University of Alberta

Laboratory Testing of Novel Sealant for Leaky Wells

Presented By

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ABSTRACT

Many abandoned gas wells in western Canada leak gas to the surface. This thesis presents the results of an experimental study to determine the possibility of using an asphalt-in-water emulsion as sealant for these abandoned leaky wells as a more efficient and cost-effective alternative to the conventional cement grout barrier. A second application of this process would be to hinder the water flow from water producing formations.

The asphalt-in-water emulsion used in the experiments had asphalt particles with an average particle size of around 4 μm and a 60 percent internal phase concentration. The emulsion exhibited a pseudo-plastic behaviour. Its viscosity ranged from 60 cp at a shear rate of 60 rpm to 145 cp at a shear rate of 6 rpm. The emulsion was found to be stable, even though it settled with time. Its original properties were retained after agitation and settling had occurred.

Core flow experiments were performed in order to simulate injection in the near-wellbore region. The cores were prepared using silica sand with a 60 to 80-mesh size. The resulting cores had a porosity range of 25 to 32 percent and a permeability range of 2.5 to 9 Darcy.

Experiments were performed under varying injection pressure conditions. In each case, solid plugs were formed and their length in the porous medium increased as a function of the injection pressure. In order to extend the length of the plugs, several anionic

surfactants were tested as preflush solutions for conditioning the surface of the sand grains. This resulted in increasing the emulsion penetration into the cores.

The basic mechanism of the process is to pressure up the emulsion next to a formation, forcing the emulsified asphalt to enter the porous medium and to form a flexible sealing plug. We surmise that the plug is formed through a combination of two pore blocking mechanism: one by blocking the pores by the larger-than-pore droplets, and the other by adsorbing onto the sand grain surfaces.

The experimental results have shown that the asphalt-in-water emulsion can be successfully used with to seal a gas or water producing formation. The study concludes with recommendations for field application and suggests ways for further research to improve the process.

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A	Total cross-sectional area
Ae	Effective cross-sectional area available to flow
C	Concentration
Co	Pore shape factor
F	Resistivity formation factor
I_r	Relative injectivity index
k	Permeability
p	Pressure
Q	Flow rate
R	Radius
r_H	Hydraulic radius
HLB	Hydrophile-Lipophile Balance
IPC	Internal Phase Concentration
ϕ_e	Effective porosity
γ	Shear rate
η	Apparent viscosity
σ	Surface tension
τ	Shear stress

CHAPTER 1

Introduction

Proper well abandonment is the final and critical step in the process of natural gas and oil recovery. Depleted oil and gas wells produce small non-economic amounts of gas, often the result of gas migration either through the cracks, fractures and voids in the formation along the outer wall of the casing, or between the original cement and the formation. The gas may escape to the atmosphere by flowing around the surface casing or migrate into shallow aquifers.

The current procedures for well abandonment involve placing a cement plug over the production zone and maintaining a column of water from the top of the plug to the surface. Sometimes, these procedures may not seal off all of the producing zones and remedial well abandonment treatments are needed. The Alberta Energy and Utilities Board indicates that there are more than 3000 orphan gas wells, many of which are leaking gas to surface. Companies report hundreds of leaking gas wells, some of which are "wells from hell". For example, two companies spent more than \$1.4 MM in their attempt to seal a leaking gas well, which continues to leak.

In order to improve the well abandonment technology, Seal-MastR Systems proposed an alternative method. Instead of plugging the well with a conventional cement grout barrier, a freestanding column of an asphaltene emulsion is injected into the well and pressurized. When the sealant solution is pressured up next to a formation, a certain amount of the emulsified asphalt is forced into the formation and forms a flexible seal, which can then support a fluid column, sealing the column through a hydrostatic head.

Another possible application of this process that places and fixes a sealant at a desired location in the formation is the shut-off of water breakthrough in producing oil and gas wells.

The objective of this study is to test this novel sealant technology proposed by Seal-MastR and to understand the effect of those parameters affecting the placement and fixing of an emulsion in the near well bore matrix, thereby hindering the flow of water or gas. To achieve this objective two types of experiments were designed. First, the

mechanism of the emulsion penetration into the porous matrix is studied making observations of the process in a transparent core holder. Second, the process is investigated using a steel core holder that allows injection of the emulsion at actual well pressures. The results show that the novel technology can be used with success for sealing abandoned gas leaking wells or water producing formations.

CHAPTER 2

Literature review

The proposed method of sealing a formation using an asphaltene emulsion has not been studied before. Yet, a lot of work has been done studying the flow of oil-in-water emulsions in porous media. Also, laboratory studies were conducted to determine if oil-in-water emulsions could act as a selective plugging agent, for example to improve oil recovery in waterfloods.

2.1 Emulsions

A number of books and articles have been written on the theoretical aspects of emulsions. Many systems have been studied, and large amounts of data have been collected. These will be reviewed, concentrating on those aspects and properties of the emulsions that apply to the particular emulsion that makes the object of this study.

An emulsion is a dispersion of one liquid (internal or dispersed phase) within another (external or continuous phase), in the presence of a third component: the surface-active agent or emulsifier. The emulsifier decreases the interfacial tension between liquids enabling the formation of a greatly extended interface, and stabilizing the interface against coalescence once it is formed.

The most common way to classify emulsions is to divide them in two large groups on the basis of the nature of the external phase, oil-in-water and water-in-oil. Each group is then divided in three classes based on the volume percentage of the internal phase concentration (IPC), low IPC <30%; medium IPC 30%-74%; high IPC >74%.

A second step in classifying emulsions is a function of the dispersed-phase dimension: coarse macroemulsions d>3 μm, fine macroemulsions d= 0.1-3 μm, microemulsions d=0.01-0.1 μm, micellar solutions d=0.003-0.01 μm, and molecular solutions d=0.001-0.003 μm.

2.1.1 Emulsification

Once the type of emulsion needed is chosen, the next step is to select the emulsifier that will produce a stable emulsion. Emulsion systems are formed and will be stable if sufficient emulsifying agent is present at the oil-water interface to form a film. One of the most widely used methods of selecting emulsifiers was initiated by Griffin in 1949 and is known as hydrophile-lipophile balance (HLB) method. It is based on the theory that emulsifying agents contain oil-soluble and water-soluble moieties and the balance between these two groups determine whether a particular surfactant would be soluble in either oil or water and the type of emulsion it might stabilize.

The HLB number indicates the polarity of the molecules in an arbitrary range of 1 to 40, with the most commonly used emulsifiers having a value between 1 and 20, as shown in Table 2.1. The HLB number increases with increasing hydrophilicity. According to the HLB number, surfactants may be utilized for different purposes.

The desired HLB numbers can also be achieved by mixing lipophilic and hydrophilic surfactants. The overall HLB value of a mixture is calculated as the sum of the fraction of individual HLB. A mixture of surfactants functions better than a single species because it provides a potentially greater variety of micelles which can adapt themselves to minor variations in the ingredients of the emulsion or to conditions to which the emulsion is subjected.

There are four major types of surfactants: anionic, cationic, amphoteric and nonionic. Because the flow of dispersed systems through porous media is modified by particle interactions with pore walls or pore throats, choosing the right type of surfactant is one of the most important aspects when one prepares an emulsion. This feature will be reviewed later in the thesis.

Some asphaltic crude oils contain enough natural emulsifiers to form oil-in-water emulsions by the addition of dilute solutions of alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, or lithium hydroxide. Seifert (1969) has shown that, in at least one asphaltic crude oil, the constituents producing the low interfacial tension necessary for emulsification are compounds of a predominant carboxylic acid type.

Because crude oils contain varying amounts of surface-active materials, varying amounts of caustic solution are needed to produce stable oil-in-water emulsions. Too little caustic does not sufficiently neutralize the organic acids to produce adequate emulsification, whereas too much sodium hydroxide produces a water-in-oil emulsion.

The last step before preparing an emulsion is to consider the factors that will determine the dispersed phase dimension. Pilehvari et al. (1988) have found that:

- At a given intensity of mixing, longer mixing times will result in smaller mean particle diameter. The decrease in droplet size with time of mixing will continue until it reaches an equilibrium particle size after which further mixing will not change the size or size distribution.
- For a given mixing time, a higher intensity of mixing results in a smaller droplet size.
- Higher concentration of emulsifier generally results in smaller droplet size. There is a maximum amount of emulsifier that would result in smaller droplet sizes; additional emulsifier would not change the droplet size.

2.1.2 Emulsion rheology

Relatively dilute emulsions at low shear rates behave essentially as Newtonian fluids. In more concentrated systems, dispersed particles frequently link together, forming temporary doublets and higher aggregates. Formation and decomposition of such aggregates are shear dependent, leading to non-Newtonian behaviour. Several classes of fluid viscous behaviour are illustrated in Fig 2.1.

The apparent viscosity is defined as:

$$\eta_a = \frac{shear\ stress}{shear\ rate} = \frac{\tau}{\gamma} \qquad (2.1)$$

The apparent viscosity is obtained from Fig. 2.1 by measuring the slope of a line drawn from the origin to a given point on one of the curves.

Most of the studies that have been carried out on oil-in-water emulsions were experimental in nature and the results are not as uniform and easy to interpret as might be expected.

Richardson (1958) correlated the data of emulsion viscosity as it varies with the concentration of disperse phase and obtained the equation:

$$m_e = m_{ex} exp(kC) \qquad (2.2)$$

Simon and Poynter (1968) found that, for oil-in-water emulsions, k = 7 up to a disperse phase concentration C = 75%, and k = 8 at higher concentrations.

Mao and Marsden (1977) studied emulsions prepared with a California waxy crude oil and reported that emulsions having IPC up to 50% behaved like Newtonian fluids, whereas emulsion with higher IPC behaved like non-Newtonian pseudoplastic fluids.

Steinborn and Flock (1983) found that emulsions of heavy crude oil follow the Richardson correlation when IPC is less than 20%. Their study also shows that the rheology of the emulsion might not always be determined by analogy with other oils and that emulsion rheology may vary between different oils and emulsifiers.

Pilehvari et al. (1988) studied the rheology of emulsions produced with four different heavy crude oils. They concluded that the rheological behaviour of emulsion is highly dependent on the oil droplet size. Reduction of droplet size can change the behaviour of the emulsion from Newtonian to a highly shear thinning fluid.

Khambharatana et al. (1998) performed experimental core floods for a system in which the drop sizes are comparable to the pore throat sizes. They concluded that the emulsion rheology during flow in a porous medium varies while the rheology in a viscometer is constant over the same range of shear rates. They suggested that the change of emulsion quality in the pores due to droplet capture causes this effect, while the emulsion quality remains the same throughout in a viscometer.

For oil-in water emulsions it can be concluded from this review that:

- Emulsions tend to have the viscosity of the continuous (external) phase.
- Emulsion viscosity increases with the fraction of the oil in the emulsion.

- Emulsion viscosity increases with decreasing temperature.
- At low IPC, emulsions behave like Newtonian fluids, whereas at high IPC emulsions behave like pseudoplastic fluids.
- Although two crude oils may have a similar viscosity, density and rheology, the rheological behaviour of their emulsions can be significantly different.
- Rheological behaviour of emulsions is highly dependent on the oil droplet size.

2.2 The plugging mechanism

McAuliffe (1973) was the first to explain the plugging mechanism of oil-in-water emulsions in porous media.

Let us consider a single droplet of oil emulsion entering a pore constriction smaller than itself, Figure 2.2. The droplet possesses a radius of curvature in the leading portion smaller than the radius of the portion of the drop still in the pore. Thus the capillary pressure is greater at the front of the drop than at the back, and pressure is required to force the droplet through. This effect can become appreciable as more and more emulsion droplets encounter pore constrictions. The pressure drop is expressed as:

$$\Delta p = 2\sigma(1/R_1 - 1/R_2) \tag{2.3}$$

If $p_1 - p_2 > \Delta p$, the droplet will move

For an emulsion to be most effective as a sealant, the droplets of oil in the emulsion should be slightly larger than the pore-throat constrictions in the porous medium. Emulsion droplets have a range of sizes, as do pore-throat constrictions in porous media. Thus, emulsification can make a relatively small volume of oil quite effective in restricting the flow, provided the pore-throat constrictions are not excessively large.

McAuliffe performed fluid-flow experiments in sandstone cores using diluted emulsions having 0.5% oil content and prepared from dilution with distilled water of high IPC emulsions, 60% or 70% oil content of various crude oils. He concluded that oil-in-water emulsions can effectively reduce the water permeability of sandstone cores, the reduction being more effective in high-permeability cores than in cores of lower permeability. The initial water permeability ranged from 395 to 1460 mD. In no case did he observe that emulsions completely plugged the porous medium. Fluid usually continued to flow at 1 to 10 percent of the initial water permeability.

McAuliffe also observed that the emulsion efficiency to reduce the fluid flow increases as the differential pressure decreases, which suggests that the emulsion will be more effective at some distance from the wellbore.

Soo and Radke (1984) observed in experiments using porous media micro models that, when droplets had a mean diameter that was large relative to the mean pore diameter, the main plugging mechanism is a straining mechanism. They also observed that droplets are not only captured in the pores with sizes smaller than their own, but also in crevices or pockets formed by the sand grains and, sometimes, on their surface. The aggregation of smaller droplets in a single pore throat has the same effect in blocking the pore throat as a large droplet would have.

Romero et al. (1996) performed laboratory experiments in consolidated and non-consolidated porous media to evaluate the plugging effectiveness of an oil-in-water emulsion. The emulsion employed in the study was obtained by diluting emulsion produced by activation of natural surfactants contained in the crude oil through the use of an alkaline solution. The effect of the emulsion on injectivity was expressed using the relative injectivity index I_r:

$$I_r = \frac{Q/\Delta P}{Q_i/\Delta P_i} \quad \text{or} \quad I_r = \frac{\Delta P_i}{\Delta P} \quad \text{for a constant injection rate} \qquad (2.4)$$

The study concluded that injection of the emulsion into consolidated, consolidated-fractured and non-consolidated porous media having a permeability range of 22 to 2615 mD produced a reduction of injectivity greater than 90%. The plugging mechanism was explained by a mechanical retention and coalescence of the crude oil drops found in the emulsion.

Khambharatana et al. (1998) performed a number of experimental core floods observing the physical mechanisms that occurred during stable emulsion flow in a porous medium. They concluded that, for systems of comparable drop and pore sizes, the emulsion droplets were found to be captured in a porous medium according to the filtration process proposed by Soo and Radke.

The overall conclusion is that the plugging mechanism is produced not only by the big droplets but also by the small droplets that adhere to the internal surface and/or to each other and tend to accumulate on these surfaces in small interstices and pockets of relatively stagnant flow. The droplet retention depends on droplet-surface interaction, droplet size distribution, droplet concentration, flow rate and morphology of the pore throat.

2.3 Wettability

As it was stated in the introduction, the scope of this study is to test the sealing quality of an asphaltene in water emulsion. This chapter will review some aspects regarding wettability and explain why an asphaltene in water emulsion was considered as the best candidate for sealing a porous formation.

The length of penetration of an emulsion into a porous medium is a strong factor of interactions between the fluid and the pore walls or pore throats.

The wettability is defined as the relative affinity of a liquid for a surface, as measured by the contact angle formed between the liquid and the surface. If the contact angle is zero, complete wettability occurs. If the contact angle is greater than 90 degrees, the condition is one of non-wettability. The contact angle is a function of the surface energies at the oil/water, oil/solid and water/solid interfaces. These surface energies, in turn, are dependent on the concentration of active species present at the interface.

Numerous studies have been conducted to determine the wettability of main reservoir rocks, how the mobile fluid interacts with the immobile porous medium and what are the important factors in wettability changes. Until now, the results arguments and conclusions seem to be highly dependent on the chemical nature of the individual oil/water/rock systems.

Kim et al. (1990), in their study on the role of asphaltene in wettability reversal, reported that asphaltene seemed substantial in altering the interfacial properties of oil/water systems.

Yan et al. (1997) reported that a significant change in wettability of sandstone resulted from asphaltene adsorption. They found that the brine composition was also an important factor in wettability changes induced by adsorption of asphaltene.

Liu and Buckley (1997) investigated the interaction that occurs after initial oil/solid contact. They found that adsorption of crude oil components onto dry glass surfaces was not strongly time dependent, while it was strongly time dependent on prewetted surfaces.

Skauge et al. (1995) characterized twelve crude oils derived from the North Sea with respect to asphaltene content, composition of saturates, resins and aromatics. Based on different acid and base content, three of the oils were subject to adhesion and contact angle experiments using the sessile drop technique on a quartz surface as a function of pH. The results showed more water-wet surface at higher acid number and more oil-wet behaviour at higher base number.

Zheng et al. (2000) studied the wetting behaviour of several systems containing a quartz surface, water, and a dense non-aqueous phase liquid (DNAPL).

Al-Maamari and Buckley (2003) demonstrated that ionic interaction and surface precipitation can contribute to the wetting alteration of mineral surfaces exposed to crude oil in the presence of water. Ionic interactions dominate in oil mixtures in which asphaltenes are in stable dispersion. Near the onset of asphaltene flocculation, a sharp transition to surface precipitation can occur, which produces more oil-wet conditions.

Hirasaki and Zhang (2004) investigated the important factors affecting enhanced recovery with alkaline surfactant solution. They found that the wettability of crude oil/brine on a calcite plate is a function of aging time, and that the degree of wettability alteration with alkaline surfactant systems ranged from preferentially water-wet to intermediate-wet and was a function of the prior aging temperature in crude oil.

2.4 The Novel Sealant

In the first phase of our experimental work, a bitumen-in-water emulsion was prepared and tested for sealing properties. Because of the large particle size of the oleic phase of this emulsion, it was decided to use a commercially-available asphaltene-in-water emulsion for this study. It will be explained in this chapter why this 60% asphaltene-in-water emulsion having a 4 μm average droplet size, was considered for sealing a porous medium.

Experimental observations have shown that the adsorption and entrapment of asphaltenes significantly decrease the accessible pore volume or even block it, when flowing crude oils or solutions having high asphaltene content through porous media.

Asphaltenes are heavy organic compounds which may exist in petroleum, heavy oil, tar sand and coal in different quantities. Asphaltene particles are believed to exist in petroleum partly dissolved and partly in steric-colloidal and/or micellar form, depending on the polarity of their oil medium and presence of other compounds in oil.

One of the best representations of the asphaltene micelle is that reported by Yen (1974). He suggest molecular weights of $1\text{-}5\times10^3$, a molecular formula of approximately $(C_{79}H_{92}N_2S_2O)_3$ and molecular shape as shown in Figure 2.3.

This structure would be formed by several flat, stacked condensed rings. Five of these rings, each containing from 8 to 16 condensed rings, could be placed at distances of 3.5 Å to 3.7 Å, and connected by systems of sulphide, ether, aliphatic chain and/or naphthene ring linkages. The condensed sheets may contain O, S and N atoms which may act as free radicals for anchor points of bound metals like Ni, V, Mo or Fe as well as polar and non-polar groups. The whole asphaltene complex would be 8 - 16 Å in diameter and 16 - 20 Å in height.

Due to their large size and their adsorption affinity to solid surfaces, asphaltenes are real candidates for sealing a porous medium.

Oils or solutions with high asphaltene content are very viscous fluids difficult to inject into porous formations. This problem can be overcome using an asphaltene-in-water emulsion knowing the fact that emulsions tend to have the viscosity of the continuous (external) phase.

The plugging mechanism of the asphaltene-in-water emulsion is produced not only by the big droplets but also by the small droplets that adhere to internal surfaces and/or to each other and tend to accumulate on these surfaces in small interstices and pockets of relatively stagnant flow.

If the plugging effect produced by the big droplets is mainly a mechanical retention process when it comes to the adherence of the small droplets to the internal surface, the wettability of the system must be considered.

Variability in the wetting properties of minerals exposed to asphaltenes is related to their composition. Most pristine subsurface systems are water wetting. This wettability is reversed following the adsorption of asphaltenes that essentially coat the mineral surface with an organic layer. When an asphaltene-in-water emulsion is injected into a water-wet porous medium, a double layer exists between the mineral and the asphaltene. The thin film of water that covers the mineral surface and the surfactant film that covers each emulsion droplet form this double layer.

For reversal of the wetting conditions, the insoluble, high molecular weight polar compounds in the asphaltenes must contact the mineral surface before adsorption can occur and the wettability can change. The destabilization of the layer between asphaltene and mineral interface occurs if the total surface force is attractive. The system will be oil wetting when the surface charges of the two interfaces are opposite or when the Van der Waals attractive forces are sufficient to overcome the electrostatic repulsion. Considering quartz, which has a negative charge above pH around 2, asphaltene that carry a positive charge should reverse the wettability.

Recent work has shown that beside the mineralogy of the porous medium, the pH of the system is another important factor that decides the wettability of a system. For example, quartz is oil wetting at low pHs and water wetting at high pH values for creosotes and coal tars. This aspect was considered in our work when deciding which preflush solution should be used for a better penetration of the emulsion into the porous medium.

As it was stated in Chapter 1, for an emulsion to be most effective as a sealant, the droplets of oil in the emulsion should be slightly larger than the pore-throat constrictions in the porous medium. It would be ideal to prepare an emulsion with a given droplet size for each porous medium that is to be plugged, but this is unfeasible from an economical point of view.

An upper limit to the diameter of a particle that can pass freely through a porous rock is roughly defined by the hydraulic radius of the rock. The hydraulic radius is commonly several times smaller than an average pore diameter.

The hydraulic radius can be defined by:

$$r_H^2 = C_o\left(\frac{L_e}{L}\right)^2\left(\frac{A}{A_e}\right)k \qquad (2.5)$$

where

C_o = the pore shape factor (~ 2.5)

L_e/L = tortuosity

The formation resistivity factor is given by

$$F = \frac{L_e A}{L A_e} \qquad (2.6)$$

and

$$\frac{A_e}{A} = \phi_e^{\lambda} \qquad (2.7)$$

where ϕ_e is the effective porosity and $\lambda \approx 1.3$ for the range of porosities usually found in reservoir rocks. Combining the above three equations and taking the square root of both sides:

$$r_H = 1.58F\phi_e^{0.65}k^{1/2} \qquad (2.8)$$

The value of F for a typical sandstone is given approximately by the following special case of Archie's law:

$$F = 0.84\phi_e^{-2} \qquad (2.9)$$

Combining the last two equations yields

$$r_H = \frac{1.33}{\phi_e^{1.35}}k^{1/2} \qquad (2.10)$$

For a typical sandstone having k = 100 mD and ϕ_e = 0.22, the hydraulic radius is found to be 3.2 μm.

The pore throat diameter d_n for a sand pack can be approximated using the model proposed by Chauveteau et al. (1996).

$$d_n = 2 \cdot C \cdot \sqrt{\frac{8 \cdot k}{\phi}} \tag{2.11}$$

where C= 1.15 for granular packs

Beside the above-mentioned facts, the availability and the proved good stability made the commercial asphaltene-in-water emulsion the ideal candidate for our proposed research.

Table 2.1: HLB Range

Function	HLB Range
Antifoaming agent	1 to 3
Emulsifier, water-in-oil	3 to 6
Wetting agent	7 to 9
Emulsifier, oil-in-water	8 to 18
Detergent	13 to 15
Solubilizer	15 to 20

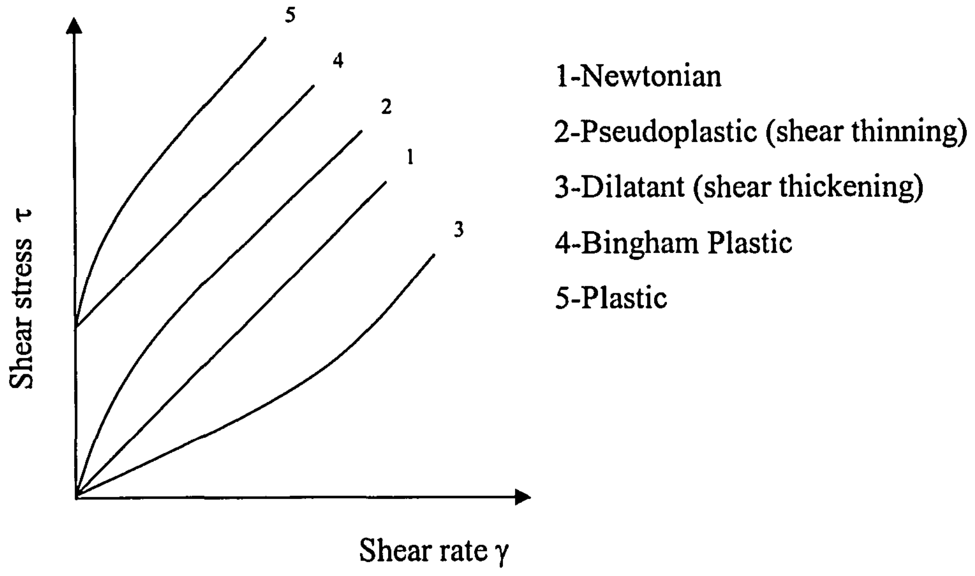


Figure 2.1: Types of fluid viscous behaviours

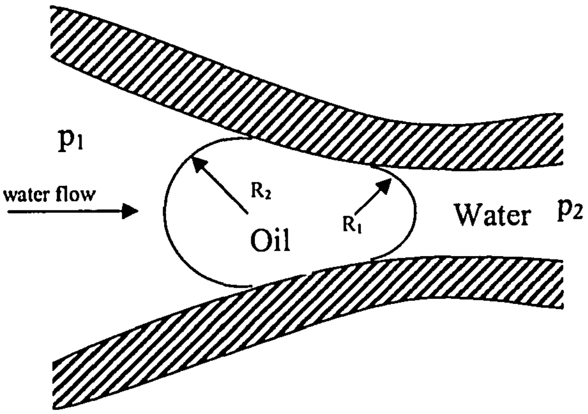
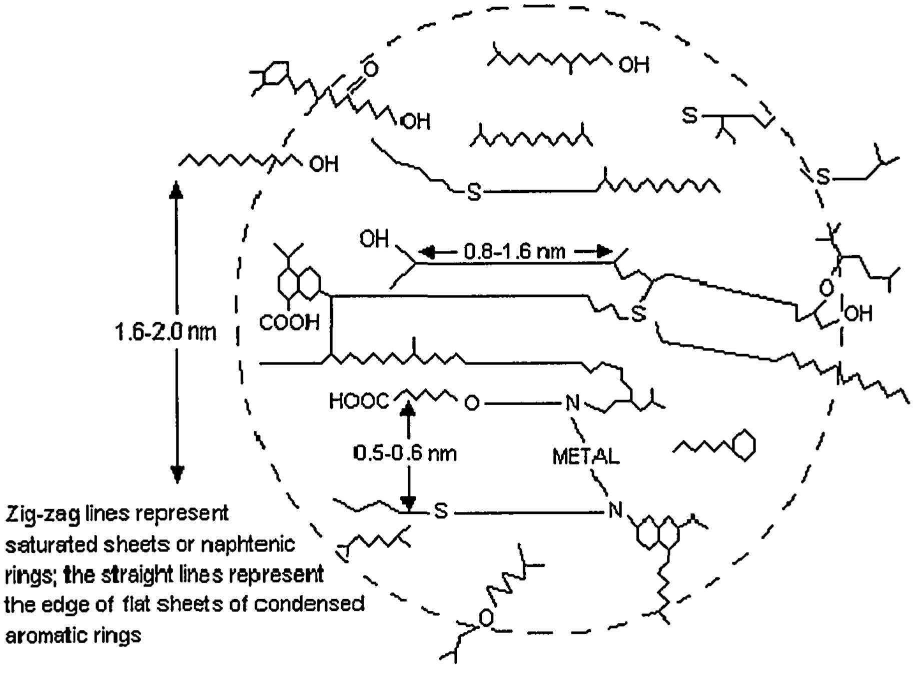


Figure 2.2: Plugging mechanism



Zig-zag lines represent saturated sheets or naphtenic rings; the straight lines represent the edge of flat sheets of condensed aromatic rings

Figure 2.3: Asphaltene molecular shape, as proposed by Yen (1974)

CHAPTER 3

Bitumen-in-water emulsion

3.1 Emulsion preparation

We performed the first experiments with a bitumen-in-water emulsion prepared in our lab. This emulsion was prepared employing one of the most frequently used techniques for obtaining medium phase ratio emulsions. The surfactant was dissolved in the external phase, water, and placed in the bowl of a Brinkmann homogenizer. The mixing was started and the internal phase, bitumen, preheated to 70^0 C, was added in small increments under continuous mixing.

Small batches of bitumen-in-water emulsions were prepared using three different surfactants: Dowfax 2A1, Dowfax 2A1 D and Dowfax 8390-D. Properties of the surfactants are presented in Table 3.1. Three different concentrations, 1%, 1.5% and 2% of the total volume were used with each surfactant. The Brinkmann homogenizer was set to provide the same energy for the same mixing time of 10 minutes in all cases. In every case, an emulsion with 60% internal phase concentration was obtained.

3.2 Emulsion viscosity

The apparent viscosity of the prepared emulsions was measured with a Brookfield dial viscometer, using variable shear rates ranging from 6 to 60 RPM. The results are presented in Table 3.2 and Figure 3.1.

With Dowfax 2A1 D, the emulsion behaviour was pseudo-plastic as the apparent viscosity increased with decreasing shear rate. Also, the apparent viscosity showed the same pseudo-plastic behaviour with a higher concentration of surfactant at all shear rates, but with increased viscosity values.

The emulsions prepared with Dowfax 2A1 and Dowfax 8390-D showed an interesting behaviour. At concentrations of 1% of total volume, the behaviour was

Newtonian (same apparent viscosity at all shear rates). At higher concentrations, the behaviour became pseudo-plastic as can be seen in the Figure 3.1 for both the Dowfax 2A1 and Dowfax 8390-D surfactants.

The increase of viscosity with the addition of surfactant could be explained by the fact that, within the concentration range considered, a larger amount of surfactant produced an emulsion with smaller droplets.

3.3 Particle size distribution

In order to understand the effect of surfactant concentration on viscosity presented earlier, a Mastersizer 2000 was used to determine the particle size distribution of the emulsions. This was initially done for two emulsion samples prepared with Dowfax 2A1 (1% and 2%). The results showed that a higher surfactant concentration produced a smaller mean droplet size of the bitumen in the bitumen-in-water emulsion. The volume weighted mean sizes were 26 μm and 23 μm, respectively.

3.4 Summary and Conclusions

The behaviour for the bitumen-in-water emulsion prepared in our lab was pseudo-plastic or Newtonian, a function of the surfactant type and concentration used. Increased apparent viscosity values were associated with a higher surfactant concentration as can be seen in the Table 3.2 and Figure 3.1.

The results of the particle size distribution analyses showed that a higher surfactant concentration produced a smaller mean droplet size of the bitumen in the oil-in-water emulsion. The droplet size was also found to be function of the mixing time.

The emulsion samples showed poor stability. After three weeks, a coalescence phenomenon could be observed followed by accelerated settling. The poor stability could be explained by the relatively large value of the droplets size and by the fact that only one surfactant, instead of a mixture of surfactants, was used for preparing the emulsion..

We originally wanted to have a bitumen particle size in the 3 to 6 μm range. The results indicated that the particle size obtained for our emulsions was out of the proposed range. This meant that a higher energy input and a longer mixing time were necessary to prepare the desired emulsion. We therefore put our efforts into a commercially available asphaltic emulsion for future work.

Table 3.1: Surfactants properties

Property	Dowfax 2A1	Dowfax 2A1-D	Dowfax 8390-D
Chemical name	Sodium sulfate	Sodium sulfate	Sodium sulfate
Appearance	Light yellow to light brown liquid	White powder	Tan powder
Solubility in water	Completely miscible	N/A	N/A
Specific gravity at 25^0 C	1.12 – 1.16	< 0.7	< 0.7
Viscosity at 25^0 C (cp)	145	N/A	N/A

Composition

Dowfax 2A1

Benzene, 1,1-oxybis, tetrapropylene derivatives, sulfonated, sodium salts	47% Max
Sodium sulfate	1% Max
Sodium chloride	<1%
Water	Balance

Dowfax 2A1-D

Benzene, 1,1-oxybis, tetrapropylene derivatives, sulfonated, sodium salts	99% Max
Sodium chloride	2% Max
Sodium sulfate	3% Max

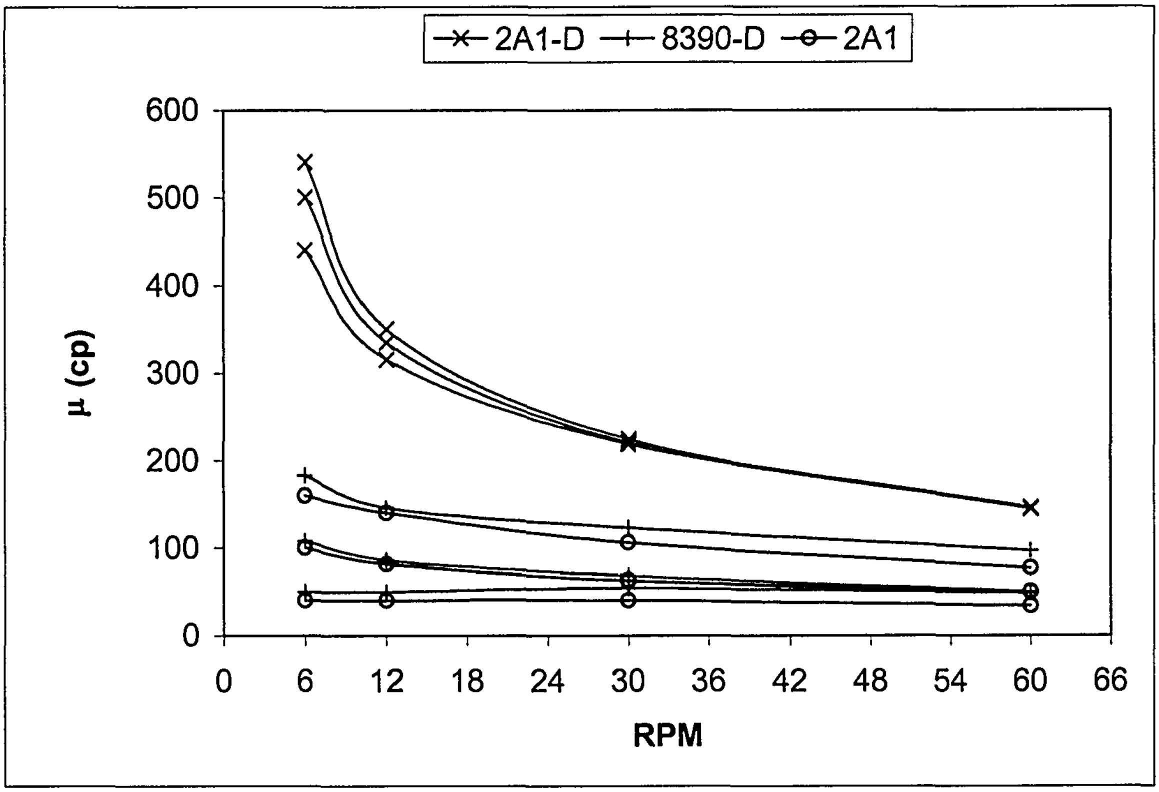
Dowfax 8390-D

Hexadecyl (sulfophenoxy) benzene sulfonic acid, disodium salt	99% Max
Sodium sulfate	3% Max
Sodium chloride	2% Max

Table 3.2: Apparent Viscosity of Bituminous Emulsions using Different Surfactants

surfactant type and concentration	viscosity @ 6 RPM (cp)	viscosity @ 12 RPM (cp)	viscosity @ 30 RPM (cp)	viscosity @ 60 RPM (cp)
Dowfax 2A1 D, 1%	440	315	218	144
Dowfax 2A1 D, 1.5%	500	335	220	144
Dowfax 2A1 D, 2%	540	350	224	146
Dowfax 8390-D, 1%	50	50	54	49
Dowfax 8390-D, 1.5%	108	86	68	50
Dowfax 8390-D, 2%	183	146	123	97
Dowfax 2A1, 1%	40	40	40	34
Dowfax 2A1, 1.5%	100	82	63	50
Dowfax 2A1, 2%	160	140	106	77

Figure 3.1: Bitumen-in-water emulsion apparent viscosities



CHAPTER 4

Visual experiments

To achieve a better understanding of the emulsion injectivity into a porous medium, visual experiments were performed in a transparent core holder

4.1 Model construction

The core holder tube was built from a transparent PVC tube 2 in ID and 6 in length with exterior threads at both ends. The lids were built from the same transparent material with interior threads for attaching to the core holder tube. Two holes were drilled in each lid, one axial and one lateral. Fittings were screwed in the holes for connecting to the tubing and pressure gages. An o-ring was installed on the bottom of each lid to create a seal. A place for a metal porous disk was machined on the inside of each lid. The fritted porous disks allowed the passage of particles less than 50 μm. Their role was to keep the sand inside the core holder during the packing process and to disperse the emulsion that entered the sand pack.

The porous medium was prepared using sand having 60-80 mesh size. A "water hat" tube was attached to the core holder and filled with water. Sand was poured into the core holder until it reached a height of 4-5 cm above the core holder edge. A vibrator was attached to the core holder and let to vibrate for 16 hours. The water was drained, the "water hat" tube removed and the upper lid attached to the core holder tube. The packing procedure is shown in Figure 4.1 and a picture of the transparent core holder is shown in Figure 4.2

4.2 Experimental set-up

The experimental set-up is presented in Figure 4.3. The transparent core holder was placed on a stand in a horizontal position. Transparent tubing lines were connected to the fittings to enable the injection of emulsion and to collect the water produced. A positive displacement pump set to deliver 1120 cm^3/h was used for fluid injection. The pump could not be set to deliver at a certain pressure and a safety valve was placed at the pump outlet. As the maximum allowable pressure for the core tube and tubing was 200 psi, the safety valve was set to 175 psi. The safety valve stayed opened as long as the pressure was below that value. Once the critical pressure was reached, the valve closed and the water was diverted to the drain. The valve opened again when the pressure decreased below the safe value. A transfer vessel was used for feeding the emulsion to the transparent core holder.

4.3 Experimental procedure

Once the packing process was finished, the water was drained out from the core and the core holder was placed in an oven for 8 hours. After the water evaporated, leaving the sand completely dry, the core was flushed with several pores volumes of carbon dioxide to remove the air. The positive displacement pump was used to inject several pore volumes of distilled water that displaced or dissolved the CO_2. The core holder was placed in a vertical position and the produced water collected. The collected water was measured and the pores volume of the core was calculated to be 31%.

Two pressure transducers were connected to the lateral fittings and distilled water was flowed through the core at a constant rate using the pump. The pressure drop was measured and the permeability was calculated using Darcy's law.

The above procedure was performed before each experiment and the permeability of the sand packs was found to be between 8.3 and 8.6 Darcy.

Three visual experiments were conducted with the above setup, one using a prepared bitumen-in-water emulsion and two using a commercially available asphalt-in-water emulsion. All experiments were conducted at room temperature and low pressure (200 psi maximum) because of the type of core used.

4.3.1 Injection of bitumen-in-water emulsion (core 1)

In the first experiment, the injection fluid was a bitumen-in-water emulsion containing 60% bitumen prepared with a 1% aqueous solution of Dowfax 2A1. The volume weighted mean size of the emulsion particles was 26 µm. The emulsion with the lowest viscosity was used for better injectivity. The apparent viscosity showed an almost Newtonian behaviour as indicated in Table 3.2.

Injection was started at 1120 cm^3/h. The pressure reached 175 psi (the safety valve pressure) after 10 minutes. For the next 4 hours, the produced water rate dropped from 1 drop/5 seconds to 1 drop/17 seconds. After 2 hours, the emulsion had penetrated 3.8 cm into the core. At the end of the experiment (4 hours) the emulsion had advanced 5.4 cm.

The next day, 16 hours later, the emulsion was found deposited on the bottom of the core tube, except for the first 3 cm at the entrance that looked like a solid plug. A reverse water flow was attempted with no success. The water moved through at a rate of 1 drop/50 seconds. When the core tube was emptied, one week after the experiment, a solid plug 3 cm long was found at the entrance (Figure 4.4).

4.3.2 Injection of asphalt-in-water emulsion without surfactant preflush (core 2)

One barrel of commercially available asphalt-in-water emulsion was obtained. The particle size of the asphalt particles of this emulsion was measured using two different samples. Sample 1 was taken from the barrel the day the emulsion was received and kept in a plastic vial. Sample 2 was taken from the barrel the day of the measurement, 14 days after the shipment was received. The barrel was rotated few times before taking sample 2. A sedimentation phenomenon was observed in sample 1, but after 1 minute of shaking, the emulsion regained its initial appearance.

The analysis report showed a weighted mean size of 4.83 μm for sample 1 and of 3.99 μm for sample 2. Considering the error associated with the measurements it was accepted that the particle size distribution of the two samples was the same. The particle size distribution graph showed an interesting composition (2 peaks) for both samples. The second peak indicated a much smaller particle size around 0.2-0.3 μm. The supplier explained that the 2-peak distribution was the result of excess surfactant in the emulsion. The results are shown in Figures 4.5 and 4.6, respectively.

The apparent viscosity of the emulsion was measured at different shear rates. The emulsion showed a pseudo-plastic behaviour, as shown below:

viscosity @ 6 RPM (cp)	viscosity @ 12 RPM (cp)	viscosity @ 30 RPM (cp)	viscosity @ 60 RPM (cp)
145	106	74	60

The same experimental procedure as in the case of the bitumen-in-water emulsion was used for the injection of the asphalt-in-water emulsion.

The injection was started at 1120 cm^3/h. The pressure reached the safety valve pressure of 175 psi at the beginning. For the next $4^{1/2}$ hours, the production rate dropped from 1 drop/10 seconds to 1 drop/27 seconds. The plug advanced 4 mm into the core. The experiment was paused for 16 hours until the next day. Because the pressure was not bled off the system at the end of the first day, the plug was found to have penetrated 8 mm into the core after the 16-hour break. Also a brown fluid (water resulting from the broken emulsion) was found deposited onto the bottom of the core. This is shown in Figure 4.7.

When the injection was restarted, the maximum pressure of 175 psi was reached again at the beginning. For the next $4^{1/2}$ hours, the production rate dropped from 1 drop/30 seconds to 1 drop/2 minutes. The plug advanced 1.7 cm into the core. After 24 hours, a reverse water flow was attempted. The core tube started leaking at the threaded connection. When the core tube was emptied, one week from the end of experiment, a solid plug 2.5 cm long was found at the entrance (Figure 4.8).

4.3.3 Injection of asphalt-in-water emulsion with surfactant preflush (core 3)

The transparent core tube was repaired and the same conditions as above were used for the emulsion injection. Prior to the emulsion injection, the sand core was preflushed with 5 pores volume of an aqueous solution of Dowfax 2A1 having a 2% concentration.

Five minutes after the injection started, a brown liquid, which looked like water from the emulsion, advanced 2.5 cm into the core. Then, the safety valve pressure was reached and the flow rate dropped to 1 drop/8 seconds. At the end of the day, after $4^{1/2}$ hours of injection, the flow rate was 1 drop/40 seconds and the plug had advanced 4 cm into the core, as shown in Figure 4.9. The pressure was not bled off.

After an overnight 16-hours break, the plug had entered 4.8 cm into the core. The injection was restarted, and the system was maintained under pressure (175 psi) for 2 hours without obtaining flow or a visible advance of the plug. Again the pressure was not bled off. After another 21 hours break, the plug was found to be 5.5 cm into the core. The core tube broke when the pressure was restored to 175 psi. The core tube was emptied and a solid plug 5.5 cm long was found at the entrance. The core holder at the end of the experiment is shown in Figure 4.10

4.4 Results of experiments

The purpose of these experiments was to visually observe the advance of bitumen-in-water and asphalt-in-water emulsions in a transparent core filled with wet sand. A reverse water flow was not performed for these experiments in order to test the strength of the plugs that formed as a result of the emulsion injection.

At the end of each experiment, the plugs were carefully removed from the core. The hardness of the plugs was determined using a Standard Asphalt Penetrometer. The penetration test measures the depth of penetration, in tenths of millimeters that a weighted needle achieves after a known time at a known temperature. The most common combination was used: 100 grams applied for 5 seconds at a temperature of 25°C. Three measurements in three different places were done on both the front (fluid injection) and the side of the plugs. The results are presented in Table 4.1. In comparison, typical values are approximately 10 for hard coating grade asphalts, 15 to 40 for roofing asphalts, and up to 100 or more for certain waterproofing materials.

4.5 Analyses and Discussion

Under the same flow rate and pressure conditions, the thickest plug was obtained when the asphalt-in-water emulsion was injected following a surfactant pre-flush. The thinnest plug was obtained in the case of the asphalt-in-water emulsion injection without a surfactant pre-flush.

The visual analyses of the plugs showed that the bitumen-in-water emulsion formed a plug with a high porosity while the appearance of the plug formed by the asphalt-in-water emulsion was much more compact. Also, the plug formed by the asphalt-in-water emulsion without surfactant pre-flush looked more compact than the one formed when the emulsion was injected after pre-flush. These observations were confirmed by the penetration test that showed that the plug formed with the asphalt-in-water emulsion without surfactant pre-flush was the hardest (smallest depth of penetration), and the one formed by the bitumen-in-water emulsion was the weakest (Table 4.1).

We could not measure the pore size of the packed sand, but from empirical correlations for sand with a grain size distribution of 180-250 μm (60-80 mesh), the pore size was estimated to be in the range of 40-60 μm. The adsorption and accumulation of the emulsion droplets onto the internal surface and/or to each other seemed to be the main blocking mechanism in our case and not the pore blocking effect produced by a droplet larger than the pore. This could explain why the asphalt-in-water emulsion with an average droplet size of 4.4 μm produced a better plug than the bitumen-in-water emulsion whose average droplet size was much larger, 26 μm.

Modifying the wettability of the porous matrix using a surfactant pre-flush seems to be the key for a good penetration of the emulsion into the porous medium. When the core was pre-flushed with a surfactant solution, a 4 cm long plug was achieved in $4^{1/2}$ hours of injection, while, without pre-flush, the plug length was only 2.5 cm after 9 hours of injection. Also, the different penetration length of the emulsion in the case of no pre-flush (4 mm the first day and 1.7 cm the following day) might be also the result of the "pre-flush process". During the first day, the oil micelles were trapped into the pores while the water advanced into the core. The water could not be visualized on first day due to its small quantity and high dispersion, but it could be seen to have deposited onto the bottom of the core on the second day. This water, which contained residues of oil and dissolved surfactant, had a pre-flush effect for the emulsion injected during the second day.

Table 4.1: Penetration test results

Plug formed by:	Length (cm)	frontal penetration (10^{-1} mm)				side penetration (10^{-1} mm)			
		1	2	3	Average	1	2	3	Average
Bitumen-in-water emulsion	3	78	81	84	81.00	76	75	72	74.33
Asphalt-in-water emulsion without surfactant pre-flush	2.5	17	20	18	18.33	12	9	10	10.33
Asphalt-in-water emulsion with surfactant pre-flush	5.5	30	40	35	35.00	24	20	24	22.67

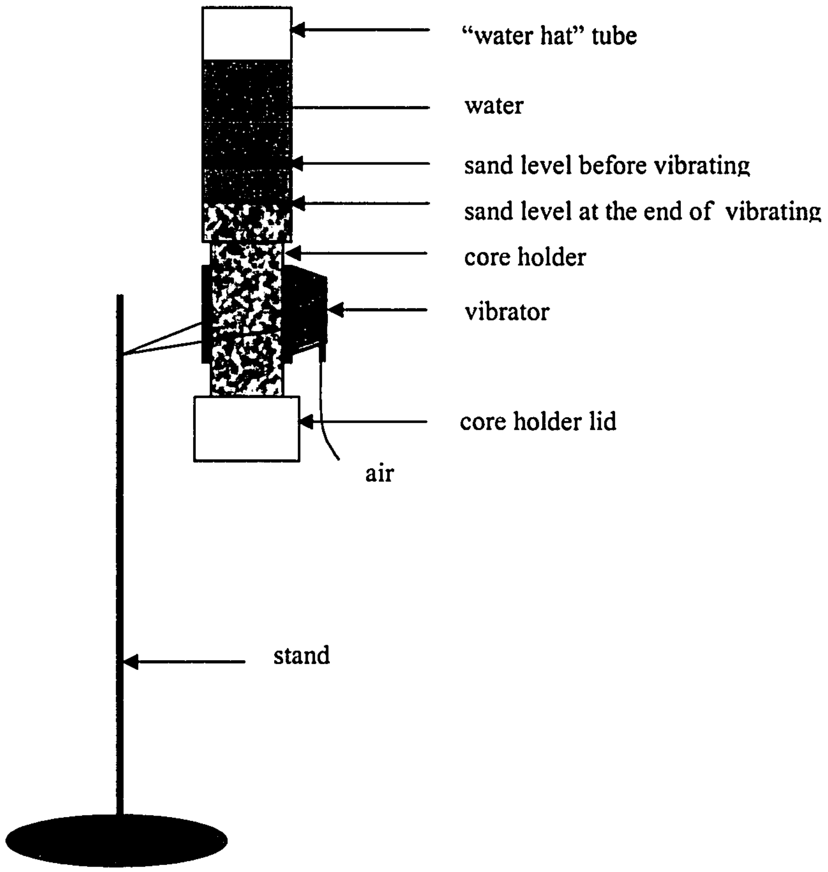


Figure 4.1: Sand packing procedure

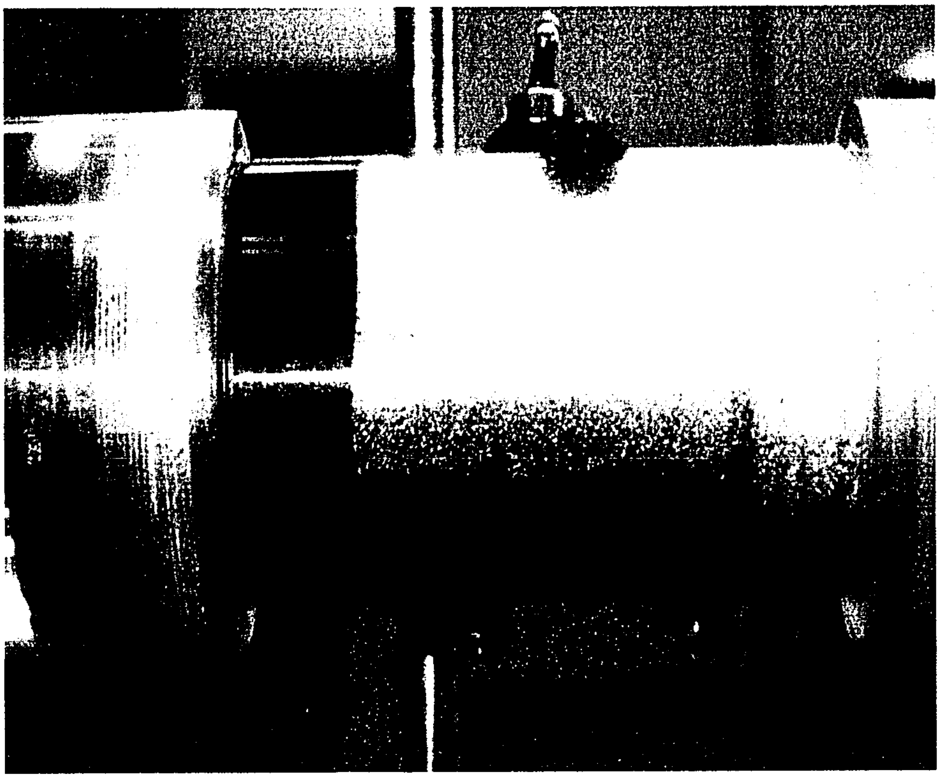


Figure 4.2: Transparent core holder

1 – Positive displacement pump
2 – Safety valve
3 – Transfer vessel
4 – Tubing
5 – Transparent core holder
6 – Stand
7 – Beaker
8 – Drain
9 – Pressure transducer

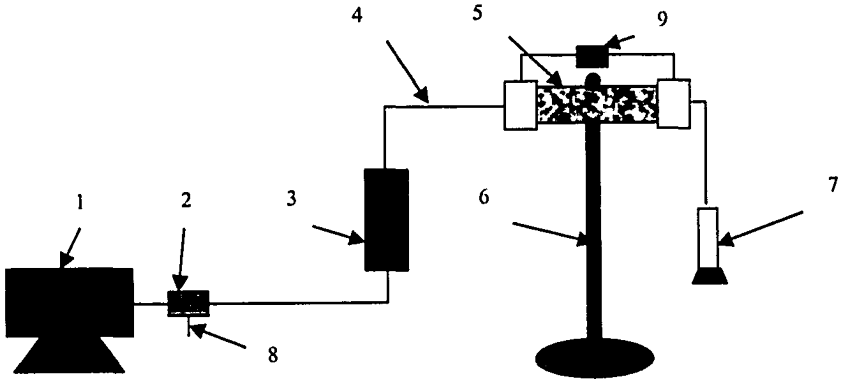


Figure 4.3: Experimental set-up

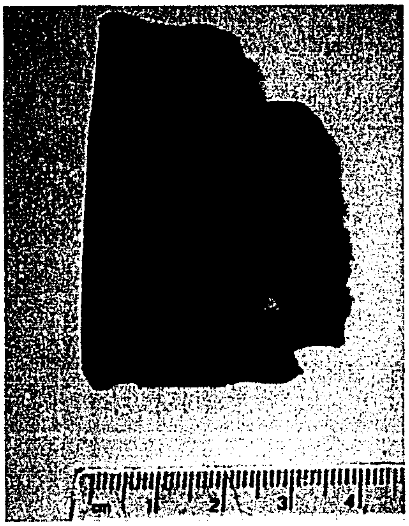
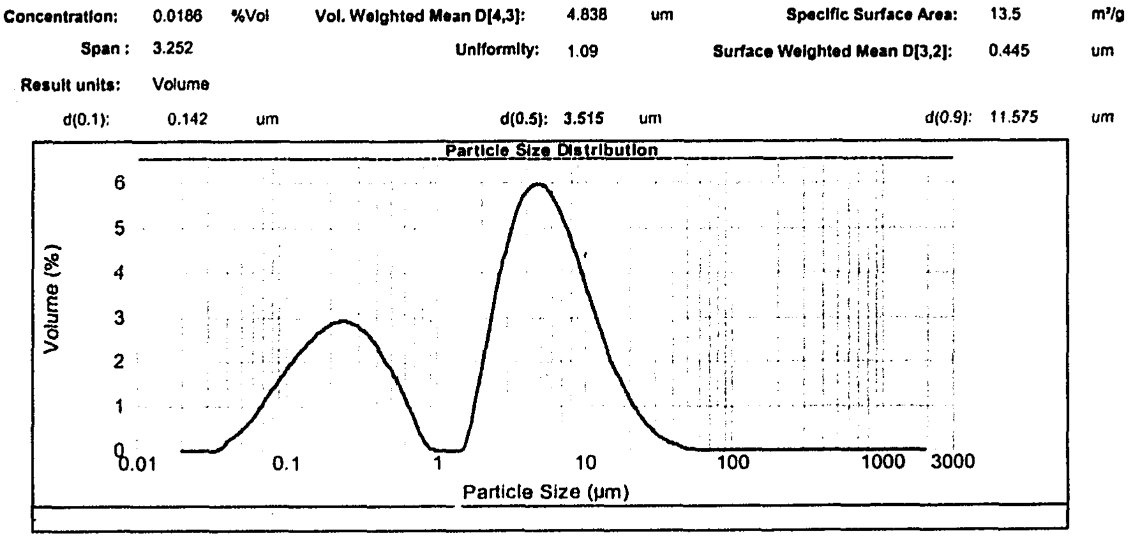
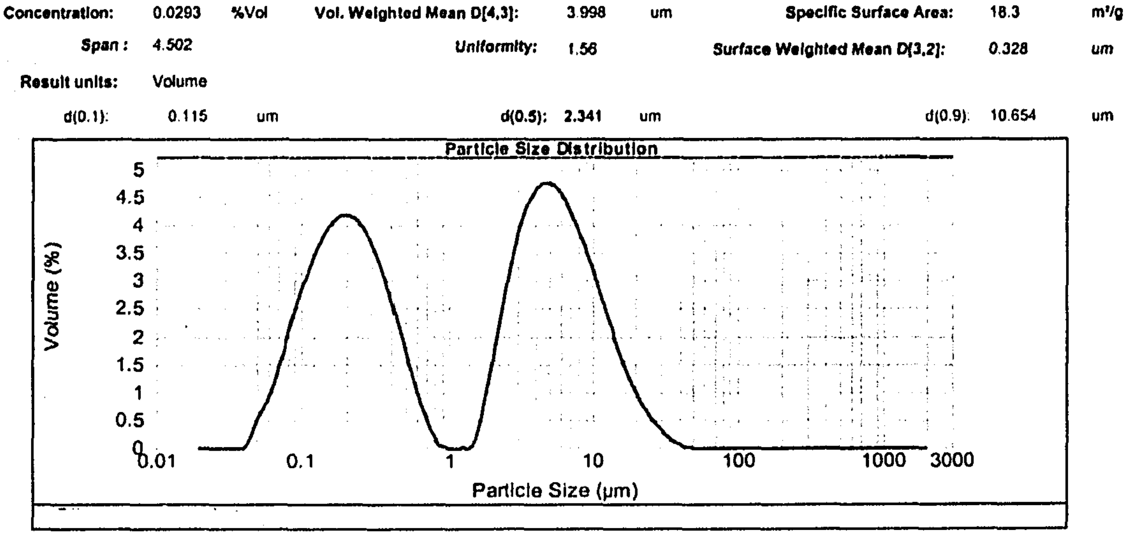


Figure 4.4: Plug formed by bitumen-in-water injection



Concentration:	0.0186	%Vol	Vol. Weighted Mean D[4,3]:	4.838	um	Specific Surface Area:	13.5	m^2/g
Span :	3.252		Uniformity:	1.09		Surface Weighted Mean D[3,2]:	0.445	um
Result units:	Volume							
d(0.1):	0.142	um	d(0.5):	3.515	um	d(0.9):	11.575	um

Figure 4.5: Particle size distribution of sample 1



Concentration:	0.0293	%Vol	Vol. Weighted Mean D[4,3]:	3.998	um	Specific Surface Area:	18.3	m^2/g
Span :	4.502		Uniformity:	1.56		Surface Weighted Mean D[3,2]:	0.328	um
Result units:	Volume							
d(0.1):	0.115	um	d(0.5):	2.341	um	d(0.9):	10.654	um

Figure 4.6: Particle size distribution of sample 2

after $4^{1/2}$ hours of injection

after 16 hours break

Figure 4.7: Visual observation of asphalt-in-water emulsion plug advance into core 2

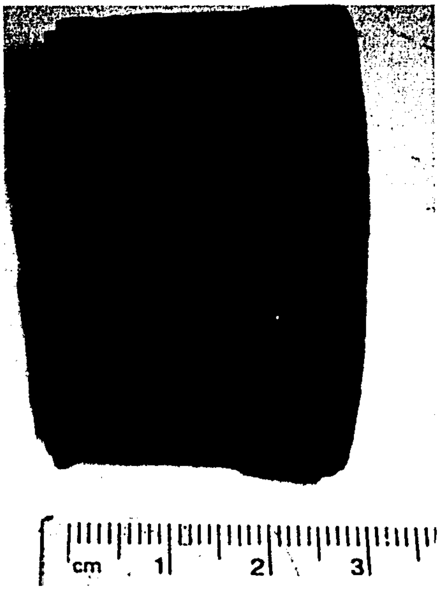
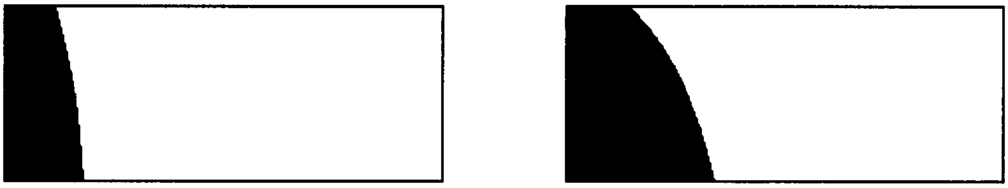
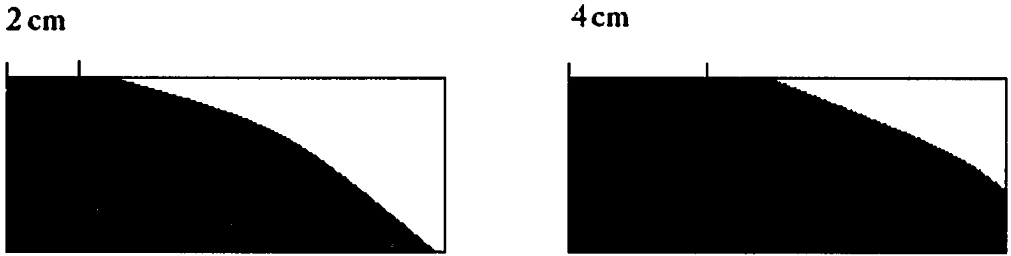


Figure 4.8: Plug formed by asphalt-in-water injection, no preflush



after 5 minutes of injection

after 20 minutes of injection,
the emulsion entered 2-3 mm



after $1^{1/2}$ hours of injection

after $4^{1/2}$ hours of injection

Figure 4.9: Visual observation of asphalt-in-water emulsion plug advance into core 3

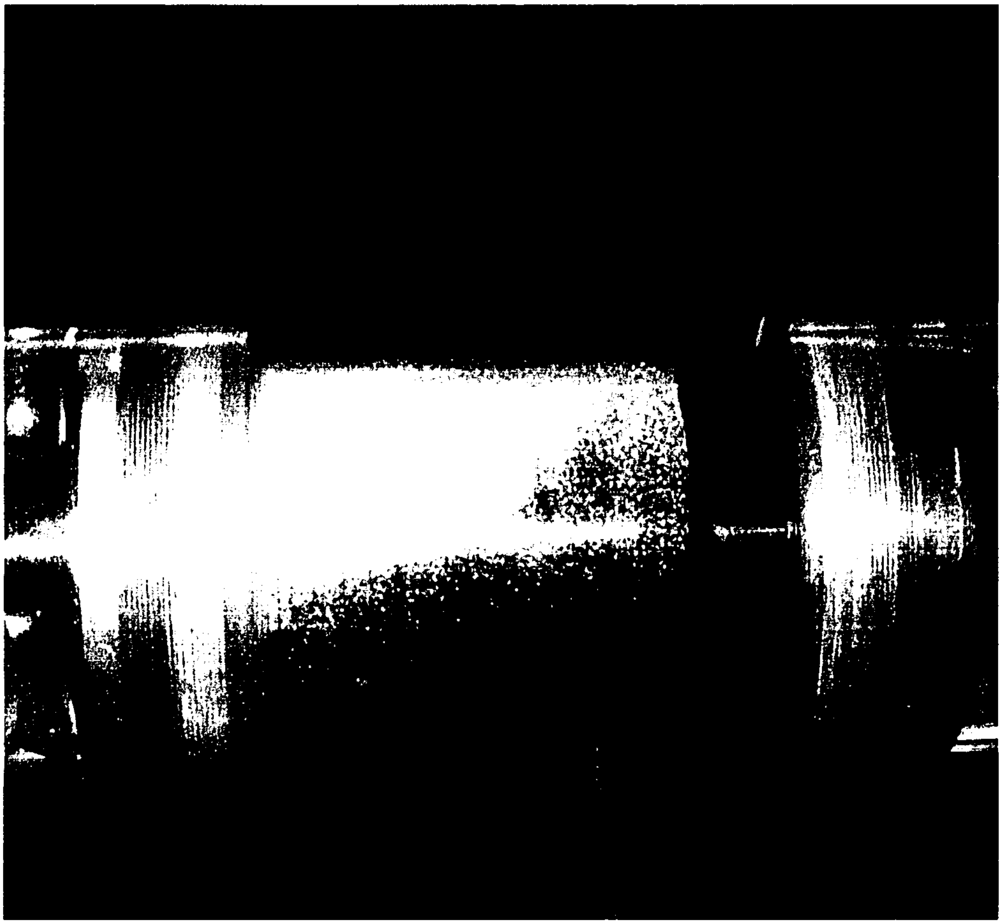


Figure 4.10: Core 3. Injection of asphalt-in-water emulsion with surfactant preflush

CHAPTER 5

High-pressure experiments

5.1 Model construction

The new core holder tube was built from stainless steel tubing, 1.5 in ID and 12 in length, with flanges welded at both ends. The lids were built from blind flanges and attached to the core holder with stud-bolts. An axial hole was drilled in each lid and a fitting was screwed in. On the inside face of the lid, a groove was machined for a rubber o-ring seal and a place for a porous fritted disk. The porous disks allowed the passage for particle less than 50 μm and their role was to keep the sand inside the core holder during the packing process and to disperse the emulsion during the injection. Pressure transducers were attached to the four pressure ports drilled along the core holder tube allowing us to measure the packed sand permeability and monitor the pressure during the emulsion injection.

The porous medium was prepared using 60-80 sand mesh and the same packing technique used for the transparent core holder was employed. A picture of the core holder during the packing process is shown in Figure 5.1

5.2 Experimental set-up

The core holder was placed on a stand in the horizontal position. Stainless steel tubing lines were connected to the core holder to enable the emulsion injection and to collect the produced water. Two transfer vessels were used for feeding the emulsion and the surfactant solution preflush to the core holder, as shown in Figure 5.2. A positive displacement pump, set to deliver 1120 cm^3/h, was used. The pressure transducers were connected to the carrier demodulator to record the pressure profile along the core. A picture of the core holder during the emulsion injection is shown in Figure 5.3.

5.3 Experimental procedure

Once the packing process was finished, the water was drained out from the core and the core holder was placed in the oven for 8 hours. After the water evaporated leaving the sand completely dry, the core was flushed with several pore volumes of carbon dioxide to remove the air. The pump was used to inject several pore volumes of distilled water that displaced or dissolved the CO_2. The core holder was placed in a vertical position and the produced water collected. The collected water was measured and the porosity of the core was calculated to be 31%.

Two pressure transducers were connected to the first and forth pressure ports and distilled water was injected through the core at a constant rate. The pressure drop was measured and the permeability was calculated using Darcy's law. The permeability was found to be between 8.3 and 8.6 Darcy.

The emulsion was injected at a rate of 1120 cm^3/h. The pressure gauge at the pump outlet was monitored during the experiment. When the pressure reached the desired maximum pressure, the pump was stopped and the time recorded. When the pressure decreased by 100 - 200 psi, the time was again recorded and flow restored until the pressure increased back to the maximum. The emulsion was injected for 8 hours, 4 hours first day and 4 hours the second day. The produced water was collected and measured.

Nine experiments were conducted with the above setup using asphalt-in-water emulsion. In two cases, the core was preflushed with a surfactant solution before injecting the emulsion. All experiments were conducted at the room temperature.

5.3.1 Experiment 1 – 900 psi, without surfactant preflush

The emulsion was injected for 8 hours at a pressure between 700 and 900 psi. The maximum pressure, 900 psi, was reached 2 minutes after the injection started. We intended to measure the pressure drop along the core to find a relationship between the advance of the emulsion into the core and the pressure (find where the emulsion front is as a function of pressure). This could not be possible because the emulsion formed a plug right at the inlet and all the pressure readings along the core were zero (the outlet was open to atmospheric pressure). When the maximum pressure was reached, the pump was stopped and the time until which the pressure decreased by 200 psi was recorded. The pressure was increased again to the maximum, and again the time until it decreased by 200 psi was recorded. These steps were repeated during the entire experiment. A chart representing the injection pressure decline (maximum pressure minus 200 psi, divided by the recorded time) versus the cumulative injection time is shown in Figure 5.4. Thirty ml of water were collected from the core outlet during the injection. A reverse water flow was tried 24 hours after the end of the injection. The pressure increased to 900 psi and drops of emulsion came out of the core. The core holder was emptied and a 3.5 cm plug was found. The plug is shown in Figure 5.5.

5.3.2 Experiment 2 – 900 psi, 1% lignin surfactant

One hour before injecting the emulsion, the core was preflushed with 5 pore volumes of a 1% aqueous solution of lignin surfactant. The injection pressure was maintained between 700 and 900 psi for 8 hours. Another attempt was made to measure the pressure profile along the core using the smallest pressure plates available for the pressure transducers. All the readings were zero. Twelve ml of water were collected from the core outlet. A reverse water flow was attempted 6 days after the end of injection. The pressure increased to 150 psi and drops of water came out of the core. When the core holder was emptied, a 1.5 cm plug was found inside. The porous disk was found deformed towards the interior of the core (Figure 5.6). The disk was plugged from the previous experiment, and the emulsion broke down before penetrating the disk in order to enter the core. Between experiments, the porous disks were cleaned using toluene and water. Probably, the cleaning procedure was not efficient and droplets of emulsion remained trapped inside the disk. This can explain the short length of the plug and the high rate of penetration (the emulsion that entered the core had a low content of oil micelles). A chart representing the injection pressure decline versus the injection time is shown in Figure 5.7.

5.3.3 Experiment 3 – 900 psi, without surfactant preflush

Experiment 1 was repeated because trying a reverse water flow at an initially high pressure (900 psi) was a felt to be a incorrect procedure. A high pressure from the beginning could create a fracture in the plug, resulting in water channelling through it. The pressure was maintained between 700 and 900 psi for 8 hours. The pressure decline curve is shown in Figure 5.8. Twenty ml of water were collected during the emulsion injection. A reverse water breakthrough was attempted 8 days after the end of injection. The reverse water flow was started at 100 psi, and water broke through. The pressure was bled off and the end cap of the core holder was taken apart. The pressure was increased again and it was found that the water was coming out between the plug and the tubing, and not through the plug, as was expected. Again, the porous disk from the entrance was found to be bent. It was then decided not to use a porous disk at the entrance end of the core for future experiments. The length of the plug was 2.5 cm.

5.3.4 Experiment 4 – 900 psi, 2% Dowfax 2A1 surfactant preflush

One hour before injecting the emulsion, the core was preflushed with 5 pore volumes of a 2% aqueous solution of Dowfax 2A1 surfactant. The pressure was maintained between 700 and 900 psi. A chart representing the injection pressure decline versus the injection time is shown in Figure 5.9. During injection, 47 ml of water were collected from the core outlet. The reverse water flow was attempted 6 days after the end of injection. The water broke through at 100 psi. The core holder was opened at one end and pressure increased to 50 psi at the other end. The water came out between the plug and the tubing, as in the previous experiment. The core holder was emptied and a 5.5 cm plug was found inside. The plug looked softer than plugs obtained without preflush. The plug is shown in Figure 5.10.

5.3.5 Experiment 5 – 900 psi, 1% lignin surfactant preflush

A second experiment with the lignin surfactant was performed this time without a porous disk at the entrance. One hour before injecting the emulsion, the core was preflushed with 5 pore volumes of a 1% aqueous solution of lignin surfactant. After the first day (4 hours of injection), the pressure was not bled off. The next day, the pressure had decreased to 280 psi, which meant that the emulsion could not penetrate at a pressure lower than 280 psi. The injection continued for another 4 hours at a pressure between 700 and 900 psi. The pressure decline versus injection time is shown in Figure 5.11. A total of 32 ml of water was collected during the experiment. A reverse water flow was attempted 5 days after the end of injection. The water came out at 150 psi, again between the plug and the tubing. The core holder was emptied and a 3.5 cm plug was found. The plug looked more compact than plugs obtained without preflush.

5.3.6 Experiment 6 – 275 psi, without surfactant preflush

When plugs obtained in the steel core holder at high pressure were compared with plugs obtained in the transparent core holder at low pressure their length was comparable and not much higher, as expected. To account for the effect of injection pressure on emulsion penetration, two experiments at low pressure were performed in the steel core holder.

For the first low-pressure experiment, the asphalt-in-water emulsion was injected using a safety valve at the pump outlet. The safety valve was set at 275 psi. After 8 hours of injection, 4 hours the first day and 4 hours the second day, a total of 22 ml of water was collected from the core outlet. At the end of the injection, when the pump was shut down, the pressure decreased from 275 psi to 210 psi. The core was left under pressure until the next day when the same pressure 210 psi was found. Six days later, the reverse water flow was attempted. The water came out from the core at 150 psi between the plug and the tubing. The core holder was emptied and a plug of 2.8 cm was found.

5.3.7 Experiment 7 – 300 psi, without surfactant preflush

A second low-pressure experiment was performed. The pressure was maintained manually between 250 and 300 psi. The pressure decline curve is shown in Figure 5.12. After 8 hours of injection over two days, a total of 21 ml of water was collected from the core holder outlet. Six days later, a reverse water flow was attempted. The water broke through at 175 psi between the plug and the tubing. The core holder was emptied and a plug of 2.7 cm was found inside.

5.3.8 Experiment 8 – 900 psi, without surfactant preflush

It was noticed in the previous two experiments that, when the reverse water flow was attempted, the water came out between the plug and tubing, and not through the plug as anticipated. To prevent water passing between the plug and tubing, the inside of the core holder was coated with contact cement before packing the core. Then sand was poured over the glue layer and was left to dry

The injection pressure was maintained between 750 and 900 psi for 8 hours (two days). The pressure decline curve is shown in Figure 5.13. A total of 24 ml of water was collected from the core outlet. Seven days later, when the reverse flow was tried, the water came out at 150 psi. The core holder was emptied and a plug of 3.5 cm was found. The plug came out from the core holder in a dried glue sleeve. The plug is shown in Figure 5.14

5.3.9 Experiment 9 – 1500 psi, without surfactant preflush

The inside of the core holder was again coated with a layer of contact cement and sand. This time, contact cement with a higher adherence to metal was used. The injection pressure was maintained between 1100 and 1500 psi for 8 hours (two days). At the end of injection, the pressure was not bled off. The next day, the system was found to be at 375 psi. The pressure decline curve is shown in Figure 5.15.

Total water produced was 59 ml. Seven days later, when the reverse water flow was attempted, the water came through at 150 psi. When the core holder was emptied, a 7.5 cm plug was recovered, partially covered with dry glue layer. The rest of the glue remained attached to the metal. The plug is shown in Figure 5.16.

5.4 Emulsion particle size distribution tests

The asphalt-in-water emulsion was analyzed using a particle size analyzer. The tests were performed to confirm that the emulsion quality had not changed in the 5 months from the date the emulsion was received. We also investigated how the average particle size could be changed for further experiments (different porous media and different size of micelles).

Four samples were taken from the container containing the emulsion after it was thoroughly shaken. The first sample was analyzed as it was. A 1% aqueous solution of the lignin surfactant found in the emulsion was added to the second sample. The third sample was mixed in a homogenizer for 4 minutes. The forth sample was mixed in a homogenizer for 8 minutes.

The resulting particle size distributions are shown in Figures 5.17 to 5.20, for samples 1 to 4, respectively. Their mean particle size is also given. As expected, the mean particle size is increasing when more surfactant is added to the emulsion as the smaller particles are coalescing (Figure 5.18). When homogenized, the mechanical action is even stronger at coalescing all of the smaller particles, resulting in a single peak (Figures 5.19 and 5.20).

5.5 Results of experiments

Nine experiments were conducted in steel core holders. It was not possible to visually observe the advance of the emulsion in the core. The only means of following the advance of the emulsion was through pressure measurements as was shown in Figures 5.4, 5.7, 5.8, 5.9, 5.11, 5.12, 5.13 and 5.15. The thickness of each plug was measured at the end of each experiment, and the results are reported in Table 5.1.

The hardness of the plugs was measured using a Standard Asphalt Penetrometer. Three measurements at three different locations were done both for frontal and side penetration. The average results are presented in Table 5.1.

5.6 Analyses and Discussion

The pressure decline curves of the six experiments for the 900 psi injection pressure were analyzed. It could be seen that, after 100 minutes, the pressure decline had reached a plateau of 5 psi/minute. The longest plug was obtained with the Dowfax 2A1 preflush but the pressure decline graph during the first day looked very similar to those obtained without preflush. On the second day, the pressure decline decreased to 3 psi/minute. It can be inferred that most of the plug was formed during the first day, and this plug hindered the emulsion penetration during the second day of injection..

Comparing the plugs obtained at 300, 900 and 1500 psi without solution surfactant preflush, no linear relationship could be inferred between the injection pressure and the length of the plug. The plug length vs. injection pressure is shown in Figure 5.21. Nevertheless, the plug length increased with increasing pressure: at a pressure of 300 psi, the plug length was 2.7-2.8 cm, at 900 psi it varied from 3.3 to 3.5 cm (5.5 cm with the Dowfax 2A1 solution preflush), and at 1500 psi it was 7.5 cm.

The above results confirmed the observations made during the visual experiments that a higher penetration of the emulsion into the porous medium is achieved by modifying the wettability of the porous matrix using a surfactant preflush. The longest plug was obtained with the 2% aqueous Dowfax 2A1 solution preflush, which gives a pH of 8-10 in an aqueous solution. Recent work by Zheng et al. (2001) has shown that quartz is oil wetting at low pH and water wetting at high pH values. The breakage of the emulsion is delayed in a strongly water-wetted porous medium.

The asphalt-in-water emulsion meets the proposed requirements for this research. The weighted-average particle size of the emulsion is in the range of 3 – 6 μm. It has good stability: if the emulsion is left to settle for long periods of time, it regains its initial quality after mixing. Also, if a larger average particle size is needed, it can be obtained by mixing the emulsion at a high shear rate.

Table 5.1: Thickness of plugs and penetration test results

Experiment	Pressure (psi)	Plug length (cm)	Preflush	Penetration (10^{-1} mm)	
				Front	Side
1	700 - 900	3.5	No	22	12
2	700 - 900	1.5	1% lignin	15	13
3	700 - 900	2.5	No	17.5	12
4	700 - 900	5.5	2% Dowfax 2A1	44	27
5	700 - 900	3.5	1% lignin	14	12
6	275	2.8	No	10	7
7	250 – 300	2.7	No		
8	700 – 900	3.3	No	18	12
9	1100 - 1500	7.5	No	17.5	11.3

Figure 5.1: Sand packing process

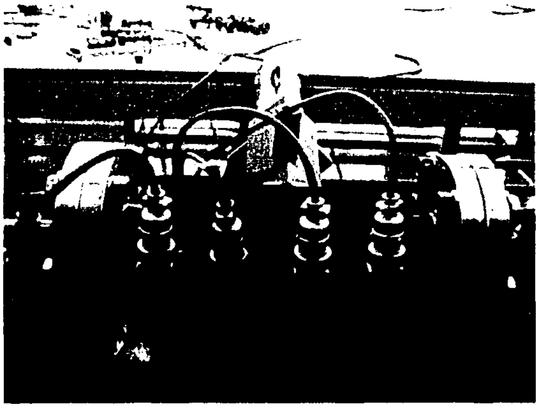


Figure 5.2: Transfer vessels

Figure 5.3: Steel core holder

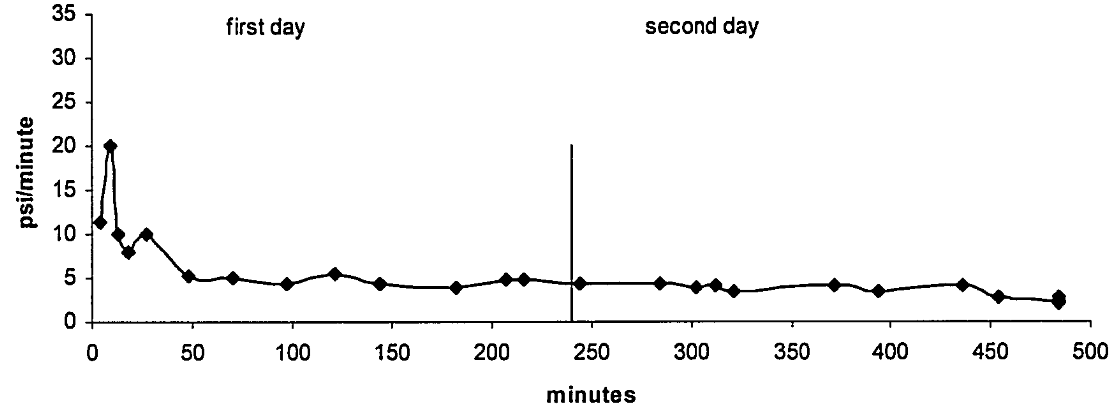


Figure 5.4: Pressure decline vs. injection time (Experiment 1)

Figure 5.5: Plug – No preflush, 900 psi

Figure 5.6: Deformed porous disk

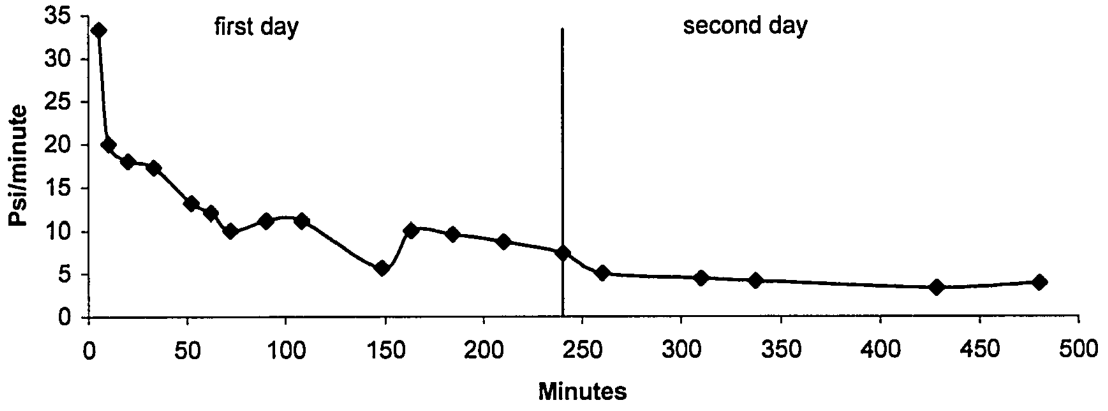


Figure 5.7: Pressure decline vs. injection time (Experiment 2)

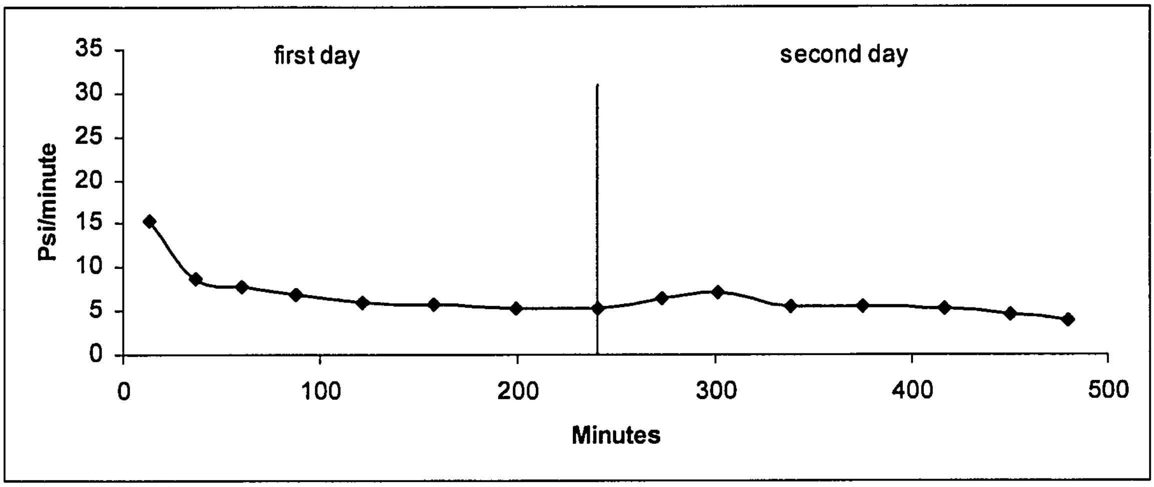


Figure 5.8: Pressure decline vs. injection time (Experiment 3)

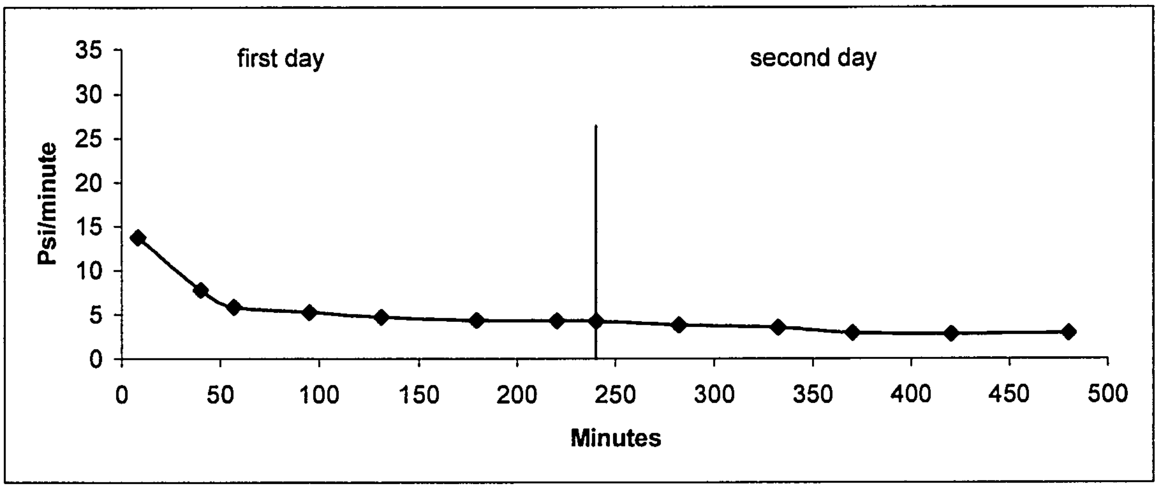


Figure 5.9: Pressure decline vs. injection time (Experiment 4)

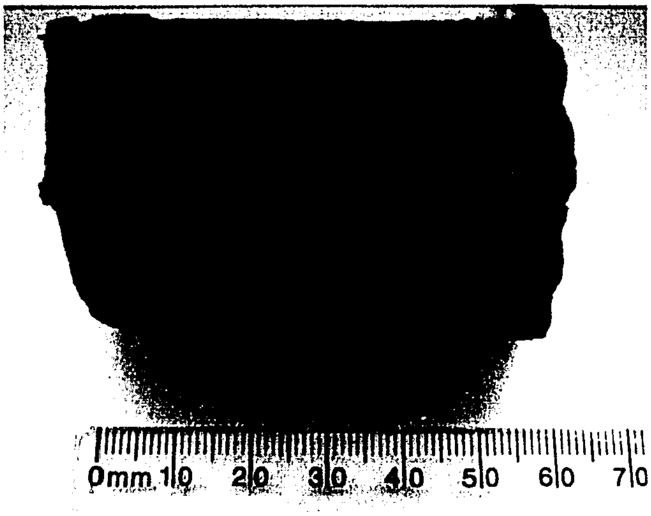


Figure 5.10: Plug – 2% Solution of Dowfax 2A1 preflush, 900 psi

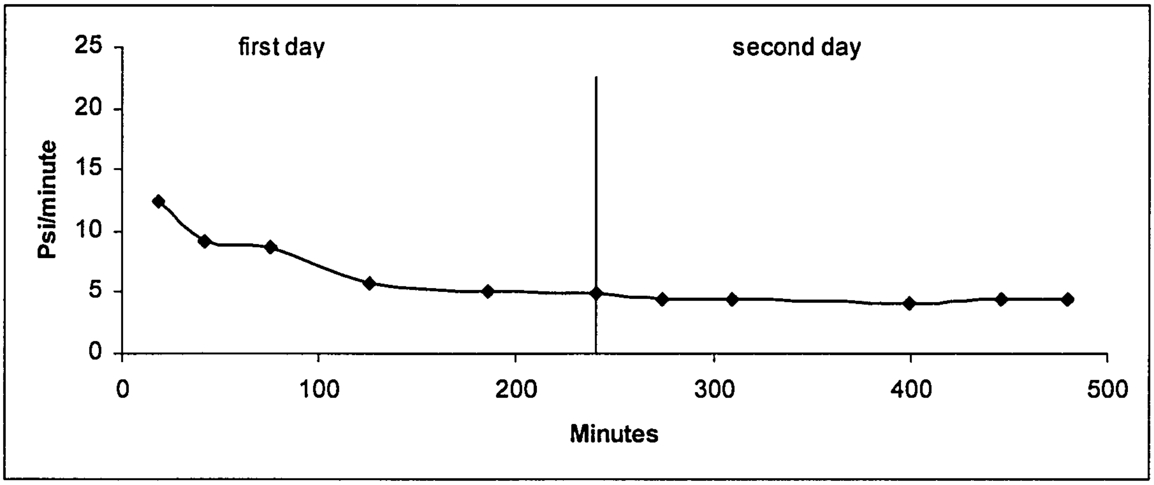


Figure 5.11: Pressure decline vs. injection time (Experiment 5)

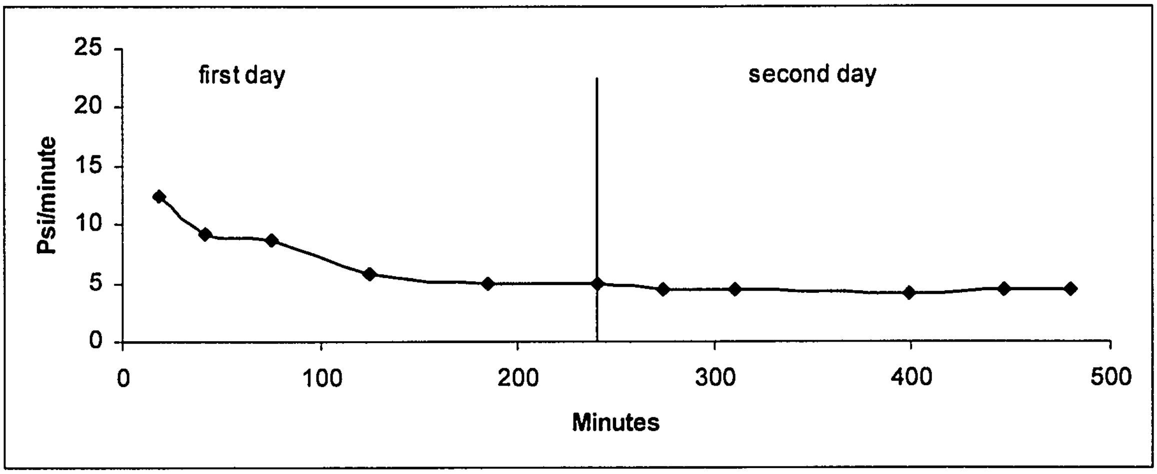


Figure 5.12: Pressure decline vs. injection time (Experiment 7)

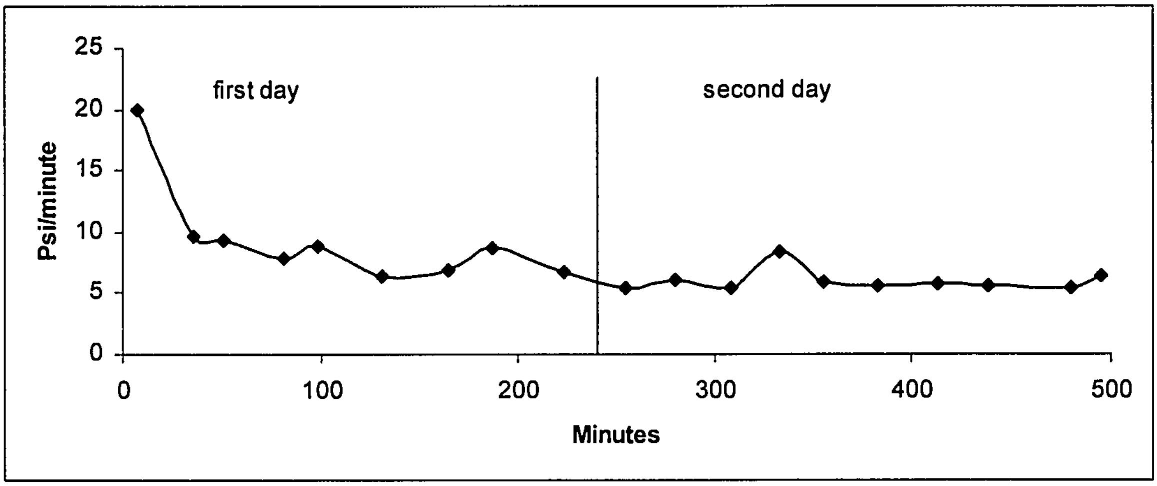


Figure 5.13: Pressure decline vs. injection time (Experiment 8)

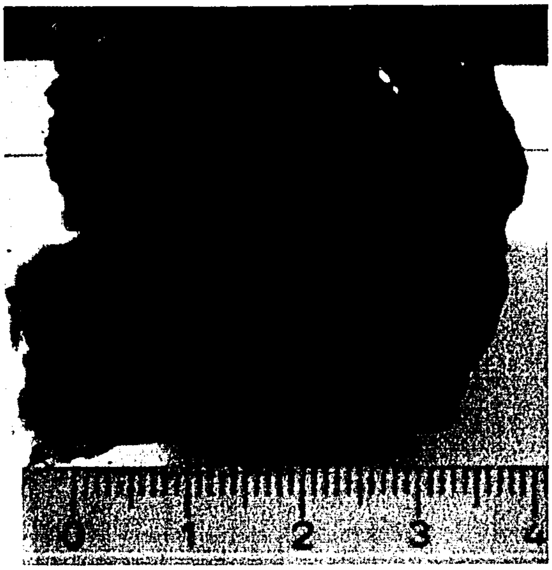


Figure 5.14: Plug – No preflush, 900 psi, glue coated core holder

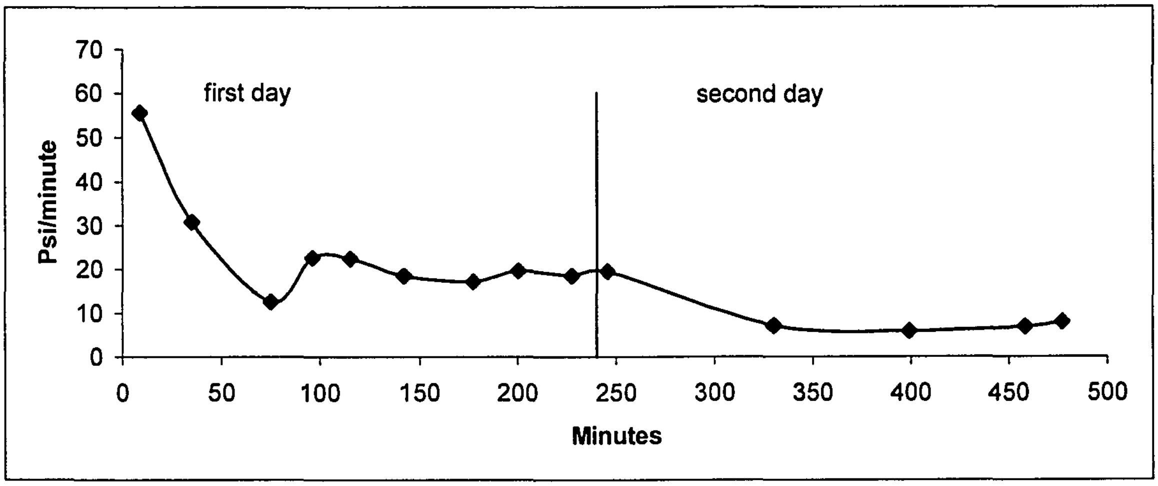
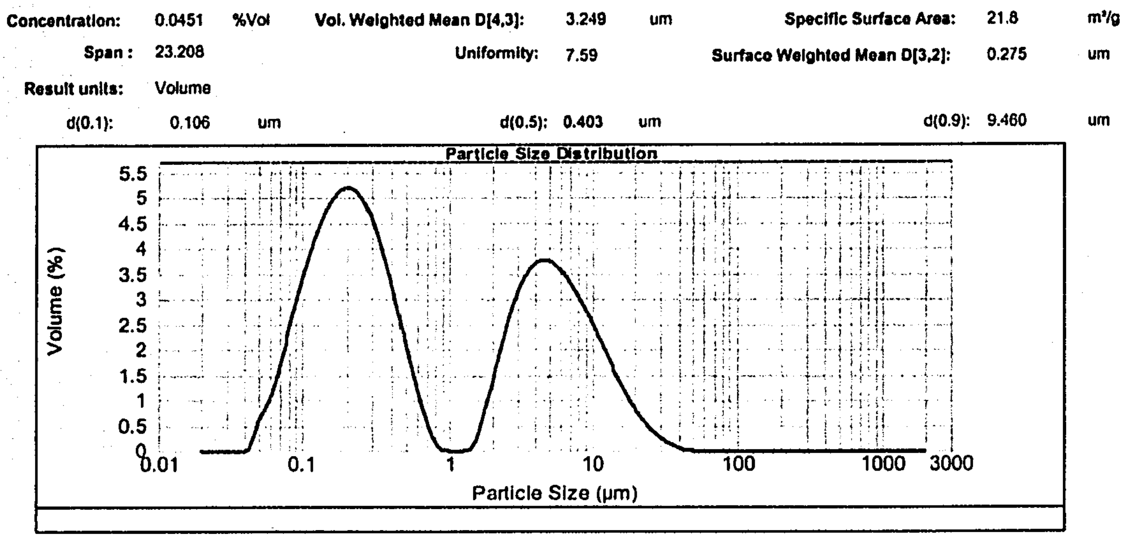


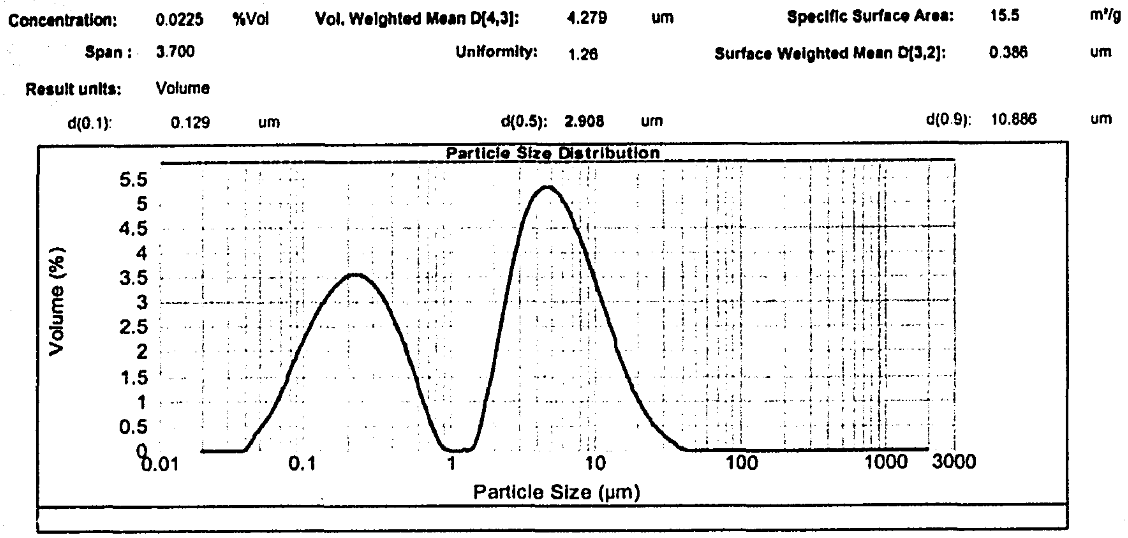
Figure 5.15: Pressure decline vs. injection time (Experiment 9)

Figure 5.16: Plug – No preflush, 1500 psi, glue coated core holder



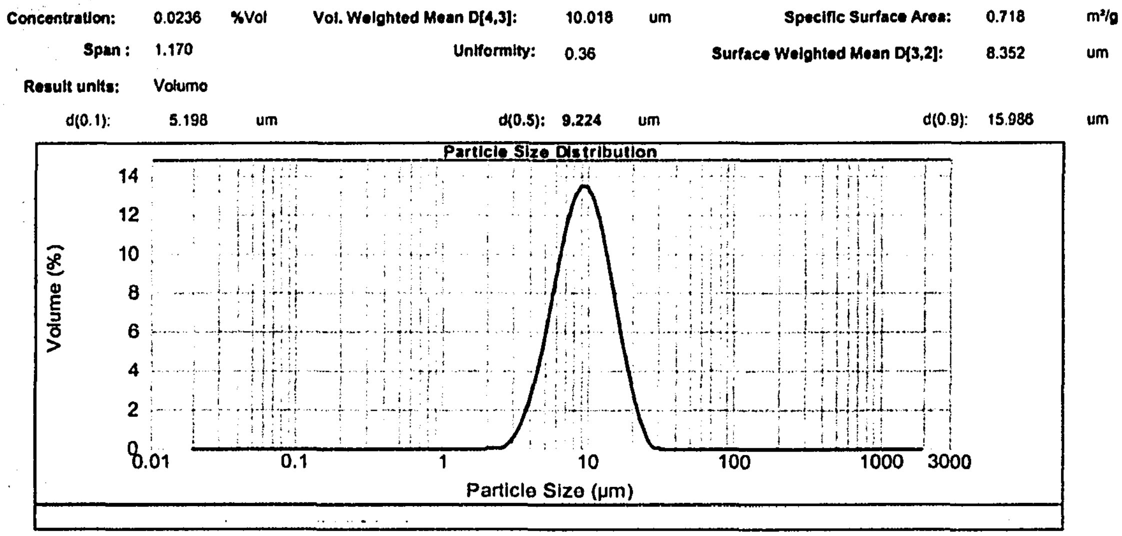
Concentration: 0.0451 %Vol
Vol. Weighted Mean D[4,3]: 3.249 um
Specific Surface Area: 21.8 m²/g
Span : 23.208
Uniformity: 7.59
Surface Weighted Mean D[3,2]: 0.275 um
Result units: Volume
d(0.1): 0.106 um
d(0.5): 0.403 um
d(0.9): 9.460 um

Figure 5.17: Sample 1 - weighted mean particle size 3.24 μm



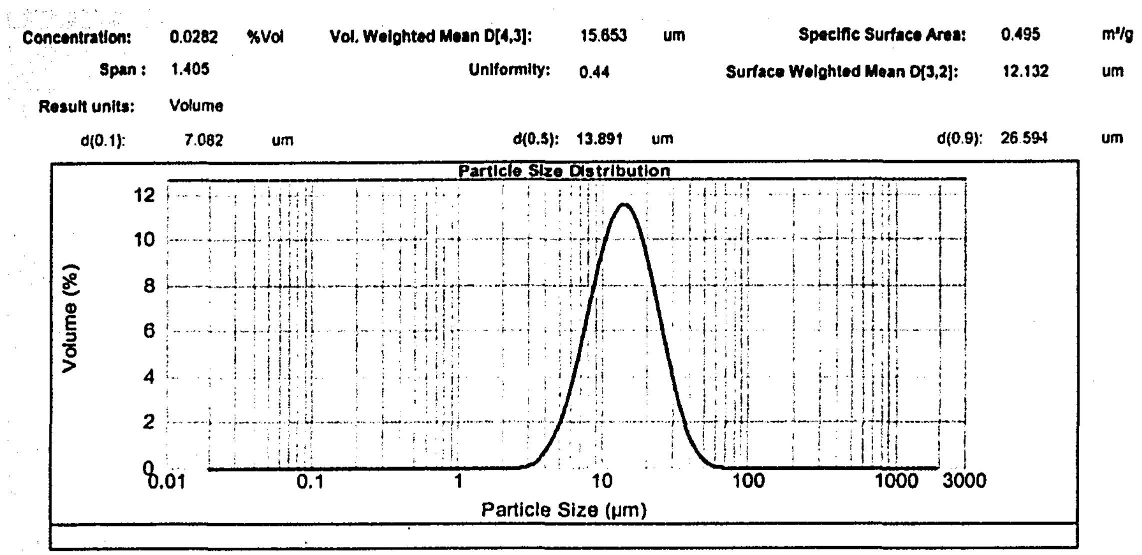
Concentration:	0.0225	%Vol	**Vol. Weighted Mean D[4,3]:**	4.279	um	**Specific Surface Area:**	15.5	m²/g
Span :	3.700		**Uniformity:**	1.26		**Surface Weighted Mean D[3,2]:**	0.386	um
Result units:	Volume							
d(0.1):	0.129	um	d(0.5):	2.908	um	d(0.9):	10.886	um

Figure 5.18: Sample 2 - weighted mean particle size 4.27 µm



Concentration:	0.0236	%Vol	**Vol. Weighted Mean D[4,3]:**	10.018	um	**Specific Surface Area:**	0.718	m²/g
Span :	1.170		**Uniformity:**	0.36		**Surface Weighted Mean D[3,2]:**	8.352	um
Result units:	Volume							
d(0.1):	5.198	um	d(0.5):	9.224	um	d(0.9):	15.986	um

Figure 5.19: Sample 3 - weighted mean particle size 10.01 µm



Concentration: 0.0282 %Vol **Vol. Weighted Mean D[4,3]:** 15.653 um **Specific Surface Area:** 0.495 m²/g

Span : 1.405 **Uniformity:** 0.44 **Surface Weighted Mean D[3,2]:** 12.132 um

Result units: Volume

d(0.1): 7.082 um d(0.5): 13.891 um d(0.9): 26.594 um

Figure 5.20: Sample 4 - weighted mean particle size 15.65 μm

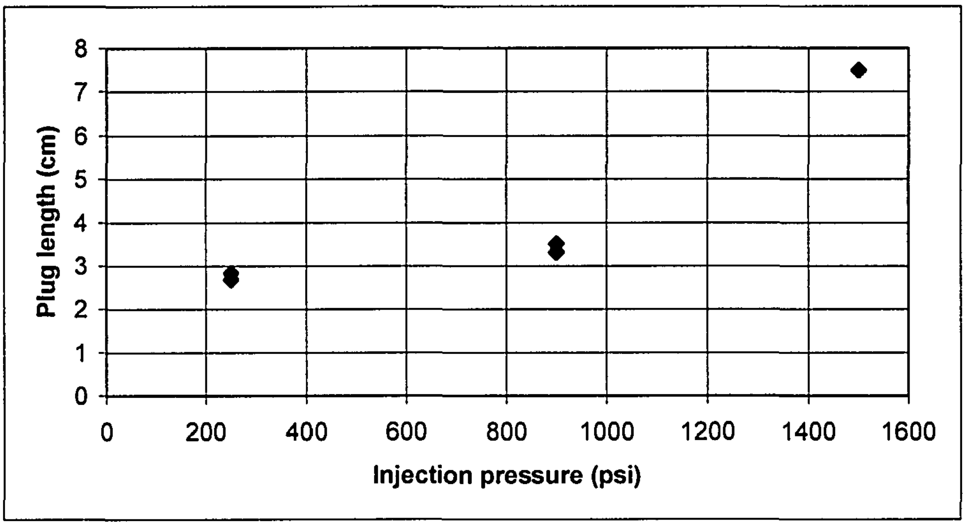


Figure 5.21: Plug length vs. Injection pressure

CHAPTER 6

Injection of asphalt-in-water emulsion in a "Hassler" core holder

In previous experiments conducted in a transparent core holder and in a steel core holder, we proved that the asphalt-in-water emulsion could be injected into a sand pack, creating a plug that seemed to be waterproof. When a reverse flow was attempted to determine the integrity of the seal, the water was found to come through between the plug and the tubing. To avert the water flow between the plug and the tubing, a "Hassler" type core holder, that allows overburden pressure to be applied, was designed and built. Six successful experiments were performed injecting the emulsion into sand packed in the new core holder

6.1 Model construction

The core holder tube was built from steel tubing, $1^{4/5}$ in ID and 9 in length. Two lateral holes were drilled and fittings were screwed in for connection to the pump used to simulate overburden pressure. A rubber sleeve, $1^{1/2}$ in ID was placed inside the core holder. Each steel end cap penetrated 2 in into the rubber sleeve, leaving room for a core having a length of 5 in. Two grooves for o-rings were machined in each end cap, one for sealing between the end cap and core holder and the other for providing the sealing between the end cap and the rubber sleeve. The core holder is shown in Figures 6.1 and 6.2.

The porous medium was prepared using 60-80 mesh sand. The core holder was placed in a vertical position with the bottom end cap attached to the core holder. The core holder was half filled with water, and sand was poured in it until it reached a height of 150 mm. The upper end cap was attached to the core holder and the screws were tightened, forcing the end cap to enter the rubber sleeve until it reached the sand level. The vibrator was started and ran for 16 hours. During the first 2 hours, when 2-3 mm advance of the end cap into the core holder was noticed, the screws were tightened further for maintaining the sand under compression. At the end of the packing, the upper end cap needed to be tightened for another 2-4 mm.

6.2 Experimental set-up

The core holder was placed on the stand in a horizontal position. High pressure tubing was connected between the core holder inlet, the transfer vessel and the pump. Transparent tubing connected the core holder outlet and the beaker used to collect the produced water at atmospheric pressure. A pressure gauge was placed at the pump outlet for monitoring the pressure during injection. A second pump was connected, using high pressure tubing, to the lateral core holder port for simulating overburden pressure on the sand pack. The overburden pressure was monitored using a pressure gauge attached to the "T" fitting from the core holder port. A bottle of compressed air was used for the gas reverse flow. The pressure of the compressed air was controlled by a regulator attached to the bottle. The experimental setup is shown in Figure 6.3.

6.3 Experimental procedure

After packing, the water was drained and the core holder was placed in an oven for 8 hours. The core was then placed on the stand and flushed with several pore volumes of carbon dioxide. After the injection of carbon dioxide, the core was saturated with distilled water. The core holder was placed in a vertical position and drained. The produced water was collected and measured for calculating the pore volume of the core. The pore volume was found to be around 25%, a lower value compared to the 31% found when the packing was made in the transparent or steel core holder. The lower value of the pore volume was a result of the packing procedure employed, the sand being compressed by the upper end cap during vibration.

The presence of the rubber sleeve inside the "Hassler" core holder did not allow for the most common method of calculating the permeability by measuring the pressure drop between two points within the sand pack. Therefore a different method was employed.

Two pressure transducers were attached to the "T" fittings from the core end caps. Water was injected into the empty core holder using the pump set at a constant flow rate of 1120 cm^3/h to measure the pressure drop between the ends of the core holder. The core holder was packed with sand, water was injected again through the core at 1120 cm^3/h, and a second pressure drop measurement was taken. The difference between the two pressure drop measurements was considered to be that of the sand pack. Using Darcy's law, the permeability was calculated to be between 2.4 and 2.6 Darcy.

The emulsion was injected for 6 hours at a maximum pressure of 1000 psi. The pump was started and left running at a flow rate of 1120 cm^3/h until the pressure reached 1000 psi. At 1000 psi, the pump was stopped and the time recorded. When the pressure had decreased to 850 psi the time was again recorded and the pressure was increased back to 1000 psi. The produced water was collected and measured.

In each case, reverse water or gas flow was attempted 6 to 7 days after the emulsion was injected. Six experiments were conducted with the above setup using the asphalt-in-water emulsion. All experiments were conducted at the room temperature.

6.3.1 Experiment 1 – 1000 psi, without surfactant preflush

The emulsion was injected for six hours at a pressure between 850 and 1000 psi without overburden pressure. The pressure decline versus injection time is shown in Figure 6.4. At the end of the injection, the pressure was not bled off. The next day the pressure gauge indicated 700 psi. The core was plugged. Twenty-six ml of water were collected from the core outlet. The water reverse flow was attempted five days later. Before starting the water injection, 500 psi of overburden pressure was applied onto the core. The pressure injection was increased to 300 psi when water started coming out. When a higher overburden pressure was attempted, it created communication between the exterior and the interior of the rubber sleeve. The core holder was emptied and a 4 cm plug was found.

During the emulsion injection, the vibrator was started for packing another core. The pressure decline increased from 4 psi/minute to 25 psi/minute. The vibrator was stopped after the faster decrease in pressure was observed.

To avoid the communication between the exterior and interior of the rubber sleeve the core holder end caps were modified adding two more o-rings as shown in Figure 6.5.

Two experiments were performed using overburden pressure before injecting the emulsion. Both of them failed. Because of the overburden pressure, the sand was squeezed inside the inlet end and formed a plug with the injected emulsion.

During the packing process both inlet and outlet ends were filled with glass wool to prevent the sand coming out of the core holder. Before starting the emulsion injection, the glass wool from the inlet end was removed to prevent plugging the inlet.

It was decided that further experiments would be conducted without overburden pressure during the emulsion injection.

6.3.2 Experiment 2 – 1000 psi, 1% aqueous solution of Dowfax 2A1-D surfactant preflush

The core was preflushed with three pores volumes of an aqueous solution of 1% Dowfax 2A1-D surfactant twenty-four hours before injecting the emulsion. The emulsion was injected at a pressure between 850 and 1000 psi. The pressure decline versus injection time is shown in Figure 6.6. At the end of the injection, the pressure was not bled off. The next day the pressure gauge indicated 500 psi. A total of 43 ml of water was collected during the injection. The reverse water flow was attempted six days later. Before starting the water injection, 1000 psi overburden pressure was applied on the core. The injection pressure was increased to 700 psi in 100 psi steps. At 700 psi, the pump was shut off and the pressure monitored for 2 hours. Neither decrease in pressure nor water coming out was noticed. When a higher injection pressure was attempted, the plug that was almost solid started being squeezed out from the core holder. The core holder was emptied and a plug 6.5 cm was found inside (Figure 6.7).

6.3.3 Experiment 3 – 1000 psi, 1% aqueous solution of Dowfax 2A1 surfactant preflush

Twenty-four hours before injecting the emulsion, the core was preflushed with three pore volumes of an aqueous solution of 1% Dowfax 2A1 surfactant. The injection pressure was maintained between 850 and 1000 psi. Twenty-five minutes before ending the experiment, a vibrator was started in the lab. The pressure decline increased from 7 psi/minute to 50 psi/minute. The pressure decline versus injection time is shown in Figure 6.8. The emulsion was collected from the core outlet. The reverse water flow was attempted 6 days later. Before injecting water, 1100 psi of overburden pressure was applied to the core. The pressure was increased to 800 psi in 100 psi. The pressure and the core were monitored for 3 hours. Neither decrease in pressure nor water coming out from the core was noticed. When the pressure was increased to more than 800 psi, the plug started coming out of the core holder. The core holder was emptied and a plug of 13 cm was found inside. There was a channel along the plug, which could explain why the emulsion filled the entire core. We think that vibrations during the experiment produced the channel. The plug is shown in Figure 6.9.

6.3.4 Experiment 4 – 1000 psi, 1% aqueous solution of Dowfax 2A1 surfactant preflush

After the core was packed and the glass wool from the inlet removed, a metallic screen was placed at the entrance to avoid the squeezing of the plug out of the core during the reverse water flow. The core was preflushed with three pores volumes of a 1% aqueous solution of Dowfax 2A1 surfactant 3 days before injecting the emulsion. The injection pressure was maintained between 850 and 1000 psi for 6 hours. The pressure decline versus injection time is shown in Figure 6.10. A total of 45 ml of water was collected during injection. Six days later, a reverse water flow was attempted. Before injecting water, 1600 psi of overburden pressure was applied to the core. The injection pressure was increased to 1400 psi in 100 psi steps. The pressure and the core were monitored for 3 hours. Neither pressure decline nor water coming out from the core was noticed. The core holder was emptied and a 6.5 cm plug was found inside.

6.3.5 Experiment 5 – 1000 psi, 1% aqueous solution of Dowfax 2A1-D surfactant preflush

The core was preflushed with three pore volumes of an aqueous solution of 1% Dowfax 2A1-D surfactant 24 hours before injecting the emulsion. The injection pressure was maintained between 850 and 1000 psi for 6 hours. The pressure decline versus injection time is shown in Figure 6.11. During the injection period, 50 ml of water were collected from the core outlet. Eight days later, a reverse air flow was attempted. Before injecting air, 1200 psi of overburden pressure was applied to the core. The air pressure, supplied from a compressed air bottle, was increased gradually to 1000 psi. The core holder was monitored for 6 hours and no air leakage was observed. The core holder was emptied and a plug 7.5 cm long was found inside.

6.3.6 Experiment 6 – 1000 psi, 1% aqueous solution of Dowfax 8390-D surfactant preflush

The core was preflushed with three pores volumes of an aqueous solution of 1% Dowfax 8390-D surfactant 24 hours before injecting the emulsion. The injection pressure was maintained between 850 and 1000 psi for 6 hours. The pressure decline versus injection time is shown in Figure 6.12. During injection, 72 ml of water were collected from the core outlet. Six days later, a reverse air flow was attempted. Before injecting air, 1200 psi of overburden pressure was applied to the core. The air pressure was increased gradually to 1000 psi. The core holder was monitored for 6 hours and no air leakage was observed. The core holder was emptied and a plug 11 cm long was found inside. The plug is shown in Figure 6.13.

6.4 Results of experiments

Six successful experiments were performed in the "Hassler" core holders. Three different surfactants were used to prepare the preflush solution. For each experiment, the advance of the emulsion was correlated with pressure measurements as shown in Figures 6.4, 6.6, 6.8, 6.10, 6.11 and 6.12. A reverse breakthrough flow was attempted at the end of each experiment using water or compressed air. The length of each plug was measured and the results are presented in Table 6.1.

The hardness of the plugs was measured using a Standard Asphalt Penetrometer. From previous experiments it was noticed that the hardness increases with ageing once the plugs are exposed to air. Measurements were made at three different times, right after the plugs were taken out from the core holder, five days and ten days later. The most common combination for the measurement was used: 100 grams applied for 5 seconds at a temperature of 25°C. Three measurements at three different locations were done both on the front (fluid injection) and on the side of the plugs. The average results are presented in Table 6.2.

6.5 Analyses and Discussion

From an analysis of the length of the plugs, as shown in Table 6.1, it can be seen that, using a surfactant preflush, the emulsion penetration increased by more than 62.5%. The best penetration was obtained with the Dowfax 8390-D surfactant preflush, 11 cm, almost triple the plug obtained without preflush, 4 cm. The measured pHs for all the 1% surfactant solutions were between 8.18 and 8.35. As expected, the alkaline preflush delayed the change in wettability produced by the organic component found in asphaltene.

The penetration measurements (Table 6.2) show that the plugs obtained with the surfactant preflush have lower hardness values. Also it can be seen that longer plugs are associated with a lower hardness.

After the core holder end caps were modified by adding 2 more o-rings, the reverse water/air flow proved that the asphalt-in-water emulsion had sealing properties. The reverse flow was performed at pressures equal to or higher than the maximum pressure used for injecting the emulsion.

From an analysis of the pressure decline curves shown in Figures 6.4, 6.6, 6.8, 6.10, 6.11 and 6.12, it can be observed that the effect of the preflush on the penetration is predominant during the first 40 minutes of injection. After the first 40 minutes, the pressure decline curves reached a plateau of around 5-7 psi/minute indicating that once the emulsion had advanced a certain distance into the porous medium, the effect of the preflush on the penetration was almost negligible. The plateau reached during injection without preflush was around 4 psi/minute.

Table 6.1: Length of plugs

Experiment	Pressure (psi)	Plug length (cm)	Preflush	Observations
1	850 - 1000	4	No	
2	850 - 1000	6.5	1% Dowfax 2A1-D	
3	850 - 1000	13	1% Dowfax 2A1	Channel in the plug, vibration
4	850 - 1000	6.5	1% Dowfax 2A1	
5	850 - 1000	7.5	1% Dowfax 2A1-D	
6	850 - 1000	11	1% Dowfax 8390-D	

Table 6.2: Penetration measurements

Plug from Experiment	**First day**		**After 5 days**		**After 10 days**	
	Front	**Side**	**Front**	**Side**	**Front**	**Side**
1	37.6	24.5	26.6	18.7	19.3	13.5
2	51.5	32.6	44.3	30.6	22.7	17.8
3	60.3	40.8	49.6	34.5	32.7	23.6
4	50.4	36.4	43.6	335	29.5	20.3
5	50.6	31.4	42.5	32.3	23.2	16.4
6	55.2	38.4	45.2	31.6	30.0	21.6

1 – End cap
2 – O-ring
3 – Port for overburden pressure
4 – Rubber sleeve
5 – Core holder body
6 – Inlet/outlet

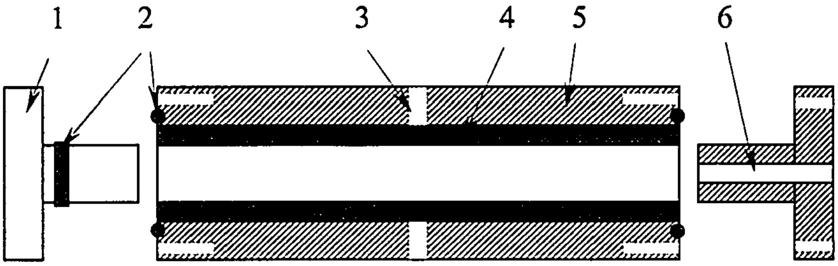


Figure 6.1: Schematic of the "Hassler" core holder

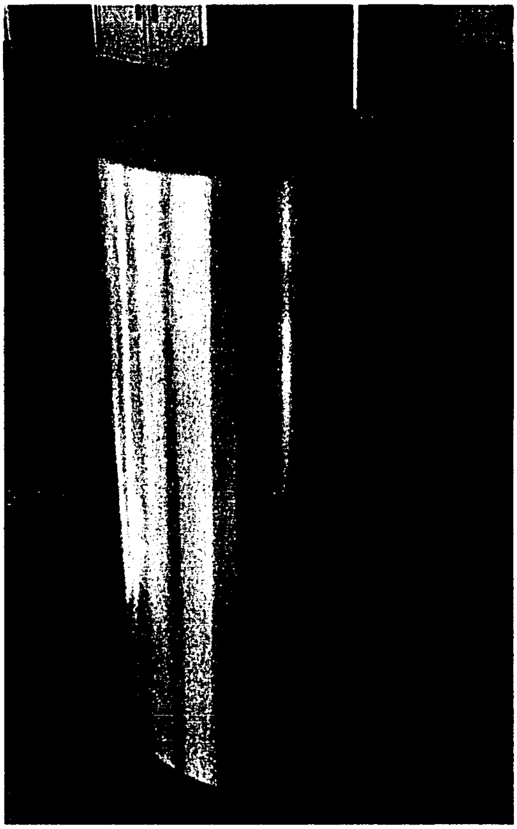


Figure 6.2: "Hassler" core holder

1 – Positive displacement pump (for emulsion injection)
2 – Pressure gauge
3 – Transfer vessel
4 – High pressure tubing
5 – "Hassler" core holder
6 – Beaker
7 – Positive displacement pump (for overburden pressure)
8 – Compressed air bottle
9 – Regulator

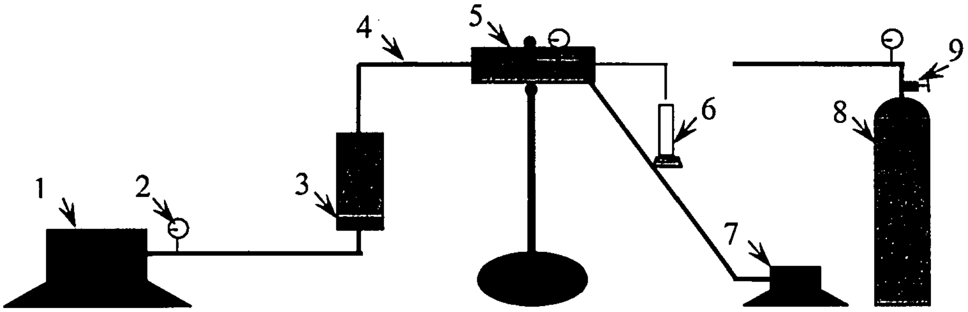


Figure 6.3: Experimental setup

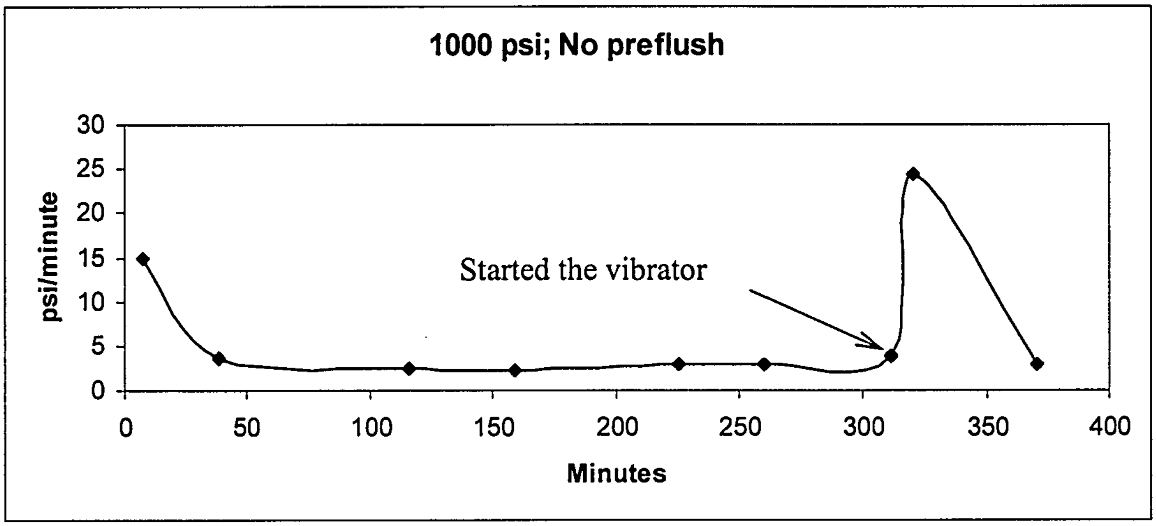


Figure 6.4: Pressure decline vs. injection time (Experiment 1)

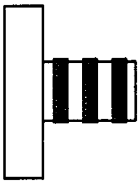


Figure 6.5: Modified end cap

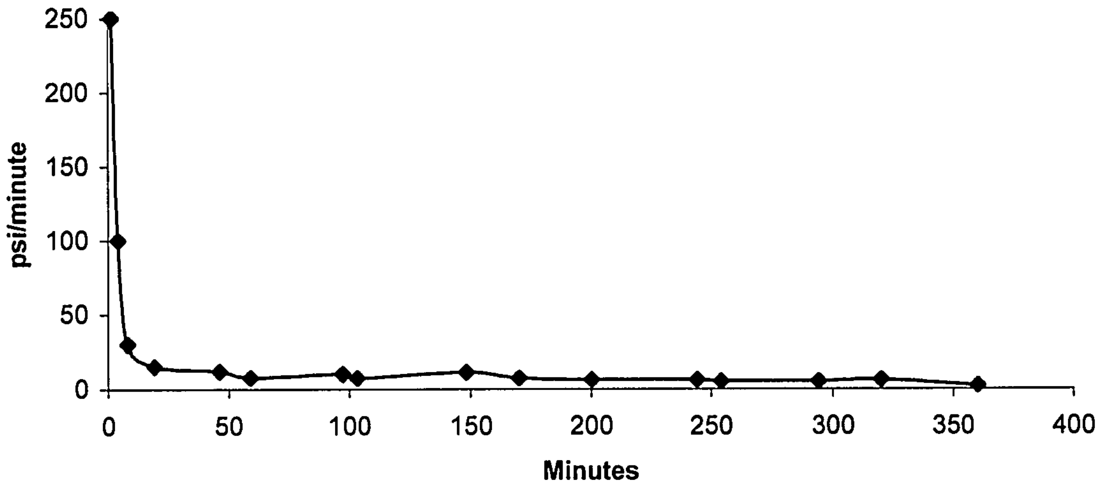


Figure 6.6: Pressure decline vs. injection time (Experiment 2)

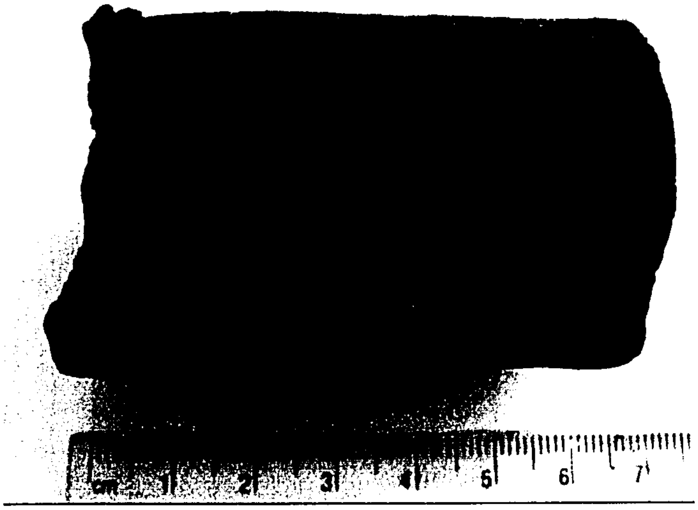


Figure 6.7: Plug – 1% Solution of Dowfax 2A1-D preflush, 1000 psi

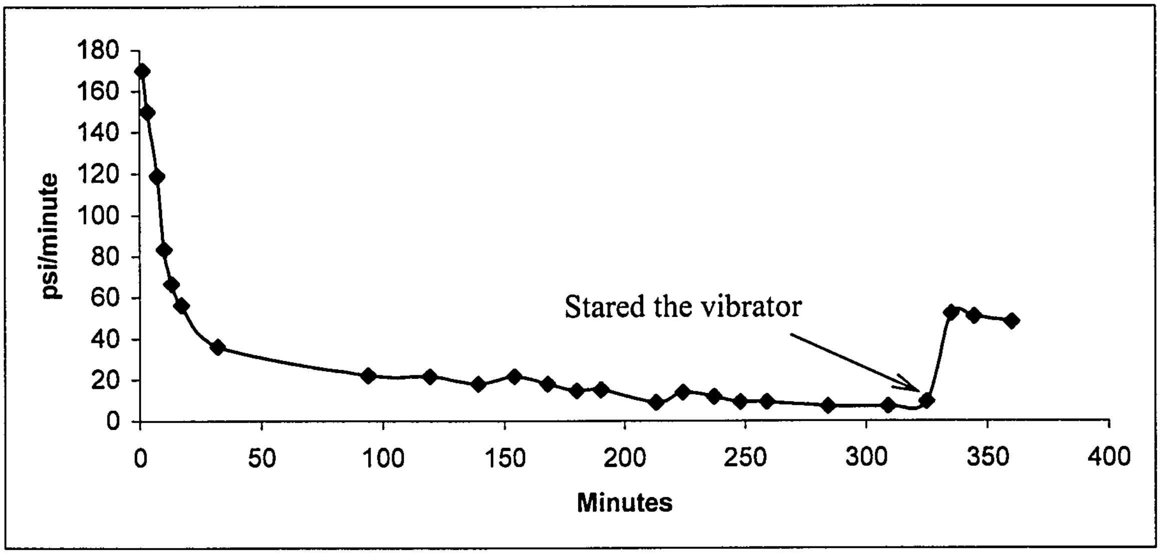


Figure 6.8: Pressure decline vs. injection time (Experiment 3)

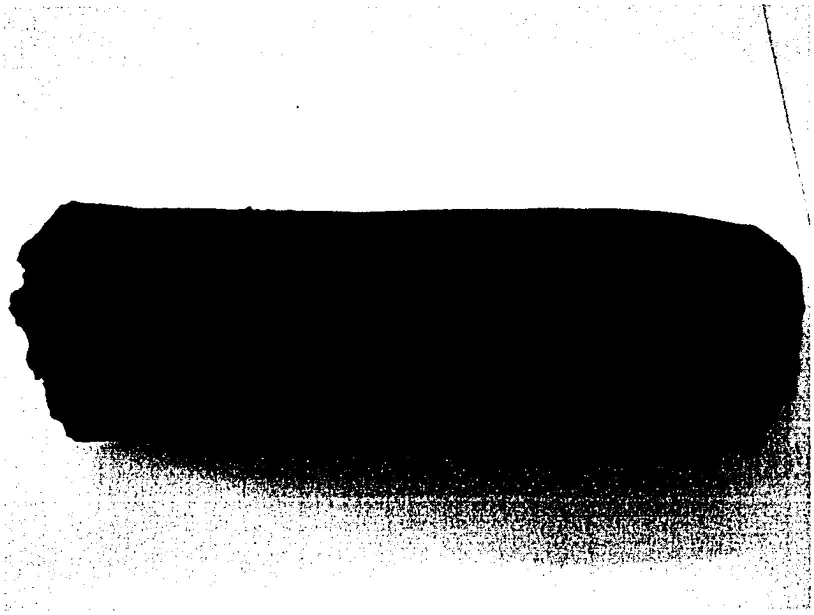


Figure 6.9: Plug – 1% Solution of Dowfax 2A1 preflush, 1000 psi

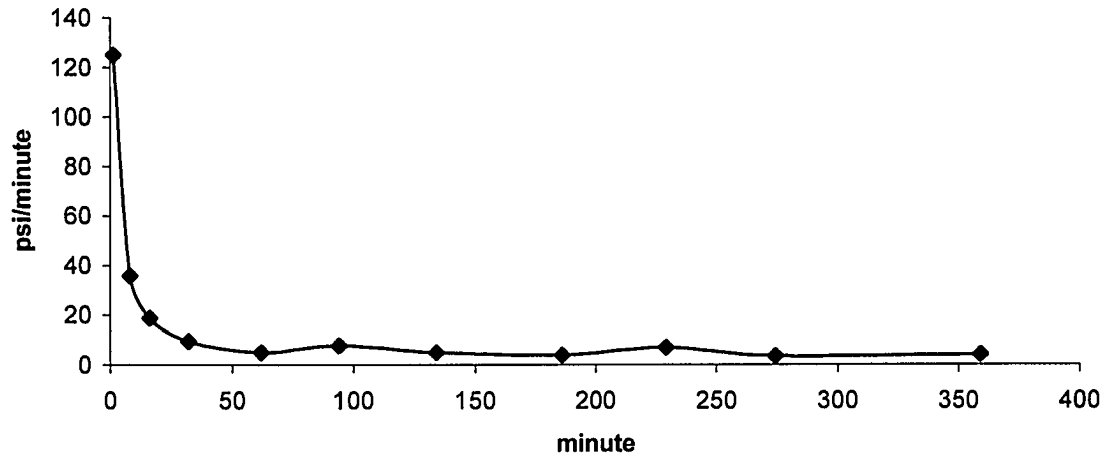


Figure 6.10: Pressure decline vs. injection time (Experiment 4)

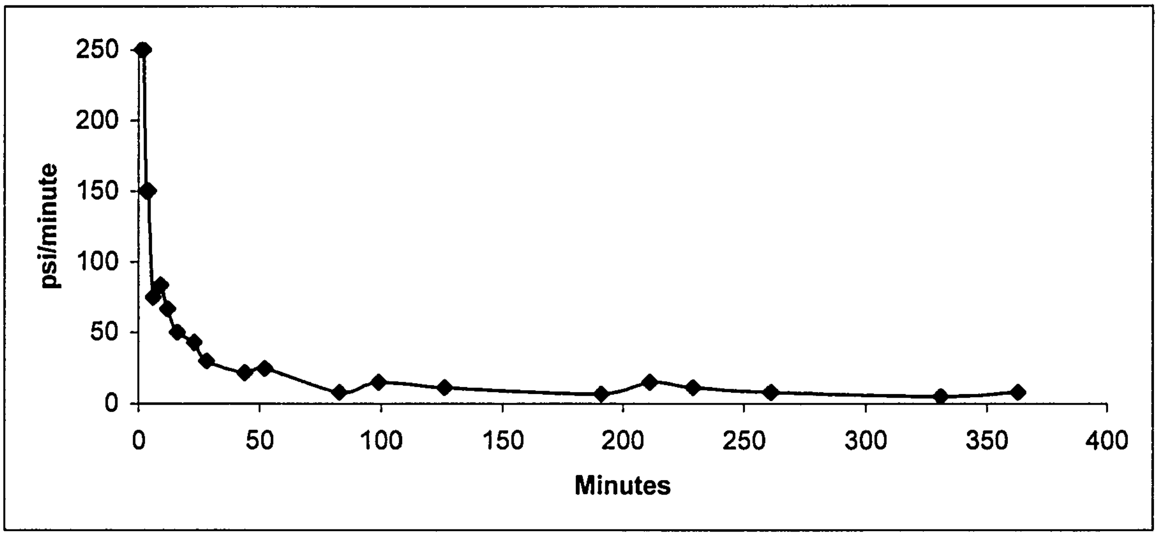


Figure 6.11: Pressure decline vs. injection time (Experiment 5)

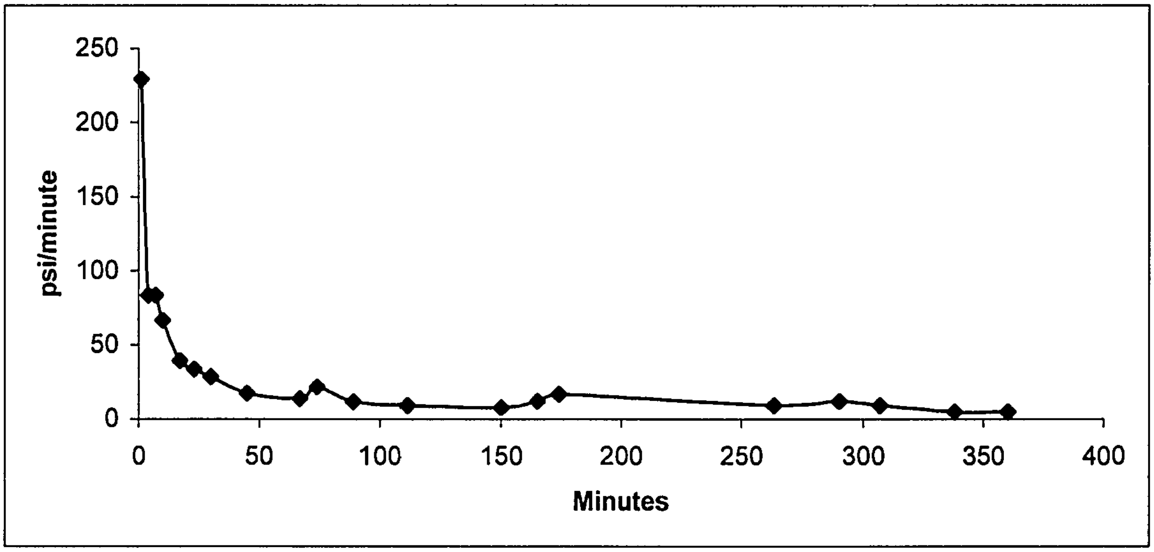


Figure 6.12: Pressure decline vs. injection time (Experiment 6)

Figure 6.13: Plug – 1% Solution of Dowfax 8390-D preflush, 1000 psi

CHAPTER 7

Conclusions and Recommendations

7.1 Summary and Conclusions

In this study, the sealing properties of an asphalt-in-water emulsion were investigated by performing injection experiments, first at low pressure in sand packs in a transparent core holder, and then using steel core holders that allowed high injection pressures. The initial experiments, performed at low pressure, allowed us to visually observe the process while the high pressure experiments focused on obtaining the "seal" that would prevent water or gas flowing back from the formation. Based on theoretical considerations, three anionic surfactants were chosen as preflush solutions that could delay the breaking of the emulsion and would produce a longer plug.

Based on the results of the study, the following conclusions can be drawn:

1. The sealant solution is an emulsion of asphalt-in-water with a 60% internal phase concentration and an average particle size of 4 μm.
2. The stability of the emulsion was evaluated five months after the emulsion was received. After sitting undisturbed for five months, the emulsion coagulated into a weak gel. The sealant was easily returned to its original state by shaking the container.
3. The pore throat diameter for the porous medium used in our experiments was calculated to be around 34 μm for the 8.4 Darcy permeability pack, and 20 μm for the 2.5 Darcy permeability pack. Looking at the pore throat diameter versus the average emulsion droplet size, 4 μm, it can be surmised that the blocking process of the porous medium was produced by the adsorption of the asphaltene onto the grain surface, followed by accumulation of small droplets that filled each pore.
4. Pre-treating the porous medium with a solution of anionic surfactant delayed the emulsion breaking and produced a higher emulsion penetration. When Dowfax 8390 – D surfactant was used the plug was almost three times longer than the plug obtained without preflush, 11 cm compared to 4 cm.

5. The sealant properties of the asphalt-in-water emulsion were demonstrated when reverse water or air flow was performed. The pressure employed during reverse water/air flow was equal to or higher than the emulsion injection pressure, and no breakthrough of the injected water or air was noticed.

7.2 Recommendations

1. If the emulsion was left to settle for a certain time and that mixing it was required, we recommend that high shear rates be avoided. When high shear rates were applied to the emulsion, the average droplet size increased. Eight minutes of high shear rate mixing produced an emulsion with an average droplet size of 15 μm.
2. The surfactant preflush should be applied at least 24 hours before injecting emulsion. When the preflush was injected right before emulsion, the plug obtained was usually 1 to 2 cm shorter. When the preflush was injected 3 days before the emulsion, no significant increase in penetration was noticed.
3. A backup pressure should be maintained in the well at least 3 days after the emulsion is injected into a formation. When a reverse water flow was performed within three days from the end of injection, droplets of emulsion came out from the core holder. Emulsion ageing inside the porous medium seemed to play an important role in obtaining a good seal.

Further research should be conducted to optimize the process. Here are some suggestions:

- Find the optimum concentration for the surfactant solution preflush that would yield the highest penetration.
- Test the emulsion in oil-wet or partially oil-wet formation. The formation wettability is a key factor in obtaining a good seal. In oil-wet porous media, the emulsion brakes faster, resulting in a smaller penetration.
- Find the optimum relation between the average emulsion droplet size and the pore size of the porous medium. Test the emulsion in formations with pore sizes similar to the average emulsion droplet size. A higher injection pressure might be necessary in this case considering that the mechanical retention of a droplet in a

pore with almost the same size would play a very important role in the blocking process beside the adsorption of the asphaltene onto the grain surface.

- Investigate the effect of vibration on emulsion injectivity.

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