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Characterization of Surfactants in the Presence of Oil for Steam Foam Application

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Abstract

The steam foam process has been applied in the oil fields since the late 1970s. The mechanism of the process, however, is not known fully; particularly the detrimental effects of oil on foam, while known, are still unexplained. This hinders field application as the behavior of surfactants cannot be predicted under field conditions. Understanding the mechanisms of foam generation, stability, and mobility of foam to improve the development of field level projects has been the focus of the attention of many workers of the oil industry. Extensive laboratory studies have been carried out, mostly without oil but some with oil. This study falls in the later category.

A one dimensional sandpack (6 ft X 2.15 in) model is used to investigate the behavior of four anionic sulfonate surfactants of varying chemical structure with steam. The study is performed with an crude oil at residual oil saturation of about 12 percent of the pore volume. The observed pressure drops across the various sections of the pack are used to study the behavior of the surfactant.

The tested surfactants vary in chain length, aromatic structure and number of ionic charges. A linear toluene sulfonate produced the highest strength foam in presence of the oil at residual saturations, as compared to the alpha olefin sulfonates. This is in contrast to the behavior of the surfactants in the absence of oil, where the alpha olefin sulfonates perform better. The reason for this change in behavior is the relative propagation rate of the foams produced by the surfactants. This conclusion is based on the observation that increase in propagation rate decreases the detrimental effect of oil; while the propagation rate is of little significance without oil.

The disulfonate performed better in the presence of oil. The improvement in the performance is embedded in the propagation rate of these surfactants as the rate of propagation in this case is also high. But the true mechanism of improvement in the strength of the foam instead of deterioration needs further study.

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Section 1

Introduction

1.1 Introduction

Steam flooding is one of the most widely used enhanced recovery methods. Factors such as heterogenety of rocks and presence of faults or permeable streaks diversely affects the efficiency of the process. Even in the absence of these factors, the gravity override, as in case of other light/ gaseous fluid injection methods, is sufficient to lead to poor sweep efficiencies.

Application of surfactant with an aim to overcome these factors , by foam formation, thus improving mobility control, has been reported to be successful both at the field level as well as at the laboratory scale. The success of the process, however, depends upon the formation of in-situ stable foam. How is foam generated and dynamically stabilized? The understanding of this question is the key to the application of the method. To simplify the process by limiting the number of parameters, most of the earlier experimental work has been carried out in the absence of oil. This work has, surely, contributed much to the objective, and theories regarding the foam generation and its behavior in two phase system have been postulated. However, the adverse affects of oil on foam generation as well as stabilization of the foam, although known since the beginning of reseach on the process, are still under investigation.

In the absence of complete understanding of the process, the field application of the process has been based on trial and error, particularly regarding the formulation of the surfactant. The project formulation is based on testing a number of possible candidate surfactants through laboratory experiments; usually these results are also published. Most of these reports, focus on a particular chemical of interest, but often do not describe enough to allow the reader to understand the reasons for the specific surfactant behavior. Further the results of these reports are not comparable because of the varying conditions and experimental techniques. There is a need for independent studies to evaluate the foam forming capabilities of various surfactants in the presence of oil under similar conditions.

This report describes an experimental program designed for testing the foam forming ability of selected surfactants at moderate temperature conditions (150 degree centigrde) typical of califorinian operations. The scope of our work, however, is limited to mainly surfactant variation and pressure drop caused by the foams. For comparison with the performance of the surfactants without oil, the results of an earlier study by Shallcross (1990) are used. This work has the following objectives:

- To study the behavior of in-situ produced foam from selected surfactants.
- To establish a link between the foamability and chemical structure of a surfactant.
- To rank the surfactant according to the strength of produced foam and their sensitivity to oil in typical Californian steam injection conditions (low temperature and pressure).
- To investigate the generality of surfactant alternating gas (SAG) injection mode.
- To compare the foamability of surfactants with and without oil.

For our purpose, all experiments are carried out under the same operating conditions. The pressure drops observed across the sandpack as well as in different sections are investigated.

Section 2

Literature Survey

Use of foam was first proposed by Fried (1961) to control the mobility in enhanced oil recovery (EOR) projects. Concurrently the injection of a mixture of a surfactant solution and a gas as oil recovery agents was proposed by Bernard and Holbrook (1961). Since then the subject has been actively investigated both in the field application as well as in the laboratory. Marsden et al (1977) did a comprehensive literature survey covering all displacing fluid techniques. At that time, the workers identified the lack of reseach on foam applications in thermal processes. Later Marsden (1986) updated the earlier work by providing a survey on the use of foam in porous media.

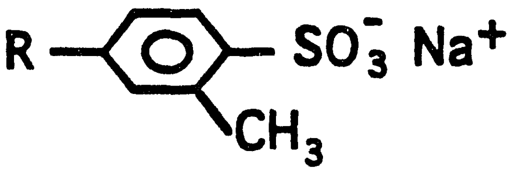
Recently three studies at Stanford were carried out on characterization of steam foams (Shallcross (1990), Hamida(1990), and Hutchison (1991)). This study follows these works. Thus, the duplication of the literature survey is avoided as far as possible. The following sections briefly discuss the types of surfactants, foam generation and stability, the effects of oil on foam,and some other factors as adsorption etc. Experiments performed using sandpack models to evaluate foam behavior are also described.

2.1 Surfactant Types

A surfactant monomer consists of two parts, a polar hydrophilic part and a nonpolar portion. Surfactants are classified into four groups depending, upon their polar part as anionic, cationic, nonionic and amphoteric. A large variety of surfactants is possible within each group depending on the position and type of the polar part, and type, length, and isomeric structure of the nonpolar part, called tail. Anionic surfactants particularly sulfonates are mostly used in steam flooding because they are relatively resistant to retention, and are thermally stable and cheap. We will concentrate on sulfonates in this study. The sulfonates are produced from pure organic chemicals, from refinery cuts and sometimes even from crude oil by sulfonation process (Lake

1989). Surfactants, after sulfonation, are neutralized with NaOH or NH_3. When dissolved in water, the two parts disassociate into a monomer and a cation. The monomer is the part which stabilizes the foam. The structure of alpha olefin sulfonate and linear toluene sulfonate are given below. Disulfonates (also known as dimers) are similar in structure but contain two polar entities.

$R-C=C-SO_3^- Na^+$



2.2 Foam Generation

A comprehensive definition of foam inside a porous media is given by Falls et al. (1986) as " a dispersion of gas in a liquid such that the liquid phase is continuous, and at least some part of the gas is made discontinuous by thin liquid film called lamella". Foam is generated by three mechanisms; snap-off, division and leave behind process.

Snap-off is a process whereby a liquid lamella spontaneously forms in a pore throat and blocks gas flow through the throat. Roof (1970) was the first to observe the snap-off in a water /oil system with oil serving as a displacing fluid. The process is governed by capillary pressure and surface tension. Roof (1970) provided a criteria stating that for snap-off to occur in the straight constricted capillaries, the front of the displacing fluid must have protruded 7 times the length of the throat radius. The snap off mechanisms have since been studied using capillaries of different shapes, glass bead packs and micro models and have further been classified as neck constriction snap-off (given above), preneck snap-off , and rectilinear snap-off. These processes have been discussed in detail by Chamber and Radke (1990). The sites where these processes occur in a porous medium are named "germination" sites.

Division process, as the name suggests, need an existing lamella along with a branching in the flow path. Ransohoff and Radke (1988) observed the mechanism using glass bead packs. Hirasaki (1989) is of the view that lamella division is the predominant mechanism for generation of foam in the presence of a large pressure gradient.

Lamella leave-behind occurs when two separate gas fronts converge on the same liquid filled pore space from different directions. If the surfactant is present to stabilize the interface and capillary pressure in the medium is not too high , then a stable, stationary lamella results (Chambers and Radke 1990). The lamella formed in this case is a weak lamella.

All the mechanisms occur in the porous medium and have been observed using capillaries of various shapes (Chamber and Radke (1990)) and in glass bead packs (Ransohoff and Radke (1988)).

2.3 Foam Texture

The texture of the foam, (i.e. the average bubble size), is determined by the type of snap-off, time of snap-off along with gas velocity, porous media geometry, surface tensions, and liquid viscosity. Some of these properties e.g. viscosity and surface tension are known to be dependent upon the surfactant structure but the quantitative understanding of such correlations is still lacking. Although, the surfactants are not needed for lamella generation "the snap-off time", and the bubble size are influenced by the changes in viscosity and surface tension, due to the presence of a surfactant. In neck-constriction snap-off, bubble size and hence the texture depends upon the time for the liquid to accumulate into the growing collar. The film thickness deposited by the aqueous phase laden with a surfactant is increased about 1.5 times as compared to a lamella produced by the aqueous phase alone (Chamber and Radke (1990)). In the case of pre-neck snap-off the bubble size is smaller than the pore throat, in any case. The bubble generation frequency for snap-off process depends upon liquid accumulation time and the time required to mobilize the lamella. For the division process, bubble generation frequency varies with gas velocity whereas bubble size is directly dependent upon the parent size (Chambers and Radke (1990)). Ransohoff and Radke (1988) and Hirasaki (1989) observed that the division mechanism occurs at high velocities. They concluded that at high velocities, snap-off and division process produces a "strong"' foam. Falls et al. (1986) are of the opinion that the texture of a foam is determined by the geometry and topology of the core. They demonstrated this by using a sandpack where the permeability was varied along the pack. The same type of texture was observed in the particular sections of the pack, irrespective of the quality of the injected preformed foam except near the inlet. Etinger and Radke (1989) also concluded that the porous media determine the foam texture through strong making and breaking of the foam. Using mixed type of surfactants Sharma (1986) observed that equal lengths of alcohol chain and sodium alkyl sulfate minimized bubble size. According to Gauglitz et al. (1988) , the bubble size may be of several pore bodies and will depend on snap-off time.

All these factors determine the bubble size. Some of the factors are found to be directly dependent on the type of the surfactant while many other are found to be dependent only in an indirect way.

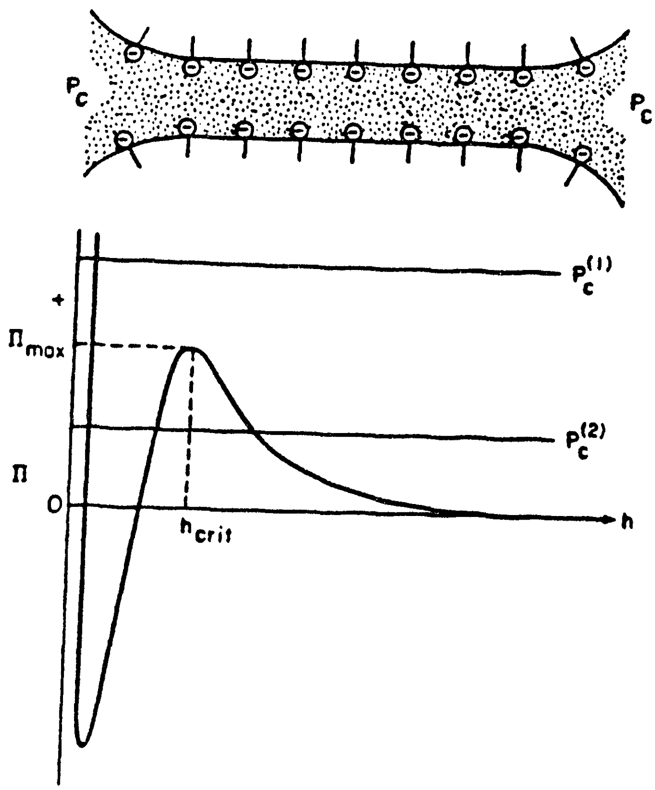


Figure 2.1: A conjoining/disjoining pressure isotherm and the capillary pressure necessary for an unstable $P_c{}^{(1)}$, and metastable, $P_c{}^{(2)}$, foam or pseudoemulsion film

2.4 Foam Stability

A lamella, produced by all processes discussed so far, is not stable if the aqueous phase is not laden with a surfactant. Lenses generated during snap-off will drain due to the capillary suction forces and the lamella will break. Anionic surfactant present at the gas liquid interface orient themselves and create repulsive forces while an attractive force, called Van der Walls dispersion acts upon the thin film due to the molecular density difference of gas and liquid phase. The combined effect of conjoining and disjoining forces, π should balance the capillary suction at this point. No foam can exist when the capillary pressure is greater than the maximum possible value of the conjoining and disjoining forces, π_{max}. The implication is that there is a minimum value of wetting liquid saturation level at which lamella cannot exist due to high capillary pressure. The lamella, however, collapses rapidly after reaching a critical minimum thickness required for stability. The process is shown in figure 2.1 (After Manlowe and Radke (1988) Fig. 6) where h is the lamella thickness, P_c capillary pressure, and π denotes conjoining and disjoining forces. Details are given in Lake, 1989; Falls et al., 1986; Chambers and Radke, 1990. It can therefore be inferred that the lamella thickness as well as the magnitude of the conjoining and disjoining forces will depend upon the surfactant structure, ionic charge and number of molecules at the gas liquid interface. However the exact shape and magnitude of conjoining and disjoining pressure isotherms is not known at concentration commonly used in foam flooding (Chambers and Radke(1990)).

There are other factors which have been postulated to cause foam coalescence in a porous media. These include pore throat to pore body ratio, mass transfer from small bubble to large bubble by diffusion or by condensation and evaporation, shear thinning of a mobile lamella, and external forces like gravity, temperature shocks, gas velocity. Injection of non-condensible, low water soluble gas, (most often nitrogen), stabilizes steam foams to an extent (Falls et al. 1986, Hirasaki et al. 1986). Demiral et al. (1991) have shown that along with stabilizing the steam foam, nitrogen forms a foam bank ahead of the steam front.

2.5 Foam Mobility

Foam mobility is much less then its constituents, gas and liquid, much more less for the gas phase. The mobility of a foam is primarily dependent upon the permeability of porous media, pore size, gas velocity, quality, strength, and texture of a foam, and the surfactant type. For fine textures, the mobility is low. Similarly increase in gas velocity or decrease in permeability will decrease the mobility. But both increasing and decreasing trends have been reported in the literature. Hutchison (1991) has explained these contradictory trends qualitatively by using the translational model. The model consists of, (a) making and breaking (MAB) mode where gas flows by constantly making and breaking the (weak) foam, and (b) bubble train translational (BTT) mode where the bubbles pass through the pore throats without rupturing (strong) foam. The mobility variations are then explained by considering foam texture, stability and transport mode. The transport mode, in turn, is predicted by using permeability, surfactant concentration, and the injected foam quality or in-situ gas saturation as criteria.

Rossen (1988) presented the theories of foam mobilization and models to predict related pressure drops. Rossen concluded that percolation theory can explain the experimental reports regarding minimum pressure gradient required to generate foam. Two cases were considered by him, the snap -off process where foam is considered to be propagated by making and breaking method, and the bubble train flow, similar to Hutchison (1991). The pressure gradient required for the mechanism was correlated statistically with the foam as fraction of pore throats blocked by lamella, geometry of the pore throat and topology of the pore network. The theoretical predicted values were unrealistically high for both cases. Rossen implied that that the snap off process occurs only near the wellbore, while the bubble train flow indicates the plugging of the flow for fine texture foam. Thus either high injection pressures would be required or coalescence should occur.

Falls et al (1986) are of the view that the mobility of the foam is mainly dependent upon the foam texture. They used the concept of continuous and discontinuous gas phase and population balance theory to correlate the gas mobilities. For two phase flow, the model results were in good agreement with their experimental results.

2.6 Oil Effects on Foam

The common notion by which oil droplets affect foam stability is spreading mechanism. It is postulated that during lamella thinning, if oil is in contact with the lamella, oil droplets are squeezed between the film surfaces and spread on the surfaces in the form of lenses (microemulsion). Eventually spreading on the film surface, the oil droplets breaks the lamella (thick film).

Nikolov et al.(1986) studied the foam stability in the presence of n-octane, n-dodecane and Salem crude oil. In the study, transmitted lights and special microscopic techniques were used to observe aqueous foam film and emulsified oil droplets. Alpha olefin surfactants of C_{12}, C_{14}, and C_{16} and a nonionic surfactant Enordet AE 1215-30 at concentration above the critical micelle concentration were used in the study, with preequilibrated oil. This study concludes that the foam destabilization in the presence of oil is a complex process, and involves the migration of emulsified oil droplets from the foam film lamella in the plateau borders where factors such as the magnitude of pseudoemulsion film, the pseudoemulsion film tension, the droplet size and number of the droplets contribute to destabilization or stabilization of the three phase foam structure. They also concluded that micellar micro-structure are formed within the film where the electrolyte concentration, and surfactant type directly influence the microstructure stability. The rupture of film occurs stepwise, number of steps increases with increase in chain length, increasing the lamella life. It was also observed that different type of surfactant behave differently with certain oils while an opposite behavior of the same surfactants may be observed with another type of oil. The study, however, is restricted to pregenerated bulk foam only. Therefore, the application of the results in porous media should be done with care. Also the reported film rupture time (10 minutes.) is very unrealistic and is much greater than the drainage time while actual rupture time in the presence of oil in a porous media is less than the drainage time.

Micromodel studies have also been carried out by Schramm et al (1990) to observe the lamella/oil interaction and a model was formulated based on surface energy concepts. Based on the results, the surfactant/ foams are divided into three categories; type A,B and C. Type A foams showed no interaction with the oil. For type

B foams, oil emulsified into smaller droplets ending up in the plateau borders. The oil-containing foams continued to flow and only a few rupture due to oil occurred. In the type C foam, oil spontaneously emulsifies into the small droplets which were drawn up in the foam, and ruptured the thinner lamella regions. The workers concluded that the foam destruction involves emulsification of oil into droplets which travel into the interior foam structure and enters the aqueous /gas interface to cause rupture.

Manlowe and Radke (1988) performed experiments using an etched-glass micromodel. The oils used in the study were hexane and dodecane and five different surfactants were used to observe the spreading effects of oil. The type of oil, spreading or non spreading, has no effect on foam performance. The approximated bubble drainage time for the three phase, gas/water/oil, system was in agreement with the observed rupture time of the foam. Manlowe and Radke confirmed the existence of oil/water emulsion on the the foam bubble surfaces, and foam stability could be linked with the pseudoemulsion film stability formed between foam bubbles and oil.

2.7 Some Other Factors

The factors other than oil which affect the performance of a surfactant at field level are thermal stability, adsorption, cation exchange with clays, and partioning of the surfactant into oil. These factors are covered in the literature survey by Hamida (1990) in detail. In summary, sulfonates are thermally stable but a few conflicting results have also been reported. Adsorption follows a Langmuir type isotherm (Al-Khafaji(1982), Lake (1989)), and depends upon the solution concentration, and is usually low as compared to other factors. Cation exchange which is due to divalent ions present in the clays, depends upon reservoir rock, and salinity. Preflushing with trona or alkali may be beneficial for field applications if the cation exchange contribution is large. Partioning into the oil is dependent upon surfactant formulation, concentration, salinity, crude oil composition and temperature. Experimental methods to evaluate the surfactant losses due to these factors are described by Friedmann (1986).

2.8 Displacement Studies

Shallcross (1990) surveyed the experimental techniques applied to evaluate the surfactant foaming capabilities. He concluded that, as a first step, prescreening of surfactants is required for any study. Earlier Castanier and Brigham (1985) described screening criteria for steam foam injection outlining three main points as, (a) thermal stability under field conditions, (b) low partitioning in oil, and (c) low retention of the surfactant in the porous media. Regarding the experimental setup, Shallcross concluded that a one dimensional sandpack gives a good indication of surfactant performance at the first stage. The factors such as higher oil saturation (above residual oil saturation), permeability variations and gravity override can then be analyzed by using either two parallel sandpacks of different permeabilities or a two dimensional vertical sandpack.

After prescreening, Shallcross tested (without oil) seventeen different surfactants representing four chemical structures namely alpha olefin sulfonate, linear toluene sulfonate, internal olefin sulfonate, and linear xylene sulfonate. A linear olefin sulfonate, AOS2024, was found to be the best, raising the pressure drop in the sandpack to maximum with single slug injection of 10 % PV of 0.1 % by wt active surfactant solution. The main conclusions besides the highest performance of AOS2024 were; (a) increasing the chain length increases the surfactant foaming capacity, (b) nitrogen injection increases the foam stability, and (c) internal olefin surfactants generate strong foams but at a higher concentration than the alpha olefin sulfonates. Later Hamida (1990), under similar conditions observed a comparable behavior of AOS 2024, again in the absence of oil. Hamida further concluded that enrichment of disufonate content in AOS2024 enhances the foam propagation but the foam strength is reduced. However, no foam was produced by any of the surfactants in the presence of the oil while simultaneous injection of steam, nitrogen, and surfactant slug (SIS) mode was applied. The other surfactant injection method, where steam and nitrogen injections are discontinued temporarily during the surfactant slug injection, surfactant alternating gas (SAG) mode was successfully applied by Demiral (1991) using AOS 2024 at 1.0% by wt active concentration at the residual oil saturation. Hutchison (1991) extended the study and optimized the slug volume and concentration. He concluded that a big slug at lower concentrations may prove to be cost effective in the field. The experiments reported in the present study are performed under the same conditions as that of Hutchison at residual oil saturations and complement his work by using different chemical compositions for the surfactants.

Hudgins and Chung (1990) studied the foam generation and propagation over long distances through porous media. A one dimensional sandpack model (30 ft X 0.25 in) was used for conducting two series of experiments using Alipal CD-128 (chemical formulation not given). Experiments were conducted with nitrogen as displacing fluid and water alternating gas (WAG) mode was applied . It was observed that different ratios of water and gas strongly affect the foam generation as well as its propagation. The injection strategy can be optimized by adjusted WAG ratios and injection sequence as injection of large slugs of water destroy the generated foam. By proper WAG ratios foam can propagate at much longer distances.

Jensen and Friedmann (1989) studied the behavior of three sulfonate surfactants of varied structure (Variation in structure , names or chemical composition not mentioned) with four crude oils and two synthetic oils. The pressure drop across a sand pack was used as criteria. The foam injected was not preformed but the gas and liquid was homogenized upstream of sand pack. The injection of surfactant solution was continued till the steady state pressure drop was achieved, and the volumes of the injected surfactant solution was compared. They concluded that oil saturation level in the core strongly affected the foam response more than the variation in the oil type. Two types of surfactants were defined, oil sensitive and oil insensitive based on the performance of the surfactant above 15% oil saturation level. The foam propagation rate was maximum for the oil insensitive surfactant.

Hansen and Dolland (1990) studied 48 surfactants using 200cm long and 2 cm diameter plastic column packed with glass beads for effectiveness of gas blockage in presence of oil. Only four surfactants successfully blocked the gas. A constant pressure gradient with stepwise increase was applied across the pack and gas flow rate was measured at each step. The properties like interfacial tensions, spreading coefficients, oil saturation, foam quality, surfactant oil solubilization and wetting characteristic were also measured but no correlation between these properties and foam behavior was observed.

Sharma et al. (1986) studied the foaming behavior along with other surface chemical properties of mixed-chain length surfactants; selecting Na SO_4 C_{12} and varying the alcohol chain length from C_8 to C_{16}. In this study, Ottawa as well as Berea sands were used as porous media and identical results were reported. For equal chain length of the two components, the breakthrough time and the fluid displacement efficiencies were maximum . Regarding physical properties, minimum bubble size and surface tension with maximum surface viscosity and bubble stability were also observed for equal chain lengths.

Duerksen (1986) tested 35 commercial surfactants and 15 CRC (Chevron Research Company) sulfonates. Prescreening of surfactants was carried out by observing the thermal stability, bulk foam generation, resistance to the flow of steam in the porous media in the absence of oil. It showed that alkyl olefin sulfonate and CRC sulfonates perform better than alkyl aryl sulfonate. The behavior of the surfactants was observed in the presence of Kern River oil using unconsolidated as well as Kern River sand at different oil saturations. The resistance factors observed showed that the alkyl olefin sulfonate are less sensitive to oil saturation while CRC gave higher pressure drops at lower oil concentrations. From the static foam stability tests, Duerksen concluded that in a porous media, foam requires constant regeneration at flowing conditions to maintain its resistance.

Wang (1986) concluded that alternative injection of surfactant (Suntech IV) solution and steam reduces the steam mobility while addition of nitrogen is beneficial as the steam mobility is further reduced.

Dilgren and Owens (1983) reported that alpha olefin sulfonate reduces the steam mobility by a factor of 25 in the absence of oil. Muijs et al. (1988) concluded that an increase in carbon chain length increases the surfactant performance for both alpha olefin and linear toluene sulfonates. The study again was carried out without oil.

Lau and Borchardt (1989) analyzed a field project and concluded that performance can be improved by faster surfactant propagation, increased foam strength, and residual oil saturation reduction. Performing displacement studies, they concluded that surfactant propagation suffers with increase in molecular weight. This, however, can be improved by increasing the disulfonation or coinjection of sodium sulfate. Here it may be pointed out that two types of propagations are mentioned in the literature, surfactant propagation and foam propagation. The two should be studied separately as they represent two different aspects, in spite of many similarities. The increased surfactant propagation shows less surfactant loss due to retention, partitioning and precipitation of the surfactant but does not necessarily lead to foam propagation. On the other hand, foam propagation may occur due to fast moving lamellas even in the areas where the surfactant propagation is still at lower levels. The higher propagation of foam, thus, shows foam performance in terms of pressure gradients while surfactant propagation indicates surfactant losses.

Regarding field application, Hirasaki (1989) reported use of AOS1618, SD1000, LTS18 in field tests alongwith some commercial surfactants of unknown formulations. A survey and analysis of some field projects have been prepared by Castanier (1989).

2.9 Remarks

From the literature survey it may be concluded that

- The commercial surfactants contain a variety of chemical species, and samples may very in chemical composition.
- The role of surfactant, directly or indirectly encompasses all facets of foam flooding. However no correlation has been identified yet.
- The mechanism of foam generation is better known than the stability critera. The two phase mechanism can be explained but the effect of oil on foam in the porous media are not fully understood.
- The displacement studies using sand packs or actual cores without oil show that alpha olefin sulfonates are the best suited surfactants in the steam foam injection. The effect of increasing the carbon chain length improves the surfactant performance. These trends, however, need to be verified in the presence of for field applications.

The mechanism by which oil affects the surfactant performance need to be studied.

Section 3

Experimental Equipment and Procedure

A one dimensional laboratory model was used to investigate the foam forming characteristics of surfactants under the same set of conditions in the presence of a crude oil. The surfactants studied included an alpha olefin sulfonate, AOS2024 , a linear toluene sulfonate, LTS18, a CHEVRON disulfonate, SD1020 and an alpha olefin sulfonate, AOS1618 . A description of the apparatus and experimental methodology used, and the experiments performed follows. The experimental conditions are summarized in Table 3.1.

3.1 Experimental Apparatus

The equipment used in this study is essentially a one dimensional sandpack model and was first built by Wang (1986). A similar equipment was also used by Maneffa (1987) , Shallcross (1989-1990), Hamida (1990), and Hutchinson (1991). A schematic of the linear sandpack model and supporting equipment is shown in Figure 3.1.

3.1.1 Sandpack

The apparatus consists of a cylindrical stainless steel tube (SS#321) 6 feet long, with a 2.16 inches inner diameter, wrapped with 2.76 in. insulating Fiberfax to reduce heat losses. It is packed with clean Ottawa sand. The porosity of the sandpack is 35% and the permeability is 90 Darcies.

TABLE 3.1

EXPERIMENTAL CONDITIONS	
SANDPACK PROPERTIES	
LENGTH	1.83m (6.0 ft)
DIAMETER	54.8mm (2.16 in)
POROSITY	33 %
ABSOLUTE PERMEABILITY	89.8 μm^2 (89.8 D)
PORE VOLUME	1500 ml (0.0502 ft^3)
CRUDE OIL:	MOBIL'S NEWPORT BEACH CRUDE OIL
INJECTION RATES	
BACK PRESSURE	580 kPa (70 psig)
STEAM INJECTION RATE	4.0 ml/min
NITROGEN INJECTION RATE	0.081 l/min
SURFACTANT INJECTION RATE	9.0 -10.0 ml/min
SURFACTANT CONCENTRATION	1.0 wt % (Active)
SLUG VOLUME	150 ml
SODIUM CHLORIDE CONCENTRATION	1.0 wt %
SURFACTANTS USED	
RUN 11	ALPHA OLEFIN SULFONATE AOS2024
RUN 12	LINEAR TOLUENE SULFONATE LTS18
RUN 13	SD-1020 (CHEVRON TRADE NAME)
Run 14	ALPHA OLEFIN SULFONATE AOS1618

Table 3.1: Experimental Conditions

3.1.2 Injection System

Fluid injection is handled with four pumps, including a GE pump and three Constametric Model III pumps. Of the Constametric types, one is exclusively used for input to the steam generator, the second is used for injection of the distilled water at a low rate and the third is used for injection of either surfactant or cleaning fluid. The GE pump provides high rate distilled water flushing and is used for cleaning.

3.1.3 Data Acquisition

Figure 3.1 shows the eighteen thermocouples located along the sandpack. They are located at a distance of about 4 in. from each other at the inlet and 8 in. from each other at the outlet. Their position alternates between the center and 0.5 in. from the top of the pack. A thermocouple is also placed in the steam generator, and in the fluid inlet and outlet flow lines.

Eight taps along the pack allow for pressure drops to be recorded (Figure 3.1). The taps divide the sandpack into four sections. The first two sections are 16 in. long while the last two are 20 in. long. The first section is further subdivided into four subsections of four inches each. Seven thin film heat flux sensors provide heat loss information. The overall heat transfer coefficient and the steam quality along the sandpack can be determined from this information. Four of the heat flux sensors are placed at the top of the pack (14, 26, 38, and 57 inches from the inlet) and the other three are placed circumferentially around the pack at the bottom, left and right side at a distance of 26 inches from the inlet.

An IBM-XT computer and an HP Model 3497A data acquisition system are used to record the pressure and temperature information from the seven transducers and 21 thermocouples. A Marshall Model #1056 steam generator is used for the generation of steam, a Mattheson Model 8141 mass flowmeter to control the nitrogen supply rate, and strip chart recorders to provide continuous analog output of pressure drops along the pack.

3.2 Experimental Procedure

The experimental procedure consists of six main stages which are explained below. Mobil's Newport Beach crude oil was used in all experiments.

3.2.1 Saturation with Crude oil

The sand pack was initially cleaned as described in section 2.6 and then saturated with water. Crude oil was injected in the pack until breakthrough was achieved. To ensure that the sand pack had reached residual water saturation, an additional 100-200 ml of crude oil was injected. Although no back pressure was applied during this step, the high viscosity of the oil caused a high pressure drop across the pack.

The sand pack was left at residual water saturation condition for a period of at least 15 hours.

3.2.2 Steam Flooding

100 % quality steam was injected at a rate of 4.0 ml CWE (Cold Water Equivalent) per minute at a back pressure of 70 psig. Steam breakthrough took approximately 3.5 - 4.0 hours and was indicated both by the temperature measurements and by visual inspection through the sight glass. Steam injection was continued for about an hour until no traces of oil were observed in the production stream.

Cold water was injected in order to cool the system and to leave it in the state of residual oil saturation for at least 12 to 15 hours.

3.2.3 Steady State Condition

Steady state conditions for the experiment were achieved by injecting steam into the cold sandpack at residual oil saturation with a back pressure of 70 psig until breakthrough was observed Nitrogen was then injected for about an hour. The total time for this step is approximately four hours.

3.2.4 Slug Injection

Three to four surfactant injections were carried out after achieving steady state conditions. Prior to the injection of a slug, the steam and nitrogen injection were stopped. Surfactant solution was then injected at a fixed rate until the desired quantity had been achieved. The surfactant injection was then stopped and the steam and nitrogen injection was resumed.

3.2.5 Shut Down

Upon completion of the experiment, the sand pack was flushed with four pore volumes of distilled water.

3.2.6 Cleaning of the Sand Pack

The same sandpack was used in the entire experimental series. Effective cleaning of the pack after every run was therefore a very important step. The following procedure was applied to prepare the pack for the next run.

Six to eight pore volumes of distilled water were injected into the sandpack. This was followed by injection of two to three PV of mineral spirits to dissolve and displace the oil. The sandpack saturated with mineral spirits was left overnight.

An additional half PV of mineral spirits followed by one and a half to two PV of tetra-butyl -alcohol (TBA), and four to five PV of hot distilled water were injected into it. The pack was then injected with carbon dioxide at a constant pressure of 45 PSIG with a back pressure of 40 PSIG for about 45 minutes to ensure that it was free from nitrogen. The system was then flushed with ten pore volumes of distilled water. The core is then assumed to be clean and ready for the next run.

3.3 Experimental Program

The objective of the study is to analyze the effect of structure of a surfactant on the foam stability in the presence of an oil. The following sections describe the selection of surfactants and the experiments performed.

3.3.1 Surfactant Selection

Four anionic surfactants, AOS2024, LTS18, SD1020 and AOS1618 are used. The surfactants used represent three broad category of sulfonates, two Alpha olefin sulfonates, a Linear toluene sulfonate and, a disulfonate. All four surfactants are commercial products. The numbers attributed to their names indicate the alkyl chain length or the range of alkyl chain length e.g. the chain length of molecules in AOS2024 varies from 20 to 24 carbon atoms. SD1020 is a disulfonated alpha olefin sulfonate of unknown chain length. The selection of three surfactants AOS1618, AOS2024 and LTS18 is based on the highest ranking of these surfactants out of the seventeen surfactants tested by Shallcross (1990) . The ranking of the surfactants was based on the magnitude and duration of response at minimum (0.1 %) concentration level in the sandpack in absence of oil. The higher pressure drops created by the foam generated by these surfactants was also reported by Hamida (1990). The selection also represents the variations in length AOS2024 vs AOS1618, variation in structure AOS2024 vs LTS18 and includes disulfonated surfactant. The above experiments were carried out for two phase system, gas(steam and nitrogen)/water. The fourth selected surfactant was, however at the lowest level in the ranking of Shallcross as there was no response (without oil) at the highest tested concentration (1.0 %).

3.3.2 Run Sequence

Four experiments were performed using the selected surfactants in the following sequence; AOS2024 was used in Run 11, LTS18 in Run 12, SD1020 in Run 13 and

AOS1618 in Run 14. In all the experiments the concentration of surfactant solution was 1.0% by weight of active surfactant, and 1.0% by weight of sodium chloride. All experiments were performed at residual oil saturation which was estimated to be 12.0% on the average (Appendix A) Each run is described briefly below.

Run11 : AOS2024

The surfactant used in this run is an alpha olefin sulfonate, AOS2024. The objectives of this run are to:

a) check the equipment performance after reassembling the apparatus in a new location.

b) check the effect of a third slug infection of the surfactant at 1% weight concentration,

c) serve as the base case for later surfactant studies.

Prior to the run, the equipment was pressure tested at 300 psi. Carbon dioxide was injected to remove the air in the system. The equipment was flushed with 10 PV of water. The pressure transducers were calibrated. The oil was injected as per procedure and steam flooding was performed. The problems encountered were corrected. The run was performed as per normal procedure.

Run12 : LTS18

The surfactant used in this run is a linear toluene sulfonate, LTS18. The normal sequence was applied during this run. During the preparation of the surfactant solution, a slight heating (60 degree centigrade) was needed. The solution was kept at 40-45 degree centigrade during the experiment. Three slugs of surfactant solutions were injected during this run as per slug injection procedure. The back pressure was set at 70 psig during this run. After the second injection, a strong foam was produced. Big foam bubbles were observed through the slight glass at the outlet. The back pressure control valve was working but a lot of fluctuations in the pressure were observed. To some extent, these were reduced by manually operating a valve provided for this purpose. The fluctuations observed in Figure 4.4-4.6 are due to this back pressure control problem.

Run13 : SD1020

This run followed the LTS18. The run was a normal run. Three slugs of surfactants were injected.

Run14 : AOS1618

The run of AOS1618 was a normal run. As no significant pressure drop increase was observed during this run, the run was extended to five slug injections. The run was stopped as per procedure. However, the results of this run were not stored due to a computer malfunction during shutdown. The results presented are produced from the log charts from backup recorders.

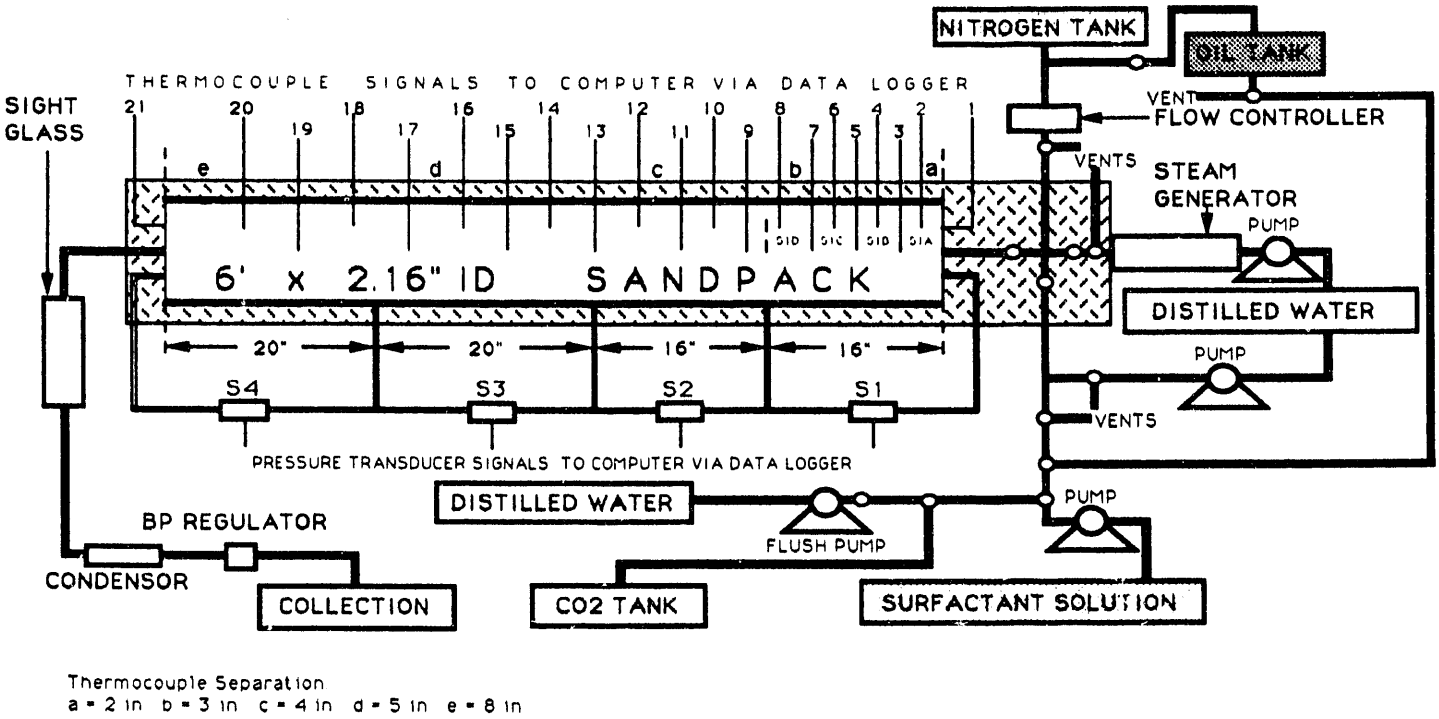


Figure 3.1: Schematic Diagram of the Equipment

Section 4

Results and Discussion

4.1 Results

The pressure drop across a sand pack is usually the main criterion used to compare the effectiveness of surfactants. The results are analyzed on this basis. This is in line with similar studies carried out using the same type of systems e.g. Dilgren et al. (1978) , Huang et al. (1985), Muijis (1987). The results of the experiments performed in this study, are shown in Figures 4.1 to 4.11 and summarized in Table 4.1.

4.1.1 RUN11 : AOS2024

The surfactant used in this run is an alpha olefin sulfonate , AOS2024. The total peak pressure drops observed along the sandpack in this run were 2.0,12.0,16.0 and 17.0 psig for the four slug injections respectively. The behavior of the pressure drop during the run is shown in Figure 4.1.

An increase in the pressure drop was only observed in section 1 when the first slug injection was performed (Figure 4.2). For subsequent slugs, responses were observed in every section except section 4 . Figure 4.2 also shows that the pressure drop across section 3 of the pack was high as compared to section 2. The trend continued with similar pressure differential for the two sections. This was due to the difference in the lengths of these two sections which are 20 inches and 16 inches respectively. Corresponding pressure gradient per foot observed in these two sections were 6.0 psi/ft and 5.04 psi/ft. The actual pressure gradient is, therefore, lower in section 3 than in section 2.

The pressure drop responses from the experiment in sections 1A to 1D are shown in figure 4.3 . No response was observed in section 1A and 1B during the experiment. A higher response was observed in section 1D as compared to 1C. This trend was observed in all experiments and will be discussed separately.

TABLE 4.1
PRESSURE DROPS

Run	SLUG NO	SECTION 1	SECTION 2	SECTION 3	SECTION 4	TOTAL PRESSURE DROP
11 AOS-2024	1	1.4	0.4	0.4	0.0	2.0
	2	2.0	6.0	6.2	0.4	12.0
	3	3.0	8.0	8.4	0.5	16.0
	4	3.4	7.8	8.4	0.5	17.0
12 LTS-18	1	2.6	2.2	0.6	0.5	6.0
	2	5.6	9.0	7.5	5.0	20.0
	3	7.0	9.4	8.2	6.0	23.0
13 SD-1020	1	3.8	1.4	0.0	0.0	5.0
	2	4.6	2.8	0.0	0.0	6.0
	3	5.6	5.4	5.0	2.0	15.0
14 AOS-1618	1	0.7	0.8	0.3	0.0	1.5
	2	0.9	0.9	0.6	0.0	2.5
	3	1.0	1.8	0.6	0.0	3.4
	4	1.0	2.5	0.8	0.0	3.6

Table 4.1: Surfactant Performance in Presence of Oil

4.1.2 Run 12 : LTS18

The surfactant used in this run is a linear toluene sulfonate , LTS18. The highest total pressure drop was observed in this run. Figure 4.4 shows that the total pressure drops were 5, 20 and 25 psi for the three slug injections respectively. The large fluctuations observed in this run are due to back pressure control problem as stated earlier in section 3.2. The increase in the pressure drop is significant from the first to the second slug injection as in case of run 11.

Section-wise results which are shown in figure 4.5 indicate that the pressure drop in both sections 1 and 2 increased after the first slug injection. The important observation of this run is the clear response from section 4 after the second slug injection. The response of section 4 is comparable with section 3. As explained in AOS2024 run, the corrected pressure gradients for sections 1, 2, 3 and 4 are 5.2, 7.0, 4.9 and 3.6 psi/ft respectively.

Figure 4.6 shows the response of sections 1A-1D which are similar to the AOS2024 case.

4.1.3 Run 13 : SD1020

The surfactant used in this run is a CHEVRON disulfonate , SD1020. The increasing trend of total pressure drop with successive slug injections followed a different trajectory then run 11 and run 12. As shown in figure 4.7, the response to the first slug was low (5.0 psi). The figure shows that the maximum pressure drop across the pack did not increase much with the second slug injection (6.0 psi). However,the response from the third slug was significant with a value of 15.0 psi.

The highest pressure drop for any section in this run was recorded across section 1 (Figure 4.8). This is contrast to runs 11 and 12 where section 2 produced the largest drop. Figure 4.8 also shows that sections 3 and 4 showed no response to the first two slug injections. For the third slug injection, an increase in pressure drop is observed . from section 3 after the third slug injection is comparable with section 2. (5.5 psi vs 5.0 psi). Section 4 of the pack also showed a response of 2.0 psi to this slug injection.

Near the inlet, the response was similar to other runs with no response from section 1A and 1B. This is shown in figure 4.9. The responses for section 1C and 1D are similar (2.6 psi vs 2.9 psi).

4.1.4 Run 14 : AOS1618

The surfactant used in this run is an alpha olefin sulfonate , AOS1618. The maximum pressure produced was 3.5 psi after the fourth slug injection. Accordingly the pressure drops observed in each section were also low.

4.2 Maximum Pressure Drop

The total pressure drop observed at the steady state conditions prior to the surfactant slug injection was in the range of 0.5 to 1.0 psi. Among the tested surfactants, the pressure drop increased to the highest level of all the experiments (23 psi) in the case of LTS18. This was followed by AOS2024 (16.0 psi) and SD1020(15.0 psi). The lowest response was observed in the case of AOS1618 (3.5 psi). (Table 4.1)

4.3 Inlet Zone

A consistent behavior was observed near the inlet of the sandpack in sections 1A and 1B . In these sections either no or a very negligible increase in pressure drop was observed irrespective of the surfactant and the number of slug injections; a maximum increase of 0.2 psi was observed in section 1B in the case of LTS18 and AOS 2024. Consequently, a zone of about 8 inches exists at the pack inlet with no pressure gradient. Away from the inlet zone (section 1C and 1 D) the pressure drop increased with varying degrees for different surfactants; with a higher increase observed in section 1D relative to 1C.

The lack of pressure drop increase in the inlet zone in all the cases, irrespective of number of slug injections is due to complete dryness/ low aqueous phase concentration because 100 % quality steam was injected in the sand pack. The other reason may be the wettability alteration. Given the fact that a maximum volume of steam has passed through these sections, the first effect is more plausible. This also explains the reason for a similar response under similar conditions when no oil was in the pack as reported by Hamida(1990).

4.4 Slug Wise Response

The pressure response for the first slug was lowest in each case. Response to the subsequent slug injections did not follow a particular pattern. In the case of LTS18, a 300% increase in pressure drop was observed after the second slug as compared to the response after the first slug(20 vs 6.0 psi) while an increase of only 15% was observed for the third slug (23 vs 20 psi). These increase rates for AOS2024 were 500 % , and 25 % ; and in case of SD1020 the respective increase rates were 20 % and 200 %.

Three factors which can contribute to the difference of these responses as well as to the low response after the first slug injection in all cases, are discussed in the following sections.

4.4.1 Possible Adsorption Problems

Oil and rock may scavenge surfactant from the gas water interface or from the surfactant solution. This mechanism will occur up to the point where oil and rock are not saturated with the surfactant. Once enough surfactant has been injected in the system and has contacted the oil /rock, this effect would be diminished. In laboratory experiments this is achieved by equilibrating oil and rock with the surfactant. In this study, however, this phenomenon would affect the surfactant performance only in the first few slugs injection. After the saturation of oil and rock with surfactant, the mechanism would not hinder in the creation or stabilization of foam as no more surfactant would be adsorbed by rock or scavenged by the oil.

The adsorption losses will be for different surfactants, brine concentration and oil saturation . In this study, these losses are not estimated. For SD1020, where the response has been delayed upto the third slug injection, these need to be determined for better evaluation of the behavior of the surfactant.

4.4.2 Macroemulsion Formation

The formation of macroemulsion has been avoided by injecting the surfactant solutions at high concentration. The critical micellar concentration (CMC) is, fortunately, usually low as its range is 0.1-0.2 percent surfactant concentrations (Al- Khafaji 1982). One percent surfactant solutions injected in the study are higher than CMC.

This is specially true at the injection end. Downstream concentration of surfactant will depend on surfactant propagation; foam propagation, surfactant solution propagation and propagation of surfactant with aqueous phase. Thus at the downstream end formation of macroemulsion cannot be totally rejected in the first few slug injections.

4.4.3 Wettability Changes

Oil may cause wettability change, from water-wet to oil-wet, and destabilize the foam.

Ottawa sand is used in the sand pack which is strongly water wet. The oil is at residual oil saturation (12 percent). In a recent micromodel study, Hornbrook et al. (1991) have observed that when a surfactant solution comes in contact with oil interface, the surface is converted to water-wet even at 100 percent oil saturation. The change in wettability (except in the dry zones as discussed earlier) is not expected even at the down stream end. The generation / propagation of foam in the sandpack also negates the the wettability alteration.

4.5 Foam Propagation Rate

The foam propagation rates are compared by the delay in response from the sections after the slug injection. For AOS 2024, no pressure drop increase was recorded in section 2 and 3 after the first slug injection, The section 2 response was immediate and a delay of 10 minutes was noted for section 3 after the second slug injection. The same trend continued for subsequent injections. However a slight improvement in the response time for the section 3 was noted (Figure 4.2)

The response for LTS 18 are as follows; the second section responded after 10 minutes of 1st slug injection. Sections 3 and 4 did not respond to the first injection. The response from the sections 2 and 3 was immediate and the pressure drop increase in section 4 was observed after three to five minutes for the subsequent two slugs.(Figure 4.5) It is, thus, deduced that the foam propagation rate is slower in the case of AOS2024 as compared to LTS 18.

The results of run 13 with SD1020 indicate an immediate response for section 2 from the injection of the first injection. For sections 3 and 4 the response was observed with a delay of 10 and 15 mins respectively after the third slug injection. (Figure 4.8) Thus the foam propagation rate in case of SD1020 is higher than AOS2024 and lower than LTS18.

The propagation rate cannot be compared for the case of AOS1618 as the response was low.

4.6 Foam Generation at Higher Saturations

The estimated residual average oil saturation in the pack is about 12%. However section 4 of the pack would be at a higher oil saturation as less pore volumes of steam have swept this area. Observations of section 4, therefore, are presented separately. The highest pressure drop increase was observed in section 4 for LTS18 (5,6 psi) for the 2nd and 3rd slug injections. A nominal increase of 1.0 psi for the AOS2024 case after the third slug injection. 2.0 psi response in the case of SD1020 was also observed after the third slug injection in this section.

Earlier in section 4.1.11, it was concluded that the propagation of foam in case of LTS-18 is faster than the other cases. Thus it can be concluded indirectly that LTS-18 is less sensitive to the oil as compared to other surfactants tested in this study.

This complements the results of Jensen and Friedmann (1988) who observed that the foam of less sensitive surfactants propagates at a faster rate.

4.7 Injection Method

The tested surfactants produced foam in the presence of oil under the slug injection technique (SAG mode). Foam was not produced when steam and surfactants were injected simultaneously (SIS mode), (Hamida 1990). The results for the surfactant AOS2024 compare favorably with the results reported by Hutchison (1991).

The different results for the two injection modes may be attributed to better in-situ contact of the gas phase with the surfactant laden aqueous phase. The generation of foam requires adequate aqueous phase saturation in the pores to create a liquid film which then forms bubbles by capillary action at the constriction neck by flow of liquid through the annulus (snap off action). Surfactant molecules at this liquid film, called lamella, stabilize it. The injection by the SAG method ensures both contact and required pore level saturation because the steam and nitrogen which is present as a noncondensible gas have to pass through the injected slug.

In other words, the gas has to make a new path through the aqueous phase. The presence of sufficient quantity of the aqueous phase, the necessary ingredient required for snap off action, is the main cause of success for this mode.

In case of SIS injection along with continuous steam injection, the concentration of surfactant at any given point will be so low that the lamella produced is not stabilized. In addition, the low saturation of aqueous phase where steam is passing may not be able to produce lamella. If a lamella is not produced at the first stage, no foam will be generated. This occurs for the SIS injection mode near the injection end. Away from the injection end , the sufactant will end up in the aqueous phase while steam and nitrogen may follow the preferential path caused by gravity override or other factors. The low aqueous phase concentration in this particular path will not create any of the foam generation phenomena.

Another possible cause of no foam generation in this case is the continuous flushing action of gas. If the rate of surfactant injection is just equal to this quantity, all or most of the injected surfactant will end up in the produced gas. The lamella produced in this case will not have the required amount of surfactant to stabilize it and thus will lead to no foam generation.

4.8 No Oil Case

The sandpack used in the above study was used to observe the behavior of surfactants in the two phase system, Steam/ water only, by Shallcross (1990) and Hamida (1990). The performance of the surfactants as reported by Shallcross are used for comparison as no oil case without reference from here on. These results are reported at a surfactant concentration of 0.1% by wt. as against 1.0% by wt. of this study.

The major observation was that SD1020 did not produce foam. AOS2024 produced maximum pressure drop with a single injection (234 psi). AOS1618 followed with a response of (132, 247) and this was followed by LTS18 (58 psi, 237 psi for 2 slugs). The durations of the pressure response, defined as the time between when the pressure drop increases at a rate less than 1 psi/min., are 85, 68 and more than 120 minutes for AOS2024, AOS1618 and LTS18 respectively.

Foam propagation rate , as indicated by section-wise responses of the surfactants, was highest for LTS18; it was followed by AOS2024, and this was followed by AOS1618. The respective time lag in response to the first slug injections were 10, 20, and 30 minutes respectively. The results, taken from Shallcross(1990), are shown in Figures 4.12...4.17.

4.9 Comparison with no oil case

Comparison of absence of oil case with its presence indicates that in the absence of oil, AOS2024 created the maximum pressure drop while in presence of the oil, LTS18 has created maximum pressure drop. The higher propagation rate of LTS18 in both cases, has increased the performance in the presence of oil. The surfactant, SD1020, did not create foam in the absence of oil . However, in presence of the oil, its performance is comparable with AOS2024. This implies that dimerized surfactants perform better in the presence of oil.

The increase in alkyl chain length of a particular structure increases the performance irrespective of the presence of oil as the results of AOS2024 and AOS1618 indicate.

4.10 Theoretical Explanations

In this section we will try to analyze the causes for the observed behavior for various surfactants in the presence of oil.

In three phase media how oil affects the foam stability is not established. However it is observed that the performance of a surfactant with fast foam propagation rate is less affected by presence of the oil.

The process can be explained by the two existing postulates regarding the effect of oil on foams.

One of the mechanism observed is the interaction between aqueous foam films and emulsified oil droplets. The foam bubble ruptures due to destabilization of the psuedoemulsion films with the emulsified oil (Manlowe and Radke (1988)). The rupture times are much faster than the drainage time which is the main cause of coalescences. However, if the oil/water contact time is less then the rupture time, the gas bubble lives the normal life. The faster propagation rate decreases the contact time, decreases the number of coalescences due to breakage of pseudoemulsion and, thus, increases the foam performance accordingly.

The second postulate links the spreading of oil on the gas bubble surface as main cause of the coalescences. However, in this case the imbibition of oil particles occurs before the spreading. While the imbibition depends upon the surface forces, the amount of oil deposited on a particular gas bubble will depend upon the oil/bubble contact time. The insufficient spreading of oil on the gas bubble will not affect the lamella and the gas bubble will collapse due to the other factors like drainage or film thinning. Obviously the amount of oil deposition depends upon the contact time , and will be less in case of a faster moving bubble. The foam propagation rate , thus, certainly affects the life of individual bubbles. Thus, it should be expected that the faster propagation will lessen the oil effects.

The observation that the higher saturation decreases the foam strength can also be explained by these postulates. Increase in oil saturation increases the average pore size where oil is present, increases the pore throat size. This increase in the contact time is due to the increase in the pore throat size where the oil/ lamella interaction is occurring. The bubble rupture rate will then increases, decreasing the foam strength. On similar analogy, the increase in the area of contact results in increasing the oil deposition on the bubble surface and , increasing the number of coalesces. How the propagation rate has increased due to the structural change of surfactant remains unanswered.

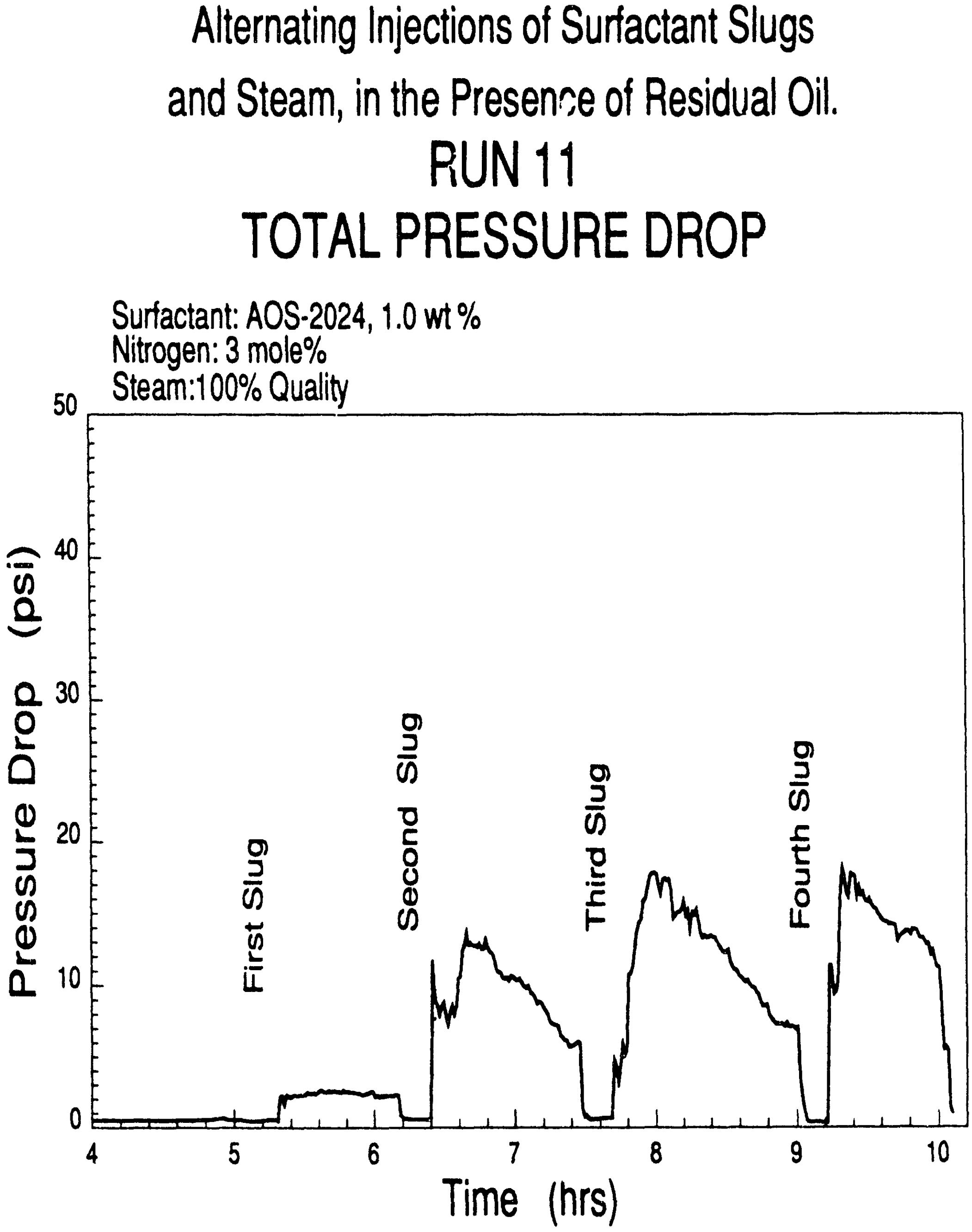
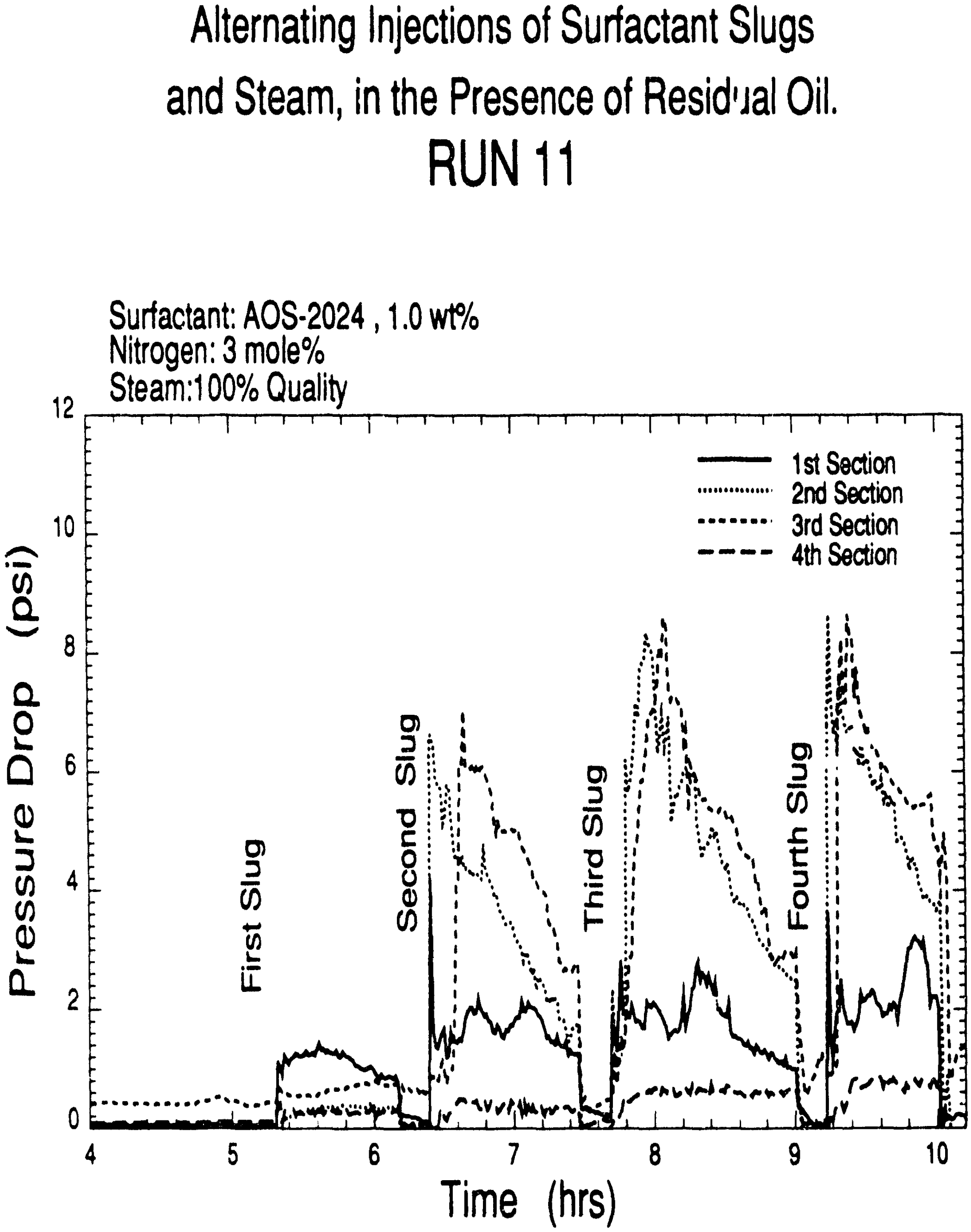


Figure 4.1: RUN 11, AOS 2024: Pressure-Drop Across the Sandpack



Alternating Injections of Surfactant Slugs and Steam, in the Presence of Resid'ual Oil.
RUN 11

Figure 4.2: RUN 11, AOS 2024: Section Wise Pressure-Drop Across the Sandpack

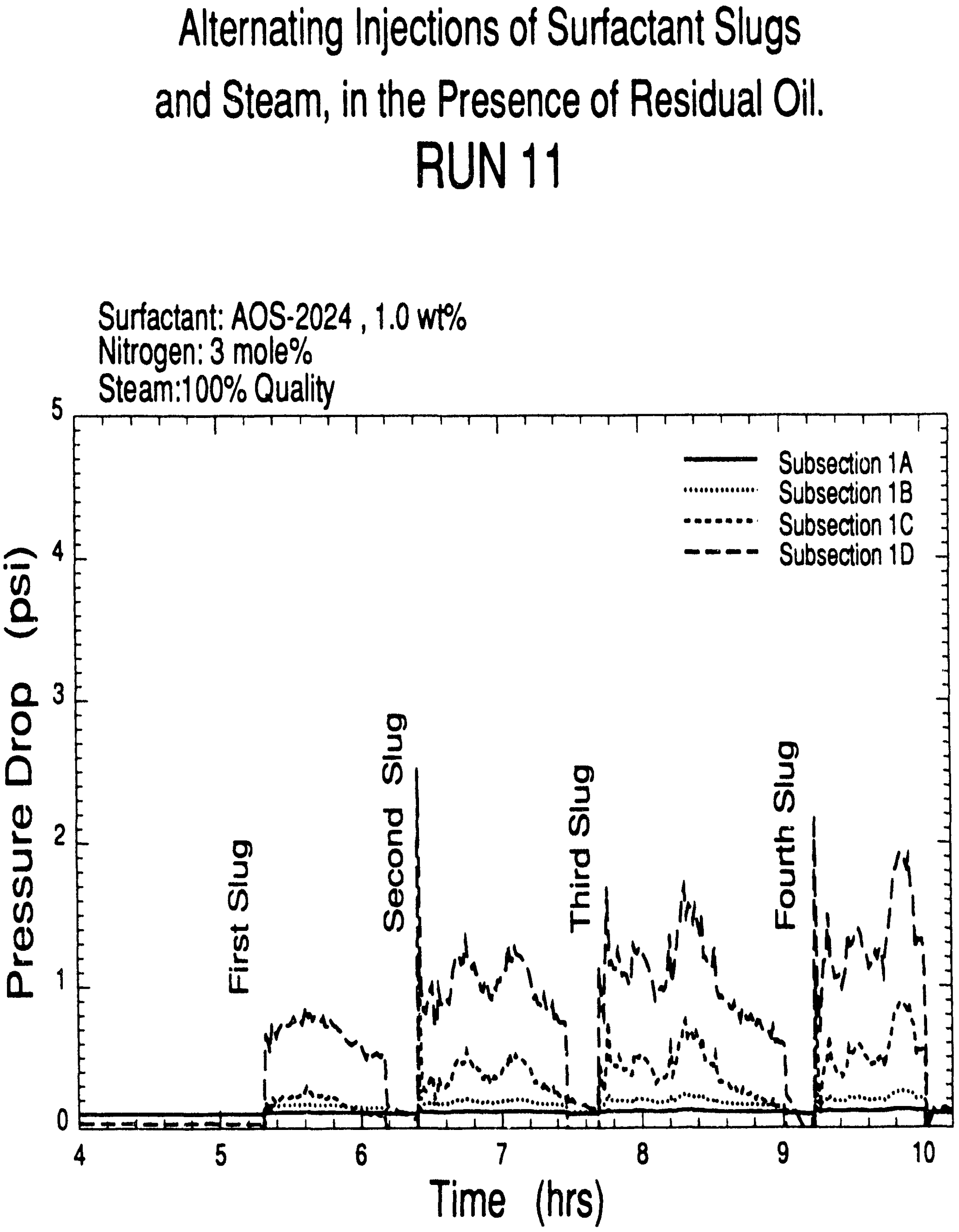


Figure 4.3: RUN 11, AOS 2024: Pressure-Drop Across the Sandpack of Inlet Sections

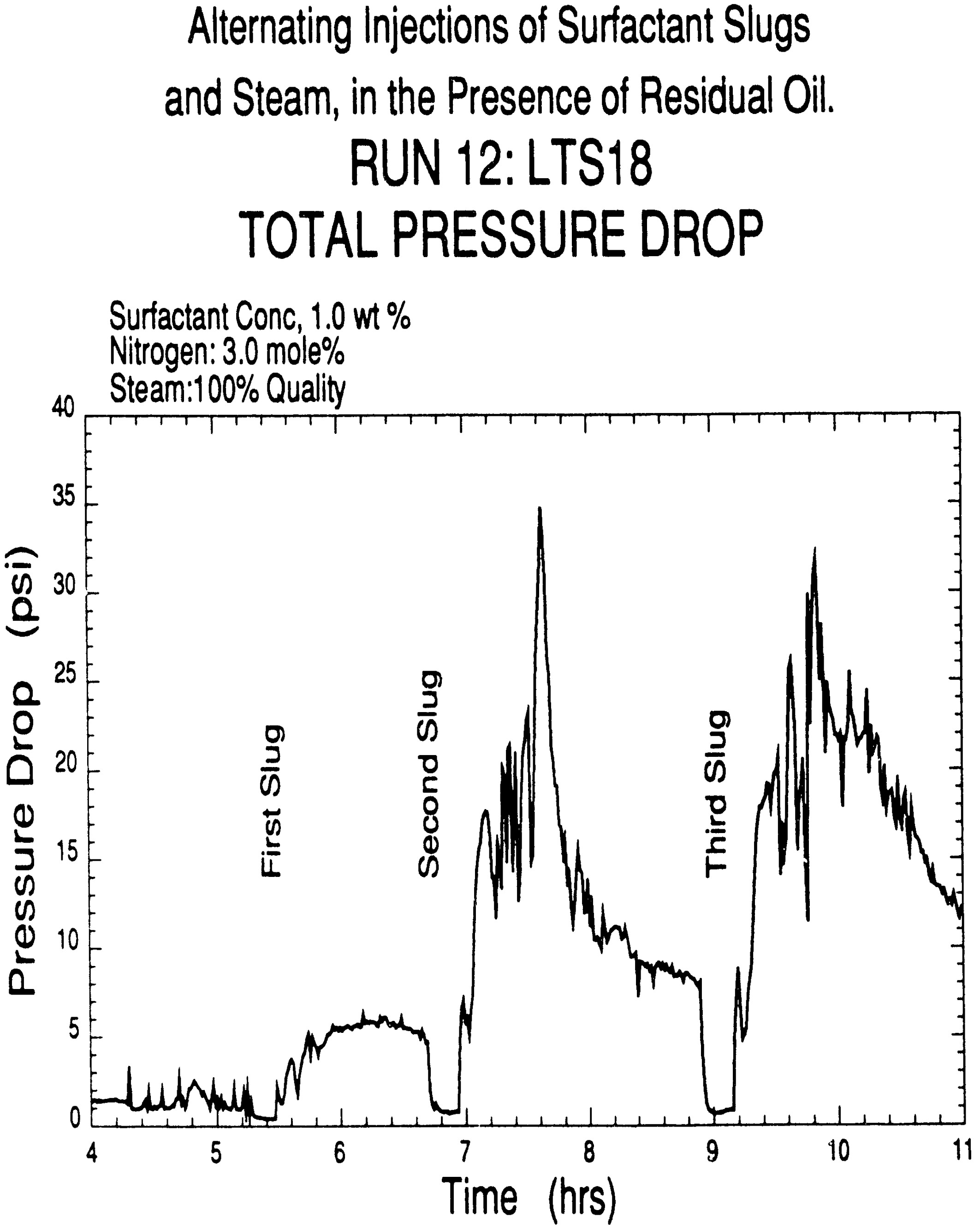
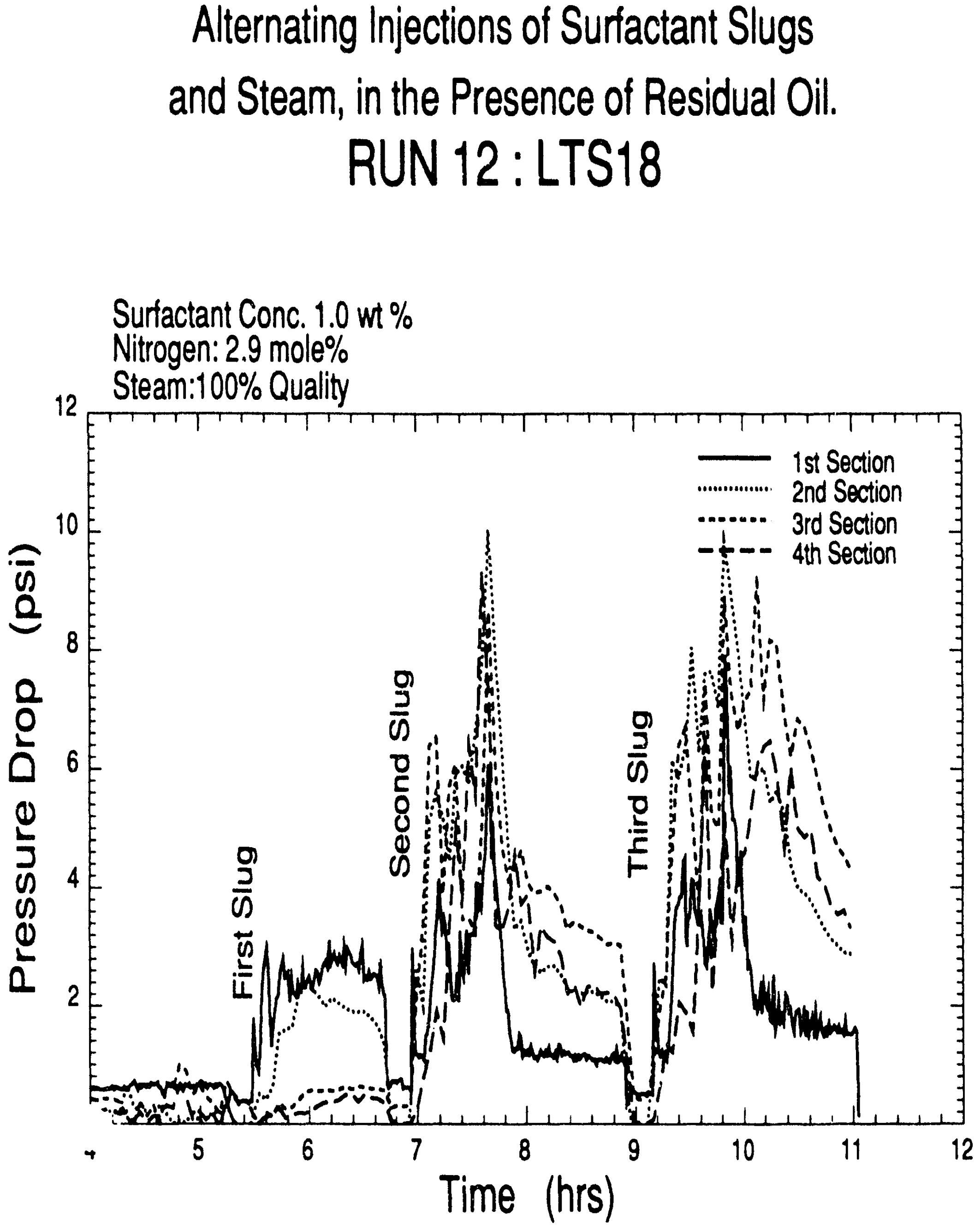


Figure 4.4: RUN 12, LTS 18: Pressure-Drop Across the Sandpack

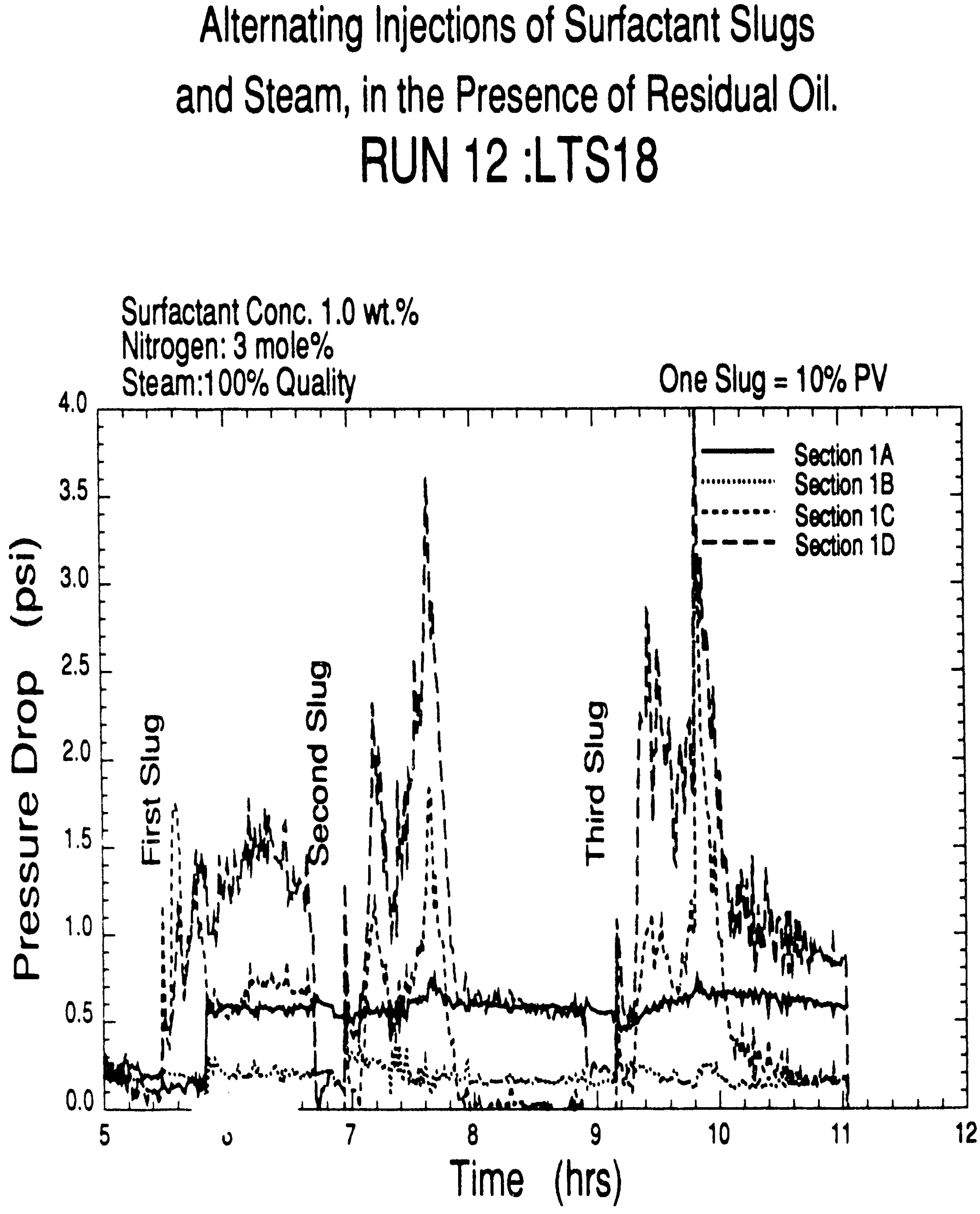


Alternating Injections of Surfactant Slugs and Steam, in the Presence of Residual Oil.

RUN 12 : LTS18

Surfactant Conc. 1.0 wt %
Nitrogen: 2.9 mole%
Steam:100% Quality

Figure 4.5: RUN 12, LTS 18: Section Wise Pressure-Drop Across the Sandpack



Alternating Injections of Surfactant Slugs
and Steam, in the Presence of Residual Oil.
RUN 12 :LTS18

Figure 4.6: RUN 12, LTS 18: Pressure-Drop Across the Sandpack of Inlet Sections

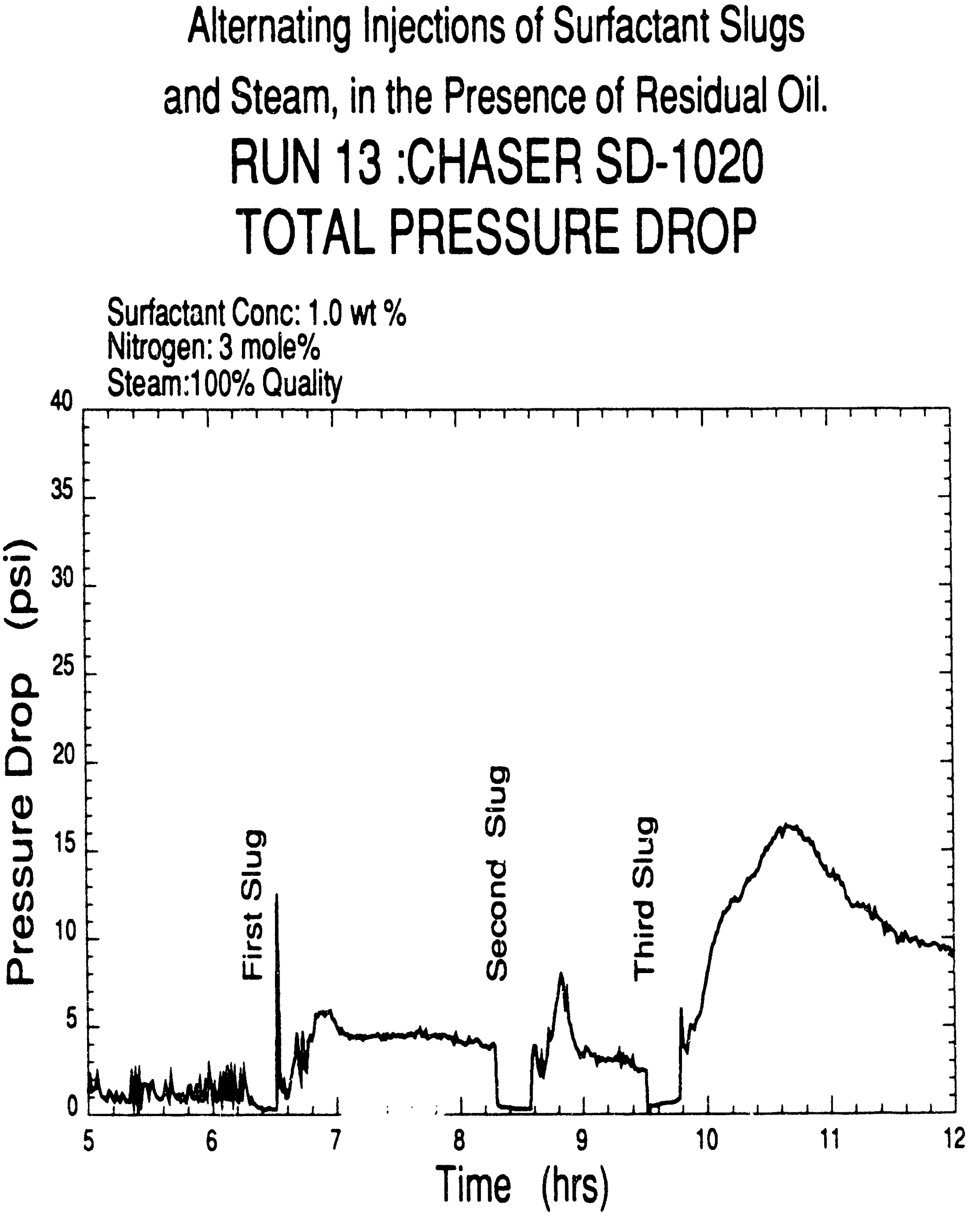


Figure 4.7: RUN 13, SD 1020: Pressure-Drop Across the Sandpack

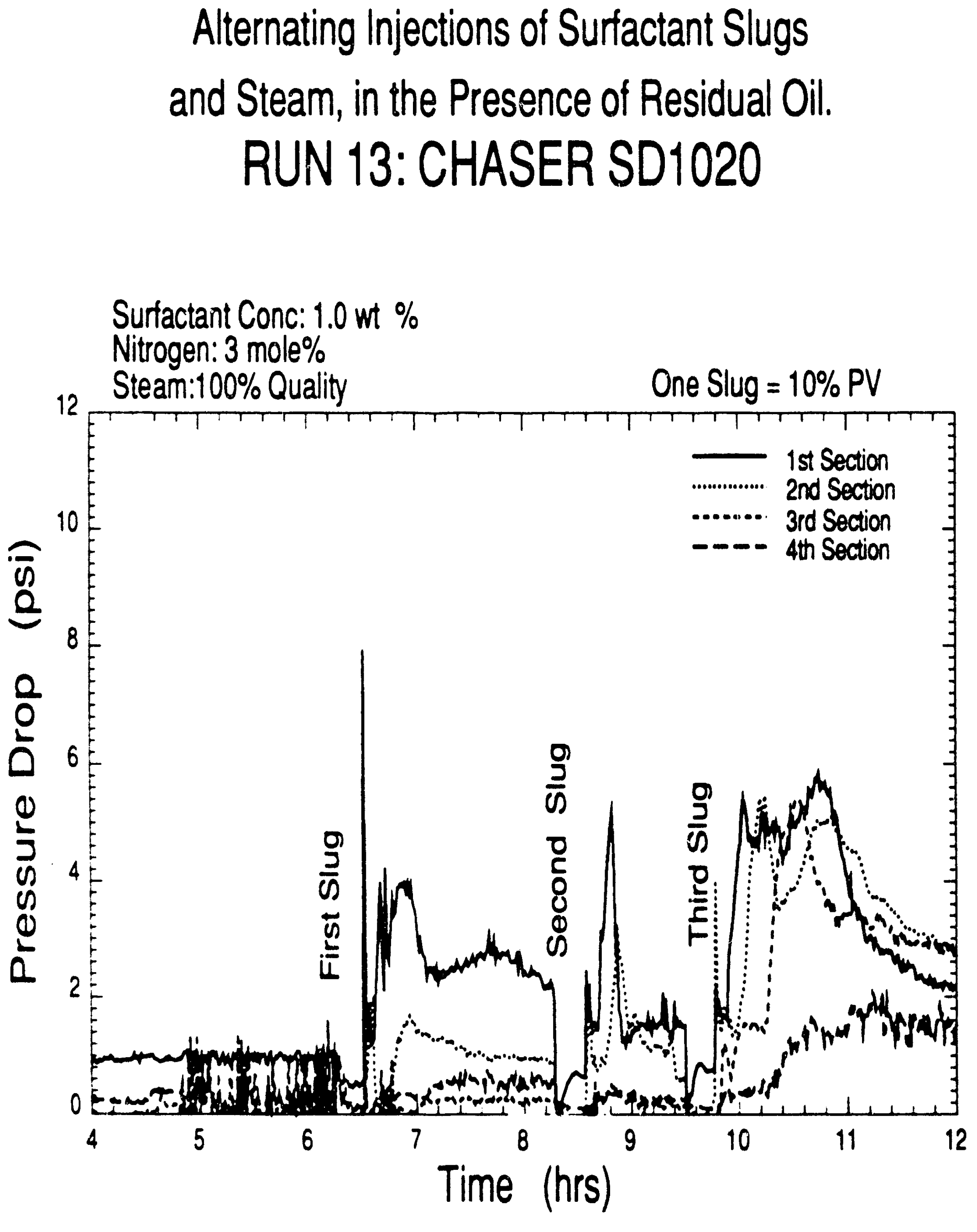


Figure 4.8: RUN 13, SD 1020: Section Wise Pressure-Drop Across the Sandpack

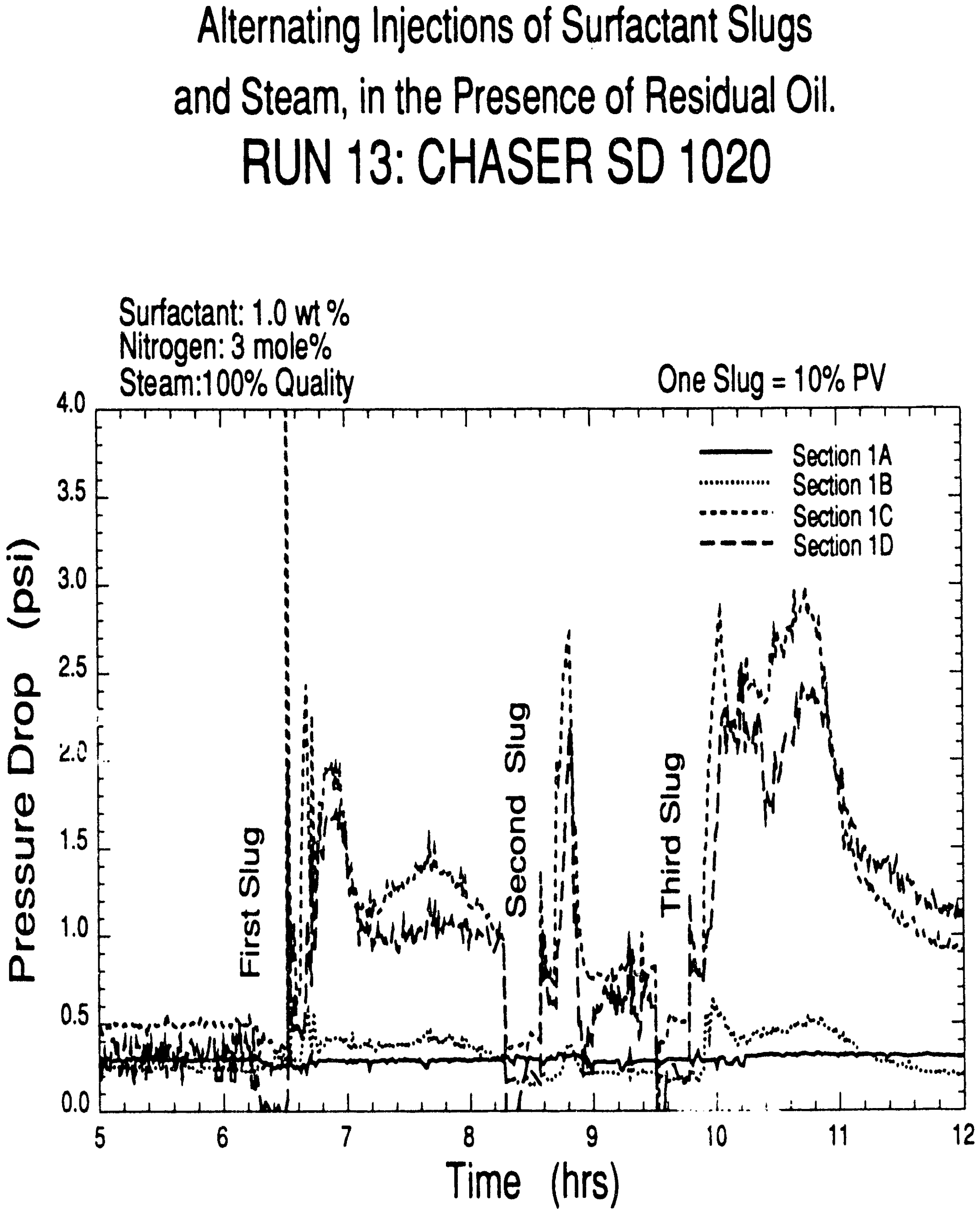


Figure 4.9: RUN 13, SD 1020: Pressure-Drop Across the Sandpack of Inlet Sections

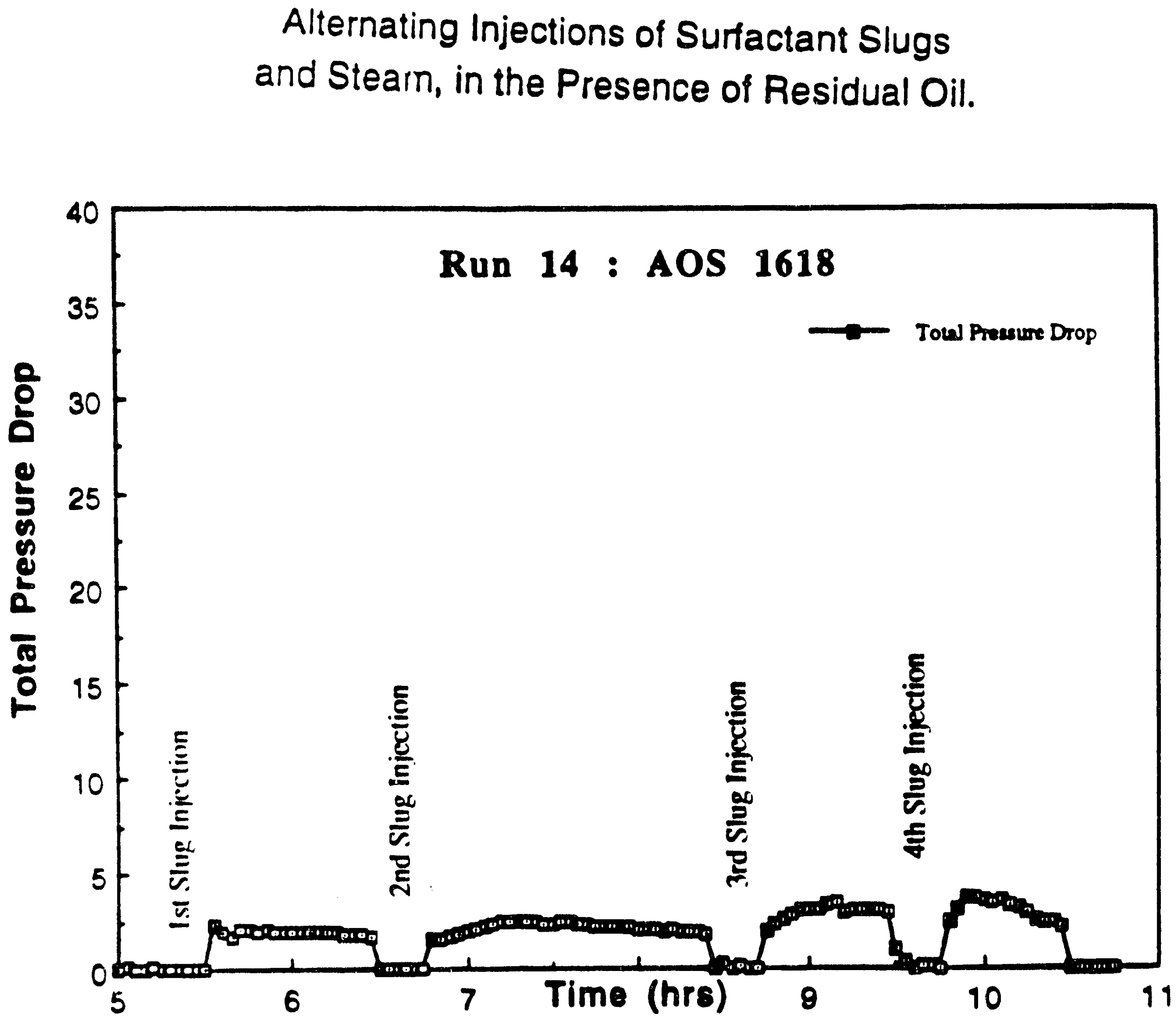


Figure 4.10: RUN 14, AOS 1618: Pressure-Drop Across the Sandpack

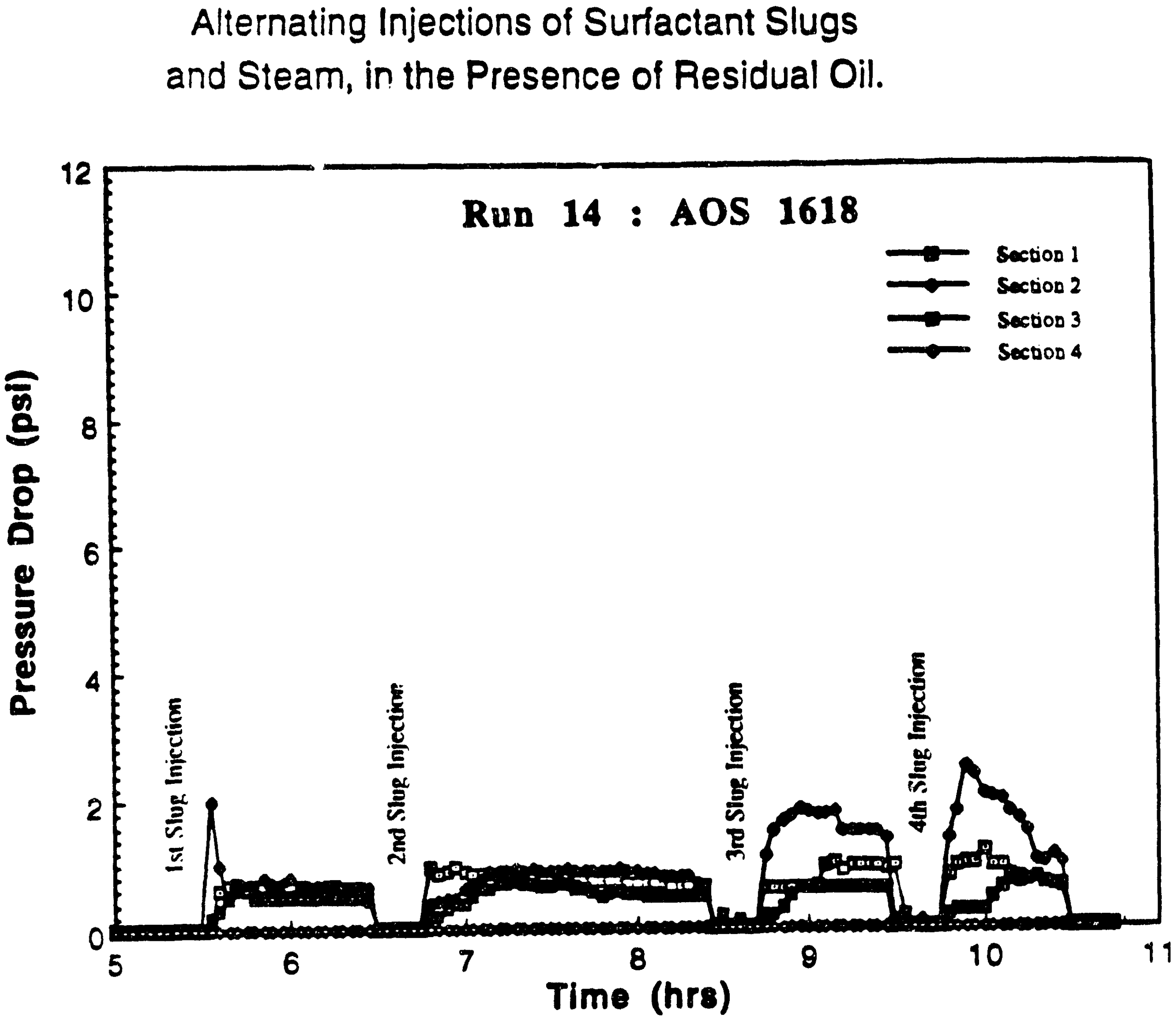


Figure 4.11: RUN 14, AOS 1618: Section Wise Pressure-Drop Across the Sandpack

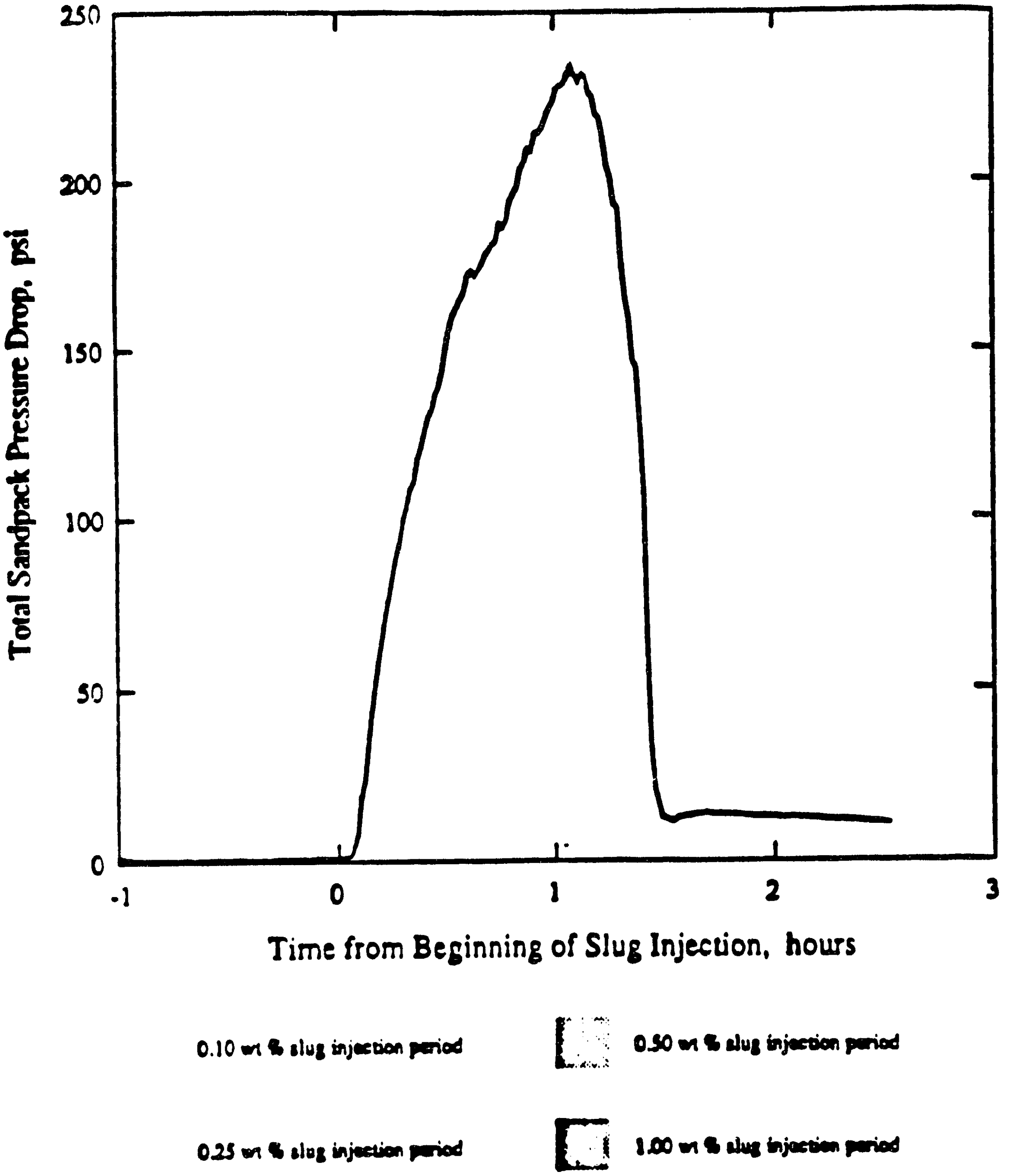


Figure 4.12: Pressure-Drop Across the Sandpack in the absence of Oil for AOS 2024, (after Shallcross Fig.5.36)

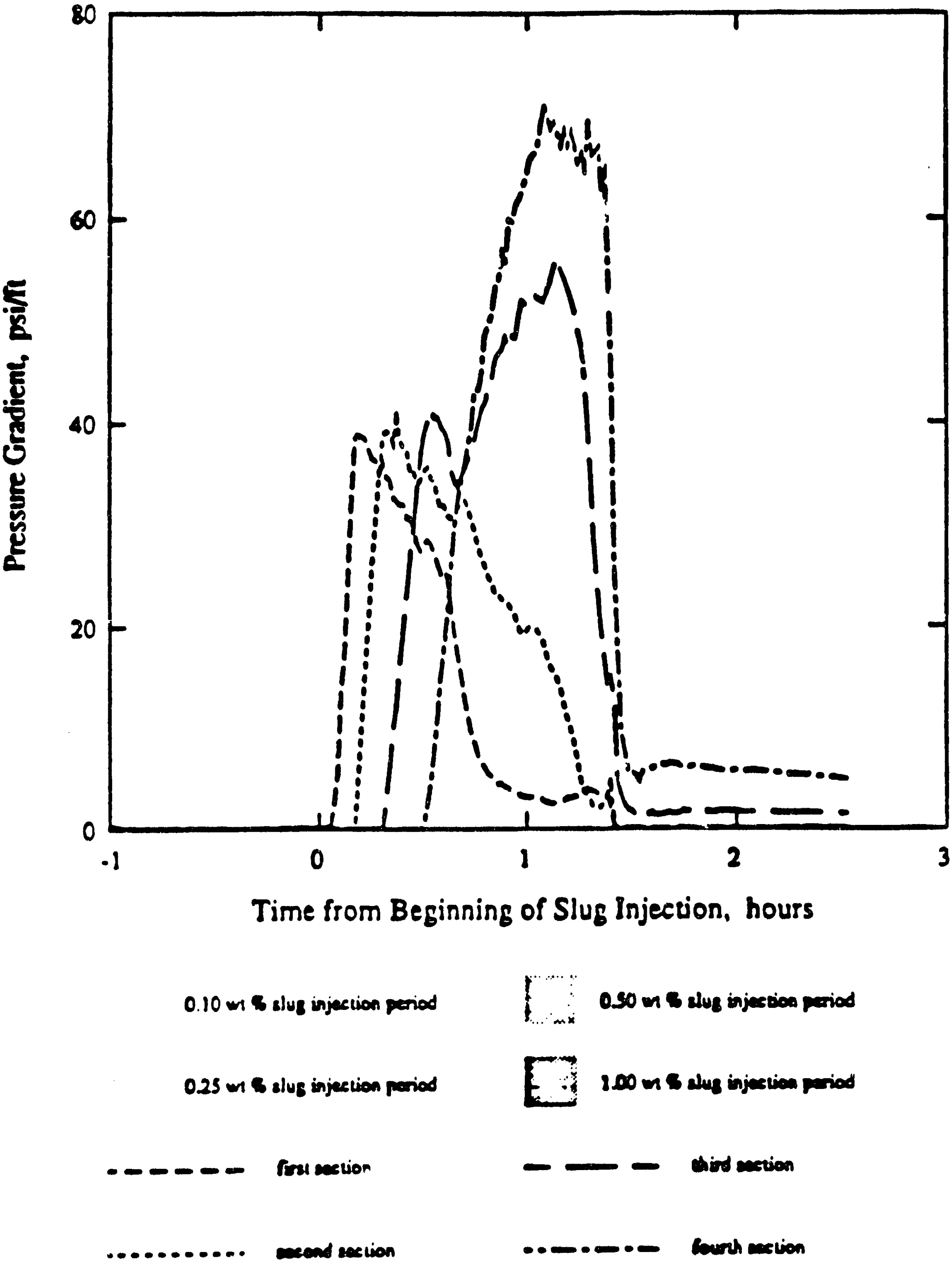


Figure 4.13: Section Wise Pressure-Drop Across the Sandpack in the absence of Oil for AOS 2024, (after Shallcross Fig.5.37)

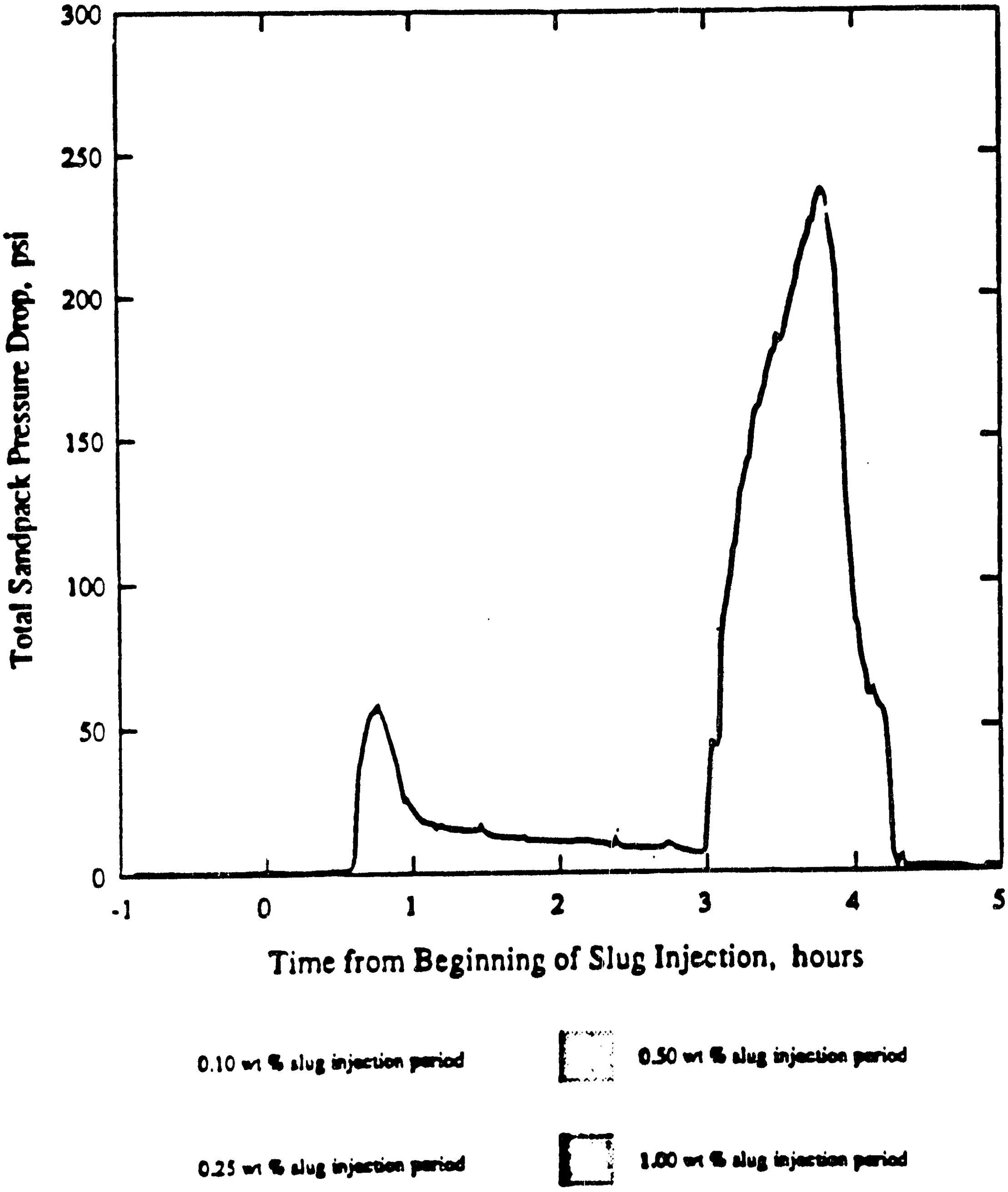


Figure 4.14: Pressure-Drop Across the Sandpack in the absence of Oil for LTS 18,(After Shallcross Fig. 5.57)

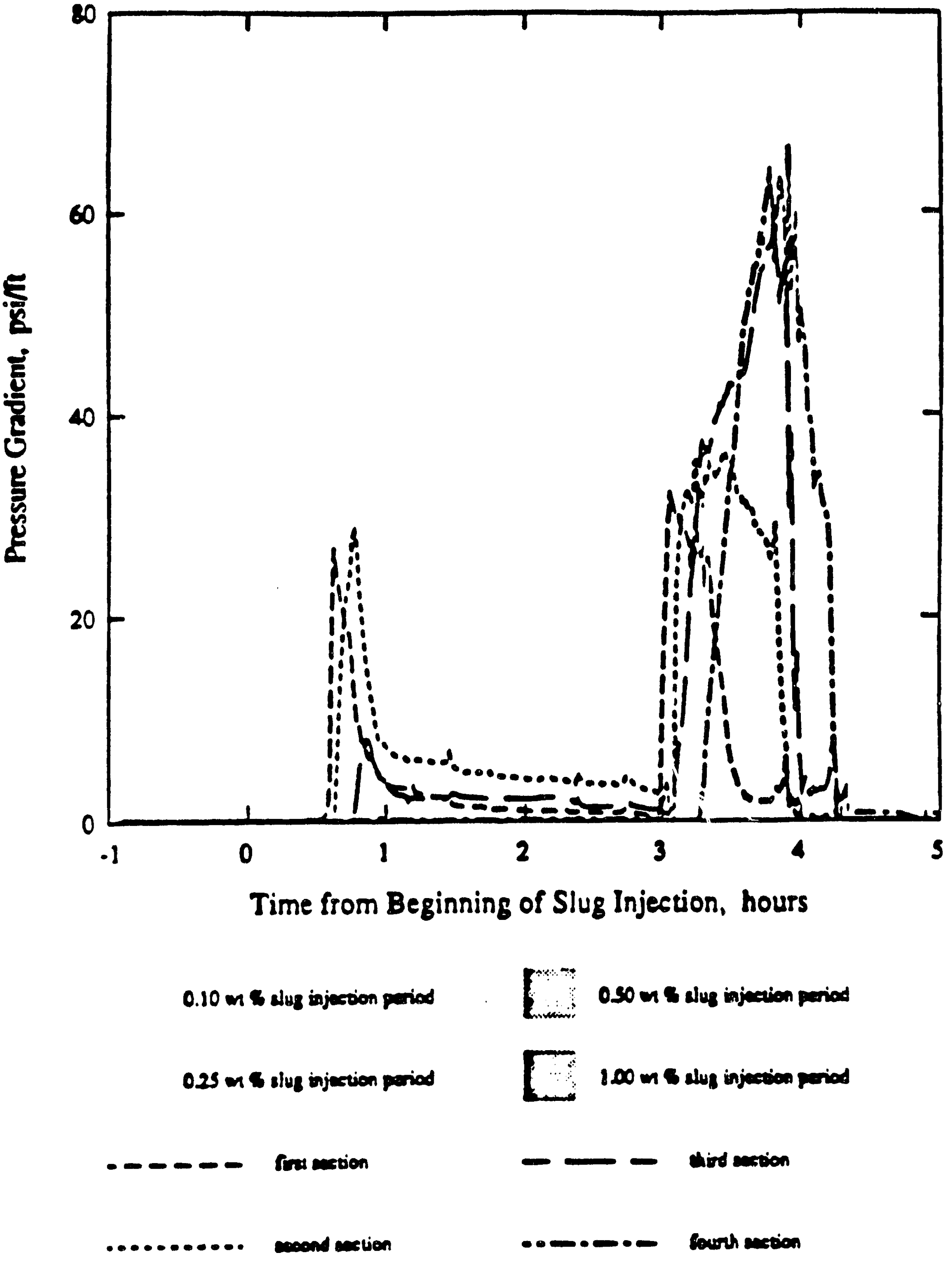


Figure 4.15: Section Wise Pressure-Drop Across the Sandpack in the absence of Oil for LTS 18,(After Shallcross Fig. 5.58)

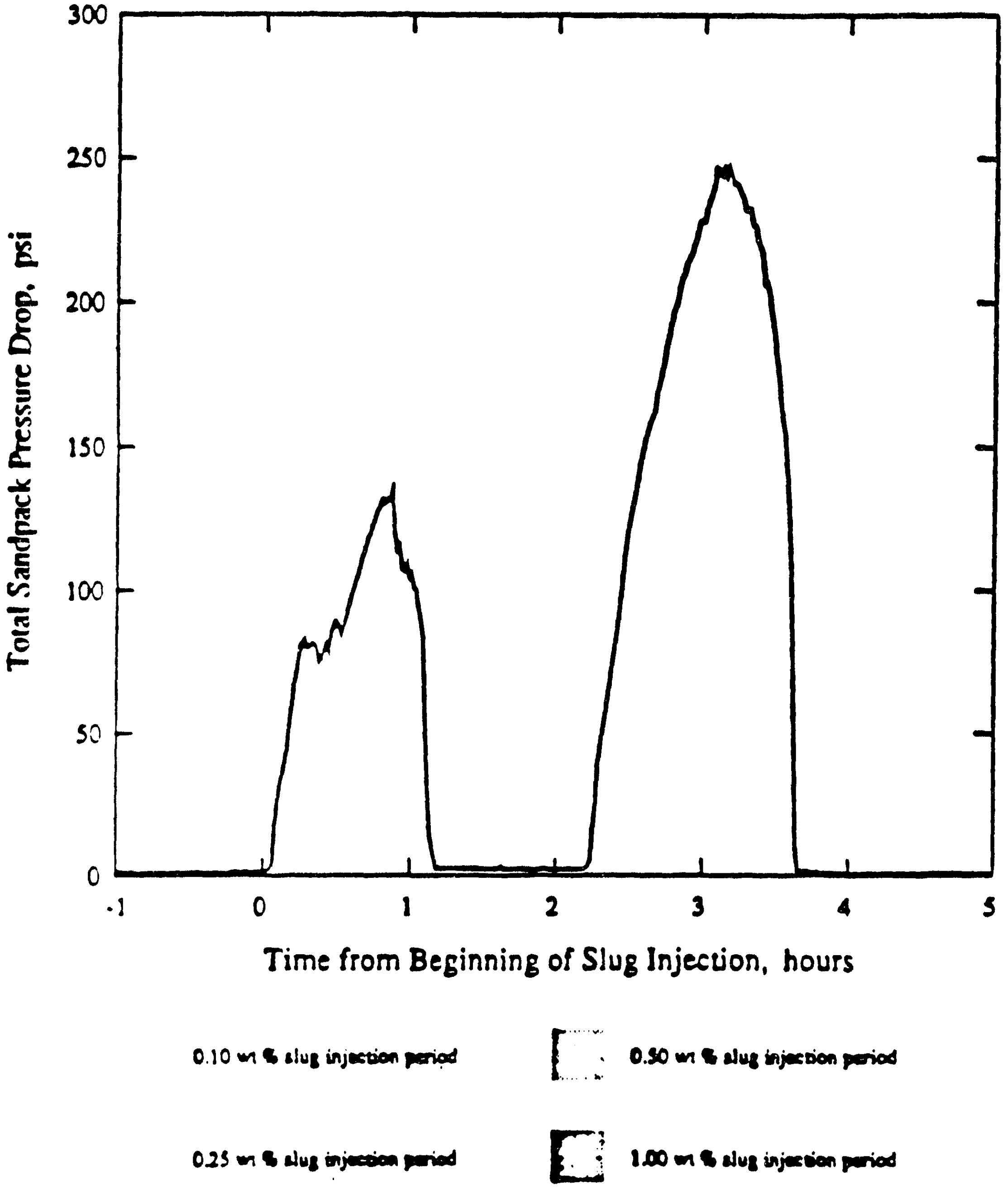


Figure 4.16: Pressure-Drop Across the Sandpack in the absence of Oil for AOS 1618, (After Shallcross Fig. 5.32)

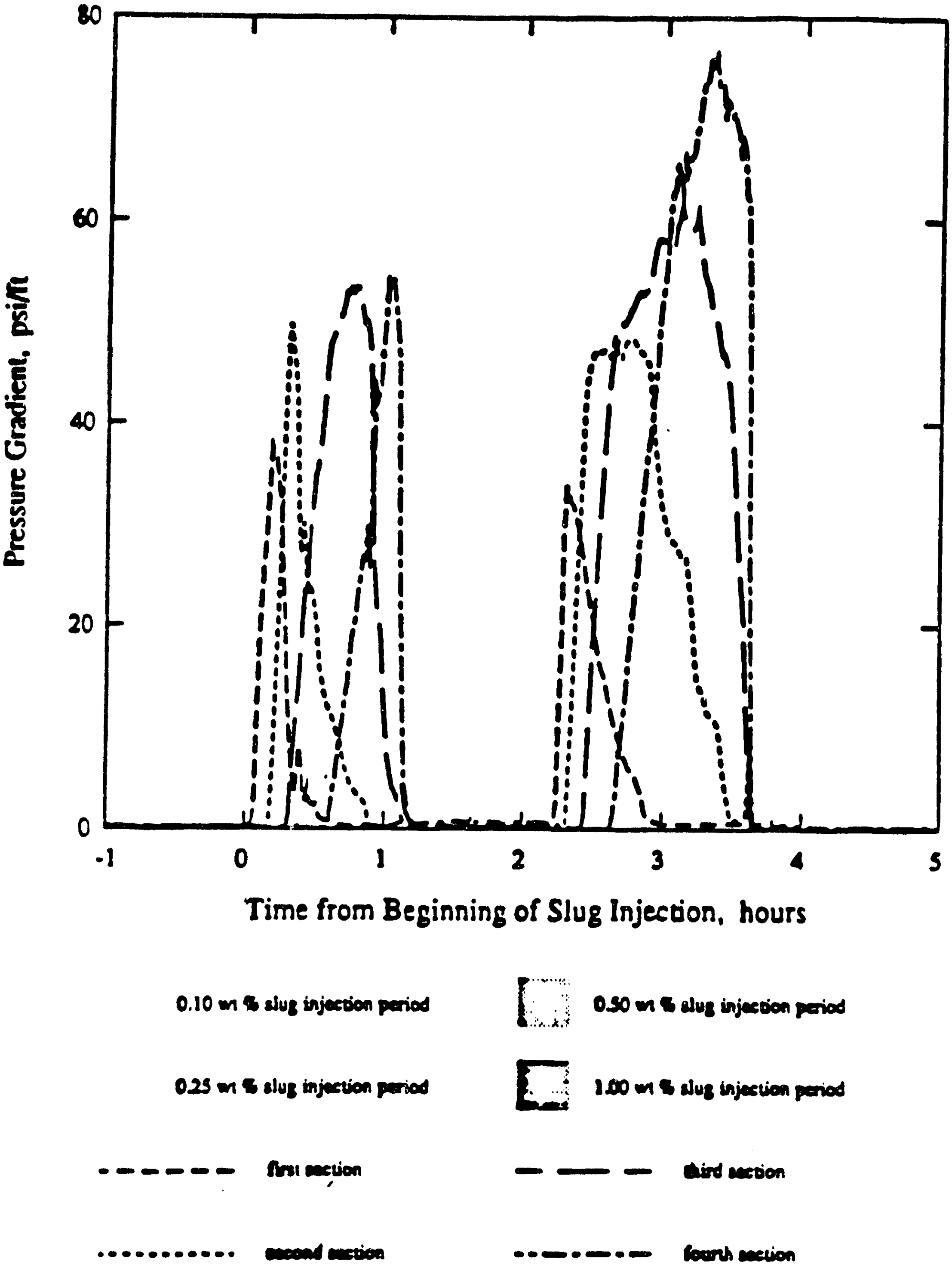


Figure 4.17: Section Wise Pressure-Drop Across the Sandpack in the absence of Oil for AOS 1618, (After Shallcross Fig. 5.33)

Section 5

Conclusions And Recommendations

5.1 Conclusions

The following conclusions may be drawn from the study.

1. Under the experimental conditions studied, a linear toluene sulfonate surfactant generated the strongest foam in the presence of the oil.
2. The propagation rate of the foam generated by a surfactant measures the foam's resistance to the oil; the faster the propagation of a foam, the more oil resistant it is.
3. Only disulfonate surfactants created stronger foams in the presence of oil as compared to the absence of oil.
4. Generally foam strength decreases with increase in oil saturation.
5. Under the experimental conditions, the linear toluene sulfonate LTS18 generated a stronger, and faster propagating foam, than the foams generated by any of the other surfactants tested in this study.
6. Under the experimental conditions the strength of foam produced by an alpha olefin surfactant increases with the increase in alkyl chain length.
7. Adsorption/ partitioning losses are greater for disulfonates as compared to monosulfonates.

5.2 Recommendations

The analysis performed in the study is complete in no way. The work, however, is an addition to the available data on surfactant behavior in presence of an oil. The following work is proposed to be carried out in order to understand the surfactant behavior. This understanding is expected to give control on steam mobility and, should consequently increase the economic benefits of steam /gas recovery methods.

1. The data of the study should be analyzed with respect to the physico-chemical properties of the surfactants and the respective oil/water/gas system formed. The proposed methodology is that the physico-chemical properties of the three phase systems be measured and used to explain the behavior of a foam formed by a surfactant.

2. The work can be extended to formulate a model capable of predicting a trend for a surfactant based on its structure.

3. The performance of disulfonate surfactants in the presence of oil can be studied by performing experiments with various oils and disulfonates of varied structure and length.

4. Combination of disulfonate in varied proportion with a strong water /gas foamer be studied in the presence of oil by performing experiments.

5. More experimental work is required to cover the range of available surfactants and to generalize the results.

Section 6

References

Al-Khafaji, A., Wang F., Castanier, L.M. and Brigham W.E., "Steam Surfactant Systems at Reservoir Conditions", SPE 10777 March 1982, paper presented at the 1982 California Regional Meeting, San Francisco, California. (also TR-38)

Castanier, L.M. and Brigham, W.E., "Selecting Foaming Agents For Steam Injection Improvement", CEP June 1985, pp 37-40.

Castanier, L.M., "Steam With Additives: Field Projects of the Eighties", Journal of Petroleum Science and Engineering, Vol 2 (1989), pp 193-206.

Chambers, K.T., and Radke, C.J., "Capillary Phenomena in Foam Flow Through Porous Media", Chapter 6 of the book "Interfacial Phenomena in Petroleum Recovery" edited by Norman R. Morrow 1990.

Dilgren R.E., Hirasaki G.J., Hill H.J., Whitten D.G., "Steam-Channel-Expanding Steam Foam Drive", U.S. Patent No. 4,086,964, May 1978.

Dilgren R.E., Owens K.B., "Olefin Sulfonate-Improved Steam Foam Drive", U.S. Patent No. 4,393,937, July, 1983.

Duerksen, J.H., "Laboratory Study of Foaming Surfactants as Steam-Diverting Additives", SPE Res Eng. Jan. 1986 p 44.

Ettinger, R.A. and Radke, C.J., "The Influence of Texture on Steady Foam Flow in Berea Sandstone", SPE 19688 Paper presented at the 64th SPE Annual Technical Conference, San Antonio, TX, October 8-11,1989

Falls, A.H., Gauglitz, P.A., Hirasaki, [illegible] and Miller D.D., "Development of a Mechanistic Foam Simulator: The Population Balance and Generation by Snap-Off" SPE/DOE 14961 Paper presented at the SPE/DOE fifth Symposium of Enhanced Oil Recovery, Tulsa , Oklahoma, April 20-23, 1986,a.

Falls, A.H.. Lawson, J.B. and Hirasaki, G.J., "The Role of Noncondensidble Gas in Steam Foams", SPE 15053 Paper presented at the 56th SPE California Regional Meeting, Okland, CA, April 1986,b.

Fried, A.N., "The Foam-Drive Process for Increasing the Recovery of Oil", USBM 5866, 1961.

Friedmann, F., "Surfactant and Polymer Losses During Flow Through Porous Media", SPE Res. Eng. May 1986, p 261.

Friedmann, F., Chen, W.H., and Gauglitz, P.A., "Experimental and Simulation Study of High-Temperature Foam Displacement in Porous Media", SPE/DOE 17357 Paper presented at the SPE/DOE fifth Symposium of Enhanced Oil Recovery , Tulsa, Oklahoma, April 17-20, 1988.

Hamida, F., "Characterization of Surfactants as Steamflood Additives", MS report Stanford University, June 1990.

Hanssen, J.E. and Dalland, M., "Foams for Effective Gas Blockage in the Presence of Crude Oil", SPE/DOE 20193 Paper presented at the SPE/DOE seventh Symposium of Enhanced Oil Recovery , Tulsa, Oklahoma, April 22-25,1990.

Hirasaki, G.J., "The Steam-Foam Process", JPT May 1989, pp 449-456.

Huang W.S., Gassmann Z.Z., Hawkins J.T., Shievelbein V.H., Hall W.L., "Method of Improving Conformance in Steam Floods with Steam Foaming Agents", U.S. Patent No. 4,540,050, September 1985.

Hutchison, D.A., "Steam Foam Studies In The Presence of Residual Oil", MS report Stanford University, September 1991.

Hudgins, D.A., and Chung, T-H., "Long Distance Propagation of Foams", SPE/DOE 20196 Paper presented at the SPE/DOE seventh Symposium of Enhanced Oil Recovery , Tulsa, Oklahoma, April 22-25,1990.

Jensen, J.A., Friedmann, F., "Physical and Chemical Effects of an Oil Phase on the Propagation of Foam in Porous Media", SPE 16375 Paper presented at the SPE California Regional Meeting, Ventura, CA, April 8-10, 1987.

Lake L.W., "Enhanced Oil Recovery", Engelwood Cliffs, New Jersey, Prentice Hall 1989.

Lau, H.C. and O'Brien, S.M., "Effects of Spreading and Nonspreading Oils on Foam Propagation Through Porous Media", SPE Res. Eng. August 1988, pp 893-896.

Lau, H.C., and O'Brien, S.M., "Surfactant Transport Through Porous Media in Steam-Foam Processes", SPE Res. Eng. November 1988, pp 1177-1185.

Lau, H.C. and Borchardt, J.K., "Improved Steam Foam Formulations: Concepts and Laboratory Results", SPE 18783 Paper presented at the SPE California Regional Meeting, Bakersfield, CA, April 5-7, 1989.

Manlowe, D.J. and Radke, C.J., "A Pore Level Investigation of Foam/Oil Interactions in Porous Media" SPE 18069 Paper presented at the 63rd SPE Annual Technical Conference, Houston, TX, October 2-5, 1988.

Marsden, S.S., Jr., Elson, T., and Guppy, K., "Literature Review of the Selective

Blockage of Fluids in Thermal Recovery Projects" Supri-TR-3, Nov 1977. (Work preformed under U.S. contract no. E(04-3) 1256 for Energy Research and Development Administration.)

Marsden S.S., "Foams in Porous Media", Supri TR 49, May 1986. (Work performed for the Department of Energy, U.S.A. under contract no DE-AC03-81SF 11564.)

Maneffa, M.G., "A Laboratory Study of Surfactants as Foam Diverting Agents", MS Report Stanford University, June 1987

Muijs H.M. Keijzer P.P.M., Wierma R.J., "Surfactants for Mobility Control in High Temperature Steam Foam Applications", Proceedings of the 1988 SPE/DOE Sixth Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, pp 663-676, April 1988

Nikolov, A.D., Wasan, D.T., Huang, D.W., and Edwards, D.A., "The Effect of Oil on Foam Stability: Mechanisms and Implications for Oil", SPE 15443 Paper presented at the SPE 61st Annual Technical Conference, Orleans, LA, October 5-8, 1986.

Ransohoff, T.C., and Radke, C.J., "Mechanisms of Foam Generation in Glass Bead Packs", SPE Res. Eng. May 1988, pp 573-585.

Roof, J.G., "Snap-Off of Oil Droplets in Water-Wet Pores", SPEJ March 1970, pp 85-90.

Rossen, W.R., "Theories of Foam Mobilization Pressure Gradient", SPE/DOE 17358 Paper presented at the SPE/DOE fifth Symposium of Enhanced Oil Recovery, Tulsa, Oklahoma, April 17-20, 1988

Schramm, L.L., Turta, A.T., and Novosad, J.J., "Microvisual and Coreflood Studies of Foam Interactions With a Light Crude Oil", SPE/DOE 20197 Paper presented at the SPE/DOE seventh Symposium of Enhanced Oil Recovery, Tulsa, Oklahoma, April 22-25,1990.

Sharma, M.K., Shah, D.O., Brigham, W.E., "Effect of Mixed-Chain-Length Surfactants on Fluid Displacement in Porous Media by In-Situ Foaming Process", SPE Res. Eng. May 1986, pp 253-260.

Shallcross D.C., Castanier L.M., Brigham W.E., "Characterization of Steam Foam Surfactants Through One-dimensional Sandpack experiments", May 1990 Supri TR 73. DOE/BC/14126-19.

Wang, F.P., Brigham, W.E., "A Study of Heat Transfer During Steam Injection and Effect of Surfactants on Steam Mobility Reduction" Supri TR-55 Oct. 1986, DOE/SF/11564-21.

Section 7

Appendix

7.1 Appendix A: Residual Oil Calculation

The residual oil saturation was calculated by material balance approach. The amount of water produced during the oil flooding was noted and taken as total amount of oil in the pack. For the residual oil saturation, the effluent during the steam flooding prior to first slug injection was collected. The oil produced in the effluent was, then measured. The main difficulty , however, was the formation of strong oil /water emulsion. In two cases the effluent were allowed to settle for a month, this resulted in lower values for the oil produced; the calculated residual oil saturation for these cases were higher. Overall an average value of 12 % can be reported.

Table 7.1: Residual Oil Saturation

Run	Produced Water During Oil Flooding (ml)	Produced Oil During Steam Flooding (ml)	Residual Oil $(Col2 - Col3)/PV$ $1PV = 1500ml$
11,AOS2024	1380	1240	9.333
12,LTS18	1420	1260	10.67
13,SD1020	1400	1150	16.67
14,AOS1618	1390	1180	14.00
mean			12.66

*U.S.GPO:1992-761-027/60061

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