phase permeability we obtain the relative permeabilities at the end points. The oil relative permeabilities do not show a very distinct trend and range between 60 and 90 percent. Values greater than 90 percent are suspect. For example, in experiment 21 a relative oil permeability greater than unity is calculated. This could be due to an error in the determination of the single phase permeability, but recent publications suggest that relative permeability greater than unity can occur if slip boundary conditions are applied [7].

Without exception the relative oil permeabilities are greater than the relative water permeabilities. The water relative permeability shows a trend among the different rock types. Bentheim sandstone samples generally exhibit the greatest water relative permeability.
These differences are also visible in the ratios of water to oil permeability (last column in Table 4.1). The $k_w/k_o$ ratios are between 2 and 3 for Bentheim sandstone, around 5 for Velsen and mainly greater than 5 for Berea sandstone.

4.8. Discussion and conclusions

Figs. 4.6 and 4.7 show that imbibition and drainage exhibit different behaviors: during imbibition the differential pressure increases more or less linearly to a plateau when water breakthrough at the far end of the core occurs, after which the differential pressure will remain constant. On the other hand, during drainage, the differential pressure initially increases sharply, until oil breakthrough. From this point the differential pressure decreases exponentially. This is a result of the rock properties of the sample the fluids migrate through.

Three types of sandstone are used in the experiments: Bentheim, Velsen and laminated Berea sandstone. These three sandstones do not show very different residual saturations. Bentheim tends to have the lowest residual water saturation, followed closely by Velsen, while Berea has the highest residual water saturation. The residual oil saturation does not vary significantly and is around 30% for all samples.

The observed fluid flow behavior in the different rock types coincides well with the rock types used in these experiments. The Bentheim and Velsen sandstones have very similar porosities, but Velsen has a fraction of the permeability of the Bentheim sandstone. Also the ratio of water to oil end point permeability is greater in the Velsen sandstone than in the Bentheim, indicating that water experiences greater resistance to flow in the Velsen samples than in the Bentheim samples. From a lithological viewpoint the principal difference between these two rock types is the grain sorting. Bentheim is a well sorted sandstone and as a result the pore size distribution is also quite homogeneous. The Velsen sandstone is poorly sorted, and contains significant amounts of lithic components. As a result the pore size distribution is much greater, causing greater obstruction to flow even though the porosity is very similar to that of Bentheim.
Permeability reflects the ease for each phase to flow through a rock. Being the cleanest and most homogeneous, Bentheim offers the least resistance to flow. Because of the very low clay content and the smoothness of the grains (well rounded), fluid flow is easier than in the Velsen sandstone. Due to poor sorting of the Velsen sandstone, significant amounts of clay and angular grains, resistance to flow is most significant, resulting in permeabilities several orders of magnitude smaller than for Bentheim sandstone, even though the porosity is very similar.

Laminated Berea has a lower porosity but an intermediate permeability compared to the other two rock types. What really sets the Berea samples apart is the ratio of water to oil permeability, which is more than twice the ratio of the Velsen. The water relative permeability is much lower in the Berea samples than in the Bentheim or the Velsen samples. This is likely to be a result of the lamination and clay content. Particularly the clay layers could retain water easily. This might also explain why the residual water saturation of these samples is relatively high.

4.9. References

5. Dynamics of TMOS in porous media

This chapter describes the placement of TMOS in porous media. The chemical reactions and dynamics are described in chapters 2 and 3, in which static bulk situations are presented. The application of a reactive mass-transfer system such as TMOS in a porous medium introduces new characteristics to the flow behavior due to the complex interaction between the fluids and the porous medium, and the coupling with flow. For instance, the kinetics is likely to change drastically as a result of the much greater surface area between oil and water in the porous medium; this could accelerate the mass transfer-process significantly. The behavior of alkoxysilanes, particularly TMOS, in water has been extensively investigated (chapter 2). The TMOS behavior in bulk two-phase systems was described in chapter 3. The behavior of pure multiphase flow in sandstones was discussed in chapter 4 and forms a baseline for the study of the flow of a TMOS solution in oil.

5.1. Introduction

The studies of the emplacement of TMOS in porous media, i.e. the injection of the TMOS into a porous media containing oil and water at different saturations, are scarce. The previous studies of TMOS in porous media [1] focused primarily on the effect of in-situ TMOS gelation on multiphase flow, and paid little attention to the emplacement itself and the dynamics involved in applying TMOS in multiphase flow conditions. The few studies [2-4] reported in the literature hint at the complex aspects of multiphase flow during TMOS injection, but fail to clarify the mechanisms of the coupling of mass transfer, reaction, and flow. The present study of TMOS emplacement is prompted by the need to discern the processes that occur during emplacement and their effect on multiphase flow and analyze the main parameters that affect placement. In a porous medium the surface area between the oil phase and the water phase is much larger than in the test tube experiments discussed in chapter 3. An illustration of the effect surface area can have is given by Fig. 5.1, which shows two different test tube experiments with the two phase oil/water system where the oil phase contains 20 vol% TMOS. By shaking one of the samples continuously a fine oil-in-
water emulsion is formed, resulting in a very large surface area between the oil and the water phases. This considerably increases the mass transfer rate as is clear from the much faster decline in TMOS in oil phase concentration for the sample that is shaken. It is therefore expected that the mass transfer rate increases due to an increase in the surface area. The same is expected to take place in a porous medium, where the surface area is also very large.

The core flow experiments were performed at different injection rates with various types of rock being used, and TMOS was dissolved in different oil types.

Figure 5.1: Two two-phase experiments run in test tubes. One sample was shaken continuously to form a fine emulsion during the mass transfer reaction process. This graph shows the normalized concentration of TMOS in oil as a function of time.
5.2. Experimental results

5.2.1. TMOS placement at high temperatures

Eleven experiments (1-11 in Table 4.1) were performed at high temperatures, using the same basic procedure outlined in chapter 4. All cores in these experiments were laminated Berea, cut parallel to the lamination. A more detailed description of the experimental procedure is given in Appendix A. The aim of these experiments was to monitor the effect of placing TMOS in a porous medium in cores that are brought to irreducible (or connate) water saturation at temperatures of 70 to 90ºC. During placement of TMOS the differential pressure over the core was monitored: the most important features in these experiments were discerned from the behavior of the differential pressure during TMOS placement. Since the cores are reduced to residual water saturation prior to the initiation of TMOS placement it is assumed that initially only the oil phase will be able to flow. This is true until mass transfer occurs: from this point the water saturation will increase to values above residual water and two phase flow will once again occur until mass transfer terminates.

Fig. 5.2 shows the differential pressure as a function of pore volumes of oil/TMOS mixture injected into the core at very low injection rates (0.2 mL/minute) during experiments 6 and 7 (Table 4.1). Two pore volumes of the oil/TMOS mixture were injected. The two experiments were compared to assess repeatability. The superposition is not perfect, possibly because the tubing volume before the core is not precisely quantified. The general shape and order of magnitude of the pressure rise are very similar though. Fig. 5.2 shows that after an initial flow regime with no change compared to pure oil flow, the differential pressure rises significantly with a factor of five to six compared to the initial differential pressure. This indicates that oil flow is significantly hampered during TMOS placement. The effect of placing TMOS at very low flow rate was a significant decrease in permeability, approximately equivalent for both the oil and water phase (see also Chapter 6). In other words, no disproportionate permeability reduction (in favor of oil flow) is observed.
Figure 5.2: Normalized pressure drop during injection of the oil/TMOS mixture at low flow rates. The curves are normalized to the initial pressure drop values. The pressure difference is initially stable and then increases.

After the very low injection rate experiments the decision was taken to increase the injection rate by a factor of 30 to 6 mL/minute, and inject another two pore volumes, because the results of placing 2 pore volumes of TMOS on the flow properties were not satisfactory (c.f. chapter 6). The results are shown in Fig. 5.3 (experiments 7 and 8). The experiments in which only 2 pore volumes of the TMOS/oil mixture were injected show reproducible results: during the initial pore volume of displacement the differential pressure decreased, after which the differential pressure remained largely constant. Because of very limited effects on the permeability the total volume of oil/TMOS mixture to be injected was increased to four pore volumes. In the first experiment with four pore volumes (experiment 9) the injection rate was also lowered to 2 mL/minute. In experiments 10 and 11 the injection rate was 6 mL/min. When the injected volume was increased, it seemed that the flattening behavior indicated by the previous experiments was not the equilibrium state for fluid flow during placement. After the first pore volume a period of possible constant differential pressure set in, although not unambiguously present in these experiments,
followed by a steady increase in differential pressure that had not ended by the time four pore volumes of oil/TMOS mixture had been injected. Furthermore, the increase in differential pressure seemed greater at lower flow rates as indicated by experiment 9.

Figure 5.3: Normalized pressure drop during injection of the oil/TMOS mixture at high flow rates. The curves are normalized to the initial pressure drop values. The pressure drop decreases first to a value representative of the lower-viscosity oil/TMOS mixture, and then rises again as mass transfer causes the oil phase to become more viscous and the water saturation to increase.

5.2.2. TMOS placement at room temperature

The experiments described above indicate that the competition between flow and mass transfer is important to the flow dynamics of TMOS in a porous medium. To further investigate the dynamics occurring during TMOS placement a series of experiments was performed in which the injection rate was varied while injecting a large volume of the oil/TMOS mixture (experiments 13-15 in Table 4.1). Two of these experiments (13 and 14) were performed with a Bentheim sandstone, experiment 15 was performed with Velsen sandstone. Both samples have a homogeneous distribution of porosity. As a result these experiments were not significantly affected by heterogeneity. Fig. 5.4 shows the differential
pressure obtained during 3 of the 10 experimental runs in this series, each at a different injection rate. The general trend of the three curves is similar. First the differential pressure decreases as a function of the number of pore volumes of oil/TMOS mixture injected until it reaches a minimum value; then the differential pressure increases until it reaches a maximum and finally it decreases again. In the first pore volume the normalized differential pressure decreases to 0.6 to 0.7, and the different curves coincide almost perfectly. After 1 pore volume the curves tend to diverge and the subsequent stages depend strongly on the injection rate of the oil/TMOS mixture. At 1 mL/min (experiment 15) the normalized differential pressure increases sharply from 0.7 to a maximum of 1.43 and then decreases back to 1 (at 8 injected pore volumes). For 5 mL/min (experiment 13) the differential pressure increases more gradually from about 0.6 to 1.1, with values lower then 0.7 between 1 and 2.5 injected pore volumes. This trend is accentuated for 6 mL/min (experiment 14) where the differential pressure trails off at the lowest values between 1 and 3.5 pore volumes before it increases to 0.95 and then decreases again. It is remarkable that no steady state seems to be reached in the experiments, except possibly in experiment 15 where the differential pressure seems to level off to a plateau at the end.

Figure 5.4: Normalized differential pressure during injection of TMOS at different flow rates. The rates are respectively 5, 6 and 1 mL/minute for experiments 13, 14 and 15.
The injection rate is different in each experiment (1, 5 and 6 mL/minute). The effect this has on the differential pressure behavior is evident: the shape is very similar for each curve, but the timing in terms of injected pore volumes for the trend changes in differential pressure varies. With increasing injection rate the behavior tends to be stretched over pore volumes. The peak in differential pressure also decreases with increasing flow rate and occurs after a greater number of injected pore volumes. An important note needs to be made on the oil/TMOS injection experiments: in several of these experiments the effluent was visually inspected frequently and in each of those the effluent was initially only single oil phase, but after the maximum differential pressure oil and water were produced.

5.2.3. TMOS placement and analysis of effluents

To further improve our understanding of the oil/TMOS placement process in porous media a series of experiments was performed in which the effluent is sampled in batches and the concentration of TMOS in the oil phase determined (experiments 22-26 in Table 4.1). These experiments are discussed in detail in appendix B. In Fig. 5.5 the results of experiment 26 are shown. The top graph shows the normalized differential pressure as a function of injected pore volumes, while the graph below shows the concentration of TMOS in the effluent as a function of injected pore volumes of the oil/TMOS mixture. The differential pressure behavior is very similar to that observed in earlier experiments. To highlight the different aspects that play a role in the placement of TMOS, Fig. 5.5 is split into segments and the behavior of each segment is discussed the following section.
5.3. **Stages of reactive transport**

The behavior of TMOS dissolved in oil in a porous medium is complex. TMOS transfers from the oil phase into the water phase, reacts and ultimately forms a gel. Although the water saturation in the cores is initially reduced to residual water saturation (i.e. water will no longer flow within the cores) the water saturation is not constant during TMOS injection. As mass transfer occurs the water phase saturation will increase and two phase flow will occur until mass transfer terminates and the excess water phase (volume of water phase above residual water saturation) is produced from the core. TMOS placement in a porous medium can be separated into five distinct phases, in accordance with the behavior illustrated in Fig. 5.5.
I. *Oil displacement by TMOS solution in oil*: The oil/TMOS mixture first displaces the pure oil phase that is present in the core. Since two characteristic times are competing here, i.e. the mass transfer reaction characteristic time and the flow characteristic time, this stage will be strongly influenced by the rate of oil/TMOS displacement. After 1 pore volume the effluent oil phase will first contain TMOS. How much mass transfer actually takes place during this initial displacement is heavily dependent upon the injection rate: higher rates will decrease residence time and decrease the amount of mass transfer that can take place during initial placement. Both in Fig. 5.3 and in Fig. 5.4 this phase occurs from 0 to at the most 1 pore volume. Experiments 7 to 11 and experiments 13-15 all show the decline in differential pressure as the oil phase is displaced with the lower viscosity oil/TMOS mixture. At low rates (experiment 15) the decline in differential pressure halts well before 1 pore volume.

II. *Steady state TMOS solution flow*: If the injection rate is high enough mass transfer will initially not impact flow significantly and steady-state single phase flow of the oil phase with the TMOS solution will occur. The differential pressure will maintain a plateau during this phase. This plateau is visible in experiments 7, 8 and 9 (Fig. 5.3) between 1 and 2 pore volumes, and in experiment 14 (Fig. 5.4), between 1 and 3-3.5.

III. *Mass transfer phase*: When mass transfer and reaction occurs methanol will be generated in the water phase, increasing the solubility of TMOS in the water phase. The concentration of TMOS in the effluent oil phase decreases during this stage, indicating that the mass transfer rate is increasing and TMOS is transferring to the water phase. The concentration of TMOS in the effluent oil phase declines rapidly as more and more TMOS moves to the water phase. In experiment 9 (Fig. 5.3) this phase is present between 1 and 4 pore volumes, during which time the differential pressure increases steadily. In experiments 13-15 each graph shows the presence of this phase.

IV. *Mass transfer decline phase*: After reaching a maximum, mass transfer will slowly begin to decrease until all TMOS that is injected is also produced at the outlet. This
phase is initially signaled by a minimum in TMOS in oil concentration in the effluent. After this point the concentration gradually rises until the concentration in the effluent is the same as is injected into the core. At this point the mass transfer has terminated. In experiments 7-10 (Fig. 5.3) insufficient pore volumes of the oil/TMOS mixture were injected to achieve stage IV, but each of the experiments shown in Fig. 5.4 contains the decline.

V. Termination of mass transfer: Once the water phase is saturated with TMOS the mass transfer flow will terminate. This stage is difficult to discern in any of the experiments, except possibly in experiment 15 (Fig. 5.4), where a final stabilization is at least approached.

The time at which each stage starts and its duration are strongly dependent on the injection rate of the TMOS solution in oil and on the physical parameters that influence the mass-transfer and reaction rate. This is most clearly illustrated by Fig. 5.4, which shows that with different injection rates the expression of the behavior described above will vary. At the lowest injection rate (1mL/min, experiment 15) the different phases are compressed and tend to begin and end after fewer pore volumes than at higher rates (5 mL/min in experiment 13 and 6 mL/min in experiment 14). Varying the rate at which the oil/TMOS mixture is injected directly controls the residence time. Theoretically no mass transfer will occur if the oil/TMOS mixture is injected fast enough, and only phase I and II would be expected. Experiments 7 and 8 (Fig. 5.3) both contain only phase I and II, mainly because insufficient oil/TMOS mixture was injected. Experiment 14 (Fig. 5.4) also shows both phase I (0 to 1 pore volumes) and phase II (1 to 3.5 pore volumes). In experiment 15 phase II is altogether absent and phase III directly follows phase I. In experiment 13 phase II is very short. Once mass transfer is possible within the residence time of the mixture phases III through V will also be visible, as is the case in experiments 13-15. Low flow rates (experiment 15) will tend to compact the different phases, making it difficult or even impossible to distinguish the earlier stages that are highly residence-time dependent. If the flow rates are low enough condensation will occur during the mass transfer stage and flow can become unstable or be blocked altogether as a result of gel formation.
Because the pore volume of Berea is smaller than the other samples, the pore volume displacement is also faster and phase II begins within the first five minutes. For the Bentheim and Velsen samples, phase II is apparent anywhere between 5 and 10 minutes after injection of the oil/TMOS mixture is initiated. The transition of phase II to III occurs anywhere between 10 minutes to an hour after injection begins. The beginning of phase V is difficult to ascertain as the volumes of TMOS injected typically do not exceed 10 pore volumes, and phase V seems to occur after injection of 10 to 15 pore volumes (Appendix B, Figs. 5 and 6).

5.4. The effect of the physical parameters

5.4.1. Effect of injection rate

When the total injected volume of TMOS is increased and the injection rate varied, a more complete pattern emerges (Fig. 5.4): the initial decline in differential pressure – which is a result of the displacement of a higher viscosity pure oil phase by a lower viscosity oil/TMOS mixture – is visible, followed by an increase that is finite: it exhibits a termination in the form of a plateau, at least for experiment 15. When the injection rate is increased, more oil/TMOS mixture needs to be injected before the peak differential pressure is reached. At the same time, the magnitude of the peak differential pressure also decreases with increasing injection rate.

It seems therefore from the experimental results that increasing the injection rate tends to stretch the stages defined in Fig. 5.5, while decreasing the injection rate will compact the different stages.

This is expected because mass transfer is residence-time dependent (the longer the oil/TMOS mixture is in contact with the water phase in the core, the more mass transfer can occur per unit of time), and the residence time in turn is a function of the injection rate (i.e., the injection rate determines how long the oil/TMOS mixture is in contact with the water phase in the core): at high injection rates the residence time of the oil/TMOS mixture in the core will be short, and as a result less TMOS will be able to transfer from the oil phase to
the water phase. As a result, more of the oil/TMOS mixture will need to be injected for the entire placement behavior to be able to occur.

The opposite is true for low injection rates: at low rates the oil/TMOS mixture will be in contact with the water phase in the core for longer, and mass transfer occurs more easily. As a result the placement behavior will be completed within fewer injected pore volumes.

This can also be observed in the experiments carried out at elevated temperatures in Fig. 5.3 (see also Appendix A), in which a distinction can be made between low injection rates (i.e. 0.2 mL/minute) and high injection rates (6 mL/minute). The low injection rates do not show the five-stage dynamics as illustrated above. Instead, pressure increases over most of the recorded experiment. The high-injection rate experiments do show the stage behavior, but because injection is limited to 2 to 4 pore volumes the curves in Fig. 5.3 exhibit only the initial three stages.

\[ \Delta P = \Delta P_0 \]

\[ \text{Injected Pore Volumes} \]

Figure 5.6: Normalized differential pressure during TMOS placement at 1 mL/min for experiments 15, 16 and 18.

TMOS injection in experiments 15, 16 and 18 was performed at 1 mL/min (Fig. 5.6). Experiments 16 and 18 suffer significant injectivity loss, with flow becoming impossible after (respectively) 4 and 3 pore volumes of the oil/TMOS mixture is injected. Experiment
15 does not show signs of full plugging. However, the final differential pressure seems to be higher than in experiments 13 and 14 (Fig. 5.4), suggesting that the core is at least partly blocked by gel forming during placement at the lower injection rate.

5.4.2. Influence of lithology

Three different rock types were used in the different experiments, to investigate if and how lithology influences placement (and gelation, which will be discussed in the next chapter). Table 4.1 gave an overview of the rock types used in the experiments and their petrophysical properties. Although only one experiment with the Velsen sandstone is available, the behavior during TMOS injection is very similar to that exhibited in the Bentheim sandstone (see Figs. 5.4 and 5.6), and the main differences can be ascribed to variation of injection rates (see also section 5.4.1.). Injecting TMOS in the Berea sandstone leads to a different behavior as is clear from Fig. 5.7: stage I is less pronounced, stage II seems altogether absent and stage III lasts for the entire duration of the experiments. Even though injection rates are higher in these two samples than in previous experiments (see Fig. 5.4), mass transfer is apparent as a rise in differential pressure almost from the beginning. Only a minor initial decline in pressure is measured in the first pore volume of displacement, after which the differential pressure steadily increases. Even after injecting 13 to 14 pore volumes mass transfer seems to be continuing steadily.

Although they vary significantly in terms of permeability, TMOS placement in the Bentheim and Velsen sandstone is very similar. This is illustrated in Fig. 5.6: Experiment 15 was performed with the Velsen sandstone, while the Bentheim sandstone was used in the other two experiments. The result for the Berea sandstone, which is laminated on a millimeter scale, is more difficult to compare with the other cores.

During two-phase flow the water saturation is not distributed evenly in the laminated Berea sandstone samples. The lower porosity layers have a significantly higher residual water saturation that the higher porosity layers. This leads to higher residual water saturation in the core as a whole of typically between 0.4 and 0.5, as opposed to between 0.2 and 0.3 for the Bentheim and the Velsen sandstone samples. The experiments detailed in Chapter 3 show that the water to oil phase ratio has a significant effect on the mass transfer rate:
higher water-to-oil ratios tend to speed up mass transfer. Furthermore, a higher water content in a core also means the absolute amount of TMOS that can transfer from the oil phase is larger. Fig. 5.7 shows both of the aforementioned effects. Mass transfer initiates earlier as is evident from the absence of phase II even at a flow rate of 8 mL/min, and the amount of mass transfer is so great that even after more than 12 pore volumes the injection profiles have not reached the end of stage III.

![Figure 5.7: TMOS injection into bea rock samples.](image)

### 5.5. Conclusions

We have studied the behavior of TMOS dissolved in oil as it is injected into a core containing both oil and water. Under the experimental conditions investigated we found for the first time that five stages can be distinguished in mass transfer reaction and flow. The first two stages represent an initial period in which mass transfer does not occur in significant amounts as a result of the initially low solubility of TMOS in water (stage I and II). Once small volumes of TMOS transfer and react to form silicic acid and methanol, solubility increases and the next period in which mass transfer occurs initiates (stage III).
This is an accelerating but finite process. The experiments show that the water phase can only contain a finite amount of TMOS. Once this maximum is reached, the differential pressure reaches a maximum indicating that the water saturation has reached a maximum and mass transfer slows down (stage IV). Ultimately the mass transfer terminates (Stage V). Solubility plays a significant role in the mass transfer reaction process. Without solubility being accounted for it would be impossible to observe phase II. Initially the TMOS is practically insoluble in the water phase. As small volumes do transfer and react, methanol is produced. Methanol increases the solubility of the TMOS, and thus speeds up the mass transfer process.

In relatively homogeneous rock (i.e. the Velsen or Bentheim sandstones) the behavior of the TMOS mixture does not vary significantly from one sample to another. In layered systems – such as the Berea sandstones – primarily the variation in water saturation between the layers has an impact on mass transfer. The overall water saturation in Berea sandstones remains high because the low permeability layers are difficult to drain. This higher water saturation translates to a larger volume of water available inside the core for mass transfer, which results in a larger storage capacity for the TMOS in the core as a whole. This is expressed in mass transfer being an important factor for much longer than in the other cores.

5.6. References


6. TMOS gelation in porous media

In this chapter we examine how the characteristics of porous media are modified by in situ gelation of TMOS. A brief outline of previous work is given, followed by the discussion of the results of gelling TMOS in different types of porous media: the correlation between the porosity and permeability reduction and the distribution of the gels in porous media. In particular we will attempt to illustrate when TMOS gels in porous media oil relative permeability is not affected significantly.

6.1. Introduction

TMOS is a new chemical system that has been proposed for performing water shutoff treatments [1-3] and relies on the difference in saturation between oil and water bearing layers (see Chapter 2). TMOS forms a gel when it reacts with water. TMOS can be dissolved in oil, and when this oil is brought into contact with water it will transfer from the oil phase to the water phase and react (Chapter 3). The oil/TMOS mixture can be used to place the chemical system in a porous medium and form a gel in situ. In principle, the oil/TMOS mixture that is injected into a porous medium will react only when it comes into contact with water and will remain inert when encountering oil in the porous medium. This makes TMOS a potential saturation-based water shutoff treatment. The situation is however complicated by the fact that water is always present: in fully oil-saturated layers the water saturation will always be at least the connate water saturation which is determined by the porous medium characteristics. TMOS can transfer from the oil phase to this present connate water phase resulting in an increase in water saturation (and a proportional decrease in oil saturation), as is also shown in Chapter 5. If water saturation is high when gelation sets in, the reduction in porosity and water and oil relative permeability due to the gelation of the TMOS can be significant.

Injection of the oil/TMOS mixture will always reduce the in-situ water saturation in the porous medium as the oil phase displaces the water phase. As a result, the back production
of TMOS (after placement in the near-wellbore region, when a treated well is brought back into production and reservoir fluids flow back towards the well) could be very important. In oil-bearing layers the oil flowing towards the well will simply flush out any TMOS that was not transferred into the water phase, since the oil will not react with TMOS. If the mass transfer is much slower than placement and back production practically all TMOS will be produced back. Back production in water-saturated layers will draw more water into the treated zone, enhancing the effects of gelation. By using this back-flush technique the mass transfer reaction can be limited to forming a gel which occupies only the residual water saturation when oil is the back flushing fluid (as would be the case in an oil saturated layer). In other words, little or no damage will be done to the oil phase permeability and fluid flow will be reduced to a single phase system containing oil and gel.

6.2. Results

Table 6.1 lists the residual resistance factors (RRF, the pre-gelation permeability scaled to the post gelation permeability) for all experiments. In experiments 1-11 and 22-26 water saturation and porosity were not measured. These are the same experiments as described in Chapter 4 and 5. An overview of the sample properties is given in Table 4.1.

In experiments 1-3 low viscosity IsoparH oil was used, and only 2 pore volumes of the oil/TMOS mixture were injected in the cores at low rates (0.2 mL/min). In experiments 4 to 6 the same low injection rate for TMOS was maintained, but a more viscous oil, Tellus22, was used for the experiments. In experiments 7 to 9 the injection rate was increased to 6 mL/min, but the total volume injected was 2 pore volumes, as in previous experiments. In experiments 10 and 11 the total volume of oil/TMOS mixture injected was doubled to 4 pore volumes.
The results from core flow experiments 12-21 (which were monitored with X-ray CT scanning) are accompanied by the pre- and post gelation porosity, the reduction in porosity as a result of TMOS placement, the residual water saturation and the residual resistance factor (RRF). The RRF is always determined for the back-produced fluid.

Experiments 22-26 were not monitored with CT scanning, so only the permeabilities before and after gelation and the RRF’s can be compared. In all four experiments oil was flushed through the core after TMOS placement. Due to technical malfunctioning the post-gelation permeability could not be accurately determined in experiments 22 and 24. In experiment 23 the permeability was reduced by a factor 2.6, indicating some deterioration, while in experiments 25 and 26 the post gelation permeability seemed to have increased compared to pre-gelation values. Why the permeability can increase after gel placement requires further investigation to learn what the mechanisms are that lead to this counterintuitive behavior. It is likely that the increase in permeability is the result of the change in surface chemistry as a result of TMOS gelation at the grain surface has a positive impact on the interfacial tension.

Table 6.1: Pre- and post-gelation data.

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<th>Experiment</th>
<th>Backflush</th>
<th>Oil Type Used</th>
<th>Flow Rate of TMOS in Oil (mL/min)</th>
<th>Pre-Gelation Porosity</th>
<th>Post-Gelation Porosity</th>
<th>Porosity Reduction (%)</th>
<th>Mean Swc (%)</th>
<th>RRF</th>
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6.2.1. **Brine back-flush**

Brine was flushed through the core in experiments 1-6, 9, 10 and 12. These experiments are intended to simulate the effect of a high water saturation zone being treated with TMOS and then back produced to draw more water into the treated near-wellbore region.

The back-flush with brine results in a high residual resistance factor (RRF), as is shown in Table 6.1. Experiments 1-3 are exceptions to this, although the exact reason is not completely clear. The low injection rates should not be responsible, since the same injection rate in experiments 4, 5 and 6 led to significant RRF’s. The type of oil used (low viscosity IsoparH) probably is also not the reason for the low RRF’s, since experiment 23 shows a permeability reduction with IsoparH, even though the back-flush is performed with oil. Fig. 6.1 shows the RRF as a function of TMOS injection rate for brine back-flush (squares) and oil back-flush.

![Figure 6.1: Residual resistance factor (RRF) plotted against injection rate for experiments with an oil back-flush (squares), and a brine back-flush (circles).](image)
The back-flush with brine makes it impossible to determine the post-gelation porosity by the method described in Section 4.4. Nevertheless it is possible to illustrate flow before and after gel treatment. Fig. 6.2 shows CT images of the Bentheim core used in Experiment 12. The upper image represents the porosity prior to gelation, the lower image shows the difference map between pre-gelation flow and post-gelation flow. The post gelation flow paths and porosity can be visualized by saturating the core with two different oils, as is illustrated in section 4.4. Since the CT number can only change if the in-situ properties change (in particular density), any change in CT numbers indicates that flow is occurring. Flow is from left to right. Light represents density changes as a result of flow, dark represents no fluid flow is possible. The difference map shows that towards the outlet the

Figure 6.2: CT scan images acquired during experiment 12. Flow occurs from left to right. The upper figure shows a porosity map along the axis of the core prior to gelation. The lower image shows a difference map that visualizes flow after gelation has taken place. Note that the area in which flow occurs after gelation decreases with distance, especially towards the outlet (right-hand side).
volume of the core that is participating in flow tapers off; progressively more of the core edge seems to be closed from beginning to end, indicating that gelation has affected flow the least at the inlet and increasingly towards the outlet by reducing the cross-section available for fluid flow.

Flow proceeds in a conical fashion (right-hand side of the core), with a decreasing flow radius towards the outlet. A significant part of the core is no longer involved in fluid flow as a result of gelation.

### 6.2.2. Oil back-flush in homogeneous porous media

In experiment 13 no significant decrease in oil permeability is noted (RRF ~ 1), although the porosity reduction is significant (almost 50 percent). This is a rather high porosity reduction, especially considering that the residual water saturation is 30 percent (Table 6.3) in this case. Fig. 6.3 shows that the porosity distribution before and after gelation has not changed significantly, i.e. it remains uniform. The entire core is still accessible to flow.

![CT scan images](image)

Figure 6.3: CT scan images acquired during experiment 13. The left image shows pre-gelation porosity, the image on the right shows post gel porosity.

Gel placement in experiment 14 decreases oil permeability by a factor of 4 (Table 6.1). Examining the change in porosity more closely we find that the overall change is lower (approximately 30 percent), but the distribution (Fig. 6.4) shows that at least towards the outlet (flow occurs from left to right) the flow is significantly hampered and the porosity in the lower right-hand corner of the core is reduced to practically zero.
TMOS placement in experiment 15 leads to a small RRF of 1.7. Prior to TMOS placement, during two phase flow characterization, this core is fractured at one end as is mentioned in section 4.1.2. This does not affect overall permeability significantly, but gel placement and especially post gelation flow is affected noticeably. Fig. 6.5 shows the pre and post gelation porosity maps along the core axis. The fracture is present in the upper left-hand side of the core, and acts as a conduit for flow, diverting a significant part of the flow away from the bottom half of the core.
Although even more of the core is not participating in flow after gel placement than is the case in experiment 14, the RRF to oil in experiment 15 is less than half the RRF in experiment 15, indicating that flow is not hampered significantly. This may be caused by the fracture that formed prior to gel treatment, creating a high-permeability channel for bypassing low-permeability parts of the core.

Both experiments 14 and 15 show a slight tendency for the lower part of the cores to be affected more than the upper part, although in the case of experiment 15 this could be an effect of the fracture in the upper part of the core. To ensure that gravity effects do not play a role, all later experiments were done with the core axis positioned vertically. This avoids blockage in the lower end of the core as a result of gravity and ensures a more even distribution of the gel.

TMOS injection in experiment 16 led to a large reduction in permeability, with an RRF of approximately 350. Also average porosity reduction is largest in this experiment (about 60 percent). The porosity distribution (Fig. 6.6) is quite homogeneous after gel treatment, with

![Figure 6.6: CT scan images acquired during experiment 16. The left image shows pre-gelation porosity, the right image shows post-gel porosity.](image-url)
exception of a small area at the outlet (at the bottom part of the core) that seems to have been fully blocked according to the drastic decrease in overall permeability. In experiment 18 the same injection rate is used during TMOS placement as in experiments 15 and 16, but with little apparent effect. An RRF of approximately 1 indicates that oil flow prior to gel placement is the same as after placement.

Fig. 6.7 shows pre- and post gelation porosity distribution in experiment 21. TMOS placement and subsequent gelation in this experiment results in no significant reduction of permeability, although porosity reduction is almost 45 percent. Porosity distribution after gelation is very similar to pre-gelation. The RRF for oil is less than unity, suggesting that oil permeability became greater than before gel treatment. The same observation was made in experiments 25 and 26.

The TMOS placement profiles can give a better understanding of this intriguing result. Fig. 5.4 shows the differential pressure during TMOS placement. After about one pore volume of injection a stable differential pressure was obtained. For experiment 13 this stable differential pressure was maintained longer than for experiment 14, but the level of stabilization is very similar. This period represents flow of the oil/TMOS mixture through the core without significant mass transfer occurring, keeping the core at residual water saturation. Once mass transfer began, the water saturation increased and the differential pressure rose to a maximum water saturation in the core. At this point mass transfer slows down and the water saturation exceeding residual water is decreased as water is displaced from the core.

If the pre- and post-placement residual water saturations were the same, the final level of differential pressure should be the same as the level observed after approximately 1 pore volume of injection. Both experiment 13 and 14 however show a lower differential pressure when the TMOS injection was stopped, and this differential pressure was still declining, indicating that not all water had been removed yet. Since the oil phase is deemed to be the same because mass transfer had terminated, this difference can be attributed to lower residual water saturation. The water phase chemistry and composition is affected by mass transfer and reaction of TMOS, and this change in water composition results in a lower residual saturation.
6.2.3. Layered cores

Experiments 19 and 20 are both performed with layered Berea sandstone cores. Fig. 6.8 shows pre- and post-gelation porosity maps for experiment 19 while Fig. 6.9 shows pre- and post-gelation porosity in experiment 20. In both experiments the effect of gelation on the RRF is limited: in experiment 19 the RRF is 3.1, in experiment 20 the RRF is less, approximately 1.4.

In the CT scans from experiment 19 and 20 layering is clearly visible parallel to the core axis and orthogonal to the scan plane. On the porosity maps the layers are also visible as high and low porosity planes (Figs. 6.8 and 6.9).
Figure 6.8: CT-scan images acquired during experiment 19. The image on the left shows pre-gelation porosity, the image on the right post-gelation porosity.

The impact of gelation on these layered samples is similar in both instances. In experiment 20 the layering is less clear after gelation than it was before gel placement. It is however clear that gelation has particularly affected the lower porosity regions more than the high porosity regions. Particularly in the upper part of the core the post-gelation porosity alternation mimics the trend present in the layering prior to gelation.
In experiment 20 the core is less plugged as a result of gelation (judging from the low RRF), and as a result the layering after gelation is also more clearly visible than in the previous experiment. For example, a low porosity streak runs over the entire core along the core axis (Fig. 6.9, left image). After gelation (Fig. 6.9, right image) this same layer is distinguishable, but its porosity has decreased significantly.

### 6.3. Discussion

Permeability reduction using TMOS is a complex process, as is already clear from the placement dynamics described in Chapter 5. The great advantage TMOS presents over other water shutoff chemicals is that the treatment has saturation-selective characteristics: dissolved in oil it is inert, but when the oil/TMOS mixture encounters water the TMOS transfers, reacts and ultimately forms a gel. A major complicating factor is that reservoir rocks always contain some water, even in oil-saturated intervals. The impact this residual
(or connate) water saturation has on gel placement and formation could be crucial to the placement process.

The capacity of a brine back flush following TMOS placement to greatly reduce the water permeability is well known [1, 4] and is confirmed in experiments 4-6, 9, 10 and 12. In these experiments TMOS was flushed out of the core by injecting brine and the resulting RRF’s are significantly higher than when oil was used to displace the TMOS out of the core (Table 6.1). The capacity of an oil back-flush to preserve oil permeability has been investigated in the experiments discussed above. Fig. 6.1 shows the relation between injection rate of TMOS and RRF. The experiments in which the TMOS was flushed from the core with brine all show a greater RRF than the experiments in which TMOS was flushed from the core with oil. The one exception to this was experiment 16, where a low injection rate of TMOS (1 mL/min) followed by an oil back-flush still resulted in an ultimate RRF of more than 350. The problems encountered with injecting TMOS at a low rate were already discussed in section 5.4.1 and highlighted by Fig. 5.6, and the risk of core plugging during injection of TMOS at low rates is significant. If the core becomes plugged during TMOS placement the back-flush fluid becomes less important, as at least part of the damage has already been done during TMOS placement.

The main results are listed in Table 6.1. The flow rate of the oil/TMOS mixture during placement seems to have some impact although this is tentative. Lower flow rates during placement could cause a greater oil phase permeability reduction, which is also apparent in Chapter 5.

An interesting observation is that in four instances (experiments 18, 21, 25 and 26) the oil permeability actually is greater after TMOS placement and gelation than before. This is also observed in some of the experiments presented in Appendix. B (experiments 4 and 5). This could be the result of wettability alterations due to mass transfer and gelation. Micromodel studies [5, 6] have shown that TMOS placement leads to a hydrophobization (a shift in wettability from water-wet to more oil-wet) of the treated samples, which in turn could lead to a reduction in residual water saturation. This could result in greater end-point oil permeability, simply because it shifts the end-point saturation.
The relationship between initial porosity and gelation-induced porosity reduction is also not straightforward. All samples experience a porosity reduction greater than the residual water saturation (Table 6.2). This is surprising, because it should be possible – at least at higher placement rates – to keep water saturations at or around residual saturation. If so, no reduction in volume open to oil flow should occur since the space occupied by water at residual water saturation is always inaccessible to oil. Add to that the possible hydrophobization of the samples as a result of treatment and a successful treatment should lead to a porosity reduction that does not exceed the residual water saturation. The fact that the porosity reduction does systematically exceed residual water saturation indicates that at least under the conditions used in these experiments it is not possible to limit the porosity reduction induced by TMOS to the volume occupied by residual water, possibly because mass transfer was still occurring when TMOS injection was terminated.

In the experiments where porosity and saturation were measured (experiments 13-16, 19, 20 and 21) gelation resulted in a reduction of porosity greater than the measured pre-gelation residual water saturation. The greatest porosity reduction (almost 60%) occurred in experiment 16. In this experiment the greatest RRF is also observed (~350), indicating that greater reductions in porosity do result in greater reduction in permeability. In experiment 14 a significant RRF was observed (4.15) even though the porosity reduction was relatively low (just over 30%) compared to the other experiments. Conversely, in Experiment 20 the porosity reduction was almost 50%, but the RRF barely 1.4.

Layered samples in which the layering is parallel to the flow direction exhibit generally similar behavior to homogeneous samples. Interesting to note is the observation that porosity reduction seems to be greater in initially low porosity layers than in the initially higher porosity layers. This could well be a result of the water saturation distribution. As outlined in Chapter 4, residual water saturation is likely to be higher in these low porosity layers and, as a result, they are more strongly affected by gelation. On the other hand, since these layers do not contribute significantly to oil phase flow, their effect on oil-phase permeability remains small.
6.4. Conclusions

Brine back-flush results in a strong reduction of water permeability, as is expected from previous work. For oil back-flush the parameters affecting permeability reduction are complex and interaction occurs between, for example, the injection rate of the oil/TMOS mixture during placement and the residual water saturation. In general there is little correlation between the porosity reduction observed and the RRF. Low porosity reductions can still result in high RRF’s and vice versa.

Although the volume occupied by gel is invariably larger than the space initially occupied by residual water, oil back production after TMOS placement at the conditions investigated generally leads only to minor amounts of oil permeability reduction. The main exception is formed by experiment 16, in which a low injection rate during TMOS placement (1 mL/min) is used. In Chapter 5 the difficulties faced with lower injection rates have also been discussed, and the fact that one of these experiments can lead to significant permeability reduction confirms that low injection rates are detrimental to permeability. Provided the injection rates are kept above 1 mL/min to avoid plugging during TMOS placement the resulting permeability reduction to oil is low to negligible.

In general layered samples exhibit similar behavior to homogeneous samples for layer-parallel flow. An interesting feature is that the layering affects gelation in that low porosity layers tend to be more affected by gelation than higher porosity layers. This is a result of the residual water saturation being higher in the lower porosity samples.

6.5. References

7. General conclusions

7.1. TMOS as a water shutoff chemical

The amount of water being produced from oil and gas fields is steadily rising and as a result remediation treatments such as chemical water shutoff are receiving more and more attention. TMOS has a distinct advantage over other water shutoff chemicals because it is a saturation-based treatment. In order for water shutoff to occur water needs to be present in the formation. Water is however always present, even in oil- or gasbearing layers, in the form of residual water.

To characterize the bulk behaviour of TMOS in a two phase system (water and oil, with TMOS initially only present in the oil phase) a series of experiments were performed to investigate the mass transfer and reaction behaviour under varying conditions. Furthermore coreflood experiments were performed to investigate the impact of mass transfer and reaction on the flow properties under different conditions. These experiments also allowed the characterization of the impact gelation has on the porous medium.

7.2. Coupled mass-transfer and reaction in water of TMOS

CT scanning of bulk experiments allows the characterization of mass-transfer behavior and to a lesser extent gelation. As a first approximation the TMOS concentration can be derived using a linear mixing law for TMOS and water. There is a 30% offset as a result of the chemical reactions that take place in the water phase. Once gelation begins, the overall concentration of TMOS in water will decrease as the gel forms a separate phase within the bulk system.

Different parameters have been varied to test their impact on the mass-transfer reaction process. Mass-transfer rates are not sensitive to varying the initial concentration of TMOS in the oil phase; gelation occurs sooner as the concentration of TMOS is increased. The ratios of oil phase to water phase have an impact that is scalable to the water to oil ratio. Water phase salinity does not affect mass-transfer significantly, but it does speed up
gelation. The pH of the water phase has an important impact: at low pH mass transfer is not significantly affected, but gelation occurs sooner. At high pH mass transfer speeds up significantly, and gelation begins almost immediately.

### 7.3. Porous media experiments

Imbibition and drainage exhibit different displacement behaviour: during imbibition the differential pressure increases linearly to a plateau, whereas during drainage differential pressure tends to decrease exponentially, not quite reaching a constant differential pressure. Three different sandstone types were used in the two-phase flow experiments. Of the three sandstones used, Bentheim sandstone (which has the highest permeability) tends to have the lowest residual saturation, Berea (with intermediate permeabilities) slightly higher residual saturations and Velsen (permeability in the milliDarcy range) has the highest residual saturation.

The Bentheim and Velsen sandstones have very similar porosities, but up to two orders of magnitude difference in permeability. The end-point relative permeability of Velsen sandstone is also lower than that of Bentheim sandstone. This is a result of grain sorting and composition: the Bentheim sandstone is a well sorted and mature sandstone with more than 99% silicate composition, whereas the Velsen sandstone is poorly sorted and contains more lithic components.

The samples of Berea sandstone used in the experiments were laminated on mm scale. They have a lower porosity, but an intermediate permeability. The principal difference with the Velsen and Bentheim sandstones is the ratio of water to oil permeability, which is almost twice that of the Velsen sandstone. The water relative permeability is also significantly lower than in the Velsen and the Bentheim sandstones. This is likely to be the result of the lamination and clay content, both of which can affect the hydraulic radius adversely.

### 7.4. Dynamics of TMOS in porous media

Mass-transfer of TMOS placement in porous media can be split into five different stages: During the first two stages no significant mass-transfer of TMOS occurs: stage I is the displacement of the pure oil phase by the oil-TMOS mixture. This stage will last no longer
than the time it takes to inject 1 pore volume (corrected for residual water saturation) of oil, and is characterized by a decrease in differential pressure during flow, because the viscosity of the mixture is lower than of the bulk oil phase. Stage II is a steady state displacement of the oil/TMOS mixture without (significant) mass transfer. The differential pressure remains constant during stage II.

The reason why stage I and II occur is because TMOS initially is poorly soluble in the water phase. Only when some mass transfer has occurred and the chemical reaction of TMOS in the water phase has formed silicic acid and methanol mass-transfer will be able to occur more easily because methanol acts as a solvent for TMOS in water.

Stage III represents the onset of mass-transfer of TMOS from the oil phase into the water phase; as mass-transfer occurs, the in situ phase saturation changes: the oil phase saturation decreases and the water phase saturation increases. As a result the differential pressure increases. The mass transfer is an accelerating but finite process. Once mass-transfer has reached a maximum, the differential pressure will once again begin to decrease (onset of stage IV), until it reaches a minimum when the saturations (and thus mass-transfer itself) remain essentially constant (stage V).

Solubility plays an important role in the placement of TMOS in a porous medium: without accounting for solubility, it would not be possible to observe stages I and II.

The five stages are sensitive to injection rate: the lower the injection rate, the more the stages will be compacted, and vice versa.

The impact of rock type is difficult to evaluate. For the Bentheim and Velsen sandstones the placement behaviour does not seem to vary significantly from one sample to the other. In a laminated system like Berea the variation of water saturations between the laminations has an impact on the mass-transfer. The higher overall water saturation results in a greater storage capacity of TMOS in the Berea sandstone cores as a whole. As a result mass transfer occurs over a longer period of time than in the other rock samples.
7.5. **TMOS gelation in porous media**

The fluid which is injected to displace the oil/TMOS mixture at the end of the placement of TMOS in a porous medium has an important effect on the permeability reduction caused by gelation: brine backflush results in a greater permeability reduction than oil backflush.

In general there is little correlation between the overall porosity reduction and the permeability reduction as a result of gelation: small reductions in porosity can lead to significant reductions in permeability, and vice versa.

Even when an oil back flush is performed immediately after TMOS placement the porosity reduction exceeds the residual water saturation. However, this can lead to only small permeability reductions, particularly if TMOS is placed at high flow rates.
Summary

Water production is a growing problem within the oil industry, as oil and gas fields mature worldwide and water breakthrough becomes more and more common. Often water production leads to reduction in productivity and reduction of the ultimate hydrocarbon recovery from a field. The challenges we face in regard to water production are outlined in Chapter 1 as are some of the solutions available today to reduce or mitigate water production. The purpose of this research project was to investigate the physical and chemical behaviour of TMOS, an oil-soluble chemical that forms a gel when it encounters and reacts with water.

Silanes such as TMOS are well known and extensive research has been done to understand their behaviour and the parameters that influence that behaviour. A summary of relevant studies is given in Chapter 2. Although well-known in single phase aqueous solutions, the behaviour in a multiphase system such as an oilfield is less well understood. For this purpose the mass transfer and gelation behaviour was investigated in a two phase system with TMOS dissolved in an oil phase in contact. The results of this study are presented in Chapter 3. These multiphase bulk experiments were performed in an X-ray CT scanner, and periodic scans allowed the reconstruction of TMOS in the oil and the water phase. TMOS is initially dissolved in the oil phase, and transfers to the water phase. In the water phase the TMOS first hydrolyzes to silicic acid, and ultimately condensates to form silica gel.

The mass transfer of TMOS from the oil phase to the water phase can be described with a simple exponential law. Gelation could be identified by the onset of high density silica clusters which show up on the CT images as bright spots. Several parameters were investigated to see their effect on mass transfer. The initial concentration of TMOS in the oil phase does not significantly affect the mass transfer behaviour, although increasing initial concentrations do tend to speed up gelation. The volume fraction of water to oil phase does have a measureable effect: when the ratio of water to oil increases mass transfer also increases. Addition of salt to the water phase does not significantly affect the mass transfer, but it does tend to decrease the gel time. The pH of the aqueous solution has a
large impact, both high and low pH lead to fast mass transfer, with a minimal transfer rate around neutral pH. The gel time is extremely shortened at high pH, with flocculation in the aqueous phase observed almost immediately. At low pH gelation is faster than at neutral pH, but slower than at high pH.

After characterizing the behaviour of TMOS in bulk, the behaviour in porous media needs to be investigated. For this purpose a series of multiphase flow experiments is performed (the experimental method is described in Chapter 4). First the multiphase flow is characterized (Chapter 5), after which the flow behavior during TMOS injection is investigated (Chapter 6). Compared to the bulk experiments mass transfer is significantly faster because the interfacial area between the oil phase and the water phase within the porous media is much greater than in the test tubes used in the experiments described in Chapter 3. Injection of TMOS in a porous medium is also more dynamic than the static bulk experiments: TMOS dissolved in oil is injected into the porous media after the water saturation is reduced to residual water saturation and only oil is mobile. Once mass transfer begins the in situ water saturation increases, and water will once again become mobile. This affects not only the viscosities of the oil and the water phase, but also the relative permeability of the phases through changing the in situ saturations.

The flow behavior during TMOS injection can be separated into five phases. The first two stages represent an initial period in which mass transfer does not occur as a result of the initially low solubility of TMOS in water (stage I and II). Once small volumes transfer and react to form silicic acid and methanol solubility increases and next a period in which mass transfer initiates (stage III). This is an accelerating but finite process. The experiments show that the water phase can only contain a finite amount of TMOS. Once this maximum is reached mass transfer slows down (stage IV) and ultimately terminates (Stage V).

TMOS placement is influenced by the rate of injection, which controls the residence time of the oil/TMOS mixture in the porous medium. Faster injection rate tends to stretch the exhibited mass transfer behavior, whereas low injection rates tends to compact the different phases, and very low injection rates can cause extensive permeability reduction due to the onset of gelation during TMOS placement. At high injection rates the core permeability is not significantly damaged by the TMOS placement.
The effect of TMOS placement and gelation is described in Chapter 7. Gelation is steered by varying the type of back flush. If the core is flushed with brine after TMOS placement the permeability reduction is large, whereas flushing the core with oil after TMOS placement leads to little or no permeability reduction, as long as the injection rate during TMOS placement was high enough to avoid gelation during the placement stage itself.
Samenvatting

Water productie is een toenemend probleem binnen de olie-industrie naarmate olie- en gasvelden ouder worden, langdurig in productie zijn en waterdoorbraak steeds vaker voorkomt. Vaak leidt water productie tot een afname van productiviteit en een afname in de totale winning van koolwaterstoffen uit een veld. De uitdagingen die we moeten aangaan ten opzichte van water productie worden besproken in Hoofdstuk 1, evenals een aantal van de oplossingen die vandaag de dag beschikbaar zijn om water productie te verminderen of volledig op te lossen. Het doel van dit onderzoeksproject is om het fysische en chemische gedrag van TMOS, een in olie oplosbare chemische substantie die een gel vormt wanneer ze in contact komt met water, te onderzoeken.

Silanen zoals TMOS zijn bekende chemicaliën en er is uitgebreid onderzoek gedaan om hun gedrag en de parameters die dat gedrag beïnvloeden te begrijpen. Een samenvatting van relevante studies wordt in Hoofdstuk 2 gegeven. Hoewel ze welbekend zijn in enkelfasige wateroplossingen wordt het gedrag in meerfasige systemen zoals een olieveld minder goed begrepen. Om die reden is het massa transfer en gelatie gedrag bestudeerd in een twee fase systeem met TMOS opgelost in een oliefase in contact met water. De resultaten van dit onderzoek worden besproken in Hoofdstuk 3. Deze meerfase bulk experimenten werden uitgevoerd met een Röntgen CT scanner, en periodieke scans stonden de reconstructie toe van TMOS in de olie- en waterfase. TMOS is initieel opgelost in de oliefase, en verplaatst zich naar de waterfase. In de waterfase hydroliseert de TMOS eerst tot kiezelzuur en condenseert uiteindelijk om een silica gel te vormen.

De massa transfer van TMOS uit de oliefase naar de waterfase kan beschreven worden met een simpele exponentiële functie. Gelatie kon geïdentificeerd worden door de aanvang van hoge dichtheid silica clusters die op de CT beelden te herkennen zijn als heldere vlekken. Meerdere parameters werden onderzocht om hun effect op de massa transfer te onderzoeken. De initiële concentratie van TMOS in de oliefase beïnvloedt de massa transfer nauwelijks, hoewel toenemende initiële concentraties het gelatie proces wel versnellen. Het variëren van de volume fractie van water ten opzichte van olie heeft wel een
meetbaar effect: wanneer de ratio van water ten opzichte van olie toeneemt, neemt de massa transfer ook toe. De toevoeging van zout beïnvloedt massa transfer ook niet aanmerkelijk, maar het doet de gelatie tijd wel afnemen. De pH van de wateroplossing heeft een grote invloed, zowel hoge als lage pH leiden tot snelle massa transfer, met een minimale massa transfer snelheid rond neutrale pH. De gelatie tijd wordt extreem verkort bij hoge pH, en floculatie in de waterfase werd bijna onmiddellijk waargenomen. Bij lage pH is gelatie sneller dan bij neutrale pH, maar langzamer dan bij hoge pH.

Na beschrijving van het gedrag van TMOS in bulk, moet het gedrag in poreuze media onderzocht worden. Daarom is er een serie experimenten uitgevoerd (de experimentele methode wordt in Hoofdstuk 4 beschreven). Eerst wordt de multifase stroming beschreven (Hoofdstuk 5), waarna het stromingsgedrag gedurende TMOS injectie onderzocht wordt (Hoofdstuk 6). Vergeleken met de bulk experimenten is de massa transfer aanzienlijk sneller omdat het contactoppervlak tussen de oliefase en de waterfase in een poreus medium veel groter is dan in de proefbuisjes die gebruikt zijn in de experimenten (beschreven in Hoofdstuk 3). De injectie van TMOS in een poreus medium is ook dynamischer dan de statische bulk experimenten: TMOS opgelost in olie wordt geïnjecteerd in het poreuze medium nadat de water saturatie teruggebracht is tot residuale saturatie en alleen olie mobiel is. Als massa transfer eenmaal begint neemt de in situ water saturatie toe en zal water weer mobiel worden. Dit beïnvloedt niet alleen de viscositeit van de olie en de waterfase, maar ook de relatieve permeabiliteit van de fasen door verandering in de in situ saturaties.

Her stromingsgedrag gedurende TMOS injectie kan opgedeeld worden in vijf stadia. De eerste twee stadia vertegenwoordigen een initiële periode gedurende welke massa transfer niet plaatsvindt ten gevolge van de in eerste instantie lage oplosbaarheid van TMOS in water (stadium I en II). Zodra kleine hoeveelheden TMOS zich verplaatsen naar de waterfase, reageren tot kiezelzuur en methanol neemt de oplosbaarheid toe en een volgend stadium waarin de massa transfer toeneemt begint (stadium III). Dit is een versnellend maar eindig proces. De experimenten tonen aan dat de waterfase een eindige hoeveelheid TMOS op kan nemen. Zodra het maximum bereikt wordt, vertraagt de massatransfer (stadium IV) en houdt uiteindelijk op (stadium V).
TMOS plaatsing wordt beïnvloed door de vloei stof injectiesnelheid, die de verblijftijd van het olie/TMOS mengsel in het poreus medium bepaalt. Snellere injectie rekt het massatransfer gedrag op, terwijl langzame injectie de verschillende fasen consolideert, en heel lage injectiesnelheden kunnen uitgebreide permeabiliteits reductie veroorzaken ten ge volge van gelatie gedurende de TMOS plaatsing. Bij hoge injectiesnelheden wordt de kern permeabiliteit niet significant verminderd ten gevolge van TMOS plaatsing. Het effect van TMOS plaatsing en gelatie wordt beschreven in Hoofdstuk 7. Gelatie wordt gestuurd door variërende vloeistofspoelingen. Als de kern gespoeld wordt met zout water na TMOS plaatsing is de reductie in permeabiliteit groot, terwijl een spoeling met olie leidt tot weinig of geen permeabiliteitsafname zo lang de injectiesnelheid tijdens TMOS plaatsing hoog genoeg is om gelatie tijdens de plaatsing zelf te vermijden.
Appendices
Appendix A: TMOS placement at high temperatures

Introduction
Experiments 1-11 were performed to investigate the dynamic behavior of TMOS at high temperatures. Initially only 2 pore volumes of TMOS were injected, but because the effect of TMOS placement on the cores was found to be limited, the injected volume was doubled.

Set-up and coreholder
The experimental setup is shown in Fig. A.1. Two double-effect P-500 Pharmacia pumps are used to inject the fluids. The coreholder is made of stainless steel and is formed by a casing with an internal diameter and two end pieces. Groves carved on the inside of the two end pieces allow a more uniform distribution of the fluids. Special glue resistant to high pressures and temperatures is used to fit the core inside the stainless steel casing. The temperature during the experiments was maintained at 70-90ºC by placing the coreholder in an air-circulated oven. The first experiments (cores 1-4) were performed without pre-heating the fluids at the core inlet. This resulted in a lower overall temperature in the core and had adverse effects on the experiments as will be discussed later. In the following experiments fluids were pre-heated prior to injection using house made heat exchanger, with a temperature regulation system.

The in- and outlet pressures were monitored and recorded using a personal computer. Two additional pressure sensors were also connected to the core using orifices at distances over the core length. However, due to frequent blocking with gel the pressures measured with these sensors were unreliable and were therefore discarded. A backpressure regulator was mounted at the core outlet, just before the fraction collector, to prevent the vaporization of fluids in the core. Vaporization was expected to occur at the temperatures used in the experiments, due to the presence of methanol produced by the chemical reaction.
Procedure

The experimental procedure for these experiments is summarized in Chapter 4, experiments 1-11. Note that the core used in experiment 9 proved to be only slightly affected by gelation after treatment with TMOS, and the decision was made to reuse it in a second gelation experiment.

As already mentioned, core is initially saturated with a synthetic brine to full water saturation ($S_w = 1$) and then the absolute permeability is determined (step 1).

Next oil is injected (primary drainage) up to connate water saturation and oil permeability at $S_w = S_{wc}$ is determined (step 2). Following oil injection the core is once again subjected to brine injection (secondary imbibition) to residual oil saturation in order to determine water permeability at $S_w = 1 - S_{or}$ (step 3). Preceding TMOS injection the core is then once again brought to connate water saturation (step 4). Two main methods of introducing the TMOS (step 5 and onward) into the core were tested:

First series of experiments: two pore volumes of the TMOS mixture are injected, followed by a two-hour shut in period (step 5 and 6); then either oil or brine was injected (step 7) to determine the effect of saturation on gel formation. After this injection phase the core is shut in for another 20 hours (step 8) to allow gelation to continue, and finally the new fluid flow characteristics are determined.

Second series of experiments: the initial fluid flow characterization phase is followed by injection of four pore volumes of the oil/TMOS mixture and shut in for two hours (step 5 and 6). After core shut in, brine is injected, followed by oil or brine injection.

Results and Discussion

2 pore volumes of IsoparH /TMOS at low injection rate:

The first series of experiments was carried out with IsoparH, low viscosity oil, as the TMOS carrier. Injection rates for the oil/TMOS mixtures were low (0.2 ml per minute).
The three cores (1 to 3) present low residual resistance factors both for oil and water indicating that there is little or no modification of flow properties in the cores. This suggested little gel formation (if any), and raised doubts whether mass transfer of TMOS from the oil to the water phase had occurred at all or in sufficient amount.

The low injection rate, high temperature, long shut in period (2 hours followed by another 20 hours) is believed to be sufficient to promote mass transfer and gelation. Several effects were therefore hypothesized to explain the lack of permeability modification. First, the composition of IsoparH could be such that it has a great affinity with TMOS and therefore mass transfer is too slow to build up significant amounts of TMOS in the water phase, over the exposure times used in our experiments. Secondly, the chemical properties TMOS and IsoparH could be such that no good mixing occurs. This would lead to segregation of the two components and therefore to settling of heavier TMOS in the bottom of the vessel. The amount of TMOS introduced into the core could be significantly lower than expected. Finally, in absence of a pre-heating system at the core inlet, the temperature of the fluids in the core could be much lower than the nominal value of 70 °C this would delay mass transfer and gelation considerably.

Table 4 shows that oil permeabilities before TMOS injection are similar to that calculated during TMOS injection based on the viscosity of pure IsoparH. This indicates that the viscosity of the injected oil/TMOS mixture differs little from pure oil viscosity and suggests that oil/TMOS mixture actually contained significantly less TMOS than expected. This supports second hypothesis.

Nevertheless, the overall experimental procedure was improved not only by using an oil with greater affinity with the TMOS, but also by pre-heating the fluids at the core inlet to address the third hypothesis.

2 pore volumes of Tellus22/TMOS at low injection rate:

For the next set of experiments (cores 6 to 8), high-viscosity oil Tellus22 was used as a carrier for TMOS. Oil/TMOS mixture was injected at the same low flow rate (0.2 ml per minute).
The TMOS injection stage yields very different pressure drop profiles from the previous series of experiments, and the fact that pressure drop behavior is the same in cores 6 and 7 indicates reproducibility (Fig. 5.2).

There are several possible explanations for the increase in pressure drop: First of all the tube volume before the core could be so large that the oil/TMOS mixture does not penetrate the core for the first 20 minutes. If such, the volume of tubing before the core should be about 4 ml. However, the total tubing volume in the entire setup is about 1.4 ml only. This leads us to believe that it is unlikely that the segment of tubing before the core inlet is responsible for the increase in pressure drop. A more plausible explanation is the change of viscosity due to mass transfer.

TMOS has a significantly lower viscosity than Tellus22, therefore a mixture of TMOS and oil will have a lower viscosity than oil alone. The viscosities determined from cores 6 and 8 are respectively 8.4 and 5.7 cP, both values being greater than the viscosity of pure Tellus22 (4.6 at 90°C). The data seem to point out an extensive mass transfer.

Once mass transfer occurs, the viscosity of the oil will increase. Mass transfer also causes an increase in water saturation and consequently a decrease in oil saturation. These effects contribute to pressure drop increase. The effect of gelation on fluid flow in these experiments is significant. Both water and oil permeabilities were reduced, showing that TMOS did act as an overall permeability reducer with no selectivity. After the experiments the core holder was dismantled and extensive gelation was observed at the core ends. The learning from this observation is that premature TMOS gelation occurred with water trapped in the gaps between the end pieces and the core.

2 pore volumes of Tellus22/TMOS at high injection rates:

In the following procedures another strategy was chosen for gel placement. The oil/TMOS mixture is introduced at high flow rate (6 ml/min, which is 30 times higher than the flow rate used in all previous experiments). Core 9 is subjected to oil flow following shut in, whereas in cores 10, 11 and 12, brine is injected following shut in. The experiments using core 11 ended with the initial brine backflush (step 7). The same was done for core 12.
low RRF obtained through gel treatment led however to the decision to reuse core 12 in the following series of experiments.

The 30-fold increase in injection rate during introduction of TMOS to the core has a strong effect on the shape of the pressure drop curves (Fig. 5.3), which deviate significantly from those seen in the previous set of experiments (Fig. 5.2). Low pressure drop indicates no premature gelling during placement of TMOS in the core. The decline in pressure drop at the early stage is explained by the replacement of Tellus22 by the lower-viscosity Tellus22/TMOS mixture.

4 pore volumes of Tellus22/TMOS injection at high flow rates:
Limited RRF values led us to inject four pore volumes (instead of two) of oil/TMOS mixture in cores 9 to core 11. The permeability reduction resulting in core 10 are by far the most promising, giving 13-fold reduction of water permeability while oil permeability is only reduced by a factor 2.5.

Field application recommendations for the TMOS
The above results indicate that the TMOS reduces selectively water permeability without affecting oil permeability too much as requested for bullhead water control treatments. The experiments also suggest that the TMOS can be used a total blocking agent, with advantages such as the low viscosity during injection.

Laboratory studies to optimize chemical composition, treatment parameters and schedule under the specific reservoir conditions are required. Parameters controlling the effect of gelation on fluid flow include: oil type used to inject the TMOS, temperature of the system, injection rate of the oil/TMOS mixture, and water saturation of the rock. TMOS placement conditions have to be carefully designed and adapted to reservoir and well conditions. The optimal injection rate for the TMOS/oil mixture will both depend on the oil used and the reservoir temperature. Serious consideration needs to be paid to effects of brine...
properties such as the salinity and pH. The pH was found in the past to have a significant impact on the morphology of the gel, where at lower pH values the gel will form a network relatively simple and open network. Higher pH values however will result in much denser gel network. The effect of TMOS gel morphology on fluid flow in porous media needs to be investigated in more detail.

**Conclusions**

The placement of a TMOS-based gel system is a sensitive system depending strongly on the oil chosen as carrying fluid, injection rates and post-placement procedure. IsoparH does not seem to be a good carrier for TMOS, whereas higher-viscosity Tellus22 gave significantly better results.

Our experiments also show that, due to the risk of premature gelling, low flow rates are detrimental to TMOS placement. Optimizing the conditions of TMOS placement strategy give high permeability reductions to water (RRFW=13) coupled with low permeability reduction to oil (RRFO=2.5), as required for a good selective water shutoff system.
Figure A.1: Schematic of the experimental setup.
Appendix B: TMOS placement at room temperature with effluents analysis

Introduction
A total of five coreflooding experiments and two bulk experiments are performed at the International Research Institute Stavanger (IRIS) to study the mass transfer and gelation behavior of TMOS in a porous medium. The results are presented below.

Experimental procedure

Materials:
As in several experiments performed in Delft in the framework of the DELFGEL project, the cores used in these experiments were all Bentheim sandstone cores. The same brine composition (WELGEL brine) is used, and IsoparH is used as oil phase. All experiments were performed with 20 vol% TMOS dissolved in the oil phase.

Experimental setup:
The experimental is shown in Fig. B.1. It consists of a hassler-type stainless steel coreholder in which the sandstone cores are mounted. A rubber sleeve inside the coreholder is pressurized to ensure that flow along the boundaries will not cause bypassing of the core. A waters P590 pump drives distilled water into cylinders containing the fluids that are to be injected. The entire system is kept at a constant minimum pressure of 7 Bar using a back pressure valve. The differential pressure over the core is monitored with a differential pressure transducer and the effluent is collected either in a burette to evaluate produced volumes or in a fraction collector when the effluent needs to be analyzed. By monitoring the volumes of effluent using a burette it is possible to determine the residual oil and water saturation with high accuracy.
Procedure:
1) The core is mounted in a rubber sleeve in a stainless steel coreholder.
2) The rubber sleeve is then pressurized to 30 Bar to prevent flow between the core and the sleeve.
3) The core is degassed with a vacuum pump.
4) INITIAL SATURATION: WELGEL brine is injected into the core to $Sw=1$, and the pore volume determined from the amount of brine that is injected.
5) Brine is injected at different flow rates to determine the absolute permeability.
6) PRIMARY DRAINAGE: IsoparH is injected into the core to irreducible water saturation ($Sw_i$), and the flow rate is varied to determine the oil permeability.
7) SECONDARY IMBIBITION: Brine is injected until $Sw=1-Sor$ (residual oil saturation), and the flow is varied to determine the water permeability.
8) SECONDARY DRAINAGE: IsoparH is injected until $Sw_i$, and the flow rate is varied to determine the oil permeability.
9) PLACEMENT: a mixture of 20 vol% TMOS in IsoparH is injected and the effluent is collected in 10 mL batches using a fraction collector. Post placement fluid flow characterization.
Porosity determination:
After being mounted the cores are evacuated using a vacuum pump. After evacuation is complete the core is filled with a high precision pump to measure the volume of fluid needed to fully saturate the core. In combination with the core geometry this volume gives the total porosity of the sample.

TMOS in oil phase effluent:
From the samples collected with the fraction collector a batch of oil phase is separated as quickly as possible to minimize the loss of TMOS to any produced water. The density of the samples is determined using a PAAR DMA-45 densiometer and after calibration can be converted to mass concentrations of TMOS in the oil phase.

Core properties:
The cores are Bentheim sandstone plugs with a diameter of 37.2 mm. The core length and the volume injected for core saturation are listed in Table B.1.

<table>
<thead>
<tr>
<th>Core</th>
<th>Length (cm)</th>
<th>Pore volume (mL)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>28.9</td>
<td>67.4</td>
<td>0.22</td>
</tr>
<tr>
<td>23</td>
<td>29.5</td>
<td>69.9</td>
<td>0.22</td>
</tr>
<tr>
<td>24</td>
<td>29.1</td>
<td>68.6</td>
<td>0.22</td>
</tr>
<tr>
<td>25</td>
<td>29.6</td>
<td>70.3</td>
<td>0.22</td>
</tr>
<tr>
<td>26</td>
<td>12.68</td>
<td>29.4</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Results
Experiment 22:
The exact procedure followed and the permeabilities obtained during each step are detailed in Table B.2. TMOS injection (Fig. B.2) did not lead to the expected behavior as detailed in chapter 6, leading to the conclusion that the experiment was unsuccessful. To test this hypothesis both oil (step 6) and water (step 7 and 8) were injected after TMOS placement. Oil permeability has decreased slightly, but brine permeability seems to have gone up significantly. Significant difficulties with the pump lead to a low reliability of these data.
Table B.2: experimental procedure during experiment 1.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Sw</th>
<th>permeability</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Initial saturation</td>
<td>Sw=1</td>
<td>1349</td>
<td>150</td>
</tr>
<tr>
<td>2 Primary drainage</td>
<td>Swi</td>
<td>476</td>
<td>60</td>
</tr>
<tr>
<td>3 Secondary imbibition</td>
<td>1-Sor</td>
<td>134</td>
<td>9</td>
</tr>
<tr>
<td>4 Secondary drainage</td>
<td>Swi</td>
<td>454</td>
<td>225</td>
</tr>
<tr>
<td>5 TMOS placement (Q = 4 mL/min)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6 Postgelation oil injection</td>
<td>Sw=0?</td>
<td>398</td>
<td>27</td>
</tr>
<tr>
<td>7 Postgel LoQ brine injection</td>
<td>Sw?</td>
<td>219</td>
<td>11</td>
</tr>
<tr>
<td>8 Postgel HiQ brine injection</td>
<td>Sw?</td>
<td>221</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure B.2: differential pressure during TMOS placement.

Experiment 23:
In this experiment effluent oil is first collected for analysis. Monitoring was not performed over the entire trajectory however, and not much can be said based on the density data that is obtained. Fig. B.3 shows the differential pressure and TMOS concentration in the effluent oil phase. It seems that an initially intermediate concentration of TMOS in the effluent (ca. 10 percent directly after oil/TMOS breakthrough) the amount of TMOS present in the effluent declines. The differential pressure curve is more reminiscent of TMOS placement as described in chapter 6 than in the previous experiment. After TMOS
placement oil is circulated through the core. The RRF is 2.6 (Table B.3), indicating that significant damage to oil flow has occurred.

Table B.3: experimental procedure during experiment 23.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Sw</th>
<th>permeability</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial saturation</td>
<td>Sw=1</td>
<td>1084</td>
<td>66</td>
</tr>
<tr>
<td>Primary drainage</td>
<td>Swi=0.17</td>
<td>639</td>
<td>40</td>
</tr>
<tr>
<td>Secondary imbibition</td>
<td>1-Sor = 0.65</td>
<td>125</td>
<td>2</td>
</tr>
<tr>
<td>Secondary drainage</td>
<td>Swi=0.18</td>
<td>714</td>
<td>28</td>
</tr>
<tr>
<td>TMOS placement (Q = 1 mL/min)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Postgelation oil injection</td>
<td>Sw=0?</td>
<td>274</td>
<td>34</td>
</tr>
</tbody>
</table>

![Figure B.3: differential pressure during TMOS placement and the concentration of TMOS measured in the effluent oil phase.](image)

Experiment 24:
Relative permeabilities and end-point saturations are detailed in Table B.4. During the TMOS placement cycle the back pressure valve was bypassed, thus keeping the entire setup at atmospheric pressure. This leads to less stable differential pressure curves, as can be seen from Fig. B.4. However, the general shape shows the same behavior as is detailed in
chapter 6. As a result of the instable pressures it is not possible to determine the permeability after gel placement. The TMOS concentration in the effluent oil phase was monitored over most of the experiment, and shows a more complete picture than in experiment 2. After 1 pore volume only a small amount of TMOS is present. This small amount disappears and the concentration goes to zero. After almost three pore volumes TMOS is once again present in the effluent and steadily increases.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Sw</th>
<th>permeability</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Initial saturation</td>
<td>Sw=1</td>
<td>1053</td>
<td>28</td>
</tr>
<tr>
<td>2 Primary drainage</td>
<td>Swi=0.25</td>
<td>467</td>
<td>78</td>
</tr>
<tr>
<td>3 Secondary imbibition</td>
<td>1-Sor = 0.63</td>
<td>139</td>
<td>2</td>
</tr>
<tr>
<td>4 Secondary drainage</td>
<td>Swi=0.26</td>
<td>567</td>
<td>112</td>
</tr>
<tr>
<td>5 TMOS placement (Q = 2 mL/min)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6 Postgelation oil injection</td>
<td>Sw=0?</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure B.4: differential pressure during TMOS placement and the concentration of TMOS measured in the effluent oil phase.
Experiment 25:

In this experiment the pump was replaced, leading to much more stable displacement than was realized in previous experiments. The flow rate is the same as in experiment 24 (2 mL/min) but displacement gives a better differential pressure curve over the entire trajectory. This can be seen clearly in Fig. B.5. Furthermore, the most complete record of TMOS concentration of the effluent oil phase is available through careful sampling. All stages described in chapter 6 are present, and can be recognized both in the differential pressure and the TMOS concentration behavior. Note that the concentration peak after 1 PV resembles the one observed in experiment 24. Oil permeability in this experiment is undamaged relative to oil permeability immediately prior to TMOS placement (Table B.5). In fact, it seems that the oil permeability has gone up with about 200 mD as a result of TMOS treatment.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Sw</th>
<th>permeability</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Initial saturation</td>
<td>Sw=1</td>
<td>1114</td>
<td>151</td>
</tr>
<tr>
<td>2 Primary drainage</td>
<td>Swi=0.25</td>
<td>528</td>
<td>92</td>
</tr>
<tr>
<td>3 Secondary imbibition</td>
<td>1-Sor = 0.62</td>
<td>153</td>
<td>4</td>
</tr>
<tr>
<td>4 Secondary drainage</td>
<td>Swi=0.22</td>
<td>596</td>
<td>102</td>
</tr>
<tr>
<td>5 TMOS placement (Q = 2 mL/min)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6 Postgelation oil injection</td>
<td>Sw=0?</td>
<td>789</td>
<td>26</td>
</tr>
</tbody>
</table>
 Experiment 26:
The final experiment is performed at a higher flow rate than the previous experiments. This has effects on the shape of the differential pressure curve (Fig. B.6). The maximum differential pressure is lowered, and the graph as a whole somewhat more spread out. The TMOS concentration profile clearly shows that the amount of TMOS initially present after 1 PV is close to the injected concentration (significantly higher than in the other experiments), and does not go lower than 6 mass percent during the decline.
As in experiment 25, the post treatment oil permeability is actually higher than the pretreatment permeability (Table B.6).
Table B.6: experimental procedure during experiment 26.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Sw</th>
<th>permeability</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Initial saturation</td>
<td>Sw=1</td>
<td>1173</td>
<td>136</td>
</tr>
<tr>
<td>2 Primary drainage</td>
<td>Swi=0.27</td>
<td>764</td>
<td>134</td>
</tr>
<tr>
<td>3 Secondary imbibition</td>
<td>1-Sor = 0.69</td>
<td>145</td>
<td>5</td>
</tr>
<tr>
<td>4 Secondary drainage</td>
<td>Swi=0.31</td>
<td>798</td>
<td>75</td>
</tr>
<tr>
<td>5 TMOS placement (Q = 5 mL/min)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6 Postgelation oil injection</td>
<td>Sw=0?</td>
<td>946</td>
<td>130</td>
</tr>
</tbody>
</table>

Experiments 22, 23 and 24 suffered from poor performance of the injection pump. Once the pump was replaced, the results clearly show the behavior also detailed in chapter 6: after an initial period of quiescence when the TMOS/oil mixture is placed in the core, mass transfer will pick up. This period of limited transfer is shown as an initial concentration peak in the effluent oil phase just after 1 pore volume has been injected (Figs. B.4-B.6). Once mass transfer begins, the concentration of TMOS in the effluent declines as more remains in the
core. Mass transfer causes an in-situ increase in water saturation as TMOS is added to the water phase. This in turn causes the differential pressure to increase. The volume of TMOS that can transfer to the water phase is finite, and reaches a maximum which is indicated by the minimum of TMOS present in the effluent oil phase. Once this volume is realized mass transfer slows down to ultimately cease. The maximum transfer coincides with a maximum in differential pressure.

Experiments 25 and 26 both show an increase in oil permeability after TMOS placement and gelation, which can indicate that the core was drained farther than irreducible water saturation during TMOS placement. This is possible, if the addition of TMOS (or its reaction products) to the water phase decreases the interfacial tension between water and oil.
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About the Author

Koenraad Elewaut was born in Gent, Belgium on December 26, 1977. Part of his elementary school was spent at ‘t Plankier in Zoetermeer, and the rest at the Sana’a International School, Yemen. Following elementary school he went to the athenaeum Alfrink College in Zoetermeer, which he once again interrupted to go abroad, this time to the USA, where he spent a year at Oakton high school in Oakton, Virginia. Having finished high school, he went to Utrecht to study geology in 1997. After specializing in sedimentology and basin analysis, he did his MSc thesis in Italy, at the earth sciences department of the University of Siena on the Neogene evolution of the Siena-Radicofani basin. He received his degree in geology in 2002, and started working on his PhD in Delft in the same year. The author is currently employed by Total E&P the Netherlands as a reservoir engineer/geologist.