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THE INFLUENCE OF SAMPLE COMPOSITION ON BITUMEN DISPLACEMENT FROM RECONSTITUTED OIL SAND

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degree of
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consultation. I thank him for the advice and direction which he provided.

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ABSTRACT

This research program was directed towards advancing an understanding of the factors which influence bitumen displacement from compacted oil sand. Of particular interest were the effects that the chemistry of the oil sand exerted on the method for determining recovery. A rapid, inexpensive test method was devised to obtain a quantitative means of assessing the effects on recovery of changes to the oil sand composition. Comparative displacement tests using alkaline solution and distilled water were performed to investigate the interactions between the oil sand chemistry and the chemistry of the displacing liquid. The two primary objectives of this research were: (1) to develop a rapid test method to study the displacement of bitumen from oil sand and (2) to use the test to investigate the influence of oil sand properties on the recovery process.

In the initial work, mined Athabasca oil sand was packed into a displacement cell and experiments were conducted at 250°C. The experimental procedure was refined until the test was capable of producing reproducible results. The method is suitable as a screening test to evaluate the effectiveness of additives in the displacing phase.

The focus then shifted to examining reconstituted oil sands. Cleaned sand, water and diluted bitumen were tumbled together to produce a batch of reconstituted oil sand. Diluted bitumen was used to facilitate the tumbling process and also to reduce the bitumen viscosity. This eliminated the necessity for conducting

experiments at high temperature, hence displacement experiments were conducted at 30 to 60°C. This technique permitted the specific alteration of an oil sand component to test its effect on the recovery process. The use of the reconstitution procedure to systematically assess the varied influences of oil sand composition on the displacement process has not previously been reported. A number of interesting results were obtained from the low temperature displacement testing of these reconstituted oil sands.

As the oil sand pack density increased, the recovery with water increased, but the caustic recovery efficiency was largely unaffected. This has been attributed to a fundamental difference between the chemically-controlled alkaline displacement process and the physically-controlled water displacement process.

The recoveries resulting from displacement by alkaline solution and water were affected by the pretreatment condition applied to the sand prior to reconstitution. Specifically, exposing the sand to temperatures up to 400°C increased the amount of incremental recovery observed with caustic. Exposure to still higher temperatures led to the difference between caustic and water recoveries being reduced to zero. The difference could be reintroduced by adding humic material back to a sand which had been previously heated to 775°C. Humic material interacted with alkaline solution to lower the interfacial forces in the oil sand, thus enhancing the recovery efficiency of caustic compared to water.

The connate water saturation strongly affected the water displacement process. As the saturation increased, the recovery due to water increased markedly. The effect on caustic displacement was much less dramatic. Again, this is believed to be related to the fundamental difference in the dominant factors influencing water and caustic displacement.

The maltene fraction of bitumen exhibited low interfacial tensions against 0.1 M NaOH, and when this fraction was used to reconstitute an oil sand sample, an incremental recovery was observed with caustic compared to water. The hydrocarbon subfraction of maltene did not exhibit low interfacial tensions, and the recoveries with caustic and water were equivalent in oil sands containing this material. This demonstrated the influence exerted on recovery by potentially surface active functional groups within the organic phase.

Elemental and Fourier transform infrared analysis of the humic material detected high carbon and oxygen contents. The organic material was closely affiliated with kaolinite possibly via a metal complex bridge. From thermogravimetric analysis, about 25% of the humic material was removed upon extreme heating. This may have included water loss and oxidation of organic constituents. Scanning electron microscopy revealed that sands which had been dried at 25°C contained aggregates which were not present in sands heated to 775°C. From x-ray analysis it appeared that the humic material was responsible for cementation of these aggregates.

Storage of reconstituted oil sand samples for extended periods of time made them much more difficult to process. This has been attributed to sample dehydration.

ORIGINAL CONTRIBUTIONS TO KNOWLEDGE

The principal contributions of this research towards advancing the understanding of the process of bitumen displacement from oil sand are listed below. These developments, to the best of my knowledge original, are as follows:

1. The reconstitution technique has been used to undertake a systematic study of the influence of oil sand composition on the displacement process. The characteristics of the inorganic matrix, the connate water and the bituminous phase were all varied and the resulting influences on the displacement process observed. This evaluation of the effects on recovery of compositional changes in the oil sand has contributed to a fuller understanding of the mechanisms by which the displacement processes occur.

2. The recovery efficiency by water displacement was observed to increase as the oil sand pack density increased. Displacement by alkaline solution was largely unaffected by the pack density. This suggested that water displacement was influenced by physical characteristics of the porous medium such as the liquid saturations and the dimensions of the flow pathways. The absence of a corresponding effect during caustic displacement indicated that alkaline flooding was chemically controlled. Changes to the interfacial energetics of the system due to in situ-generated surfactants influenced the displacement process more strongly than the physical properties of the porous medium.

3. The characteristics of the inorganic matrix were dependent upon the extent of heating applied to the sand after solvent

extraction. Sand dried at 25°C was oil-wet whereas sand dried at 300°C was water-wet. This has been attributed to the removal of traces of toluene at elevated temperatures. Further heating to 775°C caused the removal of humic material from the sand. The humic matter, and strongly affiliated clay particles, appeared to be responsible for the cementation of sand aggregates. In sands devoid of humic material, similar aggregates were not observed.

4. The recovery process was influenced by the humic content of the extracted sand. The presence of humic material on the sand enhanced the efficiency of caustic displacement, but had little effect on the water displacement effectiveness. This was due to a reaction between caustic and humic matter to form surfactants which lowered the interfacial forces in the oil sand, thus improving the recovery process.

5. The water displacement efficiency was much more strongly affected by the connate water saturation than was the caustic displacement efficiency. This phenomenon can be satisfactorily explained using the disjoining pressure concept. At low connate water saturations, the thickness of the adsorbed water layer was small, hence the attractive force between the sand and bitumen surfaces was large. This strong attractive force impaired the water displacement efficiency. During alkaline flooding, however, the produced surfactants concentrated in the interfacial region to decrease the strength of the sand-bitumen interaction. Hence caustic displacement was much more effective than water displacement at low connate water saturations. As the connate water content increased, the adsorbed water layer thickness

increased, and the strength of the sand-bitumen interaction therefore decreased. This change lead to a marked increase in the water displacement recovery because the resistance to bitumen movement was greatly reduced. The effect of increased water saturation on caustic displacement was negligible because the interfacial forces were controlled primarily by chemical-induced factors rather than the physical dimension of the water layer.

1. INTRODUCTION

As reserves of conventional oil are depleted, Canada will increasingly come to rely on its less accessible petroleum resources. The oil sands of Western Canada represent the largest alternative source of petroleum products. According to 1984 figures, Canada had 1.1 billion cubic metres of proven reserves of conventional oil and was producing at a rate of 220 thousand cubic metres per day (1). At that rate, the proven reserves represent only 13.6 years of supply. By comparison, the oil sands are believed to contain close to 160 billion cubic metres of crude (2).

The two commercial operations in the Athabasca region, operated by Suncor and Syncrude, rely on surface mining of the oil sand and its transportation to a central site for separation. Only about 10 to 15% of the resource can be handled in this manner. For the remainder, the overburden layer is too thick, hence, in situ recovery techniques must be developed to commercialize those regions. Research aimed at developing and improving in situ recovery methods will ultimately become very important because the economic and strategic benefits to Canada of exploiting the oil sands are very sizeable.

The present research program has focussed on developing a better understanding of the factors which control the efficiency of bitumen displacement from compacted oil sand. Two basic objectives were established at the outset of the program; these were:

(a) To develop a rapid, inexpensive displacement method to permit testing over a wide range of experimental conditions. The effects of these changes on the recovery efficiency were to be monitored. The goal was to create a comparative test method to observe relative shifts in the displacement efficiency.

(b) To use the developed model to assess the impact on recovery of chemical species within the oil sand. Reconstituted oil sand samples were used, introducing the ability to specifically control the characteristics of each component. The aim was to relate changes in oil sand composition to mechanistic interpretation of the displacement process. This is believed to be a novel approach which could ultimately assist in matching field operating conditions to oil sand characteristics.

In the literature review section, a brief overview of practical applications of in situ recovery techniques are presented. This is followed by a section describing laboratory methods for modelling the recovery process. Proposed models of oil sand microstructure are presented to show the evolution of knowledge in this area and also to define the characteristics of the system being studied. Next, are three sections dealing with the three principal components found in oil sand. The inorganic matrix, the connate water and the bitumen are all described in terms of their physical and chemical properties and the influence exerted by each on the displacement of bitumen from oil sand. The final section describes flow through porous media, in general, and discusses the specific displacement of oil by water. The emphasis is on surfactant and alkaline injection to alter the interfacial properties in the porous medium and thus improve recovery.

The experimental section begins by outlining the methodology for conducting a displacement test at high temperature using mined Athabasca oil sand. The discussion then shifts to similar description of the low temperature displacement test procedure. The ability to perform tests at low temperature which modelled certain aspects of the high temperature tests, and the ability to introduce perturbations to the oil sand composition, were made possible by development of a reconstitution method for preparing oil sand samples. This procedure is described. Next, the methodology for packing oil sand into the displacement cell while causing minimal sample disturbance is presented. The analytical procedure for separating the bitumen and water from the sand, and also for determining the displacement recovery efficiency is also described. Considerable effort was expended characterizing the residual organic material remaining on the sand after extraction of the bitumen and water. The approaches used to investigate the properties of this material are included. The measurement of interfacial tensions between alkaline solutions and various organic phases is described. In one portion of the research the influence on recovery of specific components in bitumen was addressed by performing a chromatographic separation into chemical types using solvents of increasing polarity. An existing method was modified for this purpose and the details are presented. Finally, other analytical techniques used throughout the course of the research are specified.

The results and discussion section is presented in approximate chronological order. The evolution of the test method is detailed and the results from the early tests at high temperature using mined oil sand are presented. The motivation for shifting to low temperature experimentation is reported. The addition of a diluent to lower the viscosity of the bitumen is justified and the properties of this mixed system of hexadecane and bitumen are defined. The selection of the reconstitution parameters is described. The properties of compacted oil sand are related to the packing strategy employed. The discussion then shifts to the results from the low temperature displacement experiments. The first results pertain to tests performed to assess the important operational parameters which must be controlled to obtain reproducible results. The second factorial design begins to examine the effects on recovery exerted by the oil sand composition. This is followed by three large subsections describing in more detail the importance of each of the principal components to the recovery process. The influences of changes to the sand surface characteristics, of changes to the connate water saturation and composition, and of changes to the organic phase composition are all described. In each case, the results are presented for two displacing phases: distilled water and alkaline solution. Next, the basic flow parameters which existed during low temperature displacement are developed. This is followed by a section discussing the results of work performed to identify the wettability state of the samples which were studied. In the ensuing section, the results from attempts to characterize the solvent insoluble organic material on the sand, the so-called humic material, are detailed. The interfacial tension measurements and the implications of those results are presented. A section of work which used non-bitumen containing organic phases to reconstitute oil sand samples is included. The Dean Stark analytical method is discussed, paying particular attention to the modifications which were introduced. Finally, a short section dealing with proper sample storage to preserve oil sand integrity is included.

The body of the thesis concludes with short sections presenting the conclusions and recommendations for future related study.

There are six appendices. The first presents the mathematical detail involved in the calculation of the disjoining pressure. The second contains a detailed description of the Dean Stark analytical test method in modified form. The third, fourth and fifth embody the details of the fractional factorial designs related to the packing procedure, and the influence of operational and compositional parameters on the recovery process, respectively. In the sixth, the flow parameter calculations are detailed.

2. LITERATURE REVIEW

2.1 In situ recovery by steam stimulation

Almost all processes aimed at in situ recovery from oil sands employ thermal methods to reduce the viscosity of the bitumen. These can be broadly divided into two categories: steam stimulation and in situ combustion. Discussion of in situ combustion is beyond the scope of the present research. A few attempts have been made to inject chemicals into the reservoir to lower the viscosity of the bitumen. Chemical-only floods are farther from commercial viability than thermal methods, but chemical co-injection to improve thermal recovery performance is a distinct possibility.

Thermal methods are used because of the pronounced effect of temperature in lowering the viscosity of bitumen, as depicted in Figure 2-1. In general discussion the terms heavy oil and bitumen are used interchangeably to refer to a very viscous oil. However, strictly speaking, heavy oils have specific gravities from 0.93 to 1.00 at 15.6°C (atmospheric pressure), and viscosities of 100 to 10,000 cp at reservoir conditions (3). Bitumens have specific gravities greater than 1.00 at 15.6°C (atmospheric pressure), and viscosities greater than 10,000 cp at reservoir temperature (3). Whenever possible, the viscosity is used to determine the appropriate classification.

Steam stimulation involves injecting high pressure, high temperature steam into a reservoir to heat the bitumen and render it mobile. The two basic strategies: cyclic steam stimulation

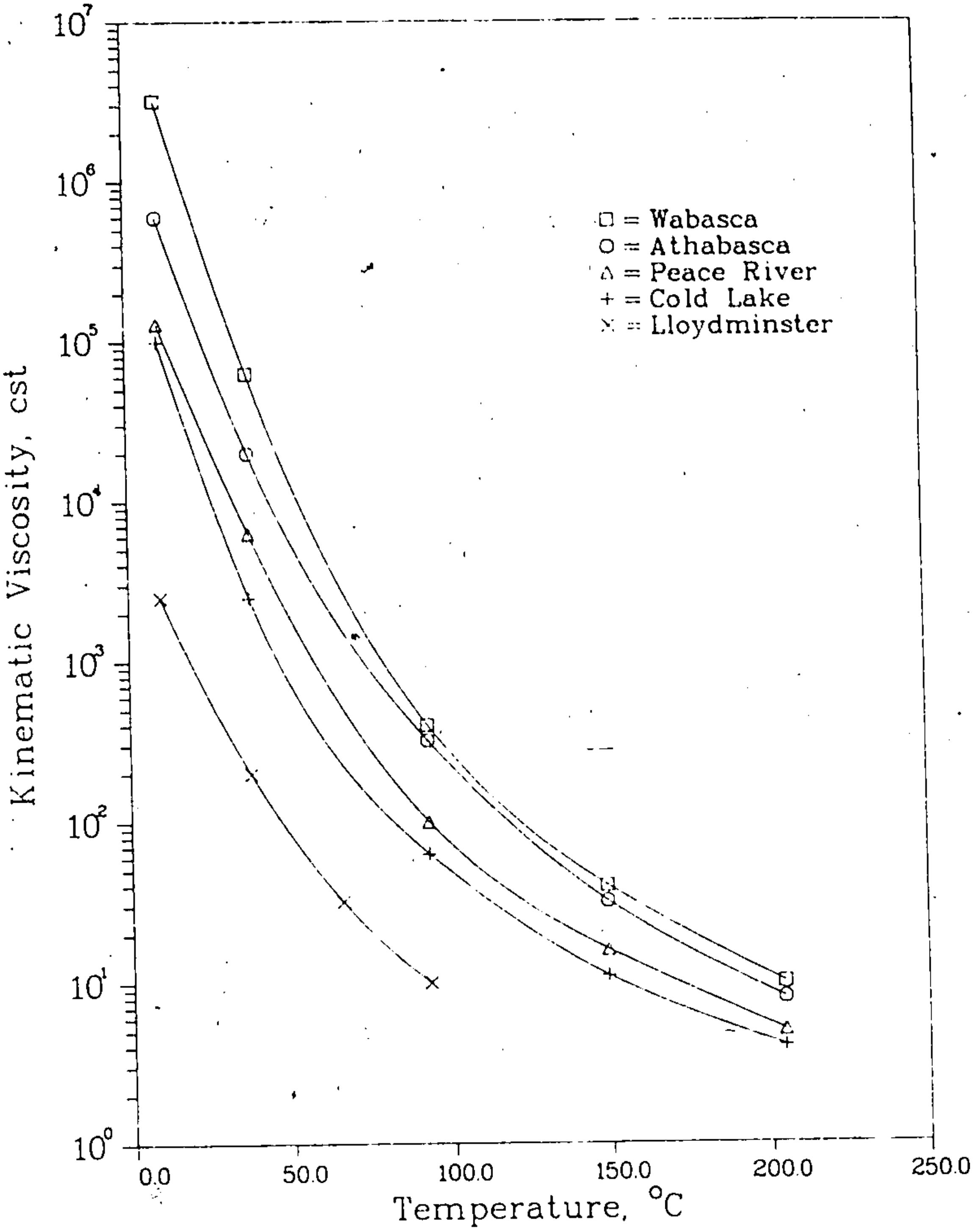


Figure 2-1. The effect of temperature on the viscosities of the principal Canadian bitumens and heavy oil (2).

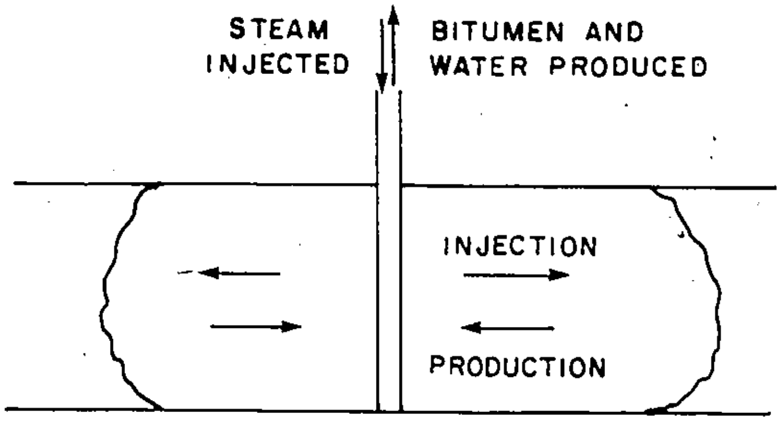
and steam drive are depicted in Figure 2-2. Oil recovery by steam stimulation has been attributed to numerous factors (4,5), including:

(a) physical displacement.
(b) distillation of volatile components.
(c) in situ solvent drive.
(d) viscosity reduction.
(e) thermal permeability and capillary pressure variations.
(f) thermal expansion.
(g) gravity segregation.
(h) solution-gas drive.
(i) emulsion drive.
(j) conventional water drive.
(k) wettability alteration.
(l) interfacial tension reduction.

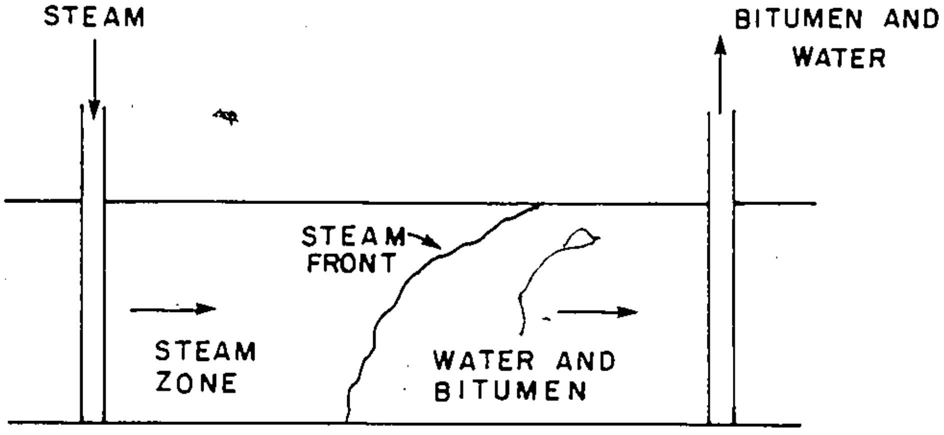
In a given reservoir formation some of these factors will be important and others will be insignificant. The oil sands contain very low gas saturations and minimal amounts of volatile material. Therefore, recoveries due to: distillation, in situ solvent drive and solution-gas drive would be minimal. Specific reservoir testing is required to ascertain the relative importance of the remaining factors.

2.1.1 Cyclic steam stimulation

Cyclic steam stimulation production (steam soak, huff and puff) alternates steam injection with oil production from the same well drilled into the oil-containing formation. For each well,



CYCLIC STEAM STIMULATION



STEAM DRIVE

Figure 2-2. Representations of cyclic steam stimulation and steam drive operations.

high pressure steam is injected for several weeks, after which the well is shut-in to allow a soak period of several days. This permits partial condensation of the steam and allows time for the injected heat to be distributed. At the end of the soak period, oil may be produced on depressurization of the heated zone, followed by pumping. Oil production is at a maximum rate initially and declines slowly over a period of months. Once the recovery rate reaches a limiting lower economic limit the production phase is stopped and the injection of steam is resumed. This cycle is repeated until the oil production ceases to be profitable.

In the higher grade oil sands, bitumen fills most of the void space in the reservoir. Since the bitumen is highly viscous at reservoir conditions it is not very mobile, and the effective porosity of the formation is close to zero. A method is necessary to heat a portion of the bitumen so that flow channels can be created. Some reservoirs contain a gas cap or bottom water zone which can be used to provide the initial heating. Where no natural channels exist, the formation is often fractured by injecting steam at a pressure greater than that of the overburden. This causes the reservoir sand to part, forming fissures into which the steam flows to heat the bitumen. These artificially created flow channels, provided they can be kept open, allow for the movement of fluids through the reservoir. Controlling the extent and orientation of the fractures is a separate problem. In a cyclic operation it is desirable to have the fractures propagate radially from the well so that a large proportion of the reservoir can be contacted. For a steam drive, it is necessary to have the fractures extending from the injection well to the production well to establish and maintain communication.

The advantages of cyclic steam stimulation are:

(a) The initial drilling costs are low because single wells can be operated.

(b) The stimulated reservoir goes on production after only a few weeks, thus a quick return on investment is realized.

(c) The operation is simple and requires little control.

The primary disadvantage is that the ultimate recovery is lower than that achieved using a steam drive. For this reason there is incentive to start in the cyclic mode but to convert adjacent wells into a steam drive operation once the heated zones from the two wells start to overlap. In this way an operator can benefit from the quick initial return provided by the cyclic operation and the better long-term economics of the steam drive.

2.1.2 Steam drive

Steam drive (steamflooding, steam displacement) involves pumping steam into an injection well and pushing it towards a production well. The injected high pressure steam serves to heat the formation and also to provide the driving force for displacement. As steam heats the reservoir it loses its latent heat of vapourization and condenses. Therefore, ahead of the steam front there is a water zone with a thermal gradient from steam to reservoir temperature.

The water zone ahead of the steam front is subject to the same fingering problems that occur in conventional waterfloods. However, the steam front tends to be quite flat because of its "self-healing" nature. If a finger of steam forms and starts to grow, its heat losses will eventually exceed the heat input from the bulk steam. When this occurs the finger condenses thereby restoring a flat steam front. An inherent problem which decreases the volumetric sweep efficiency is the tendency of steam to override the formation. Steam has a much lower density than oil and water so it migrates to the top of the reservoir under the influence of gravity. The tendency to override is a function of the steam temperature, injection rate and location of the injection port, so it can be controlled to some extent.

As mentioned, a communication channel must be established between the wells. Injected fluids preferentially flow through this channel because it is a path of lower resistance. Therefore, it becomes a major operational problem to obtain a balance between the flow through the channel to maintain communication and flow into the rest of the reservoir to get a good sweep efficiency.

2.1.3 Field pilots

A large number of in situ field pilots to recover bitumen and heavy oil have been tested. Although the present discussion focuses primarily on Canadian experiences, similar technologies have been employed in other parts of the world; e.g., the Kern River heavy oil deposits in California and the oil sands of Venezuela. Nicholls and Luhning (2) provided a detailed description of completed and ongoing field tests in each of the four principal Canadian oil sand deposits: Athabasca, Cold Lake, Peace River and Wabasca. Redford (6) presented a history of field testing in the largest single deposit - Athabasca. This review proceeds to discuss novel, largely untried recovery methods. Using the information available from these studies, the author summarizes the common trends and conjectures how future development will proceed.

The most successful of all of the in situ pilots has been the Esso-operated Cold Lake project (7,8). The operation is now of commercial rather than pilot scale. Originally, Esso had intended to embark on a mega-project to convert the Cold Lake pilot into a 25,000 m^3/d commercial facility. Under the terms of the federal-provincial energy agreement signed in 1981, Esso decided that the project was not financially attractive and placed it on hold. In 1983 the scheme was resurrected in the form of six independent phases which would ultimately produce 9000 m^3/d. The advantages of construction in a modular fashion are:

(a) The initial capital outlay is smaller.

(b) A return on investment occurs faster.

(c) Revenues from the initial phases can be used to finance subsequent construction.

Other commercial-scale ventures were planned prior to the 1986 oil price reductions. Included were a 50:50 partnership between BP Canada and Petro Canada at Wolf Lake (1100 m^3/d) and Shell Canada's Peace River project (1600 m^3/d) (9). The present status of these projects is unclear.

2.2 Laboratory modelling of steam stimulation

The development of a viable recovery method is a long process. Initially, bench-scale experiments are performed. These results are combined with the results from numerical models to construct larger and more sophisticated models, eventually leading to a field test. If the field pilot proves successful the operator is in a position to consider a commercial venture.

2.2.1 Physical models

Physical modelling in the present context refers to laboratory-scale experiments to obtain information regarding the recovery of bitumen from oil sands. In simplified terms, most experimental units require a fluid injection system, a reservoir model, a produced fluids collection system, data monitoring and analysis. Experimental simulators fall into one of two general categories: elemental or scaled models.

In an elemental model, the reservoir section contains actual oil sand. This includes repacks of mined oil sand and cores cut from the formation. Elemental models are easy to construct and operate, however, the results obtained cannot be easily scaled-up to make predictions concerning field behaviour. Nevertheless, elemental models have been used extensively to investigate the effectiveness of various recovery schemes in removing bitumen from oil sand (10,11,12).

A scaled physical model is more complex to develop and to construct. The basic concept is to establish similarity of critical parameters between the model and the reservoir to be simulated. The procedure is to manipulate the differential equations governing fluid flow, heat transfer and mass transfer to obtain a set of dimensionless groups. Similarity is achieved by equating these dimensionless groups in the model with the corresponding groups in the reservoir. A difficulty arises when a particular parameter must be scaled down to satisfy one condition and scaled up to satisfy another. This dilemma is resolved by overlooking one group in favour of the other on the basis of some rationalization regarding the relative importance of each. As mentioned, these scaled models are more difficult to construct. However, the results of a properly scaled model can be used directly to make predictions concerning field behaviour. For this reason, scaled models have been used in many applications (13,14,15).

2.2.2 Numerical models

Numerical or computer modelling attempts to predict reservoir behaviour on the basis of mathematical calculations. The differential equations governing fluid flow, heat and mass transfer are simultaneously solved to predict the movement of the fluids in the reservoir. In a sophisticated model there will be many differential equations to solve so computers are used to provide numerical solutions. This computer work must be supplemented with laboratory data to obtain values for the characteristic parameters of the reservoir fluids and rock which appear in the equations, e.g., viscosity, permeability, thermal conductivity.

If every factor affecting fluid flow could be included in the model then one could very accurately predict in a few hours what would occur in the reservoir over a period of years. Many runs could be made in which the process variables would be changed to determine the optimal method for operating a field project. Although attractive in principle, it is not (yet) possible to adequately model all of the factors that influence the reservoir performance. However, for some purposes numerical models are adequate and have been used to predict certain aspects of reservoir behaviour (16,17).

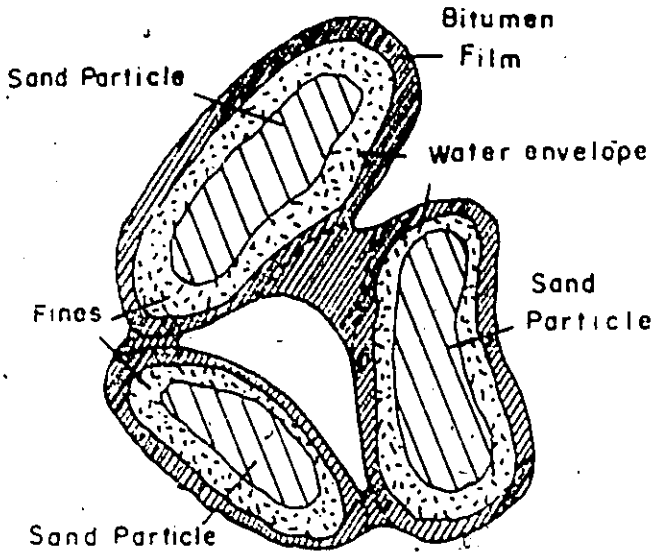
Numerical models and physical models are used interactively to refine one another. The output from the numerical simulator can be used to improve the operating conditions in the physical model, and the output from the physical model can be used to improve the accuracy of the parameters appearing in the differential equations.

2.3 Oil sand microstructure

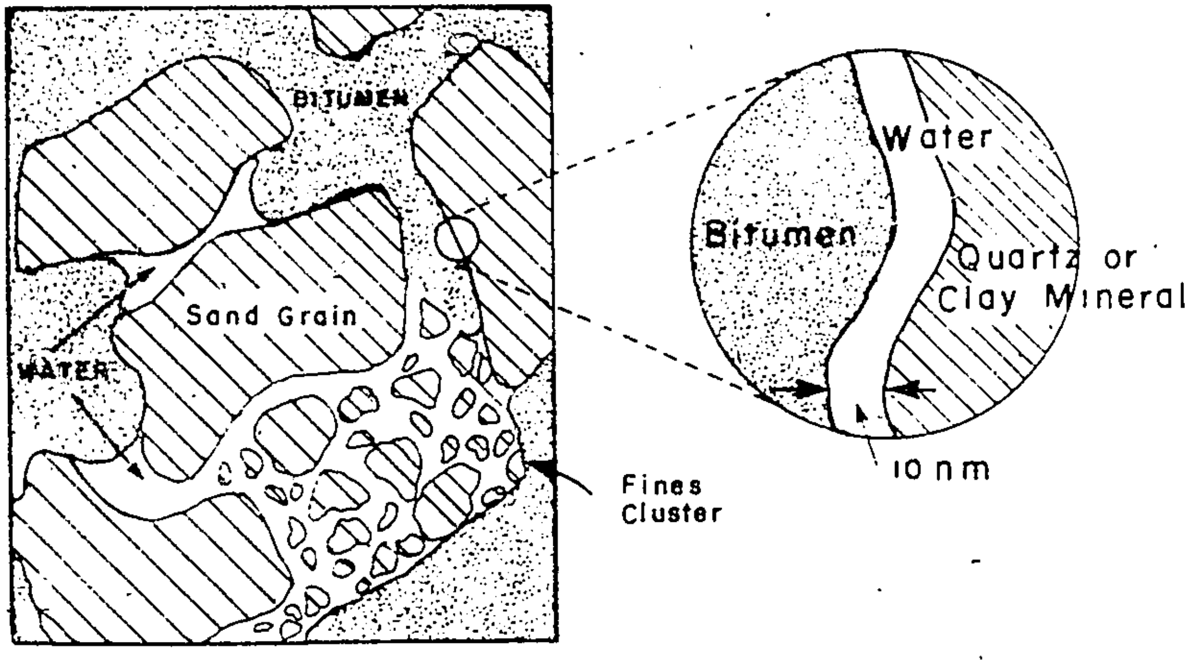
The fundamental objective of bitumen recovery schemes is to separate the bitumen from the sand. To explain observations that some processes work and others do not, various models of the microstructure of oil sands have been proposed.

High grade oil sand generally has a porosity of about 35%, and from 85 to 90% of this space is occupied by bitumen, with water and fines filling the remainder. Lower grade oil sand contains more fines, more water and less bitumen. The classical model of oil sand structure proposed by Cottrell assumes that the sand grains are surrounded by a layer of water containing suspended fines, with bitumen filling the remaining voids, as shown in Figure 2-3. This empirical model was able to account for the relative proportion of water, bitumen and fines, and was also able to explain why Canadian oil sands are water-wet. In recent years this model has undergone refinements.

Dusseault (18) refined Cottrell's model by suggesting that the sand-to-sand contacts have evolved over geological times so that adjacent grains have become "keyed" into one another through a process known as diagenesis. This means that from an initial porous medium of rounded particles with point contacts, the reservoir has evolved into a network of irregularly shaped particles having surfaces of contact. This accounts for the fact that the densities of repacked oil sand samples are not as high as the density of oil sand in the reservoir. Once this intimate structure is disturbed by mining, these highly oriented



COTTRELL'S MODEL



TAKAMURA'S MODEL

Figure 2-3. Two models of oil sand microstructure.

grain-to-grain contacts cannot be reconstructed. Rather, a random arrangement forms which will be bulkier and hence of lower density.

Takamura (19) suggested that the water is present in the form of pendular rings between adjacent sand grains and also as a thin film surrounding each sand grain, as depicted in Figure 2-3. According to this model, in lower grade oil sands the fines are concentrated in water-saturated clusters which would account for the observed changes in fines, water and bitumen saturations.

Zajic et al. (20) proposed a different model for the structure of oil sand, developed from freeze-fracture techniques and electron microscopy. Comparing the photomicrographs of oil sand samples with micrographs of known systems it was suggested that much of the water in the sample existed in the form of a water-in-bitumen emulsion. The pictures show no evidence of a layer of water surrounding the sand grains, but the limit of detection of such a layer would be about 10 nm. Takamura estimated that the water layer is about 10 nm thick, so the two proposals are not in direct conflict.

Continued research of this nature to define the microscopic orientation within oil sand will promote a better understanding of the mechanisms responsible for bitumen separation and displacement. This type of information will also help explain the effects of injected additives and will assist in the selection of preferred operating conditions.

2.4 Characteristics of the sand and clay matrix

The inorganic fraction of Athabasca oil sand is composed primarily of quartz sand. Clay is also present in significant amounts, mostly in the forms of kaolinite and illite. The clay content of a sand generally increases as the bitumen content (the grade) decreases. Bowman (21) listed a number of other minerals which have been identified in oil sand. These include: pyrite, siderite, magnetite, hematite, rutile, tourmaline, feldspar, dolomite, calcite and mica.

This segment of the oil sand can influence the displacement process in a number of ways. First, the physical size distribution of the particles affects the pore geometry and tortuosity within the porous medium. These factors will influence the sweep efficiency and the microscopic flushing efficiency during displacement. Secondly, the surface characteristics of the particles determine the wettability state of the sand which in turn impacts on the displacement effectiveness. Thirdly, strongly adsorbed organic material on the inorganic matter can, in certain circumstances, be rendered surface active. These in situ generated surfactants alter the interfacial energetics within the porous medium, thereby affecting the ultimate recovery.

In the present work the influence of the inorganic particle size distribution has only been examined briefly. Likewise, the mineral composition of the oil sand was largely unaddressed. These two factors were kept constant by using the same sand source throughout the research. However, the influence on displacement of the particle wettability state and of the role of strongly adsorbed organic material have been studied in detail.

2.4.1 Wettability considerations

There appears to be contradictory evidence regarding the preferred wettability condition to achieve maximum oil recovery. Bobek et al. (22) presented experimental results which concluded that water-wet cores flood more effectively than oil-wet cores. Morrow et al. (23) demonstrated an opposite effect. Strongly water-wet cores were preflushed with crude oil. This caused organic species in the oil to become adsorbed on the rock surfaces, rendering them only mildly water-wet. Flooding of these pretreated cores was observed to be more efficient than in the untreated, strongly water-wet cores. Wagner and Leach (24) reported that maximum recovery was achieved when the core was changed from oil-wet to water-wet during displacement by the advancing aqueous phase. This situation was superior to maintaining either oil-wet or water-wet conditions throughout the flood. Other hybrid theories have been proposed to account for experimental observations. Fatt and Klikoff (25) advanced a fractional wettability concept. The fractional oil and water wettabilities were determined by the fractional internal surface areas in direct contact with oil and water respectively. This theory addressed the fact that reservoir rock is heterogeneous and thus a uniform wettability state should not be expected. Along the same vein, Salathiel (26) explained recovery data in terms of a mixed wettability within the porous medium. Lower residual oil saturations were observed in specially constructed mixed wettability systems than in uniform, strongly oil or water-wet systems. When the preferentially oil-wet portions of the core formed a continuous pathway, then recovery would continue even at very low oil saturations. Normally, production ceases, or drops dramatically, once the oil saturation becomes discontinuous.

The range of viewpoints regarding the effect of wettability on recovery and the optimum conditions, presents a confusing scenario. It appears that the influence of wettability is very site-specific. The characteristics of a reservoir depend on the mineral composition, the types of species dissolved in the connate water and the nature of the crude oil. Since the effect of wettability can depend on any number of these parameters, it is not too surprising that different trends have been observed. A problem which has hindered the quantitative examination of the factors which control wettability is the lack of a means for measuring contact angles within a porous medium. At present this information is inferred from external tests such as imbibition and drainage behaviour. Quantitative measurements of contact angle are at present restricted to polished plates, usually made of quartz. However, these measurements do not allow for any effects due to other minerals or adsorbed organics.

2.4.2 Strongly adsorbed organic constituents

Numerous studies have demonstrated that organic species can be adsorbed onto the surfaces of mineral matter commonly found in oil sands (27-32). The heavier fractions of the bitumen, which possess high heteroatom and polar functional group contents, tend to be adsorbed. The clay fraction of the inorganic matter, with its high surface area and reactivity, is most susceptible to adsorption. Formation of these clay-organic complexes most certainly changes the surface characteristics of the inorganic matrix and thus influences the displacement process.

Baldwin and Gray (28) developed a multi-layer model which had the large aromatic or heteroatomic molecules strongly interacting with the rock surface. Next, was a layer of smaller, highly aromatic molecules which interacted less strongly, and finally, the bulk of the oil which interacted weakly, if at all, with the rock and its tighter adsorbed layers. They correctly point out that it is this altered rock surface which should be used in modelling studies. Assuming the rock surfaces to be clean introduces a gross error into the model design.

Another class of adsorbed organics, the so-called humic matter, is considered separately. Humic material (humic acids) is a generic term used to describe large organic molecules of biological origin containing polar functionalities, notably carboxylic groups. This material is insoluble in organic solvents and remains on the inorganic surfaces after extraction of the bitumen and water. In unaltered oil sand, it is debatable whether the humic acids are adsorbed on mineral surfaces or dispersed in the bitumen, and only forced onto the mineral surface during solvent extraction. The evidence favours the notion that humic acids and mineral matter, specifically the clays, are affiliated in some manner prior to any perturbation of the oil sand.

Montgomery (33) reported that the organic chemical types found in humic material are not observed in bitumen. He also stated that the humic material contained a complex mixture of acids and hence it would be expected to affect alkaline flooding. Strausz and Montgomery (34) commented that humic material has an elemental composition which resembles low rank coal more closely than bitumen. It is rational that these humic acids could be coal precursors.

Kotlyar et al. (35) described work which was performed to characterize the feed and the settled solids streams of the solvent extraction spherical agglomeration process. The sand was separated according to particle size and analyzed. It was found that as the particle size decreased, the organic and inorganic carbon contents of the samples increased. Additionally, the concentration of heavy elements, most notably iron, was higher in the finer fractions. It has therefore been hypothesized that the solvent-insoluble humic material was affiliated primarily with the clay particles in oil sand. The large concentrations of heavy elements led to the conjecture that the humic material was attached to the clay via an iron complex linkage. It is suspected that metal oxides and hydroxides serve as the complexation agents. Similar findings reported by Kessick (36) state that the adsorption of heavy organic material to clay surfaces is promoted by the ferric ion. Since the clay-organic association appears to be due to chemisorption rather than physical adsorption, separation of these species would be expected to be difficult.

Although these humic materials are insoluble in organic solvents, they can be liberated by caustic. Alkaline solution reacts with acidic functional groups in the humic matter creating a charged complex which can be solvated in an aqueous medium. Affiliated clay may be carried into suspension along with the solvated humic material. Ignasiuk et al. (37) presented an extraction sequence which can be used to obtain concentrated samples of humic material. The procedure consists of liberating the humic acids by caustic extraction, followed by acidification of the extract to precipitate the humic matter. Elemental and infrared analyses were performed on the concentrated samples of humic acids. It was observed that these species were rich in oxygen and nitrogen. The presence of carboxylic acid functional groups was suggested. Iron is again mentioned as a probable link in the clay-organic complex. They make further distinctions between humic and non-humic material. For the purpose of the present discussion, all of the toluene-insoluble organic material is classified under the generic name of humic matter.

An important consideration is the influence of these clay-organic complexes during displacement. If the displacing phase contains caustic and reacts with the humic acids, the surfactants produced may alter the interfacial forces in the porous medium so as to influence the recovery. Mobilization of the clay-organic complex can potentially exert either a positive or a negative effect. As fine particles move in a reservoir they can accumulate in, and block, narrower capillaries (38). This would be detrimental early in a flooding operation because zones of the reservoir would be bypassed. However, late in a flood it could be advantageous because the flow could be diverted into previously unswept areas. These mobilized clay-organic complexes could also serve as emulsion stabilizers (39). This would enhance the recovery efficiency, but may present troubles at the production end.

The specific influence of the inorganic matrix on oil sand processibility in the hot water extraction process has been studied. It is believed that these results have similar implications for in situ recovery. Strausz and Montgomery (34) attempted to account for the poor separability of low grade oil sand. They selected a low grade and a high grade oil sand and solvent extracted both. Cross mixtures of oil sand were prepared by combining the sand from the low grade sample with the bitumen from the high grade material and vice versa. These reconstituted oil sands were subjected to the same separability test. It was found that the nature of the inorganic material determined the recovery efficiency. The low grade sand plus high grade bitumen sample responded poorly, whereas the high grade sand plus low grade bitumen responded well. Therefore, the difference in oil sand processibilities was attributed primarily to differences within the inorganic fraction.

Smith et al. (40) related the oil sand extraction performance to the surface morphology of the sand grains. Three types of sand from different depositional areas were identified; these are: fluvial, estuarine and marine shoreface. The efficiency of processing these sands is related to the surface roughness of the grains. Some particles, both rounded and angular, possessed smooth surfaces. Other sands had been subjected to diagenetic alteration. The quartz overgrowths on these particles gave the sands a very rough, irregular surface. The processibility of sands from the marine shoreface environment was correlated with the degree of surface roughness in the sand. The more irregular the surface, the poorer the recovery of bitumen. The usual indicator of processibility is the fines content in the sand. However, in this instance the surface irregularity is a better predictor of the recovery response. This study did not consider the entire inorganic fraction, only those grains falling within a narrow size range. Nonetheless, it may provide a method for explaining and understanding apparent inconsistencies in the behaviour of oil sands from different locations.

2.5 Characteristics of the connate water

From the early days of oil sand research it has been speculated that the presence of connate water was responsible for the relative ease of Athabasca oil sand separability. However, very little research has focussed on quantifying the effects of connate water and its composition on the recovery of bitumen from oil sand. Kumar et al. (41) stated that the dissolved salts in connate water influence the oil-water interfacial tension and therefore should also influence recovery. Recently Takamura and Chow (42) and Hall et al. (43) developed similar arguments to relate the nature of connate water to the separation of bitumen from sand grains. The work of Takamura and Chow has been used as the basis for the ensuing discussion.

A parameter termed the disjoining pressure is used to predict the interaction forces existing in a model composed of charged bitumen and sand surfaces separated by an intervening layer of water – the hypothesized adsorbed water. Details of the calculation are given in Appendix 1. Conditions which yield a negative disjoining pressure favour attraction of the bitumen and sand surfaces, while conditions which yield a positive disjoining pressure favour repulsion. According to the model, bitumen separability is better when the net force is repulsive.

The model has been successfully used to explain phenomena observed in the crumble test (44). The disjoining pressure is positive for selected alkaline solutions and the rate of crumbling is high in these solutions. The addition of small amounts of Ca^{2+}

markedly retards the crumbling rate. This is accompanied by a simultaneous change to a negative disjoining pressure.

The disjoining pressure in connate water is observed to be positive. This is used as indirect evidence to support the contention that a stable aqueous film of water is adsorbed on the sand surface.

These calculations should also be useful for predicting in situ recovery behaviour since the chemistry of the system is the same. Factors which promote repulsion of the bitumen and sand surfaces would logically favour the displacement of bitumen from the porous medium. Inaccuracies in estimating the adsorbed water layer thickness introduce a complicating factor in all of these calculations. It cannot be observed so indirect estimations must be used. Its value is of critical importance because as the water thickness gets large, the disjoining pressure approaches zero for all aqueous compositions. In addition, for a given aqueous phase, the disjoining pressure can change from positive to negative or vice versa as the water layer thickness increases. Therefore, to compare and predict the behaviour of a particular system, some means of determining an accurate measure of the water layer thickness must be devised.

2.6 Characteristics of the organic phase

2.6.1 Chemical composition of bitumen

Bitumen is a complex mixture of molecular types which possess a wide range of chemical and physical properties. Component identification and characterization is accomplished by first fractionating the bitumen. Numerous separation schemes have been reported (45-52). The usual first step is to precipitate the asphaltenes. The deasphalted bitumen, maltene, is then further fractionated. Most of the separation techniques are chromatographic in nature. Fractions of increasing polarity are eluted by flushing with solvents of increasing polarity.

A typical primary separation scheme would fractionate bitumen into: saturates, aromatics, polars and asphaltenes. Within each fraction near-infinite subfractionation is possible. Trends have been detected in the physical and chemical properties of the components. Progressing from the saturates to the asphaltenes, as listed, the following changes occur:

(a) The fractions become denser and more viscous.
(b) The heteroatom content increases.
(c) The concentration of polar functional groups increases.
(d) The average molecular weight increases.

Extensive research has been performed using field ionization mass spectrometry to identify the molecular entities within the fractions (46-48). Another ongoing research interest is the development of rapid methods for characterizing bitumen and its constituents (53).

Detailed information regarding the molecular species in bitumen is beyond the scope of this work. The preliminary separation of bitumen into its chemical types and examination of those fractions has been addressed with the objective of determining which components most strongly influence the displacement process.

2.6.2 Viscosity and density correlations

For bitumens and heavy oils, the change in oil viscosity with temperature is an important consideration in the design of test conditions. A correlation which is frequently accurate, especially for lighter oils and narrow temperature ranges is the Andrade equation (54):

$$\eta = A \exp(B/T) \qquad (2.6\text{-}1)$$

where A,B are empirically determined constants, η is the viscosity and T is the absolute temperature. For very heavy oils and bitumens, the change in viscosity with temperature is very rapid, particularly in the high viscosity region. The Walther equation provides a better fit for this type of data (54):

$$\ln\ln(\nu+0.8) = -n\ \ln(T/T^*) + \ln\ln(\nu^*+0.8) \qquad (2.6\text{-}2)$$

$$\nu = \eta/\rho \qquad (2.6\text{-}3)$$

where ν is the kinematic viscosity and ρ is the density. The "best" available data point is used to determine ν^* and T^*. The parameter n is determined empirically. Use of this equation requires a knowledge of the temperature dependence of density. In the absence of experimental data, the density at a temperature t, in °C, can be estimated, if the density at 15°C is known, as follows (54):

$$\rho = \rho_{15} / [1 + (t-20) / 1047] \qquad (2.6\text{-}4)$$

In most of the present research, a mixed organic phase of bitumen and hexadecane has been used. Empirical correlations have been devised to estimate the viscosity of such mixtures. Cragoe (55) developed a correlation based on the calculation of a parameter termed the liquidity, L:

$$L = 2995.73 / (\ln \eta + 7.6009) \qquad (2.6\text{-}5)$$

where the viscosity has units of poise. For a mixture of two liquids containing a weight fraction f of liquid 1, the liquidity of the mixture (subscript m) is calculated from:

$$L_m = f_1 L_1 + (1-f_1) L_2 \qquad (2.6\text{-}6)$$

where liquidities are calculated from Equation 2.6-5 for each liquid. Knowing the liquidity of the mixture, its viscosity is determined from Equation 2.6-5. Therefore, the viscosity of a mixture at any temperature can be calculated, given the viscosities of the components at that temperature.

Shu (56) developed the following correlation for calculating the mixed viscosity, again given the component viscosities:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 \qquad (2.6\text{-}7)$$

$$x_1 = \alpha V_1 \;/\; (\alpha V_1 + V_2) \qquad (2.6\text{-}8)$$

$$x_2 = 1 - x_1 \qquad (2.6\text{-}9)$$

$$\alpha = G \;/\; \ln (\eta_1/\eta_2) \qquad (2.6\text{-}10)$$

$$G = 17.04 \;\Delta\rho^{0.5237} \;\rho_1{}^{3.2745} \;\rho_2{}^{1.6316} \qquad (2.6\text{-}11)$$

where subscript 1 refers to the more viscous component and V is the volume fraction. To use this correlation, the densities of the components at the calculation temperature must be available.

The data obtained for the hexadecane-bitumen system were fitted using both techniques. It was found that the Cragoe method more closely fit the data, hence it has been used. This supports the statement by Farouq Ali (54) that the Cragoe correlation is the most satisfactory of those available for fitting data obtained using liquids of widely varying viscosity.

The density of hexadecane-bitumen mixtures has been simply calculated by assuming ideal mixing of the two liquids. The density of the mixture is calculated from:

$$\rho_m = (M_1 + M_2) \;/\; (M_1/\rho_1 + M_2/\rho_2) \qquad (2.6\text{-}12)$$

where M is the mass of liquid. This method produced excellent agreement between calculated and experimental values.

In the low temperature displacement experiments, oil sand samples were reconstituted by mixing the inorganic material, the aqueous phase and the organic phase. Much of the work has involved introducing selective changes into the characteristics of the oil sand components and then testing the effect of the change on the displacement efficiency. Currie et al. (44) reported the results of crumble test experiments performed using reconstituted oil sand samples. In their work, only sand and bitumen were mixed together. The resulting pellets of oil sand were observed not to crumble. This is reasonable in view of the fact that water was not added during reconstitution. Strausz and Montgomery (34) did add water to the sand prior to the introduction of the bitumen. The samples thus prepared would be expected to behave more realistically.

Therefore, the use of reconstitution to prepare oil sand samples has been used previously. However, none of the reported studies have used the technique to perform the type of extensive, systematic investigation addressed in this research.

2.7 Influence of displacing phase on recovery

From a practical viewpoint, the control of an in situ displacement process is accomplished by judicious selection of the operating conditions. This includes physical parameters such as: temperature, pressure, flowrate, and injection strategy; and chemical parameters such as the use of additives in the steam/ hot water injection stream.

Flow of a single fluid in a porous medium is governed by Darcy's law, expressed as:

$$\underline{q} = (-\underline{\underline{k}}/\eta)\ \underline{\nabla} P \qquad (2.7\text{-}1)$$

where $\underline{q}$ is the linear velocity, $\underline{\underline{k}}$ is the permeability tensor, η is the fluid viscosity and P is the combined static and gravitational pressure. The equation can be simplified by introducing the following assumptions:

(a) The porous medium is isotropic (permeability the same in all directions).

(b) The flow is one-dimensional (denoted as the x direction).

(c) The flow is horizontal (gravity effects ignored).

Darcy's equation can thus be reduced to:

$$q = (-k/\eta)\ (dp/dx) \qquad (2.7\text{-}2)$$

where p is the static pressure.

Darcy's law is valid in the "seepage velocity" domain, corresponding to the parallel concept of laminar flow in pipes. The limit of applicability is obtained by calculation of the following Reynolds number (57):

$$Re = q\ d\,\rho/\eta \qquad (2.7\text{-}3)$$

where ρ is the density of the fluid and d is a "characteristic dimension" of the porous medium (e.g., average grain size or pore diameter). There is considerable discrepancy regarding the maximum value of the Reynolds number for which Darcy's law remains valid. Values ranging from 0.1 to 75 have been reported (57), hence caution must be exercised when interpreting estimates falling within this range.

Numerous attempts have been made to calculate permeability as a function of other measurable properties of a porous system. One which finds widespread usage is the Kozeny–Carman relation (57):

$$k = \phi^3 \;/\; [5\,\beta^2\,(1-\phi)^2] \qquad (2.7\text{-}4)$$

where ϕ is the porosity and β, the specific surface area, is the solid surface area per unit volume of solid. This relationship has also been employed to calculate the specific surface area of a porous medium, given its permeability.

The simultaneous flow of two or more fluids can be handled by extension of Darcy's law. For the specific case of displacement of oil (subscript o) by water (subscript w), the following additional assumptions are made:

(a) The liquids are incompressible.

(b) The liquids are immiscible.

Equation 2.7-2 can then be applied to each component as:

$$q_w = (-k_w/\eta_w)\ (dp_w/dx) \qquad (2.7\text{-}5)$$

$$q_o = (-k_o/\eta_o)\ (dp_o/dx) \qquad (2.7\text{-}6)$$

where k_w and k_o are the effective permeabilities to water and oil. It is more common to refer to relative permeabilities defined as:

$$k_{ri} = k_i/k \qquad (2.7\text{-}7)$$

From extensive investigation it appears as though the relative permeability is a function of the fluid saturation only. The similarity in shape of many relative permeability versus saturation curves has led to the development of empirical equations for determining the relative permeabilities of the wetting and non-wetting phases (57). In the present context, the wetting phase is water and the non-wetting phase is oil. The relevant equations are:

$$k_{rw} = S_w^3 \qquad (2.7\text{-}8)$$

$$k_{ro} = 1. - 1.11\ S_w \qquad (2.7\text{-}9)$$

where S is the saturation defined as:

$$S_i = V_i\ /\phi V_T \qquad (2.7\text{-}10)$$

where V_i is the volume of the ith fluid and V_T is the total system volume. Therefore, ϕV_T is the total pore volume and saturation corresponds to the proportion of the total pore volume occupied by the fluid of interest.

The pressure terms in Equations 2.7-5 and 2.7-6 are related through the capillary pressure, p_c , defined for a water-wet system as:

$$p_c = p_o - p_w \tag{2.7-11}$$

The capillary pressure can be expressed in terms of the oil-water interfacial tension, γ , using Laplace's equation:

$$p_c = \gamma(1/R_1 + 1/R_2) \tag{2.7-12}$$

where R_1 and R_2 are the principal radii of curvature of the interface.

2.7.1 Displacement of oil from a reservoir

The displacement of oil by water is never complete since there is always a residual oil saturation. The goal of a recovery operation is to lower the residual saturation at a cost which is not prohibitive. In general terms, the recovery is a product of the overall sweep efficiency and the microscopic flushing efficiency.

Sweep efficiency. The sweep efficiency of a recovery process is a macroscopic parameter which, for the present purpose, defines the volumetric proportion of the reservoir contacted by the displacing fluid. If the displacing fluid could be made to move in a flat front over the entire cross-section of the reservoir then the sweep would be complete. However, in practice, the sweep is always less than 100% efficient for the following reasons:

(a) Permeability is a function of reservoir structure, and regions of differing permeability exist. The natural tendency for a displacing fluid is to seek the path of least resistance between the injection and production points, which leads to the formation of fingers. This causes the front to assume an irregular shape as opposed to the idealized flat surface. Once a finger breaks through at the production end, practically all of the displacing fluid will pass through this channel with very little subsequent expansion of the swept volume into uncontacted reservoir.

(b) Due to density differences between the displaced and displacing phases there may be gravity segregation causing the displacing fluid to migrate to the top or bottom of the reservoir, leaving the other portion unswept. This is particularly evident in steamflooding because steam is much less dense than oil or water, hence it has a strong tendency to override the oil-containing portion of the formation.

(c) A reservoir often contains flow barriers, such as impermeable streaks, which influence the flow patterns in the formation and cause bypassing of some regions.

Considerable research has been directed towards overcoming these problems. A parameter known as the mobility ratio, M, is useful for predicting the stability of a displacement process. It is defined as (57):

$$M = \eta_o k_w / \eta_w k_o \qquad (2.7\text{-}13)$$

If the ratio is less than 1, the displacement process is stable, whereas for values greater than 1, the displacing fluid will tend to finger and the flood will be less effective. The mobility ratio can be made more favourable by increasing the water viscosity. In light oils this can be achieved by addition of water-soluble polymers. The same principle cannot be directly applied to heavier oils because the polymers degrade at the high temperatures encountered in these applications. However, with the development of more thermally-stable polymers this approach could become viable.

An alternative that shows promise for steamfloods is to use foams as blocking and diverting agents (58,59). The idea is to inject a surface active chemical with the steam which causes foam to form in the high permeability channels where gas flowrates are high. Once steam breakthrough has occurred the surfactant can be injected to create a foam to block that pathway. The formation of the foam decreases the permeability of the channel causing steam to be diverted into other portions of the reservoir. The future use of blocking agents in steaming operations appears to be attractive. Additional work is necessary to evaluate the foaming capacity of surfactants, their temperature stability and their compatibility with heavy oils and bitumens.

Flushing efficiency. Even the swept portion of the reservoir will be left with a residual oil saturation caused by incomplete displacement from the pores of the rock. Wardlaw (60,61) suggested three mechanisms by which oil can be microscopically trapped; these are termed: snap-off, bypassing and surface trapping. Snap-off is due to constriction of the flowing oil at the outlet throat of a pore by the simultaneous flow of the water. If the oil is pinched completely, an isolated blob of oil forms and it will not be subsequently recovered. Bypassing refers to the preferential flow of the displacing phase through one of a series of parallel pores, thereby isolating oil in the non-preferred pathways. Surface trapping pertains to oil adhering to oil-wettable surfaces.

Various parameters have been devised to provide an indication of the success of a displacement operation. The most prevalent of these is the capillary number, N_{ca} , introduced by Moore and Slobod (62). The general form of this dimensionless ratio of viscous to capillary forces is:

$$N_{ca} = q\eta / (\gamma \cos\theta) \qquad (2.7\text{-}14)$$

where q is the Darcy velocity, η is the viscosity of the displacing phase, γ is the interfacial tension between the displacing and displaced phases and θ is the contact angle between the displacing phase and the porous medium. In normal waterfloods the capillary number is of the order of 10^{-6} (62). It has been found that to significantly reduce the residual oil saturation, this number must be increased by several orders of magnitude (60,63,64). In an ordinary waterflood, which for economic reasons contains a minimum of additives, the viscosity, interfacial tension and contact angle are all relatively fixed. Therefore, the only way to increase the capillary number is to increase the flowrate within the constraint that the velocity be kept under the fracturing limit. To achieve still lower saturations the capillary number must be increased by altering the other three parameters in the equation. The viscosity of the water can be increased by adding water-soluble polymers. The interfacial tension can be reduced by the use of surfactants. The changes which additives have on contact angle are variable depending upon the nature of the rock.

The importance of the viscosity ratio has been incorporated into the capillary number expression by Abrams (65):

$$N_{ca} = q\, \eta_w / \gamma\, (\eta_w/\eta_o)^{0.4} \qquad (2.7\text{-}15)$$

This expression was developed by analyzing experiments done with a wide range of oil viscosities. In the work of Moore and Slobod (62), the viscosity ratio was nearly unity, therefore this modified parameter may be more appropriate for studying viscous crudes. This, and other, forms of the capillary number are often simplified by omitting the contact angle dependence. This is valid in situations where the displacing phase strongly wets the porous medium (such as Athabasca oil sand); in other cases the contact angle dependence should be included.

A second group, the dimensionless ratio of gravity to viscous forces, termed the Bond number, N_b , is important in applications where gravity segregation is important (66). Its form is:

$$N_b = \Delta\rho g\ k / \gamma \tag{2.7-16}$$

where $\Delta\rho$ is the density difference between the phases and g is the gravitational constant.

The beneficial effects of using additives in the water can be realized at two times in the production history of a reservoir. One approach is to continue the waterflood until its economic limit is reached and then to initiate the chemical flood. This would be classified as a tertiary recovery scheme. Alternatively, the chemicals can be added during the secondary production stage to conduct an enhanced waterflood. It has been shown to be more difficult to displace the residual oil trapped by a waterflood than to recover this same oil by an enhanced waterflood when the oil distribution is more continuous (6[illegible]).

In the present work, the focus has been on changing the interfacial forces within the porous medium. Indirect alteration of the sand and clay surface wettabilities may have occurred in the process. There are two different methods for altering the interfacial forces, but fundamentally they are quite similar. These are:

(a) The direct injection of surfactants.

(b) The injection of alkaline agents to react with acidic species in the porous medium to produce surfactants in situ.

2.7.2 Surfactant injection

Isaacs et al. (11,67,68) reported the results of experiments which used aqueous solutions of surfactants to displace bitumen from packed Athabasca oil sand. The results indicate that a displacing phase of water yielded the same recovery as a brine solution. The addition of surfactant enhanced this recovery, and the use of surfactant and salt was better still. The increased recovery was accompanied by a parallel decrease in the interfacial tension, which increased the capillary number, hence improved displacement efficiency would be expected.

The use of surfactants in oil sands suffers from three drawbacks. First, at the high temperatures normally encountered, surfactants undergo thermal degradation (68,69). Secondly, surfactant adsorption of the reservoir matrix may necessitate the use of prohibitive amounts of chemical in order to maintain a sufficiently high concentration at the front (11). Thirdly, the efficiency of a surfactant flood is diminished as the surfactant ages (70). These deficiencies must be overcome before field use of surfactants at high temperature becomes viable. One advantage of operating at high temperature is that the interfacial tension of most crudes examined by Flock et al. (71) decreased as the temperature increased.

A rapid test has been developed at the Alberta Research Council to screen surfactant formulations for their ability to break-up the oil sand matrix (44). The "crumble test" was devised as a means of explaining and predicting phenomena observed in the hot water extraction process. However, the information obtained may also be useful for understanding aspects of in situ-type recovery. For example, factors which facilitate the clean separation of bitumen from the sand grains should also facilitate displacement of bitumen from a pore.

Closely related to interfacial tension is the subject of reservoir rock wettability. The contact angle can be changed during a displacement process if the interfacial forces are altered. Young's equation presents the interrelationship between the interfacial tensions and the contact angle:

$$\gamma_{ow} \cos\theta = \gamma_{os} - \gamma_{ws} \qquad (2.7\text{-}17)$$

where the subscript s refers to the solid surface.

2.7.3 Alkaline injection

Alkaline flooding has been proposed as a means of lowering residual oil saturation in reservoirs which contain a high acid number oil. Tiab et al. (72) reported that caustic steamflooding is a very effective enhanced oil recovery process in acidic oils. Furthermore, Rosmalen and Hesselink (73) pointed out that alkaline flooding is one of the few chemical recovery methods presently viable at high temperatures because of the relative insensitivity of caustic to the harsh conditions.

The principle behind alkaline flooding is that the caustic reacts with the naturally occurring acids in the oil to produce surfactants in place (74-77). Once generated, these surfactants function in much the same manner as an injected micellar solution. The caustic-oil reaction is just one which is possible; reactions with inorganic species may also influence the displacement process.

The mechanisms of enhanced recovery achievable using caustic are (74,77):

(a) Interfacial tension reduction leading to emulsification and entrapment.

(b) Interfacial tension reduction leading to emulsification and entrainment.

(c) Wettability reversal in either direction.

The presence of even small amounts of Ca^{2+} increases the interfacial tension because calcium soaps are much less surface active than sodium soaps (74).

The interfacial tension between caustic and an acidic oil exhibits complicated behaviour. The interfacial tension is time-dependent; initially decreasing until a minimum is attained, then increasing. The minimum is often orders of magnitude lower than the steady-state value (75,78). Rubin and Radke (78) proposed an explanation for this transient effect. Upon contact of the oil by caustic, the acidic components in the oil diffuse to the interface, are adsorbed, react, desorb from the interface and diffuse into the bulk aqueous phase. It is postulated that initially the rate of accumulation at the interface is greater than the rate of desorption and diffusion away. At some time, the interfacial charge will reach a maximum, corresponding to the attainment of minimum interfacial tension (76). Thereafter, the rate of desorption exceeds the rate of adsorption and the interfacial tension starts to rise.

Most measurements of low interfacial tensions have been performed using a spinning drop interfacial tensiometer. In this measurement the water to oil ratio is or the order of several hundred, whereas in an actual reservoir the ratio will be close to one. Rubin and Radke (78) state that the relatively large volume of water in the spinning drop measurement exaggerates the rise in interfacial tension beyond the minimum. In an actual field test it is proposed that the operable interfacial tension is the minimum value observed in the laboratory.

The caustic-oil interfacial tension has been observed to depend on the concentration of salt in the aqueous phase (79). As the concentration of NaCl increases the concentration of NaOH required to achieve low interfacial tensions decreases, but the absolute value of the minimum increases.

Temperature also influences the shape of the transient interfacial tension versus time curve. At elevated temperatures, the magnitude of the minimum interfacial tension decreases and the time taken to reach this minimum also decreases (75). The lowering of the magnitude of the minimum interfacial tension can be explained in terms of surfactant solubility. At higher temperatures the solubility of the surfactant in water increases (higher critical micelle concentration) which in turn results in a higher surface concentration and a lower interfacial tension. The faster occurrence of the minimum can be explained in terms of reduction of the oil and water (mainly oil) viscosities. At lower bulk viscosity the organic acid/surfactant diffusion rates will be higher, so the minimum interfacial tension will be observed sooner.

Sharma and Yen (80) developed a thermodynamic model to predict the steady-state interfacial tension (i.e., after complete reaction) between caustic and oil, as a function of pH, salinity and temperature. The model is not capable of handling the time-dependent portion of the interfacial tension curve, which is the most interesting part.

Sydansk (81) reported that NaOH reacts with sandstone at elevated temperature to promote some or all of the following:

(a) dissolution of susceptible silicate minerals.
(b) increased porosity.
(c) leaching of water-soluble silicates.
(d) altered permeability.
(e) redeposition of aluminosilicate minerals.

The extent of reaction (and the extent of caustic consumption) is a function of the rock type, temperature, caustic concentration and the duration of contact. Southwick (82) suggested that problems related to silica dissolution by caustic could be reduced or eliminated by injecting an alkaline solution already saturated with the mineral species in question.

Alkaline solution can also be consumed by hydrogen ion exchange with the reservoir rock according to the reaction (83):

$$\text{Rock-H}^{+} + \text{Na}^{+}\text{OH}^{-} \quad = \quad \text{Rock-Na} + \text{H}_2\text{O} \qquad (2.7\text{-}18)$$

From the preceding it can be concluded that the practical application of caustic flooding is a complicated procedure. There are numerous factors which must be considered in the design of an efficient displacement process. The wide variation in reservoir characteristics will likely require that each potential field operation be uniquely designed.

3. EXPERIMENTAL METHOD

3.1 High temperature experiments

In the early stages of experimentation, mined Athabasca oil sand was manually tamped into the displacement cell and experiments were conducted at high temperature. The original displacement apparatus is depicted in Figure 3-1. Central to the apparatus is the cell which has an internal diameter of 2.54 cm and an inside length of 38.1 cm. The apparatus was constructed to permit either a vertical or horizontal orientation of the cell. Surrounding the cell is a 3-zoned, hinged oven built to specifications by the Industrial Heater Co., New York, NY. The rate of heating of each zone of the oven is controlled by a variable rheostat. Each zone contains a type K (chromel-alumel) thermocouple to measure the temperature and the information is relayed to a Honeywell Dialapak temperature controller. A central multicouple well was constructed to specifications by Thermoelectric Ltd., Brampton, Ont. It contains 4 equally-spaced type K wire thermocouples enclosed in a 0.318 cm outside diameter sheath. One of the cell endcaps was modified to accept the insertion of the thermocouple well into the cell to provide a temperature profile along the central axis. The inlet and outlet lines were traced with heating tape and wrapped with woven fibreglass insulation. Each section contained a type K thermocouple connected to a Honeywell Dialapak controller. All of the thermocouple outputs: 4 in the central well, 3 from the zones

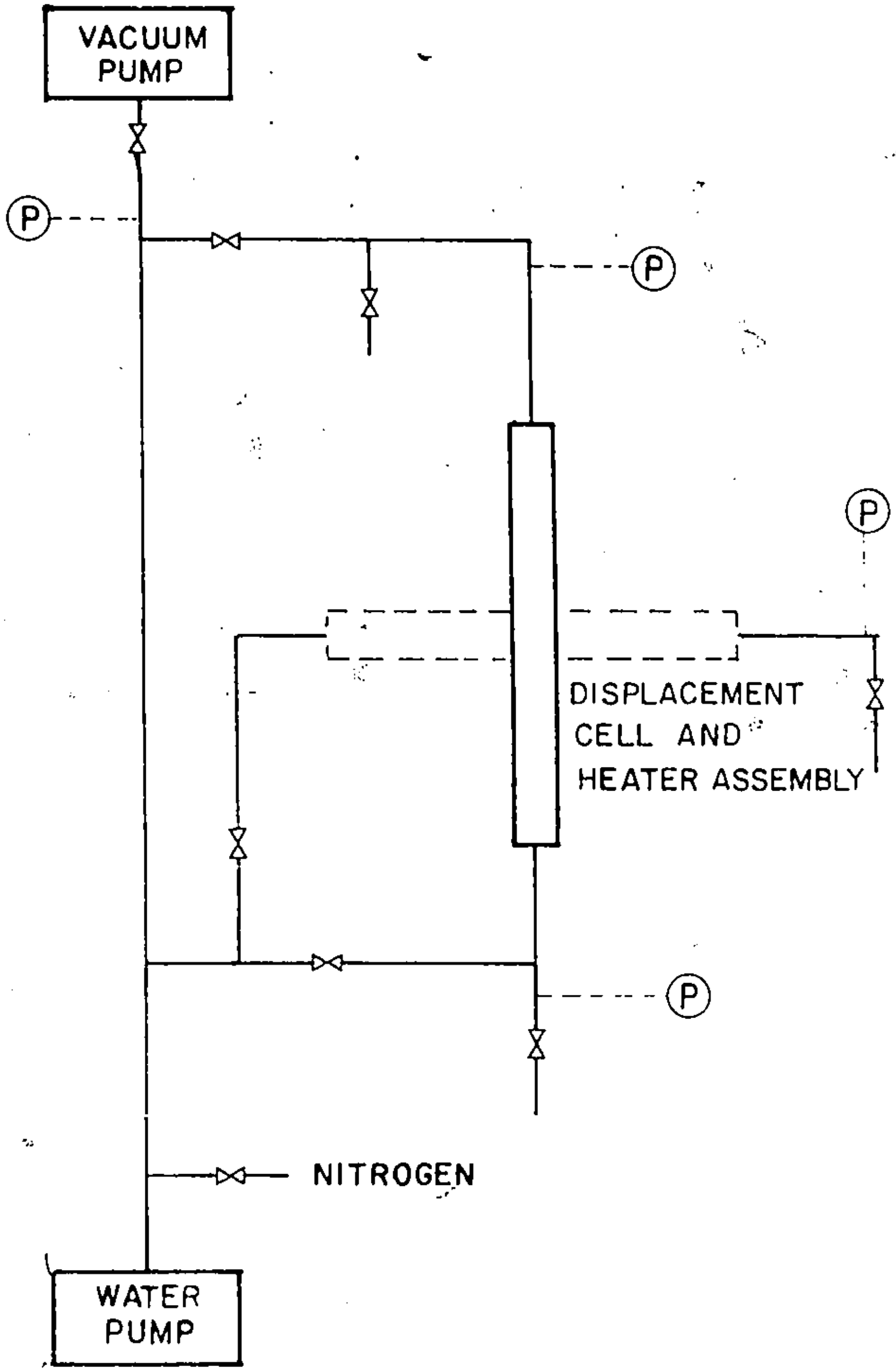


Figure 3-1. High temperature displacement apparatus.

of the oven and those from the inlet and outlet lines were plotted as a function of time on a Honeywell Model 112 12-point strip chart recorder. Other components of the displacement apparatus are a vacuum pump to evacuate the system prior to an experiment, a Lapp pump to deliver water into the sytem, and pressure gauges to measure the pressures on the inlet and outlet sides of the cell. A side line is connected to a nitrogen tank to pressure test the system.

The first step in conducting an experiment was to pack the cell. The end cap containing the central thermocouple well was secured, a wire screen positioned at the face of the cap and a section of glass beads poured into the cell. A 300 g sample of oil sand was divided into 13 equal sections. Each was manually tamped into the cell, around the central thermocouple well, using a specially constructed plunger and a rubber mallet. Glass beads were added to the void space remaining at the top, and a wire screen was placed on top of the beads. The other end cap was then secured. The packed cell arrangement is represented in Figure 3-2.

The packed cell was then mounted in the displacement apparatus. The system was evacuated and a predetermined volume of water was injected into the cell. The heaters were turned on and the system allowed to reach steady-state temperature conditions, usually at 250°C. At that time, the collection port was opened to release the built-up steam pressure and simultaneously bitumen was recovered. The recovery efficiency was measured by performing a Dean Stark analysis of the collected liquids, the outlet side glass beads and the bitumen washed out of the production side end

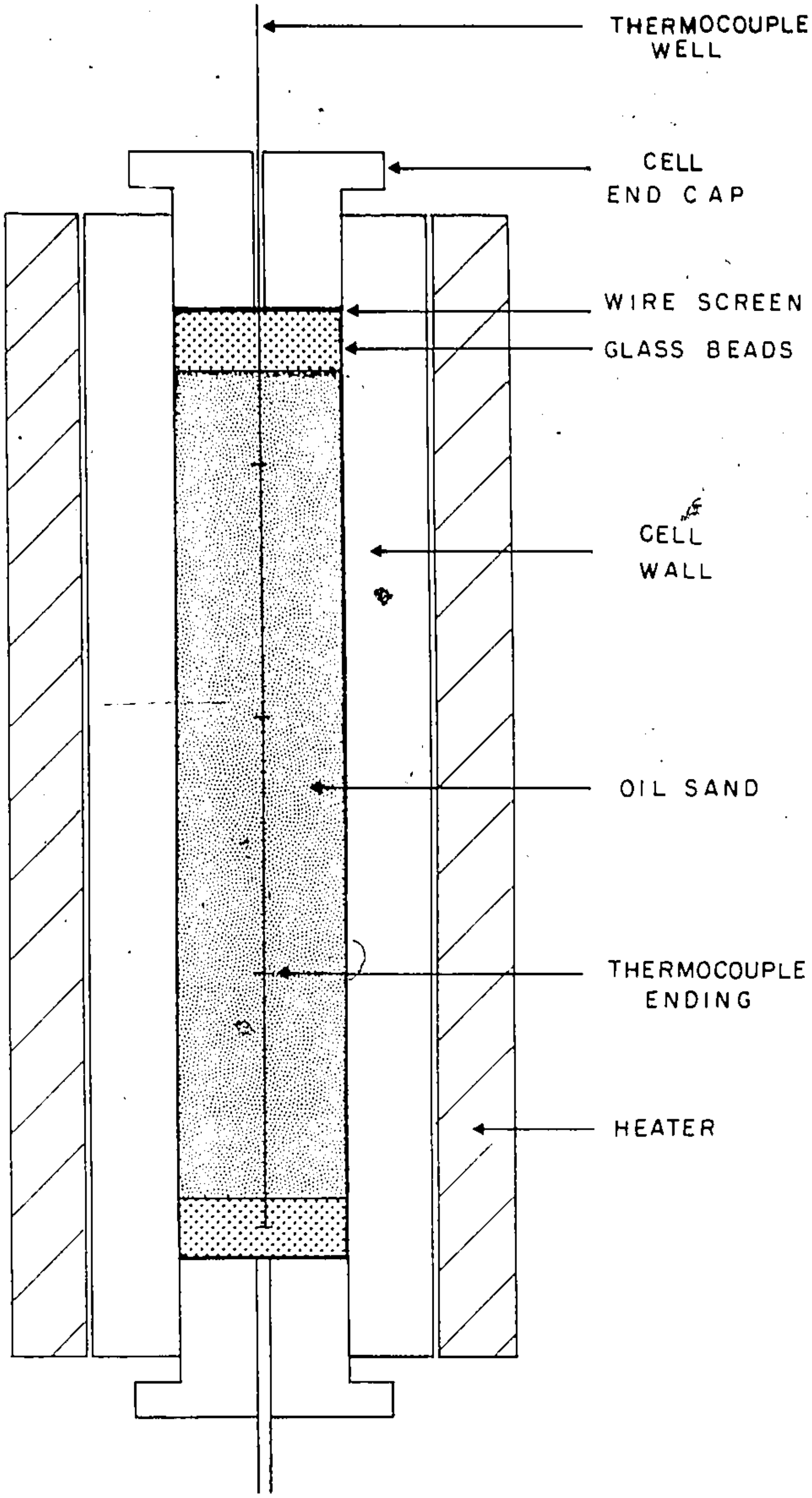


Figure 3-2. Cell arrangement after manual compaction of an oil sand sample.

cap.

The first modifications made were as follows:

(a) The mass of oil sand used in a test was reduced by a factor of 10 to simplify the experimental procedure. The smaller sample size could more readily be packed to a consistent density, and it could also be easily dislodged from the displacement cell when performing the analysis for residual oil content.

(b) The central thermocouple well was removed to improve the packing efficiency.

(c) The packing was performed in one step using a hydraulic press. This eliminated many of the packing inconsistencies embodied in the segmental, manual tamping method.

The loaded cell after introducing these changes is depicted in Figure 3-3. Experiments were performed by injecting a volume of water, bringing it up to steam conditions and then relying on the drive resulting from steam presssure letdown to displace bitumen from the packed oil sand. The recovered bitumen was determined by measuring the amounts of bitumen remaining in the oil sand pellet and calculating the amount displaced by difference.

The next modification was to shift to a system of hot water flooding. The Lapp pump was replaced by a Ruska pump which is capable of delivering more reproducible flow rates at the pressures encountered. An experiment was started by injecting enough water to occupy only a portion of the inlet side glass bead region. The system temperature was brought up to 250°C, as before. In these experiments, the displacement was accomplished by pressurizing the inlet lines to match the pressure within the

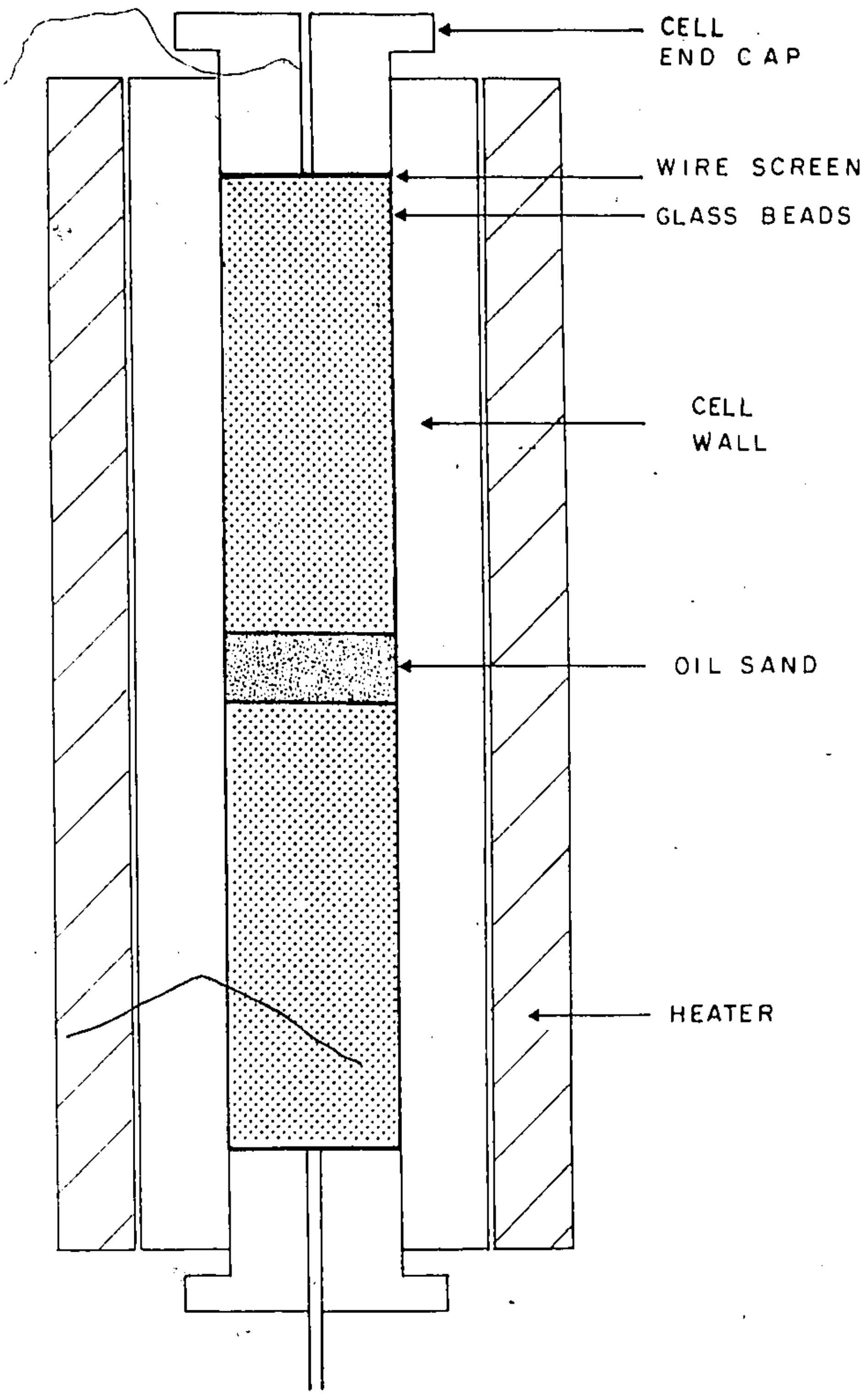


Figure 3-3. Cell arrangement after hydraulic compaction of an oil sand sample.

cell while keeping the inlet valve to the cell closed. Once the two pressures were balanced the connecting valve was opened and water was pumped into the cell, through the oil sand section, and water and recovered bitumen were collected in the outlet side glass beads. In this arrangement, the system was never opened to the atmosphere so the steam pressure was not released. As the cell filled with water, the pressure within the system increased. Controlled tests performed with the central thermocouple well in place showed that temperatures within the cell remained constant throughout the displacement operation. Again the analytical procedure was to remove the oil sand pellet, determine the amount of bitumen remaining and calculate the amount recovered by difference.

3.2 Low temperature experiments

A significant development in this research was the shift to low temperature modelling of the high temperature displacement process. Samples of oil sand were reconstituted (discussed in next section) from the basic components, thus introducing control over its characteristics. The packing sequence will be described in detail later, but the final cell arrangement is the same as depicted in Figure 3-3.

The low temperature displacement apparatus is shown in Figure 3-4. The cell and surrounding heating arrangement are the same as before, but in this case the horizontal orientation is fixed. A Ruska pump, which was introduced during the later high temperature experiments, is used to provide the driving force during displacement. The particular displacing liquid of interest is contained in the liquid reservoir.

An experiment is conducted as follows. Initially valves 1,4 and 5 are closed and the vacuum pump turned on to remove air from the system. Once full vacuum is attained, valves 3 and 6 are closed and the vacuum gauges are observed for a few minutes. Satisfied that the system is leak-tight, valves 4 and 5 are opened to allow the displacing liquid in the reservoir to be drawn into the cell and connecting lines. When the voids are filled the vacuum gauges drop back to register zero vacuum. Valves 4 and 5 are closed and time allowed to see if any vacuum redevelops. Sometimes one or both gauges indicated the reestablishment of a low level vacuum, probably resulting from the slower advance of

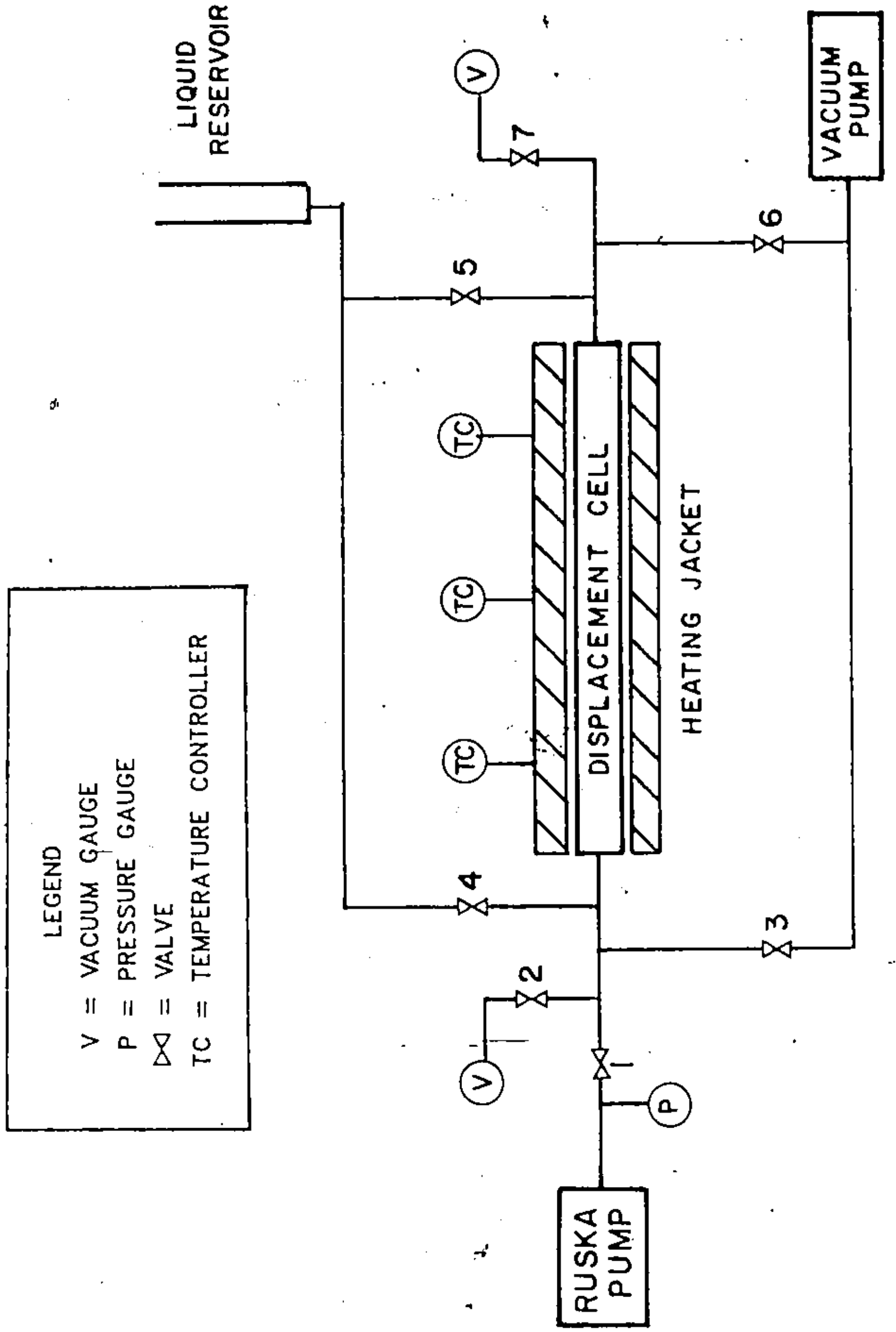


Figure 3-4. Low temperature displacement apparatus.

injected liquid into the finer pores. When this occurs, the appropriate inlet valve is opened momentarily to allow additional liquid into the system. After the system is filled with liquid, the inlet and outlet vacuum gauges are removed. The hinged oven is closed around the cell and turned on. Valves 2 and 7 are left open to maintain atmospheric pressure on both sides of the cell and to accommodate any thermal expansion which occurs during heating. Some experiments were performed with the thermocouple well in the cell. The rate of temperature increase was monitored and it was found to take 2 hours to reach a steady-state temperature of 60°C.

After reaching thermal equilibrium the displacement process is initiated by closing all valves except numbers 1 and 7, and pumping water into the cell. Water appears at the collection port in a few seconds, indicating that the voids in the cell were virtually filled with water initially. The outlet side pressure is atmospheric throughout, and the inlet pressure is monitored. Pumping continues until the desired volume has been passed through the system. The pump is shut off and valve 1 is closed. The heaters are turned off and the apparatus left to cool. Valves 2 and 7 are open during the cooling stage in case any vacuum redevelops which could cause backflow in a closed system.

3.3 Reconstitution

Reconstitution is the term which is used to describe the process of mixing together the clean sand, water and organic phase to "reconstruct" a sample of oil sand of prescribed composition. The first step is to take a sample of toluene-extracted sand and subject it to selected preconditioning. For example, this may involve heating it to a given temperature for a certain length of time or extracting it with NaOH. After pretreatment, the sand is always dried to ensure that no unaccounted for water is introduced into the oil sand. The dried sand and calculated amount of aqueous phase are added to a glass jar and manually mixed. The jar is then placed in a dry blender which tumbles with a period of about 4 s. During the first 6 hours of tumbling the blender is stopped 3 or 4 times and the contents of the jar are manually mixed. This manual stirring dislodges material which has adhered to the jar wall. The tumbling is resumed and continues overnight. The next day, a quantitative amount of the organic phase is introduced and the tumbling procedure repeated. In addition to scraping material off of the jar wall, the manual mixing serves to break up balls of oil sand which form during this stage. The following day, the blender is stopped and the sample of reconstituted oil sand removed. Just prior to using a sample, the contents of the jar are once again manually mixed.

3.4 Materials

Medium grade Athabasca oil sand obtained from the Alberta Research Council Sample Bank was used throughout this research. It was divided into 500 g packages which were stored at -18°C until needed. In all of the high temperature experiments, this oil sand was used as is.

The clean sand which was used during reconstitution was obtained by toluene-extraction of this same Athabasca oil sand. After extracting the bitumen and water, the sand was subjected to different pretreatment conditions. One, was to dry the sand overnight at temperatures ranging from 25 to 775°C. Another, was to extract the sand with 0.1 M NaOH. The procedure was to shake the sand with caustic and let it stand overnight. The next day, the mixture was centrifuged and the aqueous phase, including extracted and suspended material decanted. The extraction procedure was repeated until the supernatant colouration became very faint; this usually required four stages. Afterwards, the sand was washed with distilled water until the pH of the wash water was 7. A third pretreatment condition was to add quantitative amounts of the aforementioned extracted and suspended material, in dry form, back to a sample of sand which had been previously heated to 775°C. This will be discussed in more detail later.

In most instances distilled water has been used to represent the connate water in the reconstituted oil sand. The effect of ionic composition has been investigated by the addition of reagent grade sodium chloride or calcium chloride (Anachemia) to the water.

The bitumen which has been used is a sample obtained from Suncor. The properties of this bitumen are compared with others from the Athabasca region in Table 3-1. In much of the work to be discussed the bitumen has been diluted with certified grade hexadecane (Fisher). In some experiments, the organic phase has been composed entirely of castor oil (Fisher) or white, heavy paraffin oil (Fisher).

In the high temperature experiments which relied on steam blowdown to displace bitumen, the injected aqueous phase was always distilled water. In the hot water flooding experiments, the displacing phase usually consisted of distilled water or a solution of sodium hydroxide (Anachemia Acculute). However, in some cases solutions containing one or more of the following were used: reagent grade sodium chloride (Anachemia), Petrostep 465 petroleum sulfonate (Stepan Chemical Co.) and 5 to 6 million molecular weight polyacrylamide (Scientific Polymer Products).

In most of the low temperature experiments, the displacing phase was comprised of either distilled water or caustic. In a few experiments Anachemia reagent grade sodium chloride or calcium chloride were added.

Table 3-1. Comparison of Suncor bitumen used in this research with other Athabasca bitumens.

Analysis		This work	#1	#2	#3
Elemental, wt%	C	82.9	83.9	83.8	83.5
	H	10.1	10.4	10.6	10.3
	O	0.60	0.69	0.73	1.50
	N	0.44	0.79	0.60	0.47
	S	4.7	4.3	4.2	4.2
ppm	Fe	358	61	38	n.a.
	Ni	67	66	64	81
	V	213	211	208	204
Asphaltenes, wt%		15.3	15.9	16.3	17.2
Ash, wt%		0.5	n.a.	n.a.	0.1
Specific gravity (16/16°C)		1.009	1.013	n.a.	1.008
Viscosity, cp:	60°C	2060*	2460*	2025*	4620
	100°C	170*	302*	249*	114
Acid number		2.60	n.a.	n.a.	2.72

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data for samples 1,2,3 taken from reference 84

* interpolated or extrapolated using Andrade's equation

3.5 Packing method

The evolution of the packing methodology has been outlined in Section 3.1. The procedure used in the later high temperature experiments and all of the low temperature experiments is as follows. Plungers were machined to fit snugly into the displacement cell. One of these is positioned inside the chamber and the sample of oil sand is quantitatively transferred into the cell. The second plunger is placed on top and the whole assembly mounted vertically in a Carver press. The desired pressure is applied to the oil sand, held for a few seconds and released. This sequence is repeated until the oil sand has been compacted to a selected density. The plungers are then removed. Two wire screens of the same diameter as the chamber of the cell are positioned on top of one face of the oil sand. Glass beads are poured in to fill the rest of the space on that side of the cell. Another screen is placed on top of the beads and the cell end cap is secured. The cell is then inverted and this procedure repeated on the other side. The complete assembly is depicted in Figure 3-3.

3.6 Dean Stark Analysis

The oil content of a given sample is determined by the Dean Stark procedure developed for oil sands by the Alberta Research Council (85). Details of the method are given in Appendix 2. Two modifications were introduced to the Alberta Research Council method; these are:

(a) The extraction thimbles are taken directly from the 90°C oven and weighed, both prior to use and after evaporation of the toluene from the sand. As a result, the adsorbed water content of the thimble is the same at the beginning and end of an experiment and thus does not influence the calculations.

(b) The toluene is evaporated from the oil sand at room temperature in a fume hood, assisted by the forced air flow created by the suction of the hood. Slower evaporation of the toluene reduces the possibility of driving off constituents of the bituminous phase.

In analyzing an experiment, the ratio of oil to sand in the swept pellet is determined. Knowing the initial ratio, the amount displaced is calculated by difference.

Two types of controlled tests were performed to ensure that the method being used was accurate. In one, oil sand of known composition, or quantitative amounts of the various types of oils, were placed in the apparatus and analyzed to determine the degree of overall mass balance which could be achieved. In the second, a known weight of kaolinite was placed in an extraction thimble and refluxed to ensure that fine particles are not passed through the thimble and collected in the distillation pot.

3.7 Characterization of residual organic material on sand

Considerable effort was expended characterizing the residual organic material remaining on or in the sand after toluene extraction. Samples of whole sands exposed to varying pretreatment conditions and concentrated samples of residual organic material have been tested.

Concentrated samples of the residual organic material were obtained following a procedure similar to the one described by Montgomery (33). A sample of cleaned sand is dried at 300°C to render it water wet. It is then shaken with 0.1 M NaOH following the procedure outlined in Section 3.4. The combined reddish-brown supernatants from the successive extractions are acidified with HCl. Below a pH of about 3 the previously suspended material is precipitated. The remaining supernatant is clear and has a yellow tinge. The precipitated material is separated and dried for later use.

Samples of whole, toluene-extracted sand dried at room temperature, 200°C for 24 hours and 400°C for 24 hours were submitted for carbon, hydrogen and nitrogen analysis on a Leco CHN 600 (courtesy Analysis and Standardization Section, CANMET). Samples of these sands were also mounted and examined using coal petrographic techniques (courtesy Coal and Coke Constitution, CANMET). Samples of the reddish-brown solution extracted from 300°C-processed sand by 0.1 M NaOH were submitted for elemental analysis by inductively coupled plasma on a Jarrell Ash ICAP 9000 (courtesy Analysis and Standardization Section, CANMET), and for combined mass spectroscopy and gas chromatography on a Finnigan 4500 unit (courtesy Oil and Gas Laboratory, CANMET). Samples of sand heated to 300 and 775°C, sand which had been subjected to caustic extraction and concentrated samples of residual organic material heated to 300 and 775°C, were submitted for Fourier transform infrared (FTIR) spectroscopy using a Nicolet 60SX (courtesy Separation and Characterization, Catalysis Research Sections, CANMET). A sample of concentrated residual organic material was submitted for thermogravimetric analysis (TGA) on a Perkin-Elmer 7 Series Thermal Analysis System (courtesy Coal Liquefaction Section, CANMET). Samples of sands dried at 25 and 775°C, and samples of concentrated organic material dried at 110 and 775°C were submitted for scanning electron microscopy and x-ray analysis on a Kevex Inc. Nanolab 7 with electron microprobe (courtesy Department of Chemistry, University of Ottawa). Quantitative amounts of concentrated humic material were added back to a sand which had been heated to 775°C, and these altered sands then used to reconstitute oil sand samples for displacement testing.

3.8 Interfacial tension measurements

Interfacial tension measurements were made using University of Texas Spinning Drop Tensiometers. The Model 300 was used for experiments performed at ambient temperature and the Model 500 was used at elevated temperatures. The equipment and mode of operation have been detailed elsewhere (86). Measurements were made between 0.1 M NaOH and a solution of 20% hexadecane in bitumen at temperatures from 25 to 75°C. Other measurements, all at 25°C, were performed between 0.1 M NaOH and various organic phases including: fractions of the bitumen, castor oil and paraffin oil.

3.9 Separation of bitumen

Bitumen was fractionated to assess the importance of each component to the recovery process. The first step was to precipitate the asphaltenes. This was accomplished by mixing bitumen with roughly 30 times its volume of pentane. The mixture was sonicated to improve the contact efficiency and left overnight to digest. The next day, the mixture was briefly resonicated and gravity filtered through Whatman No. 1 paper. The collected solids (asphaltenes) were washed with pentane until the filtrate was colourless. The filtrate was rotoevaporated to remove pentane, leaving the deasphalted bitumen or the maltenes.

Further fractionation of the maltenes was performed by scaling up a procedure developed by Sawatzky et al. (50). In their procedure, the maltene is fractionated into: saturates, monoaromatics, diaromatics and polyaromatic plus polar material. In the modified version only two fractions were collected with the cut coming between the diaromatics and the polyaromatic plus polar material. The two fractions are termed hydrocarbons and polars for simplicity.

The modified procedure was to pack a vertical steel column (7.2 cm inside diameter by 121.9 cm long) with approximately 2800 cm^3 of each of silica and alumina. The silica was on the bottom. The silica was activated at 200°C overnight; the alumina was activated at 400°C overnight. Pentane was pumped into the packed system from the bottom until it appeared at the top. Then about 300 cm^3 of maltenes (containing some residual pentane) was loaded onto the column. The hydrocarbons were eluted by pumping 7 L of toluene through the system and collecting the effluent. The polars were eluted using 6 L of methanol. The collected fractions were rotoevaporated to obtain the two subfractions of maltene. Where applicable, the bitumen fractions were characterized according to elemental composition, density and viscosity.

3.10 Other analyses

The ash content of a liquid or solid sample was determined by placing a known weight of the material into a tared platinum crucible and heating the contents over an open flame. After removal of most of the volatiles, the crucible was transferred to a furnace and kept at 775°C overnight. The next day, the sample was cooled and weighed to determine the amount of ash initially present in the sample.

Viscosities of translucent liquids were measured using Ostwald-type capillary flow viscometers. Special reverse flow viscometers were used with opaque liquids.

Densities of very heavy liquids and solids were measured using pycnometers. Lighter liquids were injected into an Anton Paar DMA40 Digital Density Meter.

The elemental analyses of liquids and solids were conducted using the following instruments (courtesy Oil and Gas Laboratory, CANMET). Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer PE240C Elemental Analyzer. Oxygen was determined on a Perkin-Elmer PE240 Elemental Analyzer. The sulfur content of solids and heavy liquids was measured using a Leco SC32. The sulfur content of lighter oils was obtained on a Princeton Gamma-Tech Model 100.

The acid number of bitumen, hexadecane and a 20% solution of hexadecane in bitumen was measured following ASTM procedure D664-81 (courtesy Fuels and Lubricants Laboratory, National Research Council).

Sand size distribution was determined by placing a sample of sand on top of a tower of tared sieves and mounting the assembly in a mechanical shaker. After shaking, the individual sieves were reweighed to measure the amount of sand retained by each. The shaking was repeated until consistent weights on each screen were obtained. Sand surface areas were measured by B.E.T. nitrogen adsorption (courtesy Carbonization; Catalysis Research Sections, CANMET).

4. RESULTS AND DISCUSSION

4.1 High temperature experiments

4.1.1 Evolution of methodology

The initial high temperature experiments were performed by manually packing oil sand into the displacement cell. Pack densities of 1.80 to 1.90 g/cm^3 were obtained. The oil sand occupied about 85% of the cell volume in these experiments. The remaining space was occupied by glass beads. The porosity in the glass bead region was 42%. A temperature profile along the central axis of the cell was obtained at four points using a multiple thermocouple well. In the vertical position it was observed that there was a tendency for a thermal gradient to arise if the three temperature controller setpoints were identical (at 250°C). The temperature was 250°C at the top and 225°C at the bottom of the cell. This is attributed to convective heating in the air space between the oven and the cell. The magnitude of the gradient can be reduced by introducing a compensating gradient in the controller set points. In the horizontal position, the temperature profile within the cell was uniform. It was determined that about four hours was necessary for the temperatures measured by the central thermocouple well to achieve steady-state conditions of 250°C.

The driving force for displacement came from opening the production valve and releasing the steam pressure. Using this procedure roughly 20% of the bitumen could be recovered from the oil sand. However, the following undesirable features existed with the method:

(a) The packing was done manually so it was difficult to standardize the procedure to get reproducible pack densities.

(b) The oil sand bed was packed in segments. Therefore many individual zones, each possessing its own density gradient, were contained in the cell.

(c) Steam blowdown involved the rapid introduction of a large pressure drop in the system. The violent nature of the recovery mechanism, and the limited amount of control over it, created the suspicion that poor experimental reproducibility would result.

(d) The bitumen which was displaced from the oil sand, but trapped in the outlet lines was not included in the analysis. Observed recovery efficiencies would therefore be lower than their true values.

(e) The produced steam, hot water and bitumen were collected in an ice trap. However, the volatile components of the bitumen that were not trapped represented a noxious emission. For health reasons this situation was unacceptable.

These problems were addressed by introducing the following changes to the experimental method:

(a) The mass of oil sand used in an experiment was decreased from about 300 g to 30 to 60 g. This change meant that only 8 to 16% of the displacement cell contained packed oil sand. This left ample space to conduct the displacement operation within the confines of the cell. The change to a smaller sample size also made it practical to measure the amount of bitumen remaining in a pellet after displacement. This improved the accuracy of evaluating the recovery efficiency.

(b) The packing was performed using a hydraulic press. This introduced the ability to standardize the packing procedure.

(c) The central thermocouple well was eliminated. To use it with the hydraulic press would have required extensive unnecessary equipment modification. By that stage of the experimental program, the temperature behaviour within the cell had been sufficiently monitored.

The final high temperature operating methodology represents a procedure for performing rapid, inexpensive testing of the displacement of bitumen from oil sand by hot water. The method is ideal as a screening test to evaluate the influence on recovery of changes to the operating conditions. Development of this test procedure fulfilled one of the objectives established at the outset of this research program. In all subsequent discussion the cell orientation was horizontal to avoid temperature gradient complications.

4.1.2 Experimental results

The three operational parameters which were varied were: the nature of the displacing phase, the oil sand pack density and the temperature.

Table 4-1 presents the data obtained with various displacing phases. It is noted that the reproducibility of recovery in repeated experiments is within 1%. Therefore, comparisons can be made between experiments, with confidence that observed

Table 4-1. Recovery of bitumen from Athabasca oil sand, packed to a density of 2.00 g/cm^3, using various displacing phases at 250°C.

Displacing phase	Recovery, %
Distilled water	46.3, 46.3, 45.7
0.1 M NaOH	63.4, 63.4
2.53 wt% PS	66.5
5.11 wt% PS	65.9
3.95 wt% PS + 1.1 wt% NaCl	79.2
0.072 wt% PA	53.9
0.145 wt% PA	60.2

PS = petroleum sulfonate

PA = polyacrylamide

differences in recovery are real. The higher recovery produced by caustic compared to distilled water follows the trend which would be expected of an acidic oil. The caustic reacts with acidic species within the oil sand to generate surface active agents in situ. These surfactants serve to lower the interfacial forces within the porous medium. As predicted from the capillary number, as the capillary forces decrease and the viscous forces remain constant, the recovery efficiency would be expected to increase.

Comparing the results using petroleum sulfonate with those using water it is observed that the presence of surfactants did indeed improve the recovery efficiency. The rationale for expecting recovery to increase is the same as discussed for in situ surfactant generation. The difference in this case is that the surfactant was externally introduced into the porous medium. The presence of salt further improved the effectiveness of the petroleum sulfonate in displacing bitumen. This agrees with the observation that a certain concentration of salt must be present in petroleum sulfonate solutions to obtain ultralow interfacial tensions (87). The improvement in recovery is therefore attributed to a further lowering of the interfacial forces in the system.

The two results with polyacrylamide are again as would be predicted from examination of the capillary number. The function of a water soluble polymer in the displacing phase is to increase the water viscosity. This improves the stability of the displacement process, and thus a higher recovery is expected.

These tests demonstrate that the method which has been developed can be used to screen additives in the displacing phase. In each of these cases, the effect which would be predicted was indeed observed. The method can presumably be extended to assess additives whose behaviour is not so easily predicted, and also to rank additives according to their relative effectiveness.

The effect of the steady-state temperature on recovery is shown in Table 4-2. It is noted that as the temperature decreased, the recovery decreased. This occurs because the oil viscosity increased much faster than the water viscosity, as the temperature decreased. Therefore, the displacement process became more unstable and lower recovery would be expected and was indeed observed. Also interesting is that the reproducibility of repeated experiments at 60°C is much poorer than at 250°C. This is attributed to the very high oil-water viscosity ratio at 60°C causing the displacement process to be very unstable and hence unpredictable. It is noteworthy that the effect of temperature was not as significant for caustic displacement as it was for water displacement. This indicates that the surfactants produced by the chemical reaction between caustic and acidic components in the oil sand exerted a strong enough influence to partially overcome the adverse viscosity effects.

The effect of the oil sand pack density on recovery by water is shown in Figure 4-1. At the two highest densities water and bitumen were squeezed out of the oil sand during compaction. This is a situation which should be avoided to minimize alteration of the oil sand composition. The trend observed was that recovery increased with density.

Table 4-2. Recovery of bitumen from Athabasca oil sand, packed to a density of 2.00 g/cm^3, as a function of temperature.

Temperature, °C	Displacing phase	Recovery, %
250	Distilled water	46.3, 46.3, 45.7
165	"	38.1
135	"	34.3
60	"	11.4, 20.3, 17.5
250	0.1 M NaOH	63.4, 63.4
60	"	46.8, 48.3, 42.3

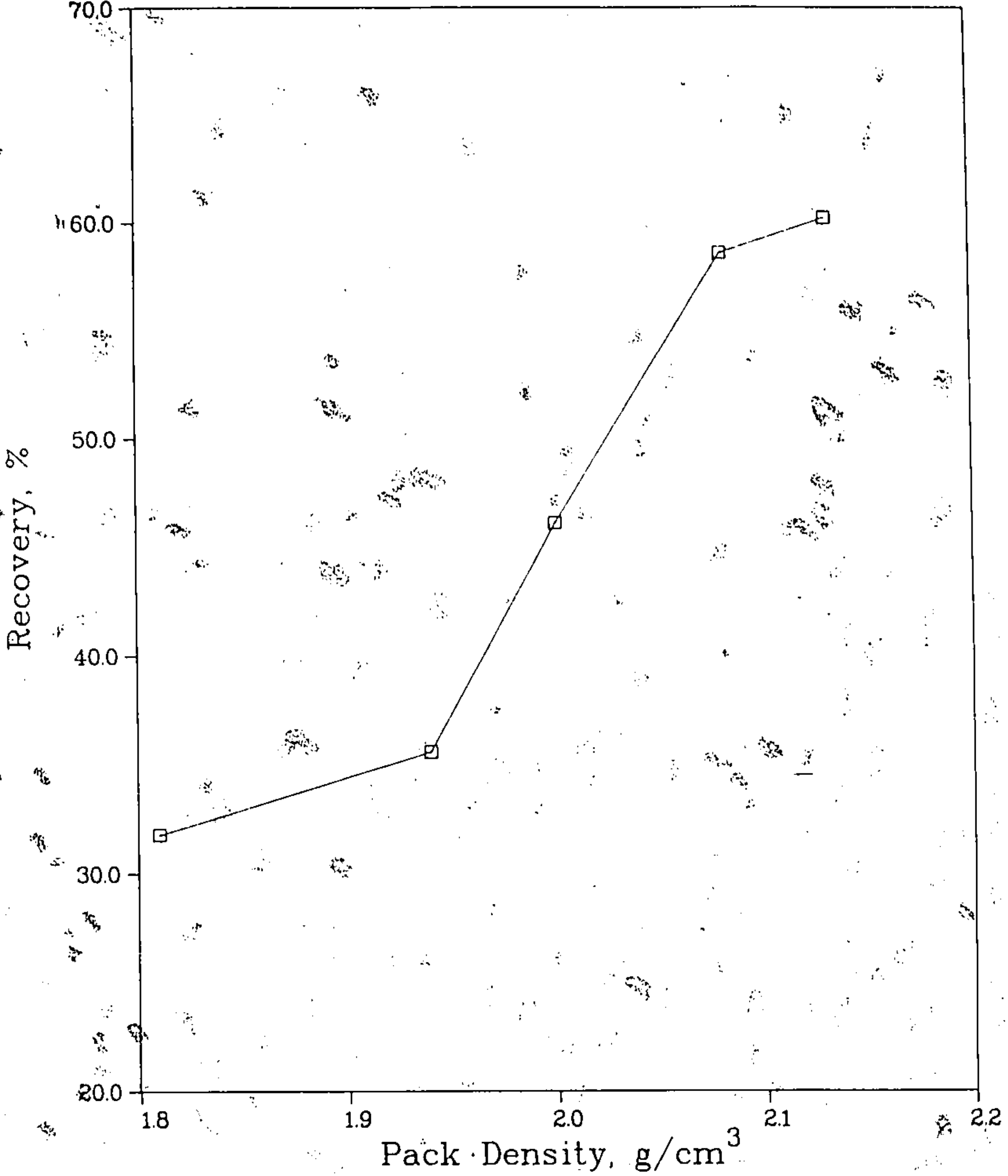

Figure 4-1. The effect of pellet density on the recovery of bitumen from Athabasca oil sand at 250°C.

This density effect must have been due to changes imposed upon the flow channels within the porous medium by the application of different packing pressures. In its natural state, Athabasca oil sand contains mineral matter, bitumen and an aqueous phase. There is essentially no additional pore space occupied by air or other gases. After mining, however, recompacted samples of oil sand will always possess some additional "artificial" porosity. The sand grains cannot be rearranged into the highly ordered state which existed underground. In the data represented in Figure 4-1, the density increases were brought about by a reduction in the amount of artificial porosity. Table 4-3 illustrates the interrelationship between the fluid distributions and the pack density for the present sample of mined Athabasca oil sand. A reduction in the artificial porosity decreases the tendency of the displacing liquid to channel through these high permeability zones. Therefore, a result of increased pack density is a better overall sweep efficiency and a higher recovery. The important conclusion forthcoming from this data is that pack density does influence recovery and therefore must be controlled to obtain reproducible results.

As previously stated, development of this high temperature displacement technique satisfied one of the goals of this research. The second, more fundamental objective, was to explore the factors which affect the displacement process in terms of assessing the roles which chemical species within oil sand exert on that process. This has been accomplished by using reconstituted oil sands in which the characteristics of each of

Table 4-3. Calculated variation of fluid volume saturations within an oil sand pellet as a function of pack density at 25°C.

Density, g/cm³	Water saturation, %	Oil saturation, %	Air saturation, %
1.80	14.5	56.0	29.5
1.85	15.5	59.8	24.7
1.90	16.5	64.0	19.5
1.95	17.7	68.5	13.8
2.00	19.0	73.4	7.6
2.05	20.4	78.7	0.9

the component parts have been strictly controlled. Whereas displacement of bitumen from Athabasca oil sand was conducted at high temperatures, in the remaining experiments the bitumen viscosity was lowered by the use of a diluent, thus enabling the displacement tests to be performed at lower temperatures.

4.2 Hexadecane–bitumen mixtures

The prime motivation for using a diluent was to lower the oil phase viscosity while retaining the chemical functionality of the bitumen. With a viscosity-reduced bituminous phase, displacement experiments could be conducted at lower temperatures. The main purpose of heating oil sand is to render the bitumen more mobile. The amount of added hexadecane has been controlled to maintain an oil-water viscosity ratio similar to that between unaltered bitumen and water at high temperatures.

In searching for a suitable diluent the following characteristics were important:

(a) The diluent had to have a low vapour pressure (high boiling point) so that it was not preferentially volatilized during a displacement experiment or the subsequent analysis stage. This is important because selective removal of a portion of the organic phase would mean that the characteristics of the displaced phase would be continually changing during an experiment. The accrued losses would also distort the calculated recovery efficiency.

(b) A material which was relatively inert to caustic and water was desirable so that the chemical reactivity of the oil phase was not affected.

(c) The diluent had to combine with bitumen to form a stable mixture.

The vapour pressure of hexadecane is 1 mm Hg at 105°C (88). From the data in Table 4-4 it is seen that the rates of

Table 4-4. Rates of evaporation of selected organic liquids.

Liquid	Temperature, °C	Evaporation rate, g/hr cm^2
Toluene	25	0.139
Bitumen	25	2.47×10^{-5}
"	90	1.51×10^{-4}
Dodecane	25	5.57×10^{-4}
"	90	2.52×10^{-4}
Hexadecane	25	2.07×10^{-5}
"	90	2.15×10^{-4}

evaporation are negligible at the temperatures encountered in these experiments. Therefore, it is safe to assume that no significant amount of hexadecane will be lost because of its volatility. Hexadecane is a pure hydrocarbon and does not contain any functional groups which would be reactive with caustic. Thus the reactivity of the hexadecane-bitumen mixture to caustic will be the same as bitumen alone, apart from any differences resulting from the dilution factor. Hexadecane and bitumen combine readily to form what appears to be a homogeneous mixture. After standing for several months no apparent gravity segregation occurs. As a precaution, stock solutions of the mixture were always stirred prior to use anyway.

Asphaltene measurements were performed to determine if the displacement process was preferentially displacing only the lighter fractions of the oil phase. The asphaltene contents of the produced and the residual samples of 20% hexadecane in bitumen after a displacement experiment were 16.2 and 15.2% by weight respectively. Therefore, there did not appear to be any selective segregation on the basis of molecular weight.

Extensive testing of the viscosity of these mixtures has been performed. Viscosities were measured for bitumen, hexadecane and a mixture of 20% hexadecane in bitumen at temperatures between 25 and 100°C. The data for hexadecane has been interpolated using Andrade's equation. For bitumen, the data has been extrapolated from 50 to 25°C from a viscosity vs. temperature plot on ASTM D 341-43 graph paper. The gradations on this type of paper are scaled according to a variation of the Walther equation. The viscosities of hexadecane in bitumen mixtures have been calculated using the Cragoe correlation. The collected data is shown in Figure 4-2. The agreement between calculated and measured viscosities for the mixture of 20% hexadecane in bitumen is within 20% at all times. This level of agreement is regarded as good because the bitumen viscosity changes by orders of magnitude over the temperature range involved. The result is that any unknown mixture viscosity can be approximated given the percentage of hexadecane present and the temperature.

The densities of mixtures containing 20 and 30% hexadecane in bitumen were measured at temperatures between 25 and 85°C. In all cases, it is noted that densities calculated by assuming ideal mixing and measured densities agree to within 0.5%. Therefore for any given temperature and dilution factor, the density of a mixture can be calculated, given the component densities at that temperature. The data is represented in Figure 4-3.

On the basis of the foregoing discussion, it has been demonstrated that hexadecane meets the criteria of a good diluent. ~~Operatio~~nally, a dilution factor of about 20% hexadecane by weight was optimal. At higher dilution, the compacted oil sand pellet tended to move inside of the displacement cell when the wire screens and end caps were positioned. At lower dilution, the hexadecane-bitumen mixture was so viscous that it was difficult to ensure good mixing during reconstitution.

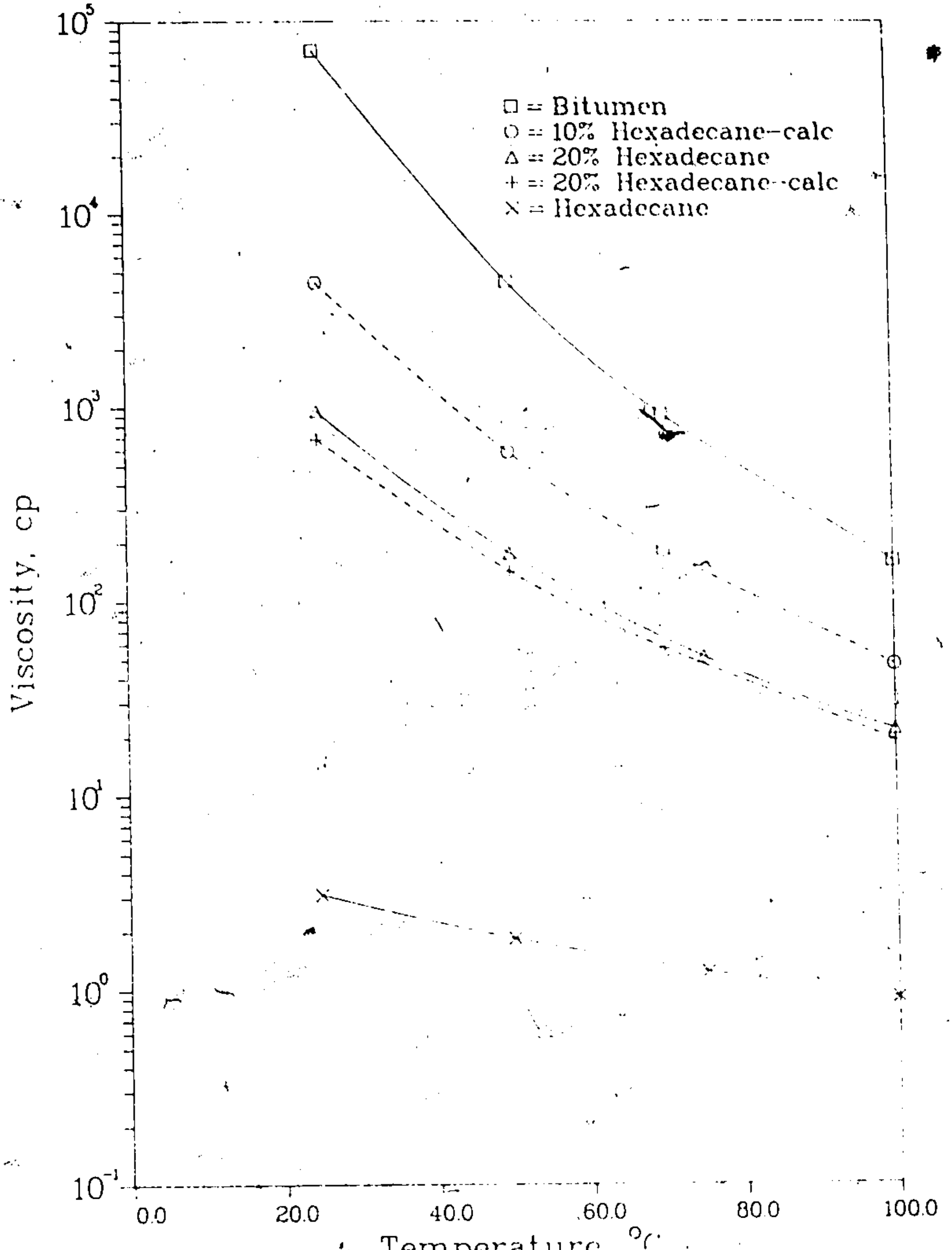

Figure 4-2. Comparison of measured mixed liquid viscosities and those calculated using Cragoe's correlation.

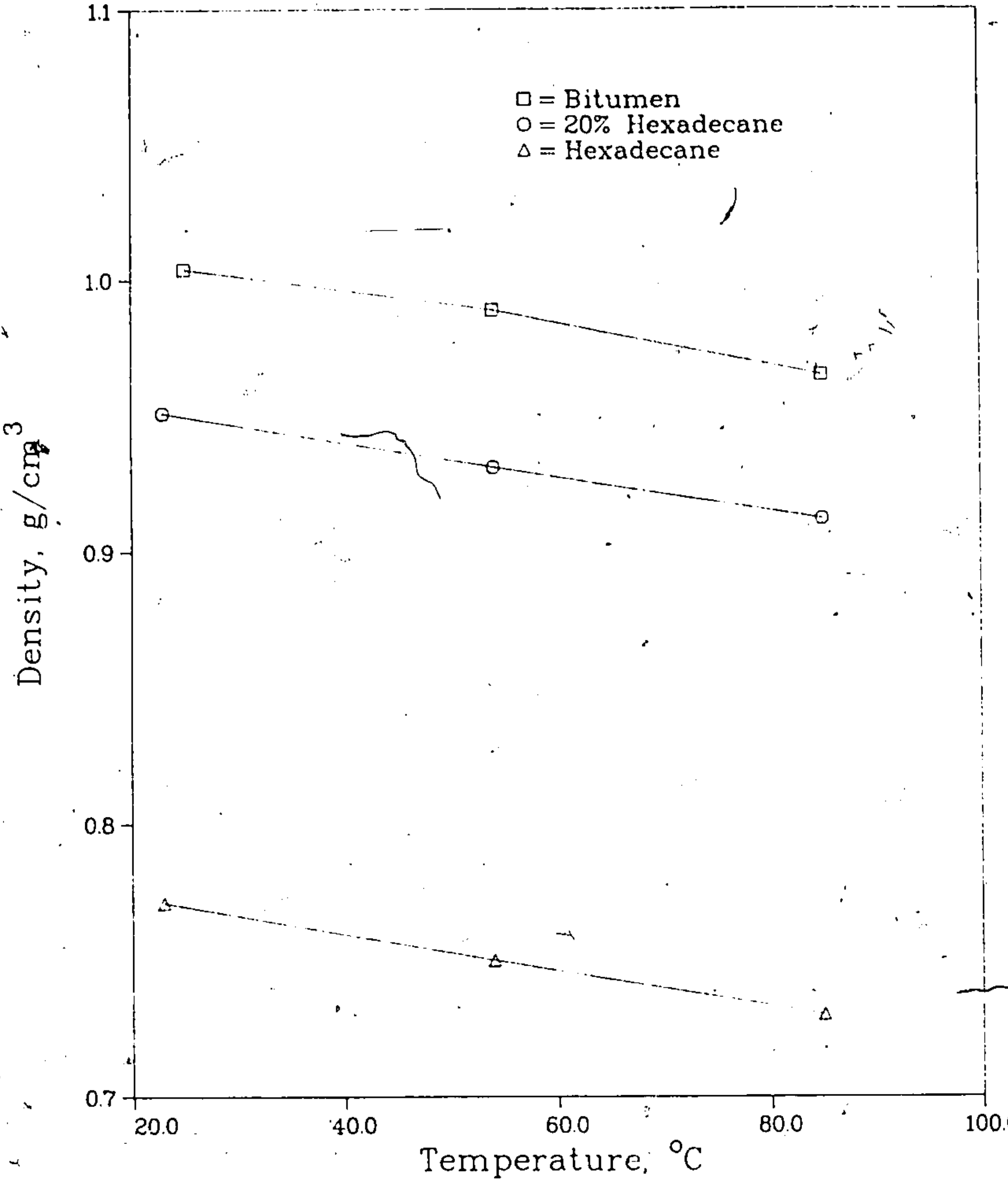

Figure 4-3. Variation in oil densities with temperature.

4.3 Reconstitution parameters

The sample of Athabasca oil sand obtained from the Alberta Research Council Sample Bank was used as a model in selecting appropriate reconstitution parameters. The composition of this oil sand is listed in Table 4-5. In subsequent calculations the unaccounted for weight, the losses, has been included in the bitumen weight following the procedure adopted at the Alberta Research Council (89). In reconstituted samples the relative volumes were kept intact because constant component saturation has more physical significance than constant relative weight. In Table 4-6 the conversion is made from weight to volume percentages for Athabasca oil sand.

In some experiments, these saturations were kept constant and the nature of the organic phase was varied. Since each of the organic phases possessed a different density, the relative weight ratios in the oil sand changed. In Table 4-7 the oil sand compositions are converted back to weight percentages because reconstitution was performed on a weight basis. For each of these oil sands the relative component weights vary but on a volume ratio basis they are identical.

In some experiments, the objective was to vary the initial water and oil saturations. If the water saturation is varied but the oil saturation kept constant, the amount of artificial porosity in the pellet would necessarily have to change (assuming that the pack density is to remain constant). Alternatively, the oil saturation can be adjusted to compensate for the changing

Table 4-5. Composition of medium grade Athabasca oil sand in weight percentages.

Sample	Bitumen	Water	Sand	Losses	Bitumen + losses
1	12.1	3.3	83.5	1.0	13.1
2	12.0	3.5	83.1	1.4	13.4
3	12.2	3.4	83.1	1.3	13.5
4	12.2	3.7	83.4	0.8	13.0
5	12.0	2.9	83.6	1.5	13.5
6	11.7	3.5	83.8	0.9	12.7
Average	12.0	3.4	83.4	1.2	13.2

Table 4-6. Conversion of the weight proportions of Athabasca oil sand to volumetric proportions (100 g basis).

Component	Wt %	Density (25°C), g/cm^3	Volume, cm^3	Vol %
Sand	83.4	2.60	32.08	66.0
Water	3.4	0.997	3.41	7.0
Bitumen	13.2	1.004	13.15	27.0

Table 4-7. Reconstitution parameters for various oil phases at constant saturations (same basis as Table 4-6).

Parameter	10% C16 in bitumen	20% C16 in bitumen	Castor oil	Paraffin oil
Sand volume, cm^3	32.08	32.08	32.08	32.08
Water volume, cm^3	3.41	3.41	3.41	3.41
Oil volume, cm^3	13.15	13.15	13.15	13.15
Oil density (25°C), g/cm^3	0.974	0.948	0.961	0.870
Sand mass, g	83.4	83.4	83.4	83.4
Water mass, g	3.40	3.40	3.40	3.40
Oil mass, g	12.81	12.47	12.64	11.44
Sand, wt%	83.7	84.0	83.9	84.9
Water, wt%	3.41	3.43	3.42	3.46
Oil, wt%	12.9	12.6	12.7	11.6
Oil:sand, w/w	0.154	0.150	0.152	0.137

C16 = hexadecane

water saturation and the artificial porosity would then remain constant. This latter option was chosen because artificial porosity presents a high permeability pathway through the porous medium and the best way to minimize the chance of this influencing the results is to keep the parameter constant. Hence the adopted procedure was to adjust the oil volume so that the sum of the initial water and oil volumes remained constant. Both the water and oil saturations were varied but there was a constant relationship between the two. The data in Table 4-8 demonstrates the interrelationship for the case of an oil sand containing 20% hexadecane in bitumen, packed to a density of 2.00 g/cm^3.

Table 4-8. Reconstitution parameters for varying water and oil contents (same basis as Table 4-6). The oil is 20% hexadecane in bitumen.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4
Sand volume, cm^3	32.08	32.08	32.08	32.08
Total volume of oil + water, cm^3	16.56	16.56	16.56	16.56
Water volume, cm^3	0.	1.00	3.41	7.82
Oil volume, cm^3	16.56	15.56	13.15	8.74
Sand mass, g	83.4	83.4	83.4	83.4
Water mass, g	0.	0.997	3.40	7.80
Oil mass, g	15.70	14.75	12.47	8.29
Sand, wt%	84.2	84.1	84.0	83.8
Water, wt%	0.	1.01	3.43	7.84
Oil, wt%	15.8	14.9	12.6	8.33
Oil:sand, w/w	0.188	0.177	0.150	0.0994

4.4 Packing method

Hydraulic pressure was used to compact the oil sand into packed beds in a reproducible manner. Considerable effort was expended in the development of this methodology.

Figure 4-4 shows the results of compacting 20 g samples of Athabasca oil sand in a 2.54 cm inside diameter steel cylinder. Two features are apparent. First, for a given compaction pressure the pack density was greater if a series of on-off pressurization cycles was used. Secondly, the pack density reached a constant value after about 5 minutes for continuous pressurization, and after 5 cycles for cyclic pressurization. The higher density resulting from cyclic pressure application has been attributed to the release of trapped air during pressure letdown. The loss of air permits a denser packing on the next pressurization step.

Figure 4-5 illustrates the dependence of Athabasca oil sand pellet density on the applied pressure and the packing strategy. The corresponding data for a reconstituted oil sand containing 20% hexadecane in bitumen are presented in Figure 4-6. It has been calculated that the maximum density of the Athabasca oil sand is 2.05 g/cm^3. In arriving at this upper bound it was assumed that the oil sand contained no artificial porosity. For reconstituted oil sand containing 20% hexadecane in bitumen, the calculated maximum density is 2.04 g/cm^3. Comparing Figures 4-5 and 4-6 it is noted that for a given pressure and packing strategy, the density is the same for both types of oil sand. This is a result

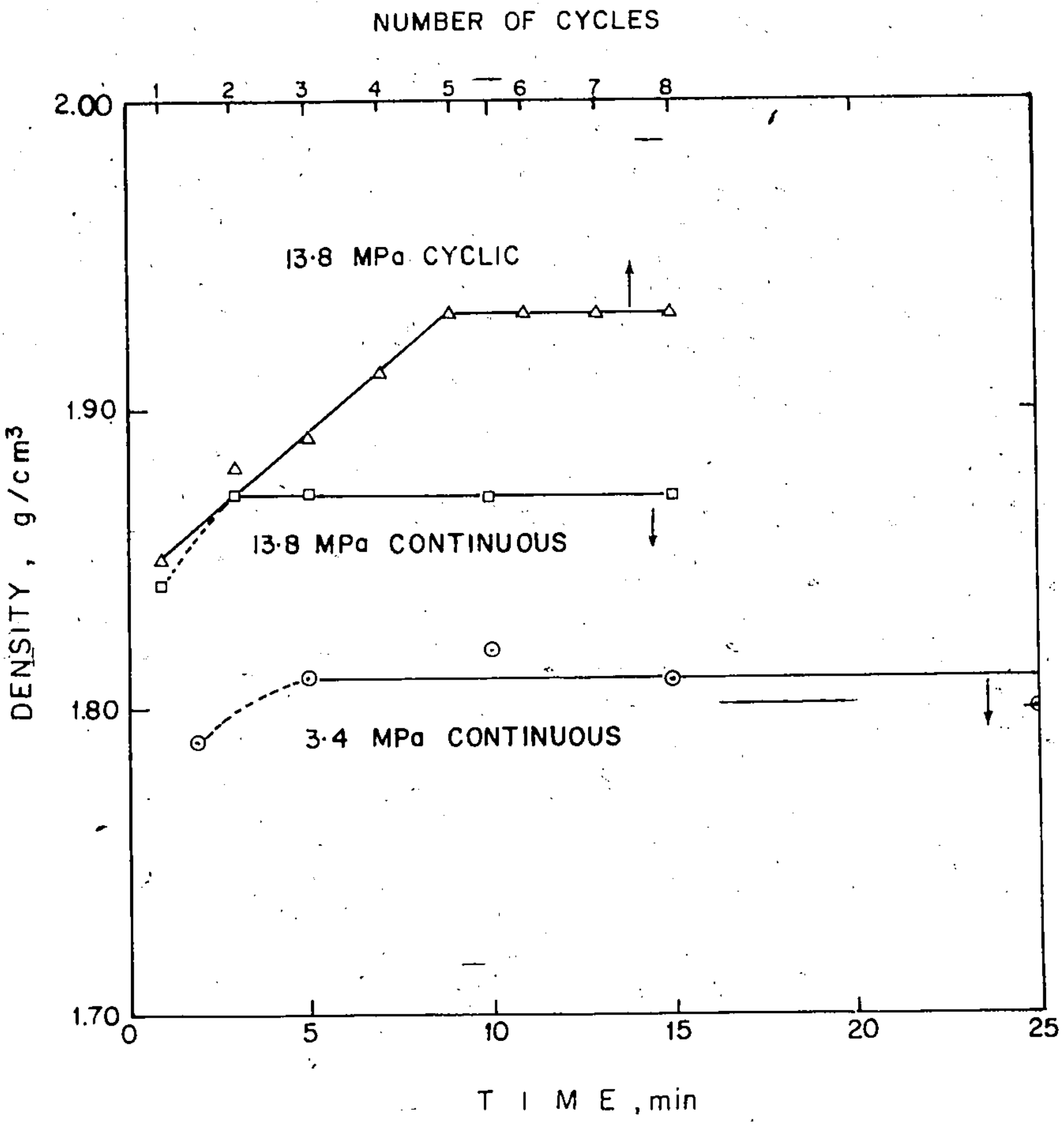

Figure 4-4. Variation in Athabasca oil sand density due to compaction pressure and packing strategy.

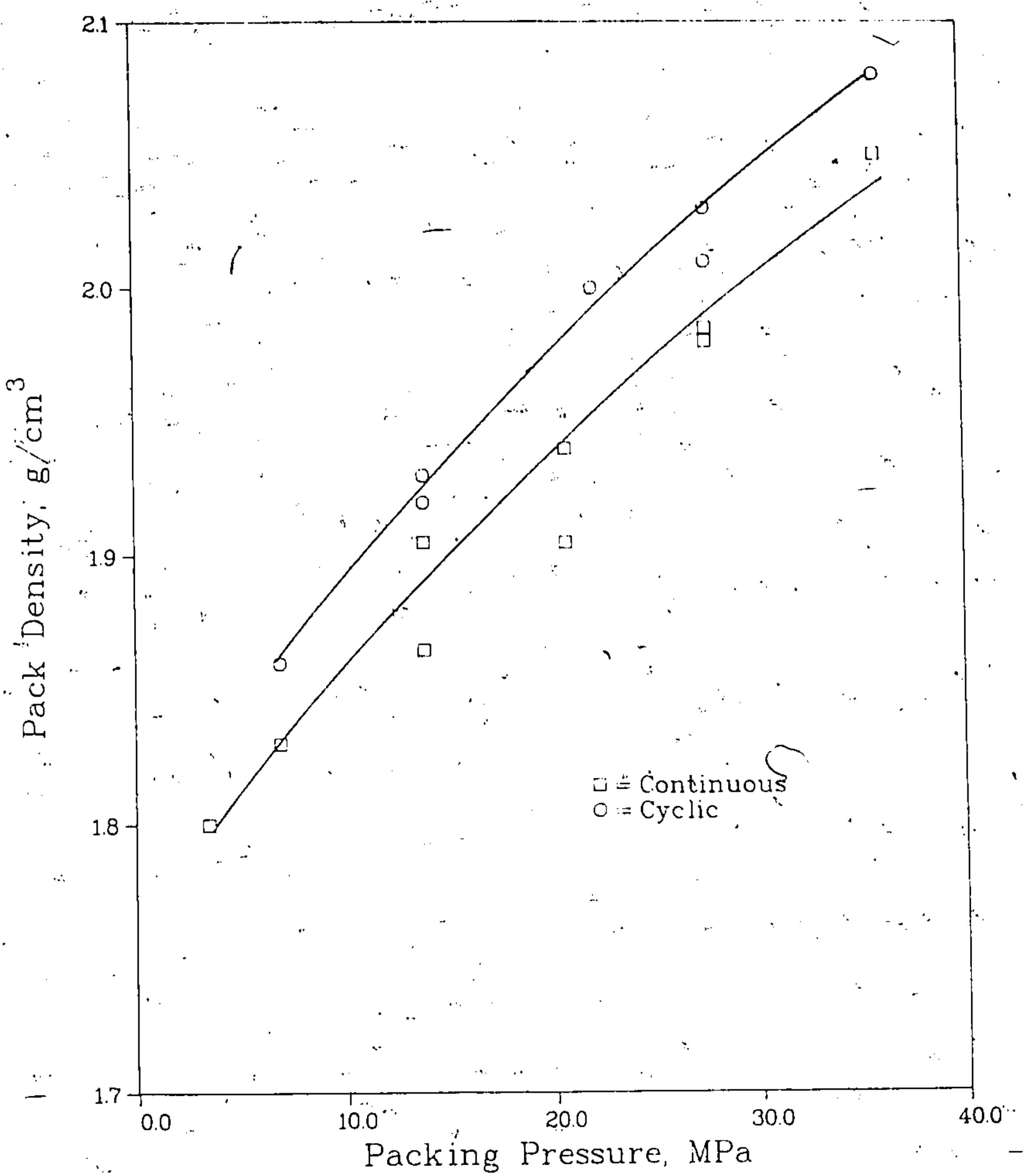

Figure 4-5. Dependence of Athabasca oil sand density on packing procedure.

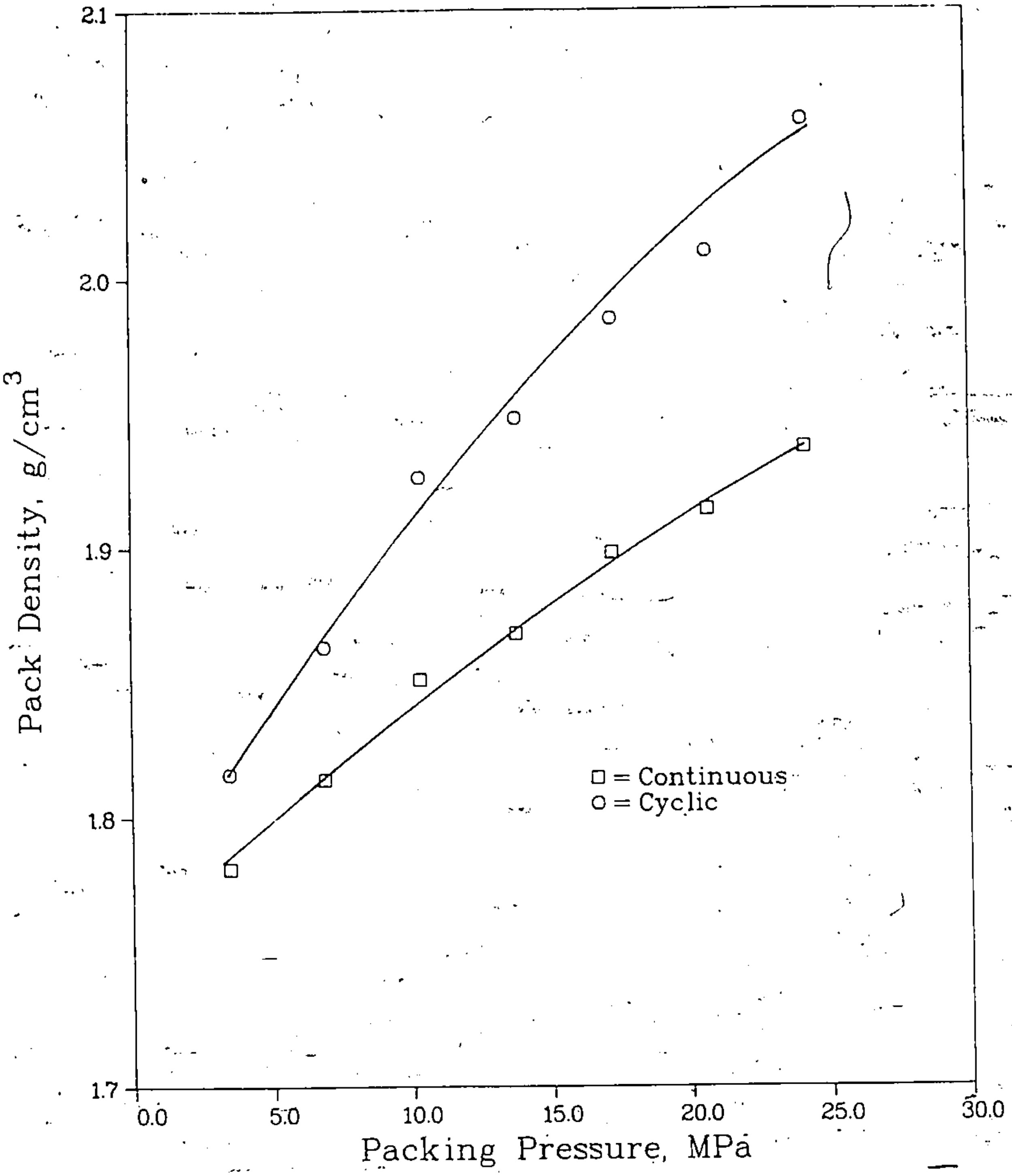

Figure 4-6. Dependence of reconstituted oil sand density on packing procedure.

of the decision to maintain the volume distribution of the Athabasca oil sand in the reconstituted oil sand.

As the applied pressure increases, part of the pack density increase is a result of crushing of the sand grains. As seen in Figure 4-7, as the amount of compaction pressure increases, the proportion of smaller particles sizes in the sample increases. A given mass of sand can be compacted into a smaller overall volume if the particle size distribution is broadened. However, this is an undesirable consequence because the surface properties of the sand grains may be altered. Another negative feature of increased pressure application is that above a certain level, water and bitumen are squeezed out of the pellet. This change in the liquid saturations within the oil sand was avoided.

Further definition of the packing procedure resulted from a 2^{5-1} fractional factorial design performed on the variables in Table 4-9. The second and third columns list the upper and lower values respectively of each of the variables. Athabasca oil sand was used in these experiments. The significant main effects were found to be: the applied pressure, the sand mass and the number of cycles. Details of the design analysis appear in Appendix 3.

As a result of these studies, the packing procedure adopted was as follows:

(a) To minimize sand grain crushing and liquid expulsion, the applied pressure was kept to a minimum.

(b) Pressure cycling was used. The same pack density can be

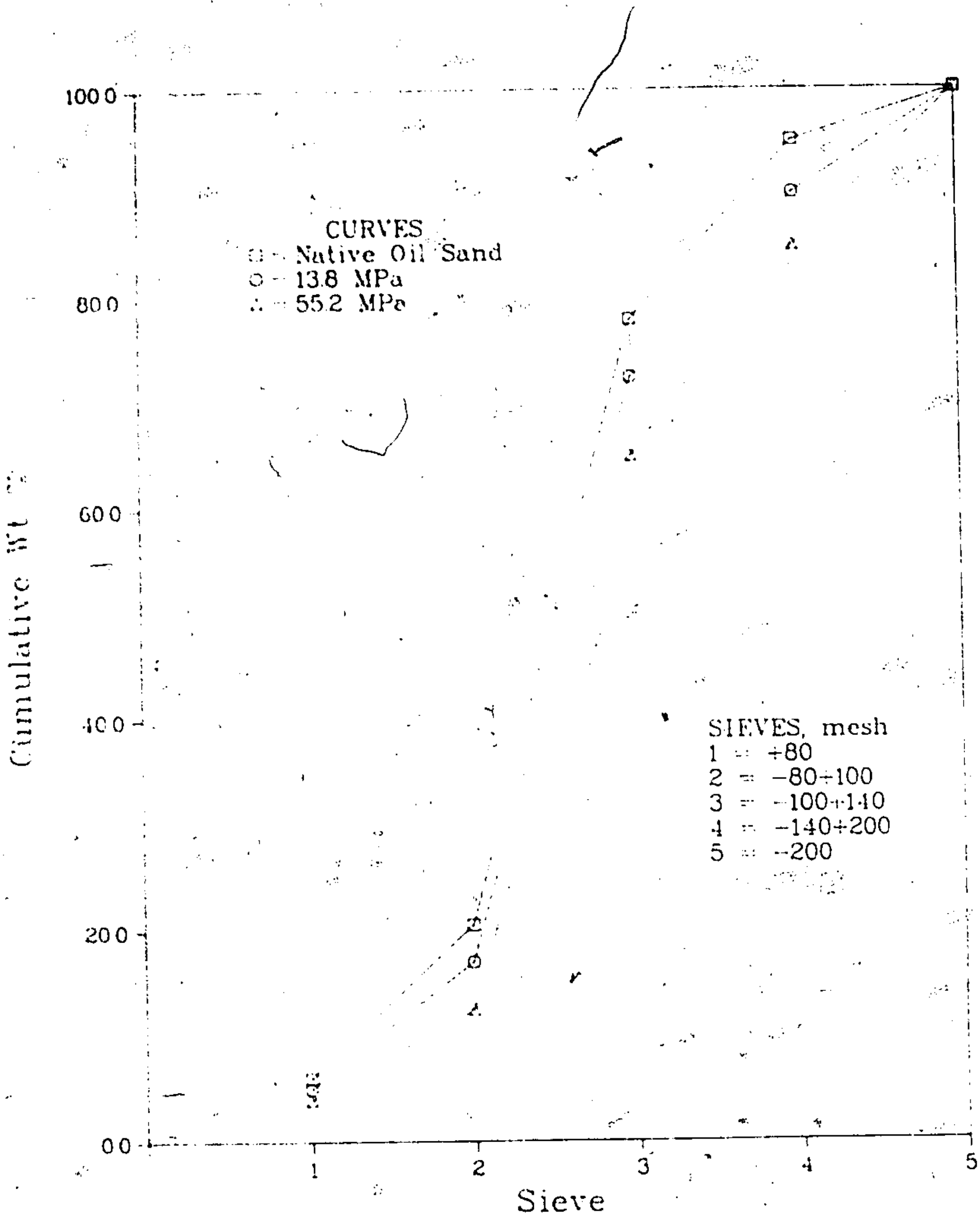

Figure 4-7. Sand size distribution after application of different pressures.

Table 4-9. Range of pack density design variables.

Variable	Upper level	Lower level
Pressure, MPa	35.1	26.6
Oil sand mass, g	60.	40.
Pressurization duration, s	10.	5.
Pressure release duration, s	10.	5.
Number of cycles	30	15

achieved at a lower pressure using cycling as opposed to continual application.

(c) The applied pressure was adjusted so that from 10 to 20 cycles were required to achieve the desired density. With this number of cycles, the final density was approached gradually. The slow increase in density minimized the severity of any density gradient which may have been present. The number of cycles was not excessively large to keep the time involved in packing a sample short.

The oil sand samples were compacted right in the displacement cell to reduce the tendency for slip flow to occur at the wall. The packing was performed at room temperature and the packed cell was heated to displacement conditons. The following calculation indicates that the thermal expansion which occurred during heating worked to negate any tendency for slip.

The linear coefficient of thermal expansion for steel is $3.7x10^{-6}$ $^{o}C^{-1}$ (88). The volumetric coefficient for solids can be estimated to be three times the linear coefficient, hence for steel it is $1.1x10^{-5}$ $^{o}C^{-1}$. For quartz the linear coefficient is $5.7x10^{-7}$ $^{o}C^{-1}$ (88), and the volumetric coefficient would therefore be $1.7x10^{-6}$ $^{o}C^{-1}$. The volumetric expansion of 20% hexadecane in bitumen is estimated from the data in Figure 4-3. Comparing the densities at 23 and 54^{o}C an average coefficient of volumetric thermal expansion over that temperature range is calculated to be $6.93x10^{-4}$ $^{o}C^{-1}$. The coefficient for water at 25^{o}C is $2.57x10^{-4}$ $^{o}C^{-1}$ (90). Using the data in Table 4-6, a weighted average volumetric thermal expansion coefficient for the oil sand can be estimated as follows:

$$\text{Average} = 0.66(1.7\text{x}10^{-6}) + 0.27(6.93\text{x}10^{-4}) + 0.07(2.57\text{x}10^{-4})$$
$$= 2.06\text{x}10^{-4}\ {}^{o}\text{C}^{-1}$$

Compared to the value of $1.1\text{x}10^{-5}\ {}^{o}\text{C}^{-1}$ for steel, it is observed that the oil sand expands more than the displacement cell. Therefore, heating will tend to favour the maintenance of close contact between the cell wall and the oil sand pellet.

4.5 Low temperature experiments

4.5.1 Operational variables

Parameters external to the sand were examined to determine the sensitivity of the displacement process to each of the selected variables. A 2^{5-1} fractional factorial design of the parameters in Table 4-10 was performed. These have been termed operational variables because they pertain to parameters which are external to the sand itself.

The temperature at which the displacement experiments were conducted was included because the viscosity of the oil phase is a strong function of temperature. The mass of an oil sand sample was selected to determine if recovery was affected by changes related to the size of the packed bed. The flowrate can influence recovery through the viscous force exerted as the displacing phase progresses through the porous medium. By varying the number of pore volumes pumped through the pellet, a measure of the completeness of the displacement process can by obtained. These experiments were to be conducted until residual oil saturation (or ultimate recovery) conditions were approached. The nature of the displacing phase was investigated to observe the effect exerted on recovery brought about by the reaction between caustic and acidic components in the oil sand.

The composition of the reconstituted oil sand was the same in all 16 experiments. It was composed of 84% by weight sand, 3.4% distilled water and 12.6% bituminous phase. The clean sand was heated at 300°C overnight prior to reconstitution. The bituminous

Table 4-10. Range of operational variables.

Variable	Lower level	Upper level
Temperature, °C	30	60
Sand mass, g	40	60
Water flowrate, cm^3/h	123	288
Pore volumes pumped	5	15
Displacing phase	water	0.1 M NaOH

phase contained 20% by weight hexadecane in bitumen. The pack density was constant at 2.00 g/cm^3 throughout.

The sole significant variable at the 95% confidence level was the nature of the displacing phase. Changes to the other variables within their test limits, did not exert a significant effect on the observed recovery. Further details of the calculations are presented in Appendix 4.

During the course of experimentation there were two differences (other than recovery efficiency) between tests done with caustic and those with water as the displacing phase. In some of the tests done with caustic, a pressure drop of the order of 1000 kPa was measured across the pellet. In contrast, when water was used, the pressure drop was of the order of 100 kPa. The second difference was that the produced aqueous phase was dark brown and cloudy after caustic displacement and colourless and clear after water displacement. This indicates that the NaOH solubilized and/or suspended species present in the oil sand. The phenomena of colouration and high pressure drop may be related. The material dispersed in the aqueous phase during alkaline flooding may have created blockages in some of the flow channels thereby causing the large pressure drop.

The negligible effect of temperature is interesting. Over the temperature range employed, the viscosity of 20% hexadecane in bitumen changes by nearly an order of magnitude, as noted in Figure 4-2. Hence the displacement efficiency is not sensitive to fluctuations of this size in the oil viscosity.

The absence of a significant effect due to the number of pore volumes pumped has an important consequence. Since recovery is the same whether 5 or 15 pore volumes are pumped, it is reasonable to conclude that residual oil saturation conditions are closely approached after 5 pore volumes. Attainment of ultimate recovery conditions was desired because it eliminated the difficulties inherent in trying to compare transient effects.

The range of flowrate test conditions was extended by performing tests at 0 and 20 cm^3/h. In the no flow case, the caustic was admitted, the heaters turned on, the system left to achieve thermal steady-state and then shut off. The results of these experiments, combined with the averaged data points at 123 and 288 cm^3/h from the operational design, are shown in Figure 4-8. At zero flow about 12% recovery still occurs. This may result from displacement by: imbibition, thermal expansion or cross-pellet flow during the filling of the cell. It is noted that above 20 cm^3/h, flowrate can by varied by an order of magnitude without altering the recovery effectiveness.

An operational variable studied independently was the oil sand pack density. The effect which this variable had on recovery is illustrated in Figure 4-9. Recovery with water was strongly affected, while recovery with caustic was largely independent of the pack density. The behaviour of the water recovery experiments was very similar to the corresponding results obtained with Athabasca oil sand at 250°C, presented in Figure 4-1. The absence of an effect for caustic displacement is indicative of a mechanistic difference in its method of displacement. With caustic, the displacement process is chemically controlled, as

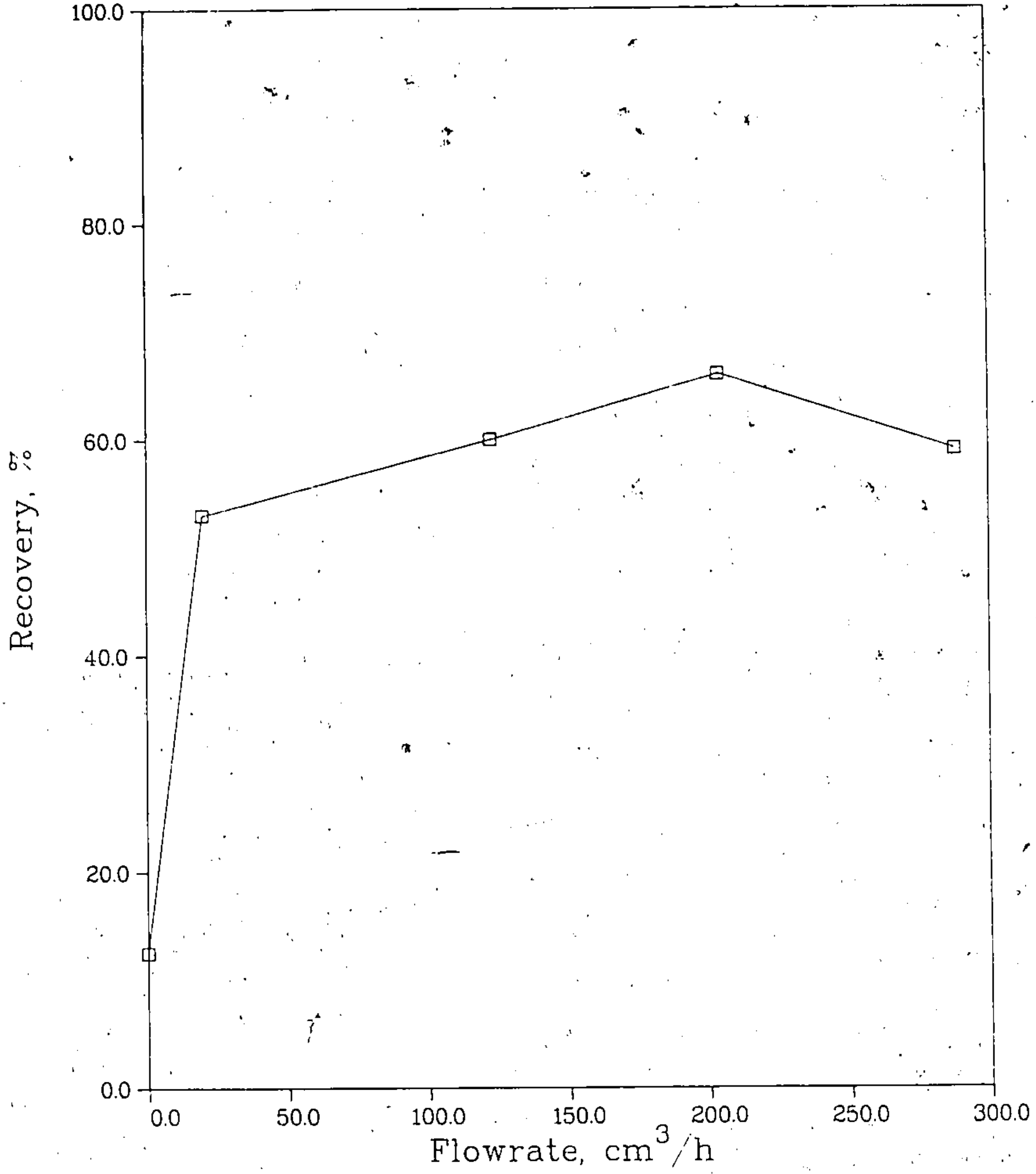

Figure 4-8. The influence on recovery of flowrate of a displacing phase of 0.1M NaOH.

opposed to water displacement which is more physically controlled. The chemical reactions between the caustic and the oil sand produces an effect which is dominant over the physical effects of changes to the pore sizes and liquid saturations. In water displacement this chemical factor is not present and changes to the physical properties of the oil sand pellet do influence recovery.

Comparison of the data at low and high temperatures reveals some similarities. The recoveries by caustic and water, and the difference between the two are numerically similar. Also, the influence which pack density exerted on recovery by water was the same at both temperatures. These parallel trends provide an element of verification that the low temperature model is representative of the high temperature process.

4.5.2 Compositional variables

A 2^{7-3} fractional factorial design was performed on six variables related to the internal composition of the oil sand. The variables and their upper and lower limits are listed in Table 4-11. The displacing phase composition was the other variable. The operating conditions for a displacement test were selected based on the results of the previous factorial design. The conditions listed in Table 4-12 were used throughout this set of experiments.

The sand drying temperature was selected because after heating at 300°C the sand was water-wet as detected by the imbibition of water, whereas after drying at 25°C the sand was still

Table 4-1F. Range of compositional variables.

Variable	Lower level	Upper level
Sand drying temperature, °C	25	300
Sand size distribution	entire	-80+200 mesh
Added kaolinite, wt%	0	3
Hexadecane dilution, wt%	10	20
Connate water content, wt%	1.0	3.4
NaCl in connate water, M	0	0.1
Displacing phase	water	0.1 M NaOH

Table 4-12. Operating conditions.

Variable	Value
Temperature, °C	45
Sand mass, g	40
Flowrate, cm^3/h	204
Pore volumes pumped	10

toluene-wet. This change in surface characteristics of the sand could have been a factor influencing the displacement process. Controlling the sand size distribution and specific addition of kaolinite were intended to alter the geometry and pore size distribution within the oil sand pellet. The hexadecane dilution factor was included to ascertain the effect on recovery of this modification to the bituminous phase; there were potential chemical and viscosity effects involved. The connate aqueous phase is hypothesized to reside between the bitumen and sand surfaces and thereby occupies an important position in the oil sand during displacement. For this reason, the water content and composition were varied.

A complication was encountered in these experiments due to the differences in clay content and sand size distribution from sample to sample. It was not possible to physically recreate the same inorganic matrix in each experiment. The sand grain size distribution was a variable, therefore it was not desirable to inflict differing levels of crushing during packing. The procedure adopted was to use the same packing pressure and the same number of cycles in all experiments. The result was that the oil sand pack density varied from experiment to experiment. As previously observed, pack density does influence recovery for water displacement, hence the complication. The problem was addressed by normalizing the recovery results to constant density. The normalization procedure was applied as follows:

(a) For a displacing phase of caustic no adjustment was made.

(b) For water displacement, the observed recovery was adjusted by applying a multiplication factor obtained from the data in Figure 4-9.

Three sets of parameter estimates were calculated. In one, the data was used as collected. In the second, the recoveries were normalized to a reference density of 2.00 g/cm^3. In the third, the recoveries were normalized to a density of 2.10 g/cm^3. The normalization procedure was done at two points to ensure that the results were not dependent upon the selection of the reference density. In all three cases the results are the same. The significant variables at the 95% confidence level are the nature of the displacing phase and the water saturation. Details of the calculations are presented in Appendix 5.

An interesting outcome of this design is that the oil phase viscosity was varied by nearly an order of magnitude yet this was not translated into a significant effect on recovery. This corroborates the observation that temperature had no significant effect in the operational factorial design. The oil to water viscosity ratio must necessarily influence the recovery process. However, within the range encountered in this work, it appears that the viscosity must change by more than an order of magnitude to exert a significant effect on the recovery.

4.5.3 Alteration of sand surface characteristics

The results of the compositional design indicate that the recovery was not affected by the initial wettability state of the sand grains. However, at temperatures above 300°C in the presence of air the sand undergoes further changes, as signalled by a

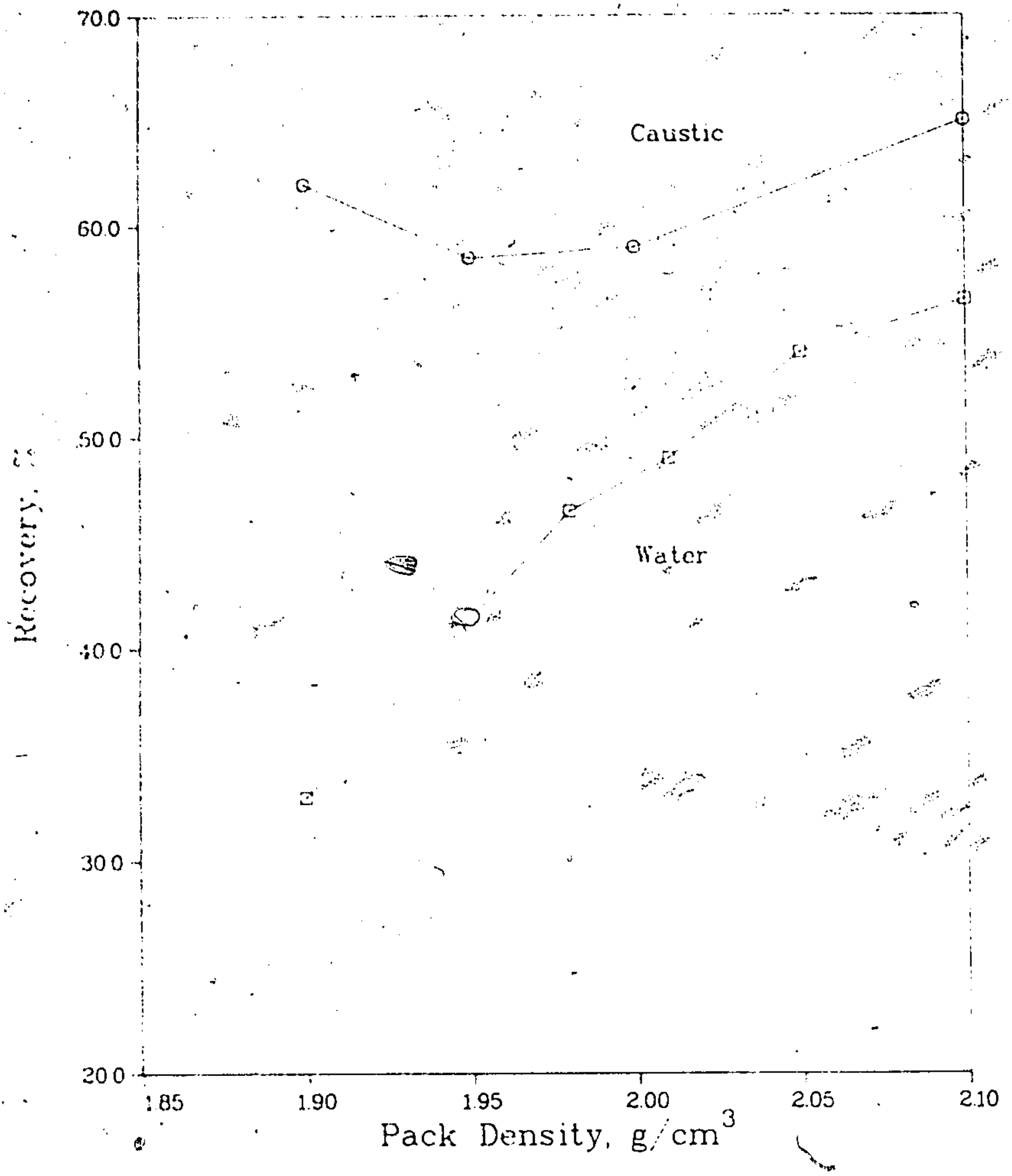

Figure 4-9. Water displacement effectiveness at various reconstituted oil sand densities.

progression to a lighter colour. The results of experiments performed using oil sand samples reconstituted from clean sands heated at temperatures ranging from 25 to 775°C are presented in Table 4-13. The most significant features to be withdrawn from this data come from examination of the difference parameter. The difference parameter is defined as the recovery by caustic minus the recovery by water. It is noted that the difference increased up to 400°C and then decreased to zero by 650°C. Therefore, the recoveries with caustic and water became equivalent if the oil sand was reconstituted from a sand which had been exposed to temperatures of 650°C or higher. This is very noteworthy because the reconstituted oil sand still contained bitumen, hence acidic species would have been present, yet their reaction with caustic did not enhance its recovery effectiveness compared to water alone. At high temperatures, in air, it is believed that heavy organic species (humic material) on the sand are oxidized and removed. Apparently, these species are partially responsible for the incremental recovery evidenced with caustic compared to water.

A second pretreatment method was to contact the sand with 0.1 M NaOH. The sand was shaken with caustic, the extract decanted, the sand washed with distilled water until the supernatant was neutral and then the sample dried. Samples of sand which had been heated at 300 and 775°C were subjected to this preconditioning step and were then used to reconstitute batches of oil sand. In all of these experiments the oil sand composition was: 84.0% by weight sand, 3.4% distilled water and 12.6% of a mixture of 20% hexadecane in bitumen.

Table 4-13. Effect of sand drying temperature on recoveries with caustic and distilled water.

Temperature, °C	Recovery with caustic, %	Recovery with water, %	Average difference, %
25	55.8	46.6	9.2
90	56.7	45.3	11.4
200	45.7	33.0,28.6,31.9	14.5
300	58.5	43.5	15.0
400	51.6,50.5,46.2	28.6	20.8
500	46.5	36.5	10.0
650	50.1	50.9	-0.8
775	45.2,39.2,39.8	43.9,43.2,44.0	-2.3

When the 300°C-processed sand was mixed with caustic, the supernatant became reddish-brown and cloudy. It was evident that portions of the sand were reacting with the caustic and thus were solubilized or suspended. The effect on recovery as a function of the number of extraction steps employed is shown in Figure 4-10. It is observed that the initial preconditioning steps served to increase the recoveries by both caustic and water. After 3 and 4 extraction stages, the recoveries by caustic and water and the difference between them were all decreasing. These trends are rationalized as follows. After 1 or 2 extraction steps, some of the humic matter will have been removed, but more importantly, some remains on the sand in a surface active state. When this preconditioned sand is used to reconstitute an oil sand and displacement tests performed, the recoveries with caustic and water are both enhanced due to the presence of these surfactants. After 3 or 4 extractions, the extent of humic acid removal is so large that there is no longer sufficient material to provide the same reduction in interfacial forces. As a result, the recovery efficiencies of both caustic and water decrease, and the relative superiority of caustic is diminished.

The same extraction procedure applied to 775°C-processed sand produced markedly different behaviour. The supernatant remained clear and colourless, indicating that no reactions occurred. The displacement results using this precontacted sand are shown in Table 4-14. It is noted that prior contact with caustic did nothing to alter the recoveries with either caustic or water. These observations further support the view that sand heated to

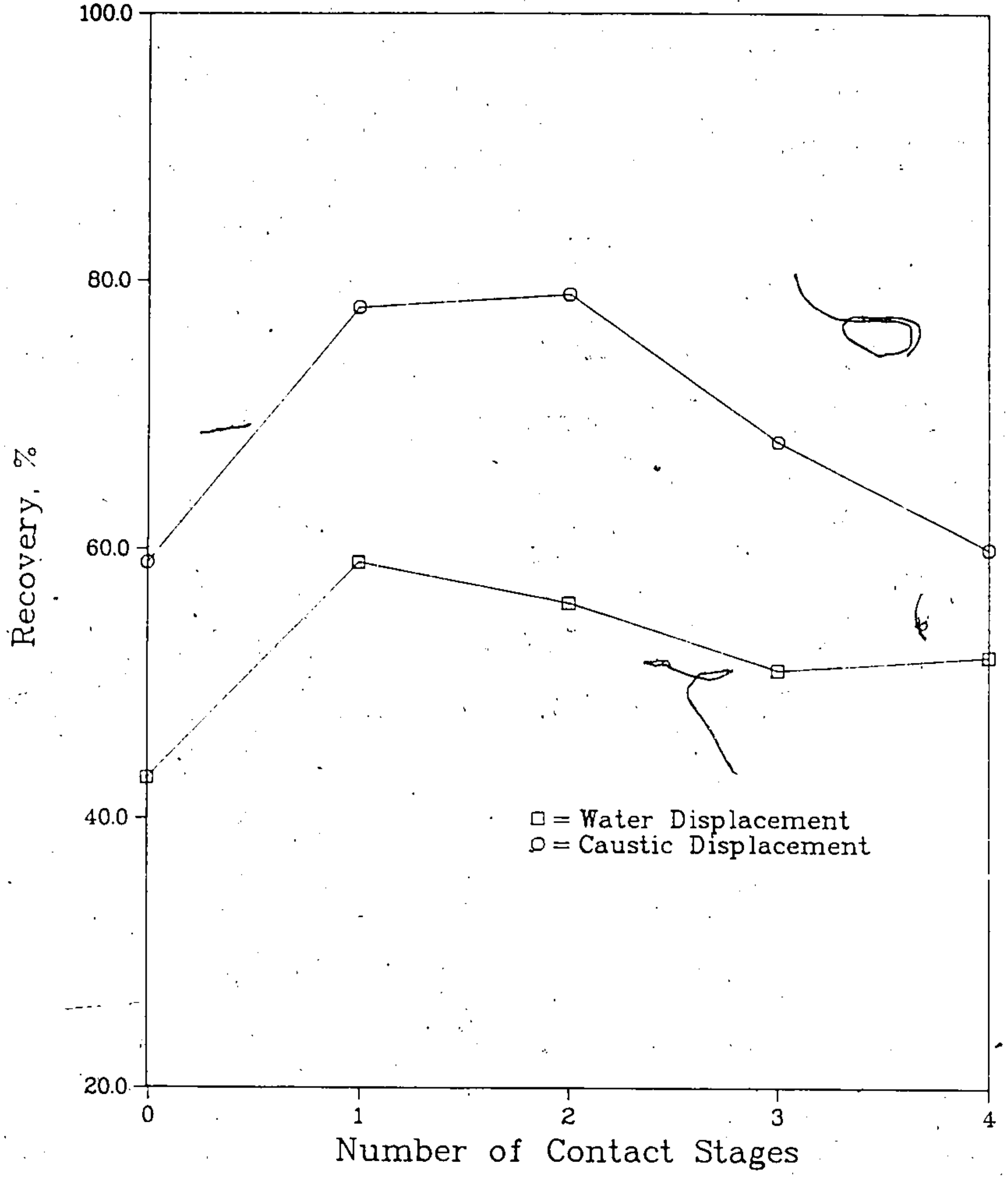

Figure 4-10. Influence on recovery of extracting 300°C-processed sand with 0.1M NaOH prior to reconstitution.

Table 4-14. Effect of NaOH extraction on sand previously heated to 775°C.

Sand pretreatment conditions	Recovery with water, %	Recovery with NaOH, %
Heated at 775°C	43.9,43.2,44.0	39.2,45.2,40.6
Heated at 775°C, extracted 3 times with 0.1M NaOH	44.3	39.4

775°C no longer contains species which can react with caustic to improve its recovery effectiveness.

This hypothesis was tested by adding quantitative amounts of humic material to 775°C-processed sand prior to reconstitution. The humic material was obtained by caustic extraction of a sand dried at 300°C, followed by acidification of the extract and drying the precipitate. This yielded concentrated samples of the humic material in solid form. Addition of this humic matter was an attempt to reintroduce some reactivity to caustic into the 775°C-processed sand. The recovery data in Figure 4-11 are for oil sands composed of: 84.0% by weight sand plus humic matter, 3.4% distilled water and 12.6% of a mixture of 20% hexadecane in bitumen. It is noted that the introduction of the humic material did restore some caustic reactivity as evidenced by the incremental recoveries obtained with caustic compared to water. A sample of the 775°C-processed sand plus 0.34% humic material was again subjected to heating at 775°C overnight. The aim was to see if the heating denatured the humic material which has been specifically added. In Figure 4-11, for a humic content of 0.34%, the recoveries with caustic and water were 52.5 and 42.2% respectively. When the sand plus humic matter were reashed prior to reconstitution, the corresponding recoveries were 41.2 and 42.7%. Therefore, the extreme heating reestablished a condition in which caustic and water displacement were equivalent. Since the sand had already been heated to 775°C, the change must have been due to the removal of the humic material. This provides additional substantiation for the claim that the humic material in

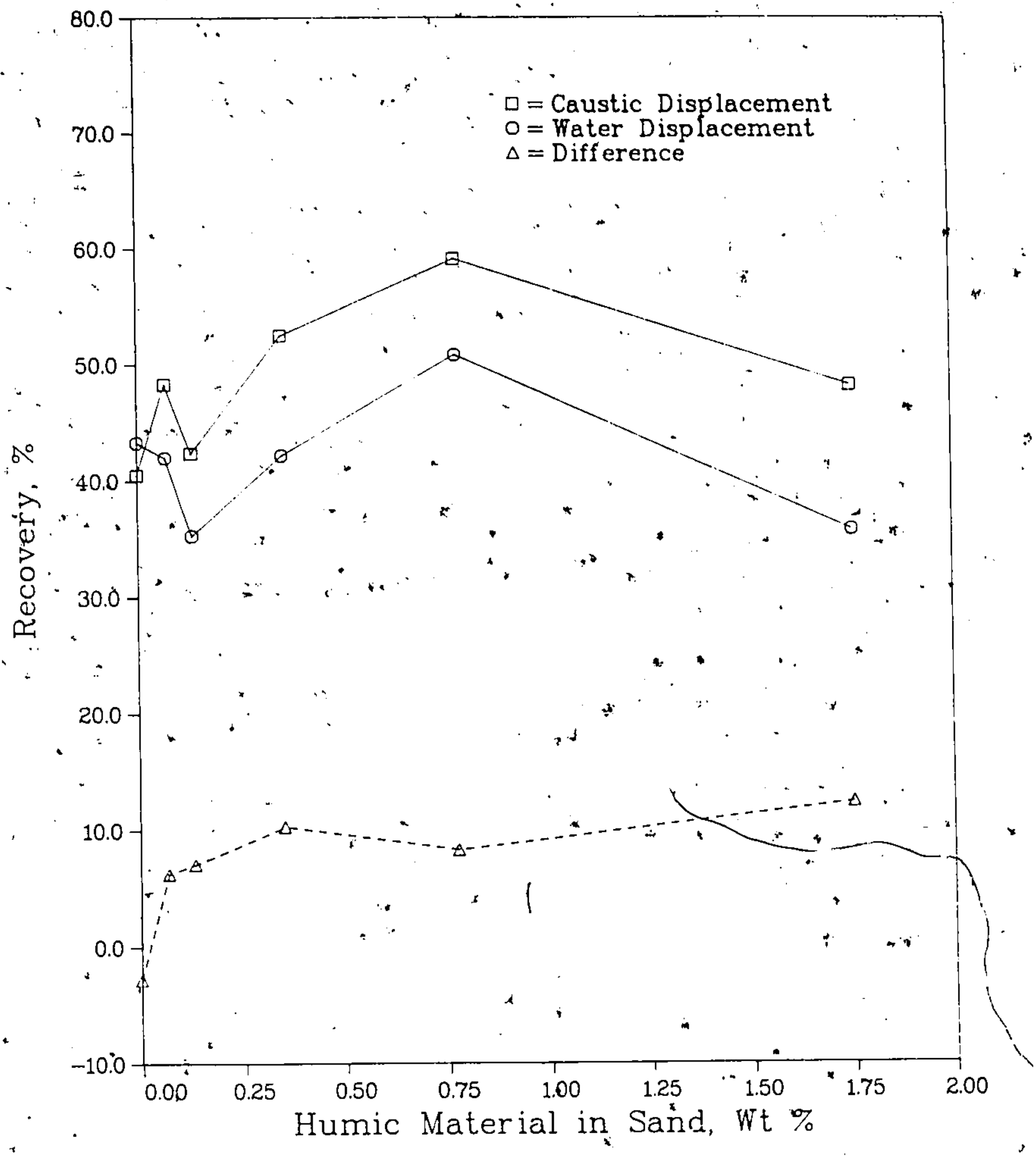

Figure 4-11. Reappearance of incremental recovery using caustic by the addition of humic material to 775°C-processed sand.

the oil sand is partially responsible for the greater effectiveness of caustic displacement.

4.5.4 Influence of connate water composition

The displacing pressure concept presented by Takamura and Chow (42) has been successfully applied to interpret behaviour observed using the crumble test. An effort was made to extend the concept to permit prediction of the efficiency of displacement from packed beds of oil sand. In principle, factors which promote attraction between the bitumen and sand surfaces would be expected to lead to lower recovery efficiency than factors which promote separation of the two surfaces.

The applicability of this concept was tested by drawing directly on the data of Takamura and Chow, and thereby making the following implicit assumptions:

(a) The zeta potentials of the hexadecane-bitumen mixture used in this work were similar to those obtained using bitumen alone in the cited work.

(b) The sand surfaces in the two cases possessed the same zeta potentials.

On this basis, a solution of 0.1 M NaCl should have promoted repulsion of the bitumen and sand surfaces and a solution of 0.01 M $CaCl_2$ in 0.006 M NaOH should have promoted attraction. These solutions were used to represent the connate water during reconstitution of oil sand samples. Experiments were conducted at two saturation levels. A water content of 3.4% by weight was selected to be consistent with the bulk of the previous work. The other value, 0.7%, was selected for a specific reason. The surface area of the clean sand was measured to be 1.16 m^2/g. The thickness of the water layer around each grain is much less than the grain diameter hence it is assumed that the water film can be regarded as planar. If all of the water is evenly distributed over the sand surfaces, its thickness would be 7.2 nm when the connate water content is 0.7%. This is the maximum thickness which a uniform water layer could have. Since some of the water will reside in pendular rings the thickness of the water layer would be less than 7.2 nm. It is for small water layer thicknesses that the disjoining pressure becomes most significant. Therefore a water content of 0.7% was selected to ensure that the film thickness is in the region where disjoining pressure is most sensitive. Table 4-15 lists the water layer thickness for other water contents calculated using the same assumptions.

The displacement results appear in Table 4-16. Comparing tests 1,5,6 and 12 it is seen that the ionic composition of the connate water exerted no influence on the efficiency of water displacement. To overcome the possibility that the connate water was being diluted by the displacing distilled water, the displacing phase was modified to be of the same composition as the connate water. The recovery in test 7 was essentially the same as those in tests 1,5,6 and 12.

When the connate water content was reduced to 0.7%, the displacement efficiences decreased markedly. Recoveries for 3.4% water were about 40% whereas recoveries for 0.7% connate water were about 10%. Importantly, the recoveries at low water content

Table 4-15. Relationship between connate water content and adsorbed water layer thickness assuming that all of the water resides in a uniform planar film.

Water content, wt %	Water layer thickness, nm
0.2	2.1
0.4	4.1
0.6	6.2
0.7	7.2
0.8	8.2
1.0	10.3
2.0	20.5
3.4	34.9

Table 4-16. Effect of connate water composition and saturation on recovery.

Test	Water composition	Water content, wt%	Displacing liquid	Recovery, %
1	water	3.4	water	43.2
2	"	"	NaOH	59.4
3*	"	0.7	water	5.0
4*	"	"	NaOH	49.0
5	Ca/NaOH	3.4	water	39.4
6	"	"	"	35.7
7	"	"	Ca/NaOH	41.3
8	"	0.7	"	10.3
9	"	"	water	1.2
10	"	"	"	18.9
11	"	"	NaOH	55.8
12	NaCl	3.4	water	42.8
13	"	0.7	"	9.1
14	"	"	NaOH	54.6

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* interpolated from Fig. 4-12

Ca/NaOH = 0.01M $CaCl_2$ in 0.006M NaOH

NaOH = 0.1M NaOH

NaCl= 0.1M NaCl

were independent of the water composition. Connate water phases of distilled water, 0.1 M NaCl and 0.01 M $CaCl_2$ all behaved similarly. According to the disjoining pressure model these aqueous phases were expected to behave differently. Possible reasons for the absence of an effect are:

(a) The displacement process is dynamic whereas the crumble test is static. The viscous forces applied by the flow of the displacing phase may override the influence of the disjoining pressure.

(b) The zeta potential data published by Takamura and Chow may not be directly applicable to the present system.

(c) The presence of salts in the clean sand used in reconstitution may have had a dominant influence ~~in~~ governing the connate water composition. During Dean Stark extraction the water is distilled over, but previously dissolved salts remain behind, probably in the sand. Reintroduction of water to the sand would solubilize them again. Whether the native or the specifically added salts predominates depends on their relative concentrations; an unknown in this case.

(d) The differences may have been masked by the experimental uncertainty of the tests.

The net result is that the addition of salts to the connate water did not exert a significant effect on the recovery. For convenience, distilled water alone was used to represent the connate water in subsequent experiments. However, water saturation was observed to strongly influence the recovery process.

4.5.5 Influence of connate water saturation

Additional experimentation was performed to explore the influence of the connate water saturation on recovery. Differing amounts of distilled water were added during reconstitution. The amount of oil phase introduced was always adjusted to compensate for the variable water volume. The constraint placed upon the reconstitution procedure was to maintain a constant total volume of connate water and oil. The results are reported in terms of the weight per cent of water added. Other equivalent units for describing the variable water content are presented in Table 4-17.

Samples of oil sand containing variable water content were reconstituted and displaced with 0.1 M NaOH and distilled water. The results for oil sand containing sand previously heated to 300°C are presented in Figure 4-12. A parallel series of experiments was performed using sand which had been heated to 775°C prior to reconstitution. As before, the initial water content was varied and the effect on recovery observed. The results are shown in Figure 4-13.

The phenomena observed in Figures 4-12 and 4-13 can be explained quite well using the disjoining pressure concept. In this discussion it is assumed that conditions which increased the disjoining pressure improved the recovery efficiency. Each of the four recovery curves will be discussed individually.

In Figure 4-12 the water recovery at zero initial water content was very low. In this situation the bitumen and sand were in direct contact and thus a highly attractive force would have existed between the two surfaces. It has been reported that the existence of an adsorbed water layer in Canadian oil sand is

Table 4-17. Equivalent descriptions of the relative water and oil contents for an oil phase of 20% hexadecane in bitumen and an oil sand pack density of 2.00 g/cm^3.

Water, wt %	Water saturation, %	Oil saturation, %	Oil wt %
0.	0.	90.5	15.8
1.0	5.5	85.0	14.9
2.0	10.9	79.6	13.9
3.4	18.6	71.9	12.6
5.6	30.6	59.9	10.5
7.8	42.6	47.9	8.4

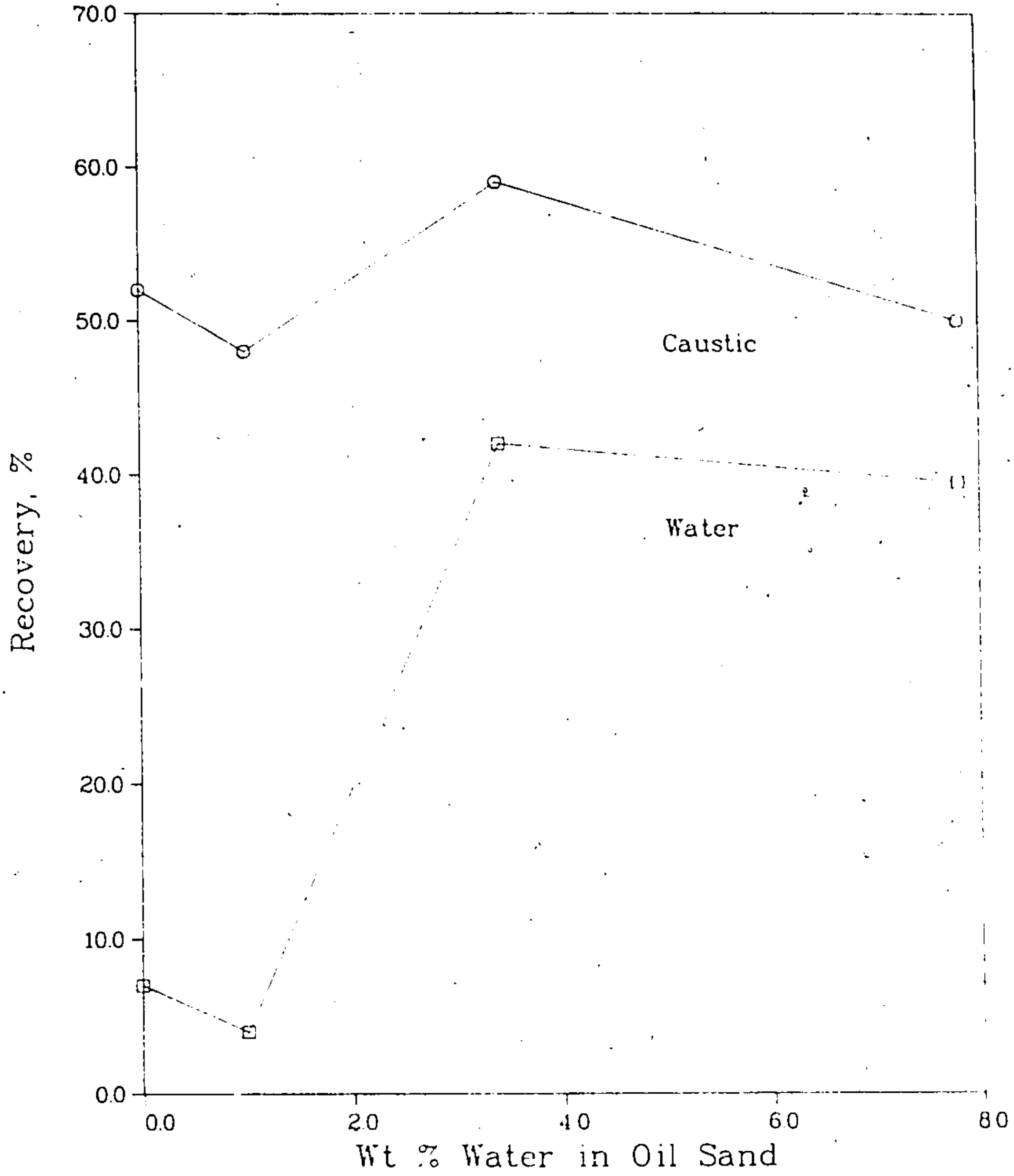


Figure 4-12. Recovery in samples containing 300°C-processed sand and variable initial water contents.

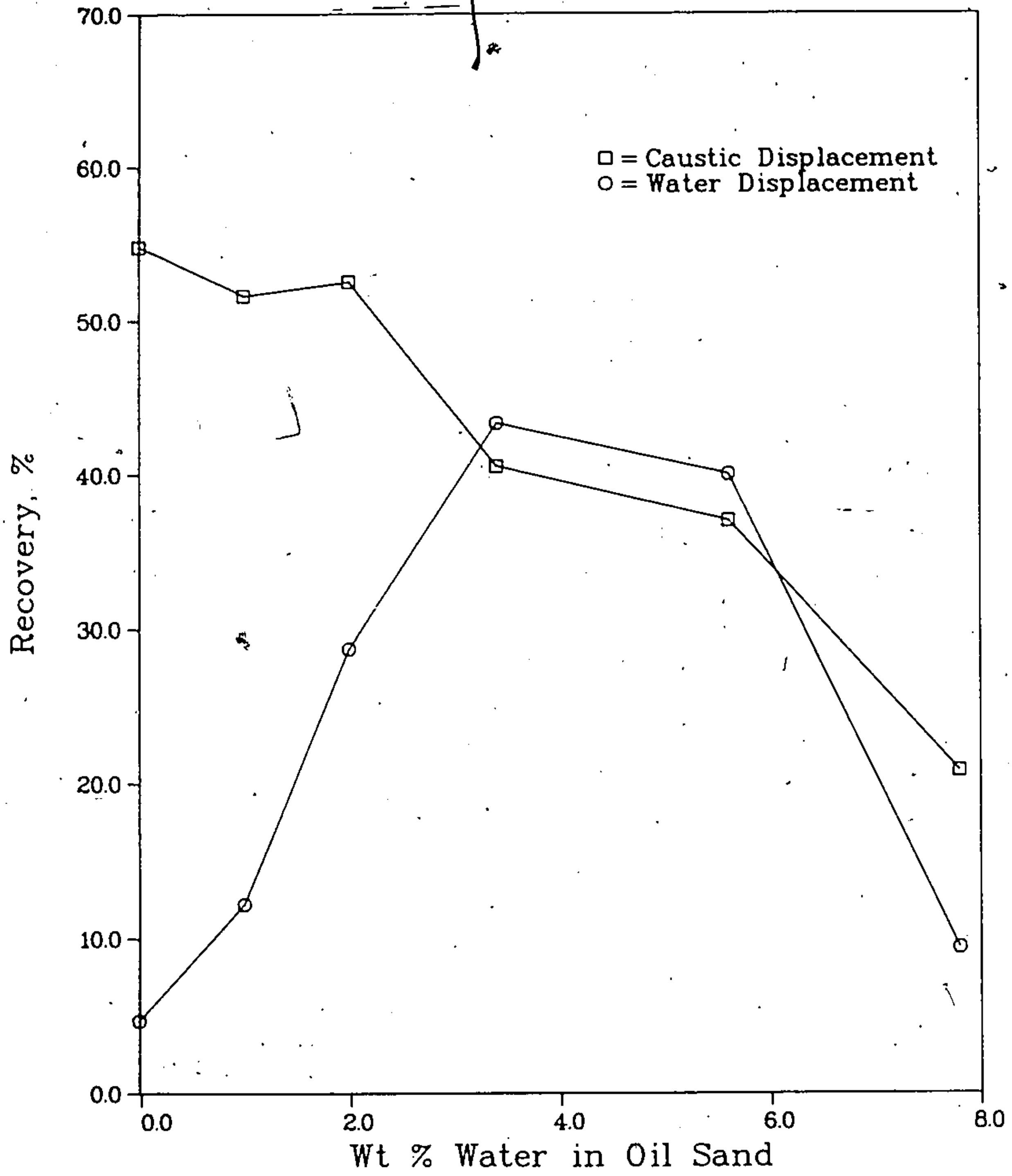


Figure 4-13. Recovery in samples containing 775°C-processed sand and variable initial water contents.

primarily responsible for its relative ease of processability compared to oil sands which do not possess such a film (42). Therefore, the high attractive force between the bitumen and sand (large, negative disjoining pressure) resulted in very low recoveries using water. The addition of 1% connate water did not improve the recovery behaviour so presumably the thickness of the resulting adsorbed water layer was not sufficient to significantly reduce the attractive force between the two surfaces. At 3.4% connate water, the recovery efficiency had increased dramatically. The behaviour can be explained if it is assumed that some of the additional water resided in the adsorbed layer. As the thickness of the layer increases the disjoining pressure eventually approaches zero because of the distance between the bitumen and sand surfaces (42). An increase in the disjoining pressure to near zero would explain why the recovery jumped so sharply. Further increases in the connate water content did not change the recovery. The disjoining pressure was already near zero so further water addition did not provide any beneficial effect.

The behaviour for caustic recovery in Figure 4-12 is quite different. At zero water content the caustic recovery was much higher than the corresponding water recovery. This was due to the caustic induced reactions which occurred. The caustic reacted with acidic species in the oil and with the humic acids on the sand. The accumulation of the resulting surfactants at the bitumen-sand interface served to lower the attractive force, or increased the disjoining pressure. Simultaneously, the production of surfactants in the porous medium would lower the capillary forces which in turn would improve the displacement efficiency. The end effect was that caustic recovery was substantial even in the absence of connate water. The recovery with caustic was largely independent of the connate water content and thus also independent of the adsorbed water layer thickness. This suggests that the caustic recovery process was controlled by the generation of surfactants rather than by the proximity of the bitumen and sand surfaces.

The behaviour of the water recovery data in Figure 4-13 was similar to that presented in Figure 4-12. The only notable deviation occurred at 7.8% connate water. The recovery efficiency was much higher when the oil sand was composed of sand containing humic material. This may have been due to the difference in sand wettability brought about by the removal of the humic material. Additional work would be required to ascertain the preferred wettability state and to determine why its influence on recovery became evident only at high water contents.

The recovery with caustic in Figure 4-13 is quite different from that in Figure 4-12. In the oil sand which did not contain humic material the caustic recovery decreased with increasing water content. This implies that the products of caustic reaction with humic material were responsible for the corresponding higher recoveries evidenced in Figure 4-12. It is interesting to compare the features of Figures 4-12 and 4-13 at 3.4% connate water. In the former case, caustic recovery was significantly higher than water recovery, while in the latter case the two recoveries were equivalent. This was unexpected because in both cases the oil phase contained potentially surface active species which would lead to a prediction of better performance with caustic than with water. That this did not occur demonstrates that the oil-water interfacial tension alone is not always a reliable predictor of recovery behaviour. As depicted in these two sets of data, the observed recovery is a function of the sand characteristics and the water content as well.

It should be pointed out that the behaviour of the present system behaved differently from the one described by Takamura and Chow (42). In the cited work, it is reported that an aqueous phase of pH 13 led to very slow disintegration of an oil sand pellet using the crumble test. This was supported by calculations which showed that the disjoining pressure peaked at about pH 12 and by pH 13 the maximum disjoining pressure was near zero. In the present work, however, it was observed that a displacing phase of 0.1 M NaOH (pH 13) produced the highest recovery, for at least one set of operating conditions. This is shown in Figure 4-14. The oil sand composition in these experiments was: 84% by weight of 300°C-processed sand, 3.4% distilled water and 12.6% of a mixture of 20% hexadecane in bitumen. Therefore, for the conditions encountered in this research it is believed that a displacing phase of pH 13 was near optimal.

One of the implicit assumptions made in the preceding discussion was that the adsorbed water layer thickness increased as the connate water content increased. This conjecture is speculative but it is believed to be reasonable, at least at low water saturations. At higher saturations the water layer

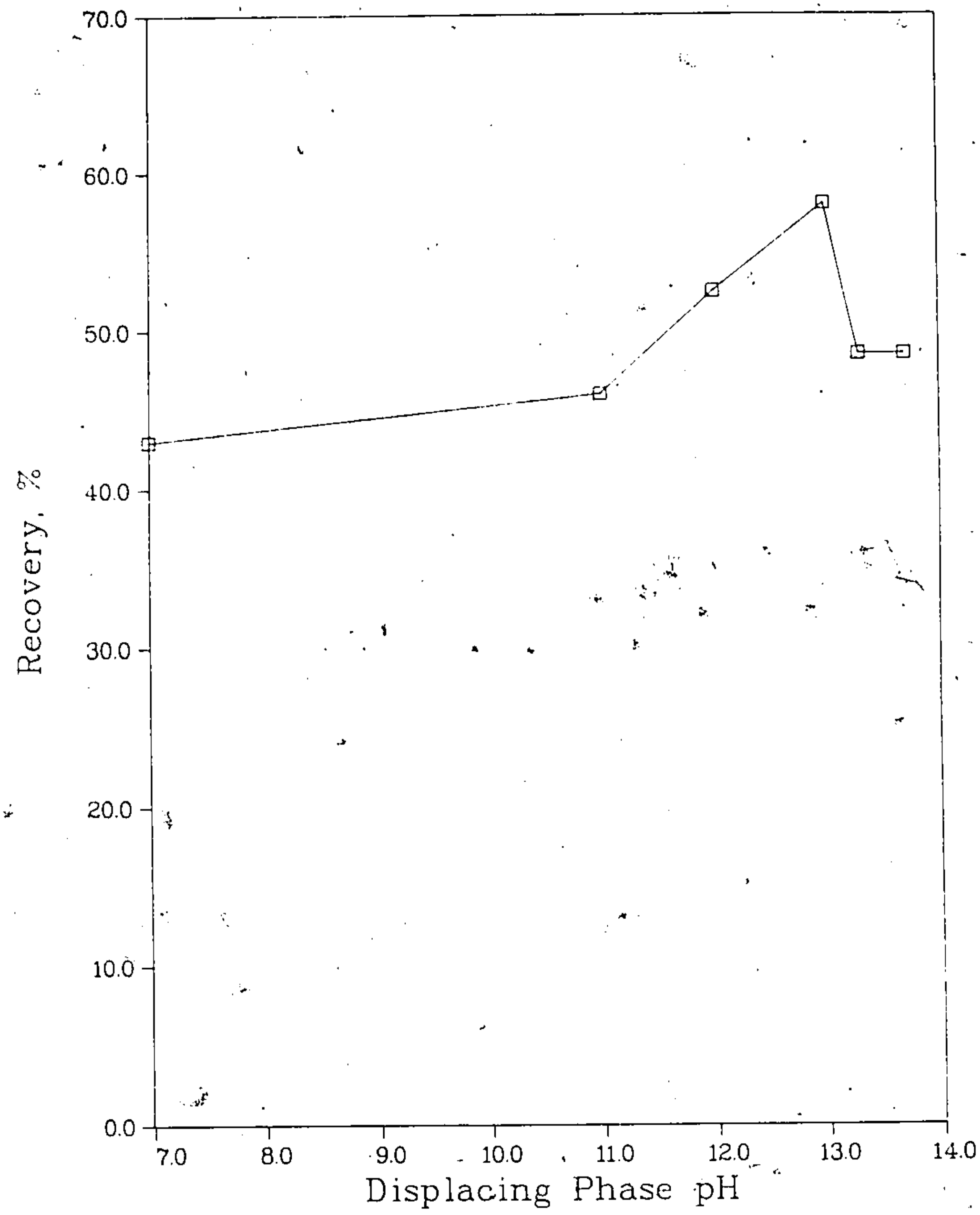


Figure 4-14. Dependence of recovery efficiency on displacing phase pH.

thickness may reach a plateau level with further water being distributed throughout the porous medium rather than around the sand surfaces. Whether this occurs is not crucial because the disjoining pressure function is most sensitive at low water layer thicknesses.

Since the initial oil content of these samples was varied, there are several ways of representing the recovery data. For example, suppose the percentage recovery is constant for all water (and oil) contents. As the oil content decreases, the absolute amount of oil produced decreases. Therefore, the greatest mass of oil would be produced when zero water is initially present. An alternative frame of reference is to compare the residual oil saturations. For constant percentage recovery, the residual oil saturation decreases as the initial oil content decreases. This method of representation is depicted in Figure 4-15 using the same data which generated Figure 4-12. Although the curve shapes are different, the same general features appear. There is a large difference in residual oil saturations resulting from caustic and water displacement at low connate water contents. The difference becomes much less pronounced at higher water contents. Also, the residual oil saturation decreases sharply between 1 and 3.4% water for water displacement. For caustic displacement, the residual oil saturation decreases more uniformly. Therefore, regardless of the mode of presentation, the significant features which require explanation remain the same. In the subsequent discussion dealing with systems of variable liquid saturations the data is presented in terms of percentage recovery only.

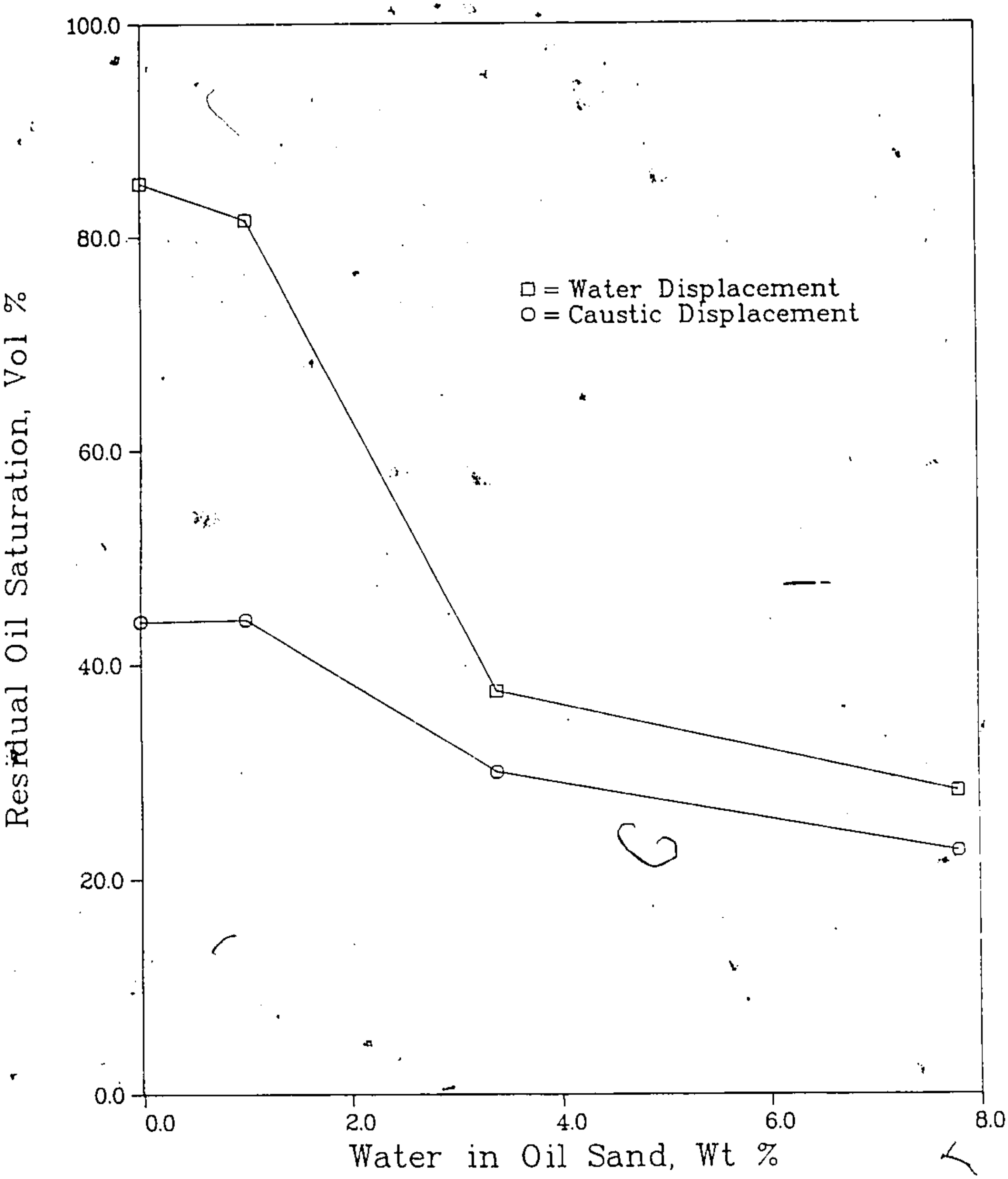


Figure 4-15. Residual oil saturation in samples containing 300°C-processed sand and variable initial water contents.

4.5.6 Influence of bitumen fractions

Comparison of the bitumens in Table 3-1 indicates that the material used in this study is very similar to the others and hence is representative of bitumens from the Athabasca region. The only marked deviation is an iron content several times higher than in the others. This may be due to the fact that the bitumen was originally contained in a steel drum and iron may have been leached into the oil.

As detailed in the experimental section, the separation sequence was to first separate the bitumen into its asphaltene and maltene fractions, and then to further fractionate the maltenes using liquid chromatography. The asphaltene comprises about 15% by weight of the bitumen. The maltene fractionation was not conducted quantitatively. Using the data of Payzant et al. (46), Athabasca maltene typically contains 70% hydrocarbons and 30% polar material. The elemental analyses of the separated fractions are shown in Table 4-18. It is noted that the asphaltene and polar fractions contain the highest proportion of heteroatoms. This was expected because there is usually a concentration of heteroatoms in the heavier fractions of any oil. The heteroatom content of the hydrocarbon fraction is lower, indicative of a relative absence of polar functional groups.

The density and viscosity measurements in Table 4-19 again confirm predictable trends. Maltene is lighter than bitumen due to the removal of the very heavy asphaltenes. Maltene splits into

Table 4-18. Elemental analysis of bitumen and its fractions in weight percentages.

Sample	C	H	N	O	S
Bitumen	82.9	10.14	0.44	0.60	4.70
Asphaltene	78.8	8.01	0.66	1.41	7.58
Maltene	83.5	10.74	0.36	0.77	3.67
Hydrocarbon	85.3	11.00	0.25	0.00	3.05
Polar	81.1	9.42	0.64	2.32	4.67

Table 4-19. Other properties of bitumen and its fractions.

Sample	Density, g/cm^3 (25°C)	Viscosity, cp (100°C)	Ash, wt %
Bitumen	1.013	162	0.6
Asphaltene	---	---	3.0
Maltene	0.973	32.7	---
Hydrocarbon	0.955	6.59	---
Polar	1.022	---	---

lower density hydrocarbon and higher density polar fractions. The viscosity data reflect the same changes. The ash content of the asphaltene accounts for nearly all of the ash in the bitumen, therefore, the other fractions were essentially ash-free.

Oil sand batches were reconstituted using these fractions. The objective was to assess the influence on recovery of the various chemical functionalities. The results presented in Table 4-20 contain several interesting features. The removal of the asphaltenes caused opposite effects in caustic and water displacement. Caustic recovery was greater in an oil sand containing maltene than for an oil phase composed of 20% hexadecane in bitumen. The reverse occurred for water displacement. Reconciliation of these opposing trends requires that the coincidental removal of asphaltenes and also hexadecane be considered.

For caustic displacement, the asphaltene fraction does nothing to enhance the interfacial activity of the bitumen (as will be seen in Section 4.9). Therefore, its removal does not impair the generation of surfactants which facilitate the displacement process. Hexadecane is inert to caustic hence its presence serves to dilute the concentration of reactive species in the bitumen. Since there was no hexadecane in the maltene, the higher incremental recovery observed with the maltene-containing oil sand is attributed to a higher concentration of reactive species in the oil. Provided the oil-caustic interface was not previously saturated, the generation of a higher concentration of surfactants should further lower the interfacial forces and thus increase

Table 4-20. Influence of organic phase composition on recovery efficiency.

Oil composition	Recovery with caustic, %	Recovery with water, %	Difference, %
20% hexadecane, 80% bitumen	59.4	43.2	16.2
maltene	72.5	32.1	40.4
20% polar, 80% maltene	72.9	19.1	53.8
hydrocarbon	62.3	65.3	-3.0
2% polar, 98% hydrocarbon	58.5	59.6	-1.1
10% polar, 90% hydrocarbon	65.5	63.2	2.3

recovery.

For water displacement, the lower concentration of polar species in the hexadecane-bitumen mixture due to dilution decreases the strength of the interaction between the sand and bitumen surfaces. Therefore, the capillary forces are lower for a system containing the hexadecane diluted bitumen than in one composed of maltene. This results in the recovery observed with water being lower in the oil sand comprised of maltene.

Additional polar material was added to the maltene with the aim of enhancing the reactivity and surface activity of the maltene. The results show that the caustic recovery of this combined oil was the same as for an oil phase of maltene alone. This is attributed to one of two factors:

(a) The concentration of polar material necessary to enhance recovery may reach a saturation level with further addition having no incremental effect.

(b) Simple remixing of the maltenes and polars does not guarantee that the molecular species in each will exhibit the same chemical properties that they possessed in the original bitumen. Therefore even if the potentially surface active species are in the polar fraction they may be in an orientation which renders them inactive.

For a sample of oil sand containing only the hydrocarbon phase the recoveries with caustic and water are the same. This occurs because of the absence of polar functional groups in the hydrocarbon fraction. It is these polar groups which are responsible for the reaction between caustic and bitumen.

The hydrocarbon fraction was doped with 2 and 10% by weight of the polar fraction in an attempt to reintroduce some reactivity into the oil. The results show that recoveries were not affected. This may have been due to one of the following factors:

(a) There may be a threshhold concentration of polar material required before displacement by caustic will be significantly greater than displacement by water.

(b) The simple recombination of polar and hydrocarbon subfractions does not guarantee that the chemical functionality of the mixture will be restored. It is possible that during the separation process, the chemical or physical properties of the molecules were altered and upon remixing these changes may not be reversible. If not, then the properties of the recombined oil could be quite different from those of the parent material.

4.6 Flow parameters

The flow parameters for a typical low temperature displacement experiment are calculated in Appendix 6. The representative oil sand upon which these calculations are based was composed of: 84% by weight sand, 3.4% distilled water and 12.6% of a mixture of 20% hexadecane in bitumen. An oil sand pellet density of 2.00 g/cm^3 was assigned.

An upper limiting Reynolds number was calculated to be 0.0039. All of the displacement experiments had Reynolds numbers less than or equal to this, hence all of the tests were in the seepage velocity domain as defined in Section 2.7.

It is calculated that the pressure drop across a loaded displacement cell occurred primarily across the oil sand pellet. The glass beads at either end contributed negligibly to the overall pressure drop.

The effective permeability to water during water displacement was determined to be 3.86x10^{-10} cm^2 during the initial stages of an experiment, and 1.93x10^{-10} cm^2 towards the latter stages. The saturation conditions at the start and end of an experiment were known, hence the relative permeabilities to water could be estimated. At the initial saturation conditions, the relative permeability to water was 0.0188 and at the final conditions it was 0.176. On this basis, the absolute permeabilities were estimated to be 2.05x10^{-8} and 1.10x10^{-9} cm^2 at the beginning and end of an experiment respectively.

Therefore, as an experiment progressed, both the effective permeability to water and the absolute permeability decreased. This has been attributed to the movement of fines in the porous medium which tended to block some of the flow paths. During caustic displacement experiments, the pressure drop was, in some cases, an order of magnitude higher than in the water displacement experiments. Since all of the other parameters in Equation 2.7-5 were the same, this difference must have been due to a decrease in the oil sand permeability. This is reasonable because during caustic flooding the aqueous phase became clouded and coloured indicating that the migration of fine or colloidal material was intensified.

4.7 Wettability considerations

The wettability state of a porous medium strongly influences the displacement process. However, quantitative determination of the wettability indicator, contact angle, within a porous medium is difficult if not impossible. A number of qualitative experiments were performed to estimate the wettability characteristics of extracted sand and oil sand.

After toluene extraction of bitumen and water, the clean sand was in a toluene-wet state. This was evidenced by the observation that toluene imbibed into this sand whereas water balled on top. When clean sand was heated to 300°C, the sand imbibed water, hence a reversal to a water-wet state had occurred. This has been attributed to the volatilization of traces of toluene adsorbed on the sand surface. Further heating to 775°C changed the humic content of the sand, but the wettability state was not noticeably affected.

A semi-quantitative verification of the change from water non-wet to water-wet during heating was obtained by placing three microscope slides in the Dean Stark extraction apparatus, and conducting a toluene reflux. Afterwards, the slides were dried at 90, 200 and 300°C overnight respectively. A water droplet placed on the slide dried at 90°C exhibited a contact angle of about 45°. On the slide dried at 200°C, the angle decreased to about 30°, and on the slide dried at 300°C, the water droplet spread to form a film thus the contact angle was near 0°. It is likely that a parallel trend occurred in the extracted sand due to its chemical similarity to glass.

The presence of caustic in the aqueous solution did not change the wettability behaviour of the sand markedly. Sand heated to 300°C and alkaline solution came into intimate contact very rapidly, as detected by the immediate colouration of the aqueous phase. However, sand dried at 25°C was not easily wetted by caustic. Even after several days of contact, the alkaline solution was only faintly coloured.

The presence of caustic did influence the relative affinities towards glass of the aqueous phase and a mixture of 20% hexadecane in bitumen. The organic mixture was placed on top of distilled water in a test tube and the tube tilted back and forth. When a portion of the tube which had been in contact with water was contacted by oil, the oil remained on the glass in preference to the water. However, when alkaline aqueous solution was used, the oil surface advanced and receded as the tube was tilted. This indicated that caustic was able to wet the glass in preference to the organic phase. An explanation of this behaviour is that the polar species in the bitumen interacted so strongly with the silica that water could not dislodge the oil. In contrast, caustic reacted with these polar species to produce surfactants which lowered the oil-solid interfacial tension sufficiently that caustic became the preferential wetting agent.

Water was also placed in contact with compacted samples of oil sand. Droplets of water positioned either above or below a compacted sample of mined Athabasca oil sand exhibited initial contact angles of about 90°, but after a few minutes the drops disappeared into the pellet. The same behaviour was observed in reconstituted oil sand pellets containing diluted bitumen. The high initial contact angle was probably due to the inability of water to wet the organic phase. The subsequent imbibition indicates one of two things. Either the water was able to contact a water-wettable surface or the overall system energetics were better with water, rather than air, occupying the artificial porosity in the pellet.

4.8 Characterization of humic material

Several approaches were taken to characterize the humic material. Initially, whole samples of clean sands were submitted for analysis. The results of elemental analyses of three sands heated to different temperatures are shown in Table 4-21. Two of the sands had carbon contents of about 0.1% which is near the detection limit of the apparatus. Samples were also examined using Fourier transform infrared (FTIR) spectroscopy and petrographic techniques. The principal feature of the FTIR spectrum of the sand dried at 25°C was a series of peaks in the 3600 to 3700 cm^{-1} region. These are attributed to OH stretching within kaolinite present in the sand. The sands heated to 200 and 400°C exhibited much weaker OH stretching indicating that thermal dehydration of the kaolinite had occurred. The lack of organic peaks means that the organic content of these sands was less than about 1% (91). Petrographic analysis of the darker portions of the sand which had been dried at 25°C revealed the presence of lignitic species; this substantiated the findings of Strausz and Montgomery (34). A sample heated to 400°C contained no such structures. Combined mass spectroscopy and gas chromatography was unable to detect organic species. This implies that any organic species on the sand were composed of more than about 40 carbon atoms and thus were too heavy to be volatilized at the temperatures attainable with the instrument.

To better characterize the humic material a concentrated sample was obtained by the method described in Section 4.5.3. The

Table 4-21. Weight percentages of carbon, hydrogen and nitrogen in whole sands heated to different temperatures.

Temperature,°C	C	H	N
90	0.08	0.01	0.05
200	0.09	0.01	0.05
400	0.00	0.01	0.10

elemental analysis of this concentrated material is shown in Table 4-22. From this data it can be said conclusively that organic material was on the clean sand and it was extracted by caustic. Polar organic functional groups and waters of hydration probably accounted for the oxygen content of the sample.

Thermogravimetric analyses of the concentrated material was conducted and the results shown in Figure 4-16. The sample was observed to lose about 25% of its weight upon heating to 1000°C in the presence of oxygen. Almost all of this weight loss occurred between 300 and 500°C. When the analysis was conducted in nitrogen the overall weight loss was the same, but the shape of the curve was different. In the nitrogen atmosphere, the major weight loss occurred over a wider range of temperatures.

Fourier transform infrared spectra of this concentrated material and a sample of concentrated material ashed at 775°C were obtained. The spectra appear in Figure 4-17. The unashed sample exhibited a set of peaks at 1600 to 1700 cm^{-1}. This is indicative of carbonyl groups or doubly bonded carbon. The other noteworthy peaks were at 3600 to 3700 cm^{-1}, the same OH stretching peaks which had been observed using whole sand. In the ashed sample, these two sets of peaks at 1600 to 1700 and 3600 to 3700 cm^{-1} disappeared. This is attributed to oxidation of the carbonaceous material and thermal dehydration of the kaolinite respectively.

The basic extract obtained by shaking 300°C-processed sand and caustic was analyzed for heavier elements using inductively coupled argon plasma. The principal constituents of the solution and their relative abundances are shown in Table 4-23.

Table 4-22. Elemental analysis of material extracted from clean sand, dried at 300°C, using NaOH.

Element	Weight %	Atomic ratio to carbon
Carbon	7.39	1.00
Hydrogen	1.47	2.39
Nitrogen	0.37	0.042
Oxygen	10.19	1.03
Sulfur	0.45	0.023

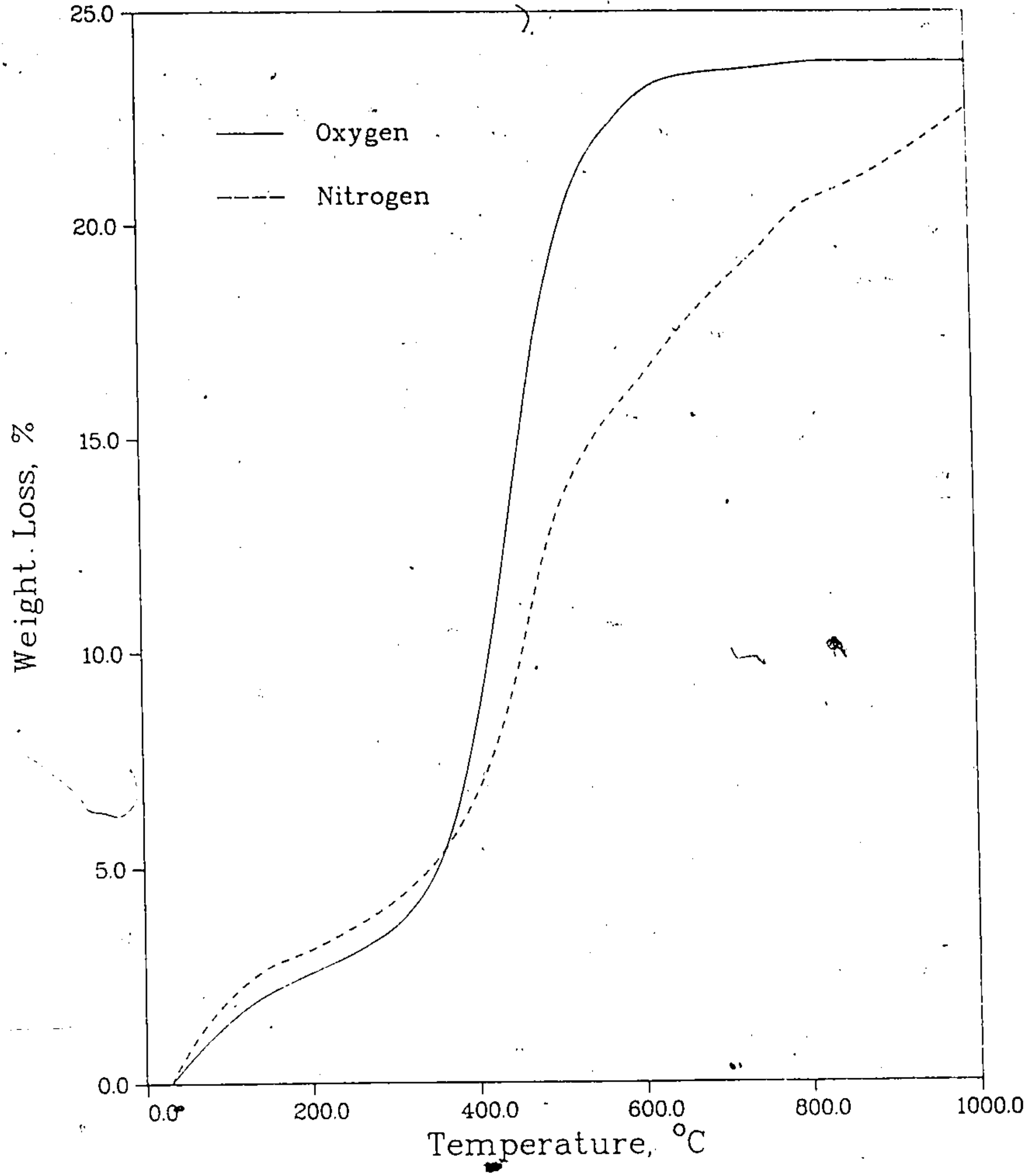


Figure 4-16. Thermogravimetric analysis of humic material.

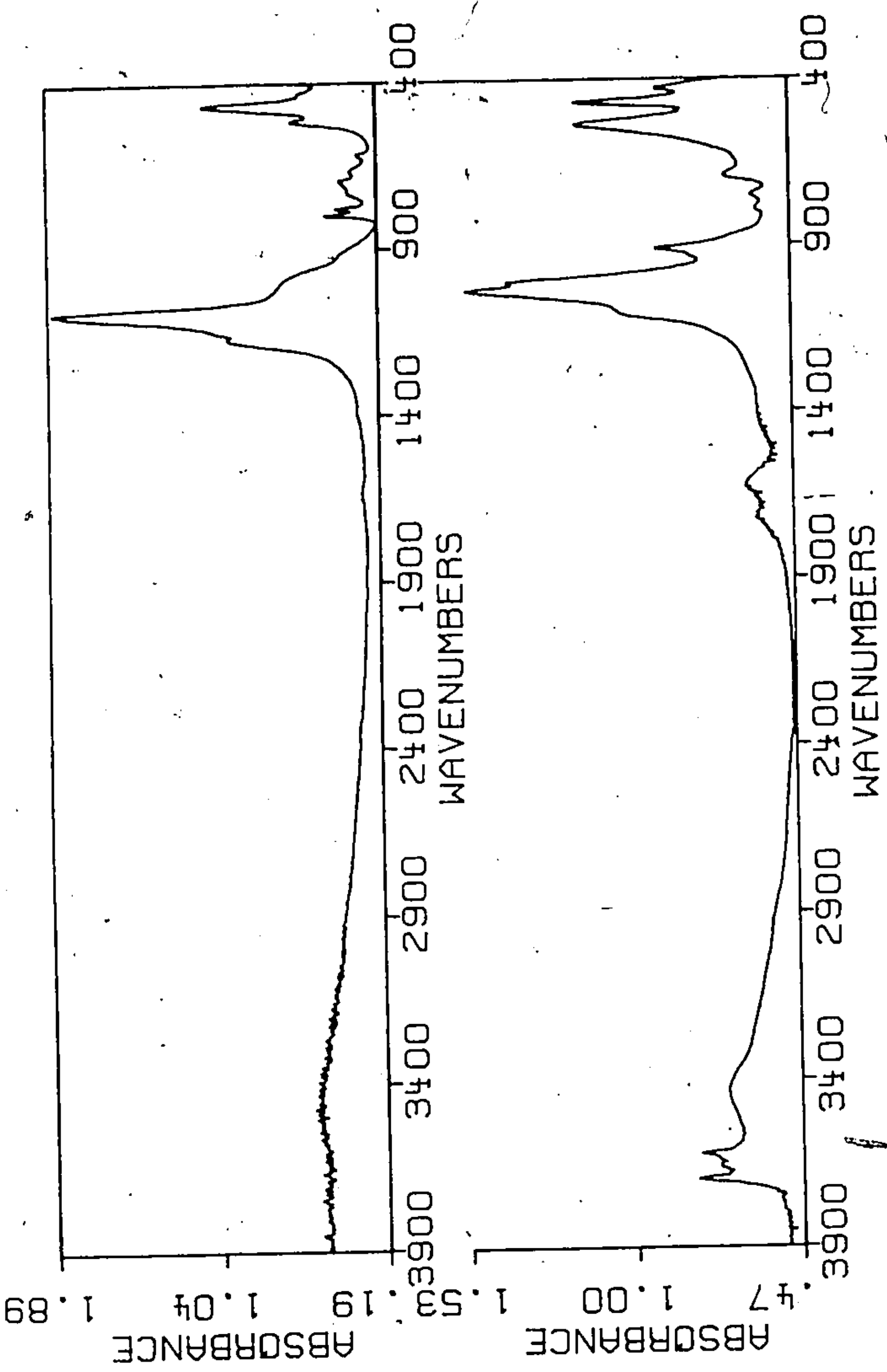


Figure 4-17. Fourier transform infrared spectra of ashed (upper) and unashed (lower) humic material.

Table 4-23. Elemental analysis by inductively coupled plasma of material extracted by 0.1M NaOH from clean sand heated to 300oC.

Element	Element:silicon mass ratio	Element:silicon atomic ratio
Si	1.	1.
Al	0.756	0.787
Fe	0.140	0.070
Ti	0.046	0.027
Ca	0.113	0.079
Mg	0.064	0.074
K	0.122	0.088
S	0.636	0.557
V	0.005	0.003

Scanning electron microscopy was used to examine samples of whole sand dried at 25 and 775°C, and samples of concentrated humic material dried at 110 and 775°C. The whole sand dried at 25°C is shown at two magnifications in Figure 4-18. In the lower magnification photo it is noted that most of the particles are in the 60 to 100 micron range, but two large particles are evident. The one in the foreground, particularly, appears to be an aggregate of smaller particles. The large particle in the central part of the photo is shown at higher magnification in the second photo. From this picture it is seen that its surface is very rough.

In Figure 4-19 the subject is the sample of whole sand which had been heated to 775°C. From the low magnification photo it is noted that the particles are all of approximately the same size. There is no evidence of the aggregates observed in the previous photo. The magnified shot of one of the particles shows these sand grains to be very smooth.

The scanning electron photomicrographs of samples of humic material which had been heated to 110 and 775°C are shown in Figures 4-20 and 4-21 respectively. These samples appear to be very similar.

The principal conclusion drawn from this work is that the whole sand dried at 25°C contained aggregates bound together by a material which imparted a high degree of surface roughness to the particles. After the sand was heated to 775°C these aggregates were not present indicating that the binding agent was removed or at least rendered inoperative by the exposure to high temperature.

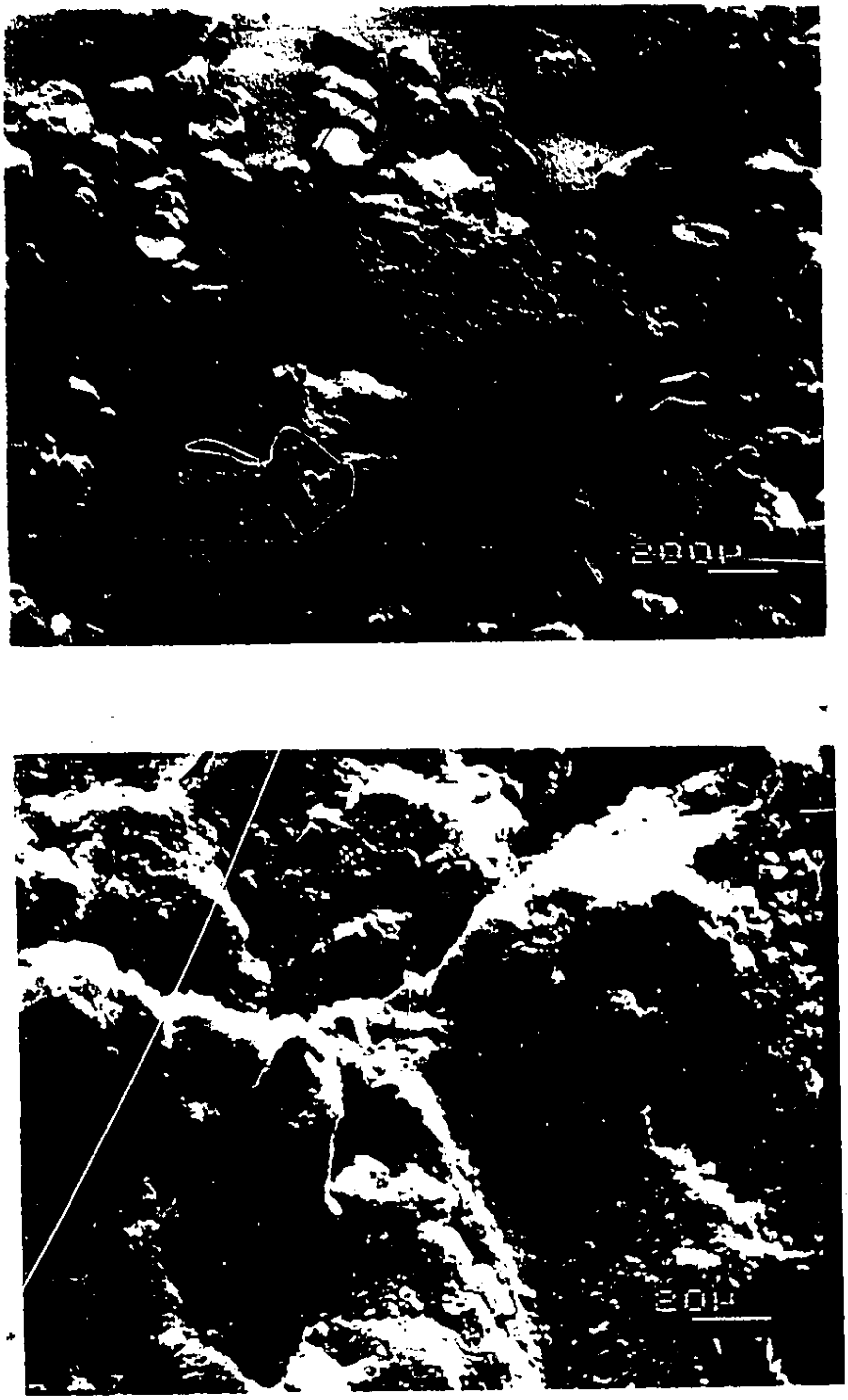
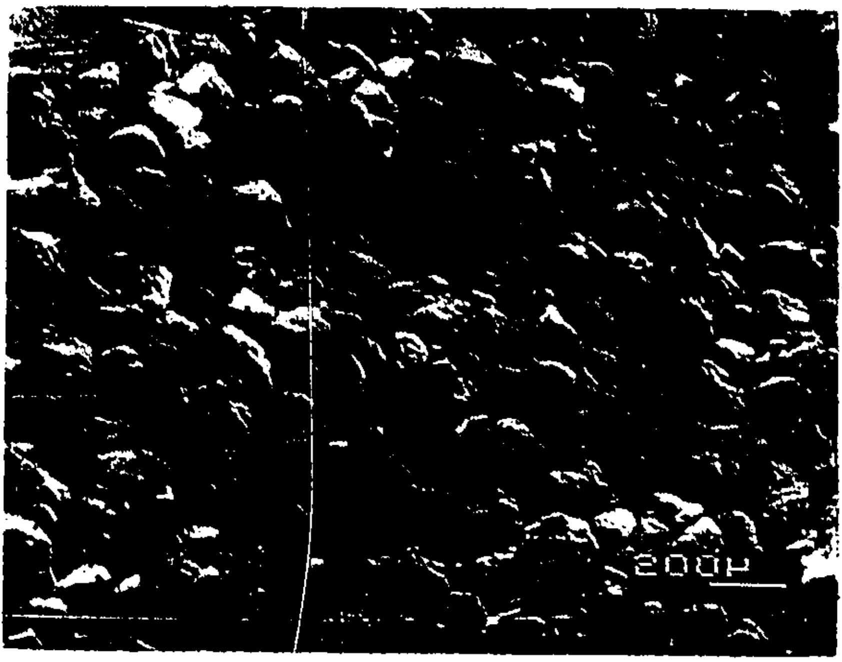


Figure 4-18. Scanning electron photomicrographs of sand previously heated to 25°C.



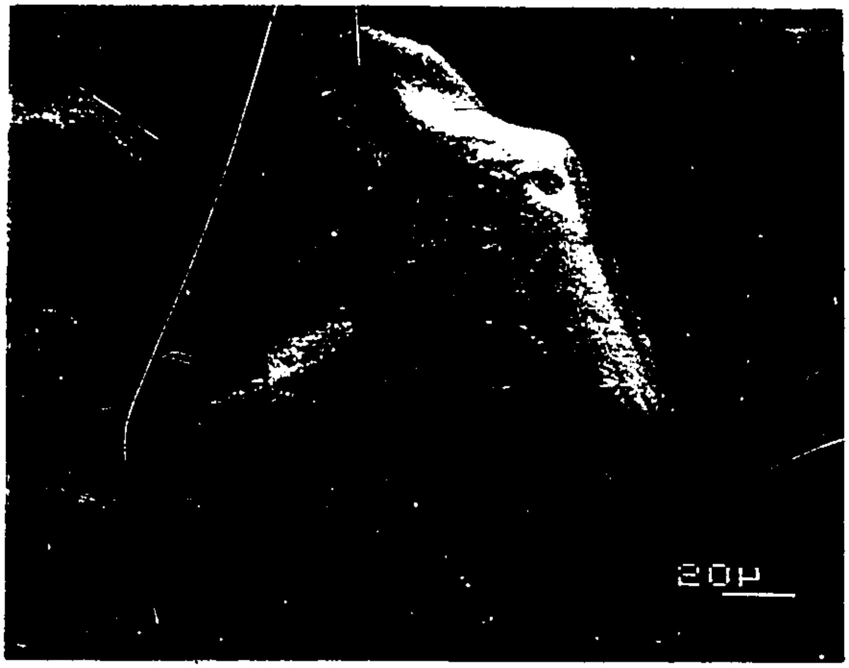


Figure 4-19. Scanning electron photomicrographs of sand previously heated to 775°C.

Figure 4-20. Scanning electron photomicrographs of humic material previously heated to 110°C.

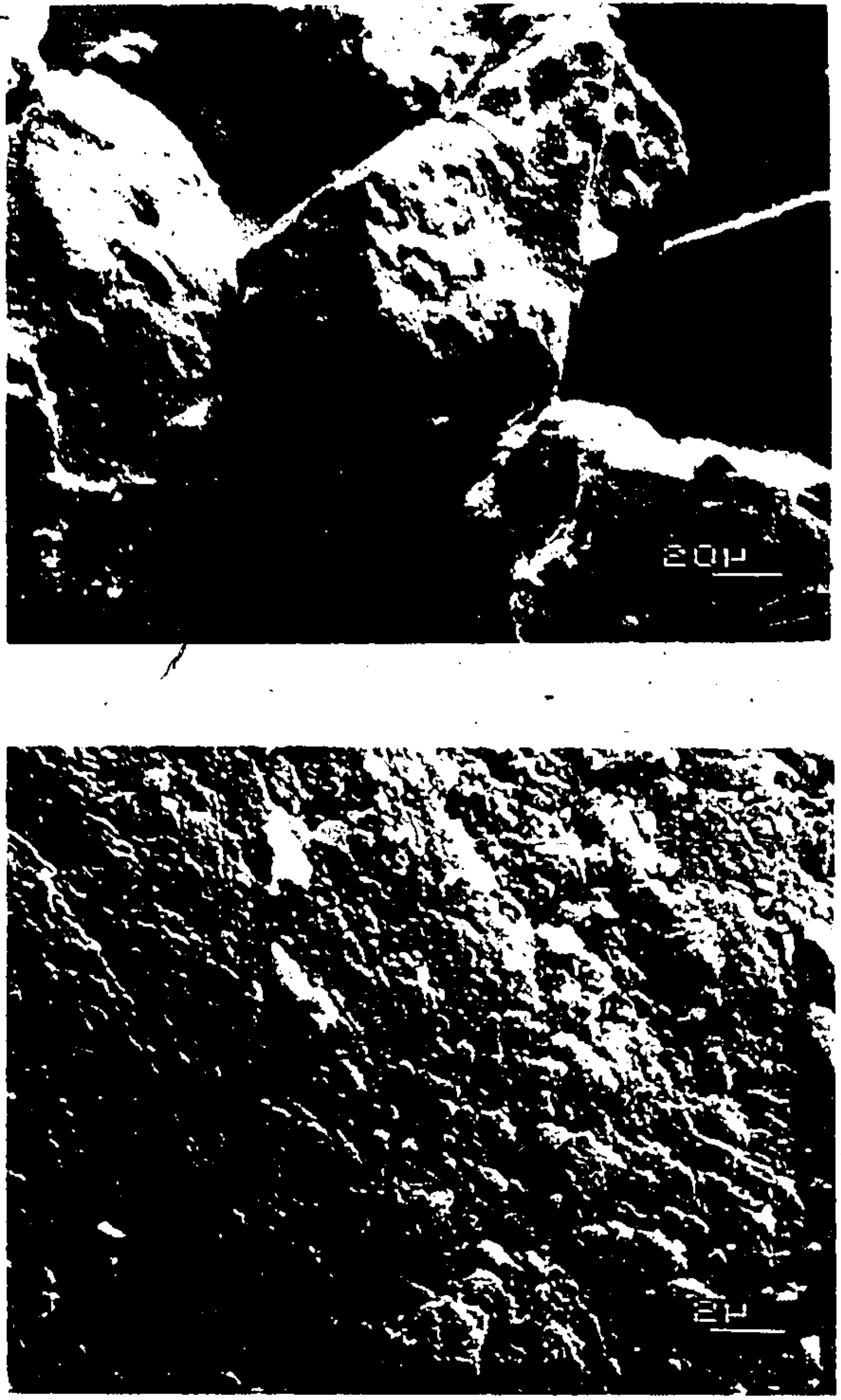


Figure 4-21. Scanning electron photomicrographs of humic material previously heated to 775°C.

This binding agent is believed to be the humic material and affiliated clay particles. Similar behaviour was observed elsewhere during the experimental work. After performing a Dean Stark analysis of a swept oil sand pellet, the cleaned sand remained in its cylindrical form in some cases and in others the sand was entirely disaggregated. A strong correlation was present between the final state of the sand and the temperature at which it had been heated prior to reconstitution. When pretreated at low temperatures the sand tended to hold its shape while sands heated at high temperatures tended to disaggregate. This phenomenon can also be explained by the binding agent mechanism just outlined.

Sections of the samples which were used for scanning electron microscopy were mounted for x-ray analysis as well. Each analysis revealed two types of information. First, the relative abundances of elements of atomic number greater than about 10 were determined. Secondly, the relative abundance of lighter elements such as carbon and oxygen could be inferred from the detected count frequency. A relatively high count frequency meant that the surface under observation was clean. That is, very little interfering or diluting material, such as organic matter was on the surface. Contrarily, a relatively low count frequency implied that the surface contained appreciable amounts of interfering material. The combined results are shown in Table 4-24. Comparison of the data in Tables 4-23 and 4-24 show that for the most part the same elements were detected in the caustic extract using inductively coupled plasma and x-ray analysis. However, the

Table 4-24. X-ray analysis data.

Sample	Atomic ratio to silicon				Count
	Si	Al	Fe	K	frequency, s^{-1}
Whole sand, 25°C aggregate	1.	0.171	0.077	---	25
Whole sand, 25°C single grain	1.	0.034	---	---	300
Whole sand, 775°C	1.	0.005	---	---	450
Humic material, 110°C *	1.	0.319	0.054	0.071	70
Humic material, 775°C **	1.	0.321	0.033	0.085	200

---

* also traces of S, Ti

** also traces of Sb, V, Cu, Ti

relative abundances as measured by the two techniques vary considerably.

The following trends are evident from the x-ray data:

(a) In whole sand dried at 25°C, the large aggregated lump of sand possessed higher iron and aluminum contents than the discrete sand grains. In addition, the count frequency was much lower for the aggregate than for the single particle. This infers that the aggregate contained a higher concentration of material on its surface which was undetectable by the technique. These two observations support the conjecture that humic material was on the sand surface and was responsible for the cohesive force which kept the cluster intact. The corresponding high iron and aluminum contents support the findings of Kotlyar et al. (35) that the humic material is attached to clay via an iron complex linkage.

(b) The whole sand heated to 775°C contained no measurable amount of iron, low aluminum content and the count frequency was high. Therefore, the humic material and affiliated inorganic species were not on the sand surface. This supports the hypothesis that the humic acid is removed at high temperatures. There was not much difference between the sand heated to 775°C and the individual sand grain in the sample heated to only 25°C. It appears that even in the sand dried at 25°C, some of the particles were devoid of humic material. Obviously, the iron and aluminum detected on the aggregate in the 25°C-processed sand were not volatilized during heating to 775°C. Rather it is supposed that when the humic material was removed, the associated minerals collapsed into very fine particles which were not observed in these analyses.

(c) The samples of humic material show high concentrations of aluminum, iron, titanium, potassium and lesser amounts of sulfur,antimony, vanadium and copper. The high aluminum content is indicative of the high concentration of clay in the samples. Except for aluminum and iron, the listed elements were not identified in other samples. The analyses of the samples heated at 110 and 775°C were very similar. The distinguishing parameter is the count frequency. The sample heated at 110°C had a low frequency presumably due to the presence of carbonaceous material on the surface. The sample heated to 775°C had a much higher count frequency because the carbonaceous material had been burned off.

On the basis of the foregoing, the following hypothesis has been formulated. In untreated Athabasca oil sand, there are segments which are rich in humic material and kaolinite. The organic components are not solubilized by toluene and remain in the clean sand after Dean Stark extraction. This humic matter reacts with caustic to produce surfactants which improve the recovery efficiency. Upon extreme heating the organic material is removed from the sand. This reduces the reactivity of the sand matrix to caustic and leads to a decrease in the efficiency of caustic displacement relative to water displacement.

4.9 Interfacial tension measurements

The interfacial tension data obtained between 0.1 M NaOH and 20% hexadecane in bitumen at temperatures from 25 to 75°C are shown in Figure 4-22. Comparison of these curves reveal the following trends:

(a) At higher temperatures, the minimum interfacial tension occurs faster.

(b) At higher temperatures, the system exhibits low interfacial tensions for a shorter period of time.

(c) The magnitude of the minimum interfacial tension is essentially unaffected by the temperature.

It has to be remembered that the water to oil ratio in a spinning drop measurement is many times larger than the corresponding ratio within the porous medium. Therefore, the transient effects of interfacial tension observed in the spinning drop will occur much slower in the oil sand during displacement. The more important aspect of these experiments is that the magnitude of the minimum interfacial tension is not a strong function of temperature over the range studied.

Interfacial tension measurements were made between maltene and an aqueous phase of 0.1 M NaOH containing variable amounts of suspended and extracted humic material. The results are presented in Figure 4-23. It is seen that the interfacial tension decreased as the amount of humic material in the aqueous phase increased. This demonstrates that the humic material on the sand did indeed interact with alkaline solution in a manner which may account for the incremental recovery observed with caustic in comparison to

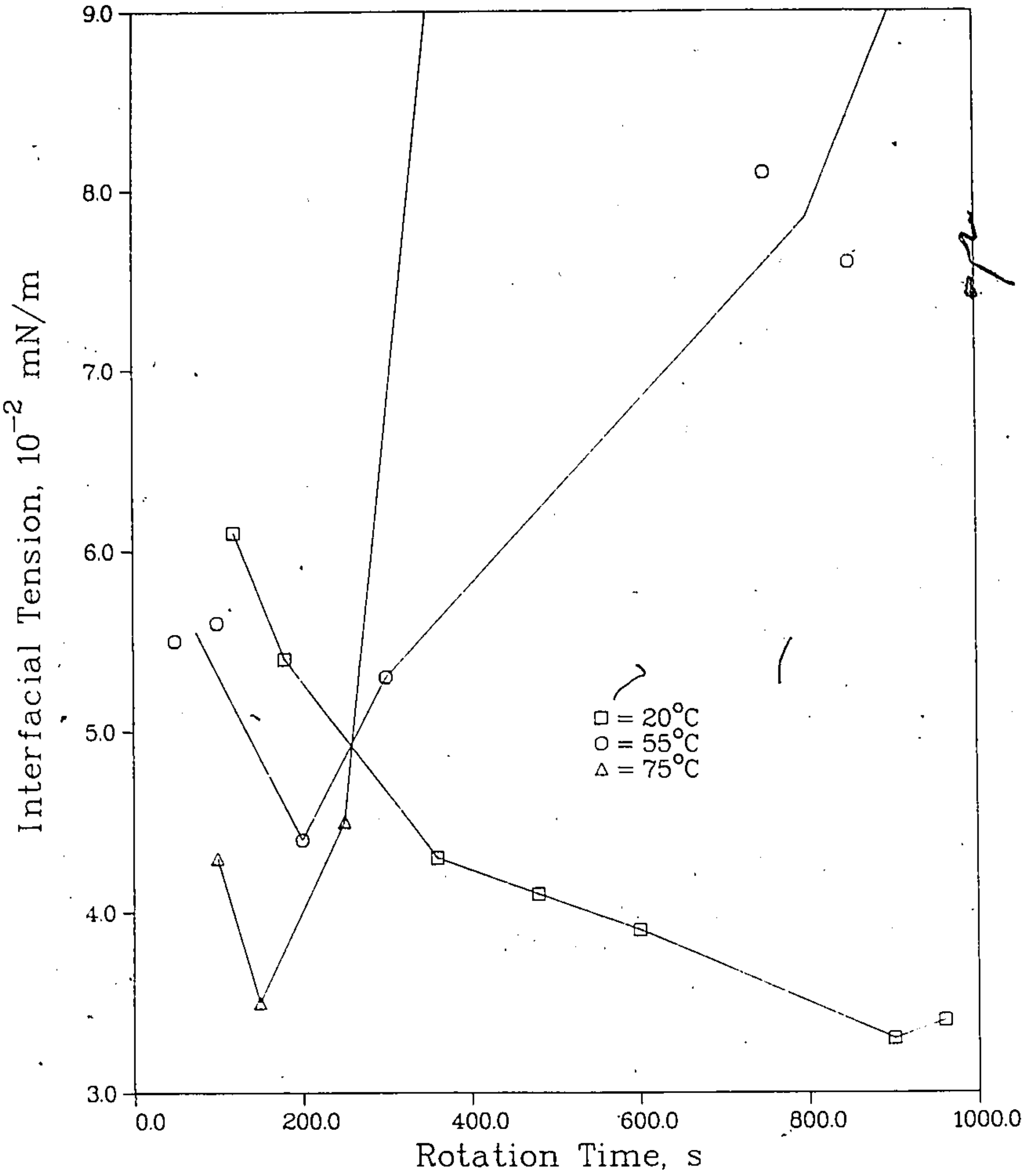


Figure 4-22. Time and temperature dependence of interfacial tension of 20% hexadecane in bitumen vs. 0.1M NaOH.

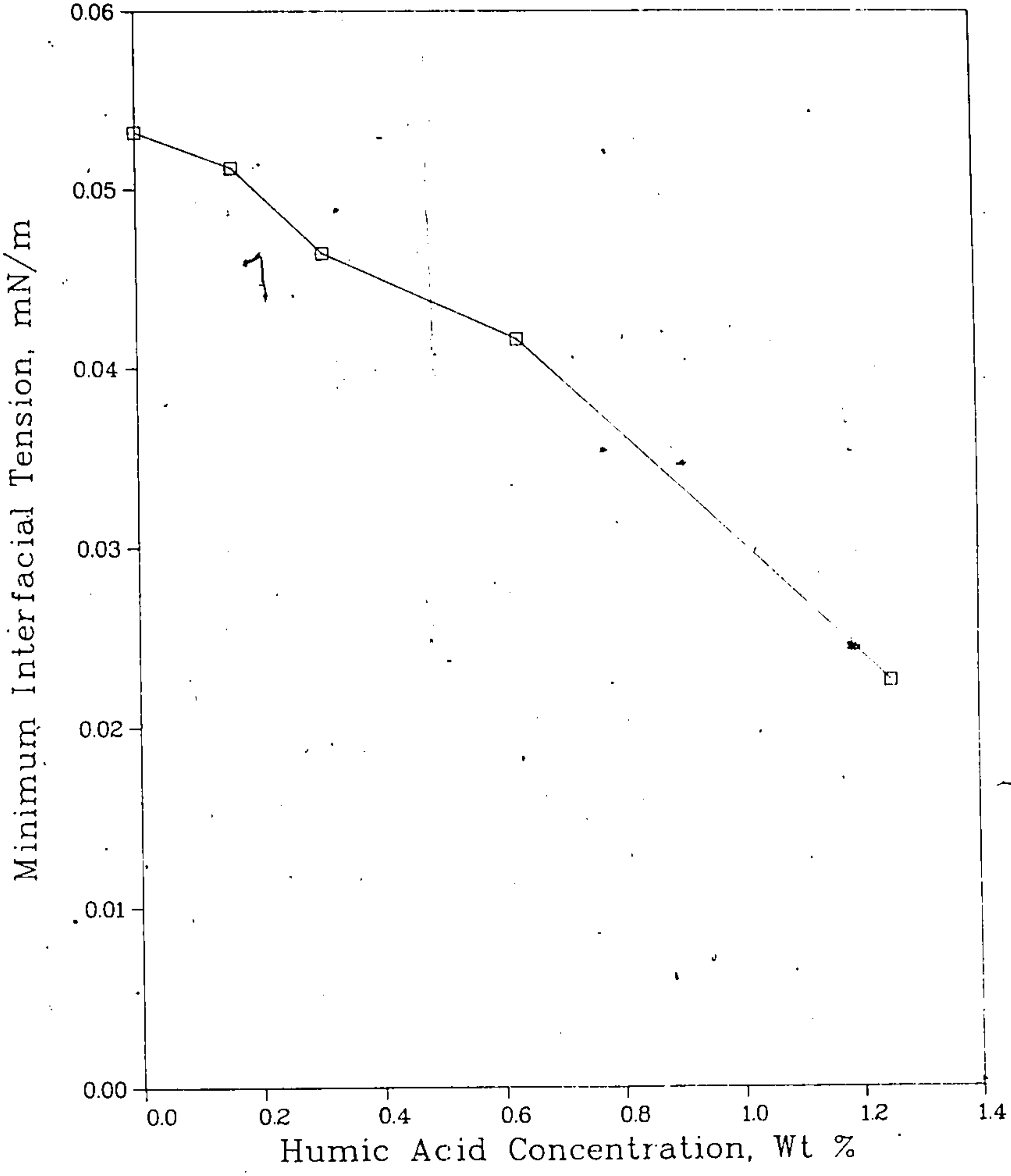


Figure 4-23. Interfacial tension between maltene and 0.1M NaOH plus variable amounts of humic material.

water. The mechanism is basically the same as the one proposed for reaction of caustic with acidic species in the oil. In both cases it is hypothesized that the caustic reacts to produce surfactants at the interface. These surfactants lower the capillary forces within the porous medium thus facilitating more effective displacement.

When NaCl was present in the aqueous phase, the transient interfacial tension effects were accelerated. During spinning, the droplet elongated and contracted much faster than when salt-free aqueous phases were used. In some instances, the minimum interfacial tension was attained before the initial drop width measurement could be completed.

Interfacial tension measurements were also performed using the bitumen fractions. The aqueous phase was 0.1 M NaOH. The results are listed in Table 4-25. In some cases, the oil droplet did not elongate at all, indicative of a high interfacial tension. This situation was denoted as an interfacial tension >1. Comparing the first two sets of data it is noted that the removal of the asphaltenes does not alter the interfacial tension. Although the asphaltene fraction is composed of polar entities, its removal does not impair the reactivity of the bitumen towards caustic. Similar behaviour of crude and deasphalted heavy oil have been reported elsewhere (92).

The interfacial tension between caustic and the hydrocarbon fraction was very high. This correlates with the observed equivalence of caustic and water recoveries from an oil sand containing the hydrocarbon phase. There are no reactive species

Table 4-25. Minimum interfacial tensions vs. 0.1M NaOH at 25°C.

Oil	Oil density g/cm^3	Interfacial tension, mN/m
20% hexadecane 80% bitumen	0.948	0.0320
maltene	0.973	0.0331; 0.0449
hydrocarbon	0.955	>1
7% polar 93% toluene	0.876	>1
58% polar 42% toluene	0.950	>1
37% polar 40% hydrocarbon 23% toluene	0.956	>1
47% polar 51% hydrocarbon 2% toluene	0.983	>1
4% asphaltene 96% toluene	0.879	>1
20% asphaltene 80% toluene	0.927	0.101

present in the oil, so caustic and water become equally effective displacement agents.

None of the oil mixtures containing the polar fraction exhibited low interfacial tensions. This explains why the addition of polar material to the maltene and hydrocarbon fractions did not enhance the effectiveness of caustic displacement. Again, the explanation for this may be due to a problem with simple recombination of fractions to try to recreate the conditions which existed in the parent material. Alternatively, it may be that the interfacially active fraction of the maltene remained on the chromatographic column during the separation sequence. This could also account for the fact that maltene exhibits a low interfacial tension against caustic, whereas neither of its fractions do.

4.10 Other organic phases

The influence which the organic phase exerted on recovery was studied by substituting for the hexadecane-bitumen mixture. Castor oil and paraffin oil were used to reconstitute oil sand and experiments parallel to those represented in Figures 4-12 and 4-13 were performed. Properties of these two oils are listed in Table 4-26. Castor oil was selected because it is a viscous oil which contains acidic components, as evidenced by its acid number of 0.89. Its comparatively low interfacial tension against caustic indicates that these acidic groups reacted to produce surfactants. Therefore, the behaviour of castor oil was similar to hexadecane-bitumen in this regard. The paraffin oil was selected because of its lack of reactive acidic components.

As before, oil sand batches were reconstituted using sands which had been previously heated to 300 or 775°C. The plots of recovery versus initial connate water saturation are shown in Figure 4-24 for an organic phase of castor oil and in Figure 4-25 for paraffin oil.

The behaviour of the oil sands containing castor oil follow many of the same trends as were exhibited in oil sands containing hexadecane-bitumen. Alkaline recovery started out much higher than water recovery. Again this is attributed to the reactions which occurred to produce surfactants. As the initial water content increased, the recovery with water rose rapidly while caustic recovery changed only slightly. As a result, caustic and water recoveries became equivalent at certain water saturations

Table 4-26. Properties of castor and paraffin oils.

Property	Castor oil	Paraffin oil
Viscosity (20°C), cp	986	61
Density (25°C), cp	0.961	0.870
Acid number, mg KOH/g	0.89	<0.01
Minimum interfacial tension vs. 0.1 M NaOH, mN/m	0.170	>1

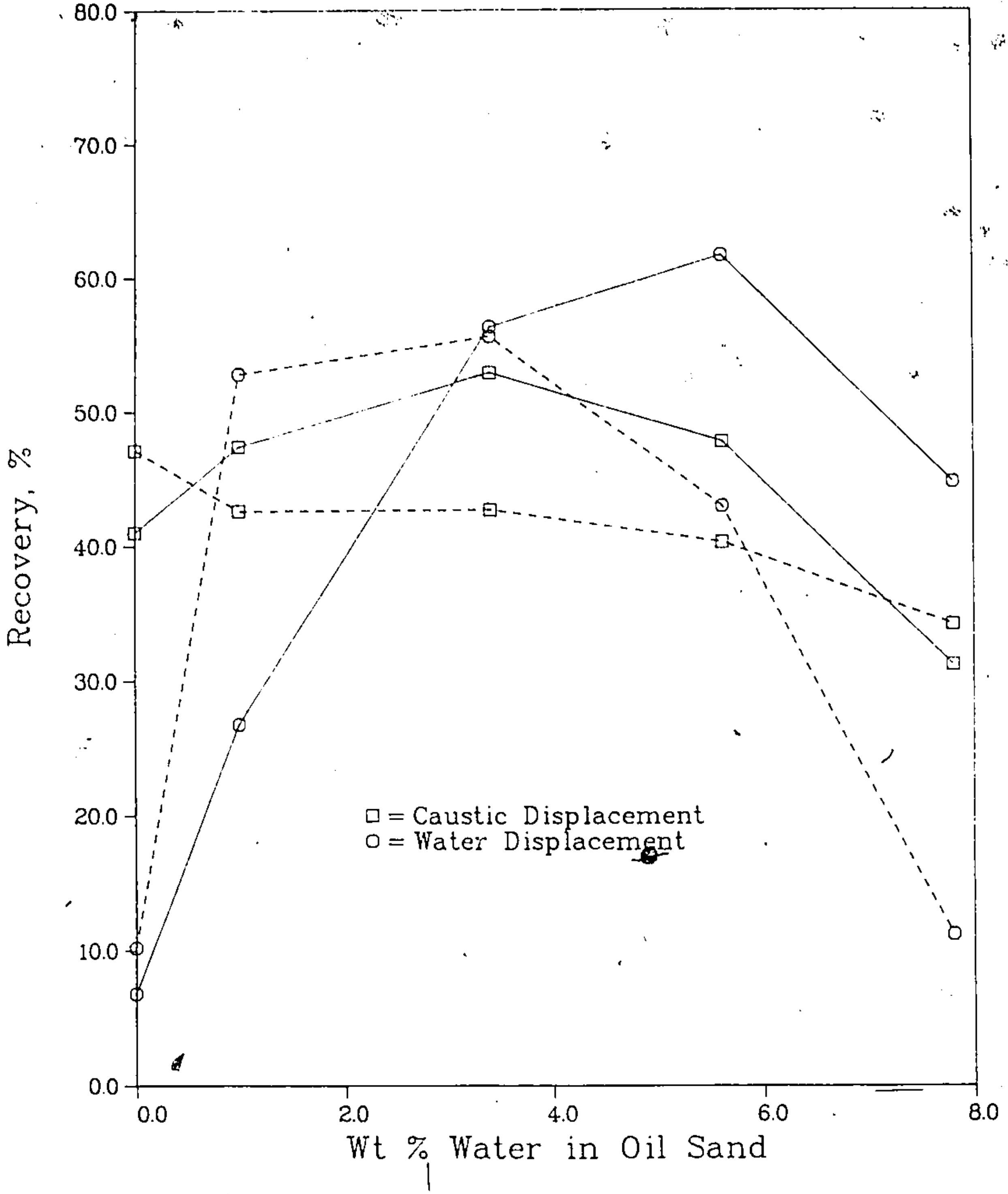


Figure 4-24. Recoveries from oil sands reconstituted with castor oil: sand pretreated at 300°C (——) and 775°C (---).

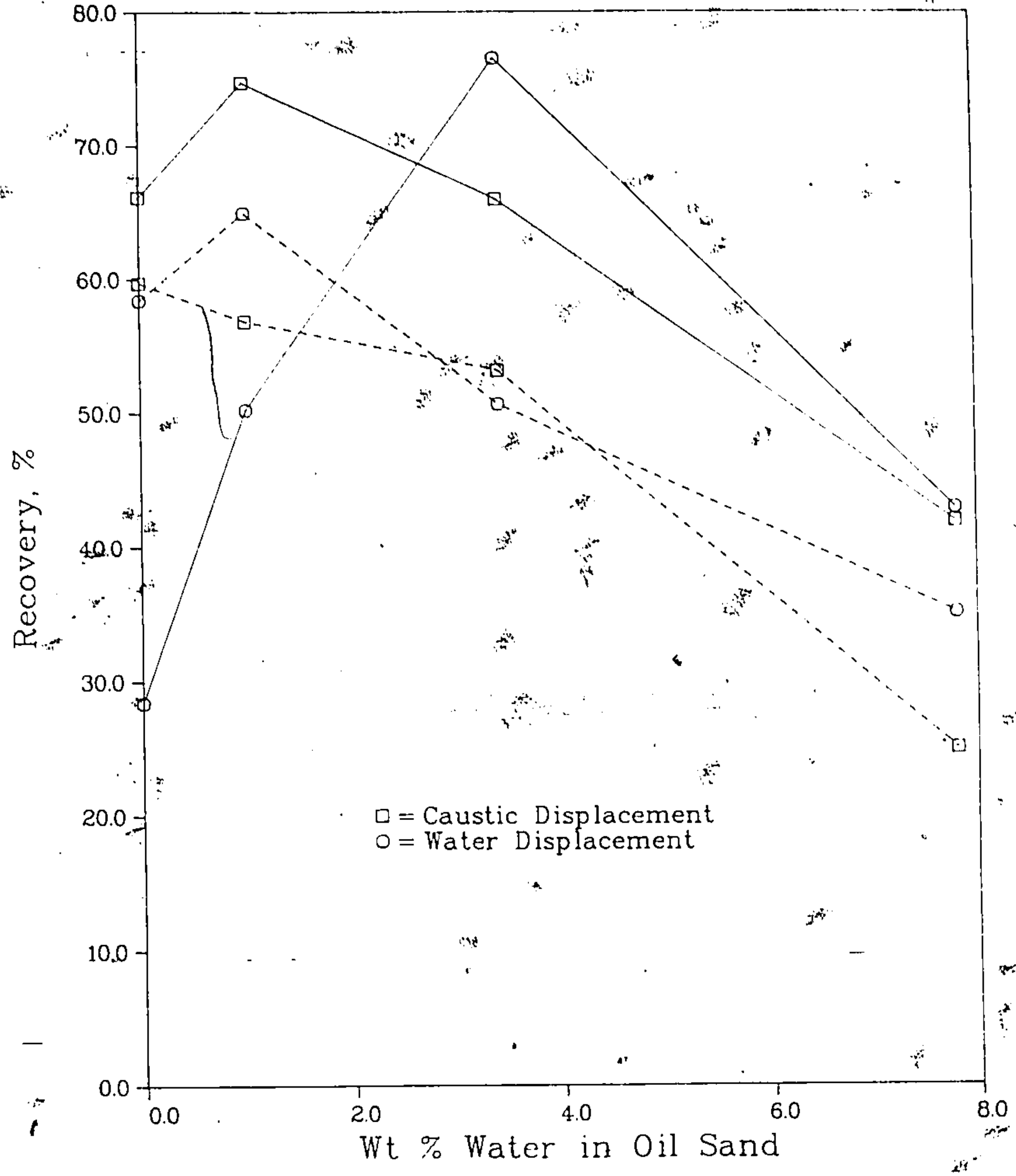


Figure 4-25. Recoveries from oil sands reconstituted with paraffin oil: sand pretreated at 300°C (——) and 775°C (---).

and in fact water appeared to be superior to caustic as a displacement agent in some cases.

The results obtained using the paraffin oil as the organic phase, in Figure 4-25, contain two features of note. First, at zero initial water content the recovery using caustic was much better than that using water for the oil sand containing 300°C-processed sand. Recalling that this oil contained no acidic groups, this result suggests that the interaction between caustic and humic material on the sand was responsible for its incremental recovery. Secondly, when the oil sand was composed of sand heated to 775°C, the recoveries with caustic and water became equivalent for all water saturations. In this case, neither the sand nor the oil contained reactive acidic groups hence caustic was no more effective than water as a displacing liquid.

These results confirmed earlier observations and explanations. The displacement process is a function of the surface characteristics of the sand, the connate water content and the nature of the organic phase. Furthermore, interactions between these three variables have been observed. The influence exerted by any one of them depends on the conditions prevailing in the other two.

4.11 Dean Stark analytical method

The most significant deviation of the present Dean Stark procedure from the one developed at the Alberta Research Council (85), is the evaporation of toluene from the oil at room temperature rather than at 90°C. The motivation for this change was a concern that at 90°C, the volatility of the oil (particularly components other than bitumen) could give rise to significant amounts of the oil being evaporated with the toluene, thus distorting the recovery data.

The rates of evaporation of toluene, bitumen and hexadecane are shown in Table ~~4-4~~. It is noted that the rate of evaporation of hexadecane at room temperature is approximately equal to that of bitumen and both are about four orders of magnitude lower than the rate of toluene evaporation. Therefore, the selective removal of toluene was easy even at room temperatures. The experimental method adopted was to record the weight of the drying pan and its contents until two successive weights obtained an hour apart agreed to within 1%. This ensured that there was not a significant amount of toluene remaining in the sample to influence the subsequent calculation of the recovery efficiency.

Controlled tests of this method were conducted by placing known weights of hexadecane and bitumen along with toluene into the Dean Stark apparatus and refluxing the mixture for three hours. Afterwards, the contents of the flask were emptied into a drying pan and the evaporation procedure followed as outlined. In these tests, possible losses during reflux as well as during evaporation were compounded. After drying to consistent weight it was found that the agreement between the known initial weights and the measured final weights was within 2%. Further controlled testing of just the room temperature evaporation stage was performed using known weights of hexadecane and bitumen in weight ratios ranging from 10 to 30% hexadecane. In all cases, following the established procedure, the initial and final weights agreed to within 2%.

In some experiments the organic phase was composed of castor or paraffin oils. The modified Dean Stark procedure was tested using a known weight of castor oil and the agreement between initial and final weights was within 1%. A controlled test was not done with paraffin oil because it is basically a heavier analogue of hexadecane. Therefore, it has been concluded that following the analytical procedure described herein, it is possible to accurately measure the oil content of an oil sand sample for all of the organic phases which were used.

A controlled test was also done to determine if fine particles in the sand passed through the extraction thimble during reflux. Known weights of kaolinite and sand were placed in an extraction thimble and refluxed. Afterwards the thimble was removed from the apparatus and the toluene removed. The final weight agreed exactly with the initial weight hence none of the kaolinite was carried over by the toluene or passed through the pores of the extraction thimble.

The recovery reported in this research was calculated by measuring the amount of oil and the amount of sand contained in a swept pellet. The final oil-sand weight ratio was compared to the initial oil-sand weight ratio to calculate the recovery according to the formula:

$$\text{Recovery} = [(\text{oil/sand})_{\text{init}} - (\text{oil/sand})_{\text{fin}}] / (\text{oil/sand})_{\text{init}}$$

Comparing the oil to sand weight ratio provides a more accurate estimate of the recovery than would be obtained by comparison of the masses of oil alone. Some of the oil sand gets left on the walls of the displacement cell when the pellet is dislodged. If it is assumed that the oil-sand ratio in this lost sand is the same as in the pellet, the calculated recovery is not affected by these losses. However, if absolute masses of oil were compared, then the oil left behind while dislodging the pellet would incorrectly appear in the calculation of recovery as displaced oil.

An overall oil mass balance was measured by comparing the initial known weight of oil in the pellet and the sum of the produced and residual oil weights, after displacement. An overall sand balance was measured by comparing the initial sand weight with the sum of the sand weight in the swept pellet plus the weight of sand left in the displacement cell. The overall oil mass balance was 98% complete and the sand balance was more than 99% complete. Therefore, oil sand components were not lost in significant amounts during the experimental sequence. The high oil balance provided the justification for analyzing the residual oil content of a pellet and calculating the recovery by difference. Since the balance was good, this procedure did not introduce significant error into the calculated results.

4.12 Preservation of oil sand samples

The batch of oil sand received from the Alberta Research Council Sample Bank was divided into 500 g packets and stored at -18°C. At this temperature, the rates of water evaporation and oil oxidation are very slow, and the oil sand characteristics remain essentially constant for extended periods of time (89).

The reconstituted oil sand samples were stored in capped jars at room temperature. A change was noted in the recovery performance of these oil sands if they were stored for long periods. Table 4-27 shows the recovery data for an oil sand comprised of: 84% by weight 300°C-processed sand, 3.4% distilled water and 12.6% of a mixture of 20% hexadecane in bitumen. It is seen that after storing for 32 days the recovery was much lower than it had been in experiments performed when the oil sand was fresher. This difference is attributed to a lowering of the water saturation within the oil sand. When stored for long periods of time, significant amounts of water may be evaporated from the oil sand. A similar trend was observed in Figure 4-12. At low connate water saturations, the recovery with a displacing phase of water was relatively low.

Therefore, if samples of reconstituted oil sand are to be saved for longer term use, additional precautions would have to be taken. The batches could be stored at lower temperatures or the containers could be hermetically sealed to prevent the escape of water vapour. The problem was avoided in this work by using only freshly prepared oil sand samples.

Table 4-27. Influence of storage time, after reconstitution, on the efficiency of displacement by water.

Storage time, days	Recovery, %
4	52.5
5	54.9, 54.6
6	54.5
32	11.3
46	2.1

5. CONCLUSIONS

The following conclusions have been formulated:

1. A rapid, reproducible elemental model test method has been developed for studying the displacement of bitumen from compacted oil sand. The method shows promise as a screening procedure for assessing the influence on recovery, of changes to the displacement conditions.

2. A reconstitution procedure was developed which permitted the formulation of specifically designed oil sand samples. The characteristics of each of the components comprising oil sand was controlled, and the resulting samples tested to observe the effect of introduced changes, on the recovery efficiency. The test can be used to assess the effect of very specific changes to the oil sand composition.

3. The use of hexadecane diluent to lower the bitumen viscosity introduced the ability to perform displacement experiments at near-ambient temperatures while retaining most of the oil sand chemistry. The viscosity of mixed solutions can be estimated to within 20% using the Cragoe correlation. The density of hexadecane-bitumen combinations can be calculated to within 0.5% by assuming ideal mixing.

4. As the oil sand pack density increased, the recovery by water increased and the recovery by alkaline solution remained constant. This difference has been attributed to a physically-controlled displacement mechanism for water compared to a chemically-controlled mechanism for caustic solution. Therefore

consideration must be given to controlling the oil sand pack density, or accounting for its influence on the displacement process.

5. The connate water saturation added during reconstitution significantly affected the recovery behaviour. Its influence was more pronounced in water displacement experiments. At low saturations, the recovery by alkaline solution was much higher than the recovery by water. As the saturation increased, the recovery by water increased dramatically, while the recovery by caustic remained largely unchanged. According to the disjoining pressure concept, the sand-bitumen interaction is strongest at low water saturations. This factor apparently influences water recovery, but is overcome by the chemically-controlled caustic displacement process. Therefore, in the course of conducting displacement experiments it is essential that the water saturation characteristics within the porous medium be known.

6. The recoveries resulting from displacement by caustic and water were a function of the temperature at which the clean sand had been heated prior to reconstitution. For a connate water content of 3.4% by weight, the difference between caustic and water recoveries increased up to a pretreatment temperature of 400°C and then declined to zero by 650°C. Although recoveries with alkaline solution and water were equivalent when the clean sand had been heated to 775°C prior to reconstitution, the incremental recovery due to caustic was restored by addition of humic material back to such a sand. This behaviour is ascribed to the initial presence of humic material which was oxidized and

removed upon extreme heating. The humic acid interacted with caustic to lower the interfacial forces in the oil sand thus rendering displacement by alkaline solution more efficient than water displacement. After removal of the humic material, caustic and water became equally effective displacing phases. These findings have important consequences in modelling studies. The sand fraction of oil sand should not be regarded as a mixture of inorganic species, rather the presence of a surface layer of organic material and affiliated kaolinite should be incorporated into the model design.

7. Analysis of the humic material detected high carbon and oxygen contents. The organic material was intimately affiliated with kaolinite, possibly through a metal complex linkage. Scanning electron microscopy revealed that sands which had been dried at 25°C contained aggregates which were not present in sands heated to 775°C. From x-ray analysis it appeared that the humic, and affiliated, material were responsible for cementation of these aggregates.

8. In samples of reconstituted oil sand containing only the maltene fraction, an incremental recovery with caustic compared to water was observed. The interfacial tension characteristics of caustic vs. maltene and caustic vs. hexadecane-bitumen were similar. Thus the removal of the asphaltenes did not affect the interfacial activity of the organic phase. None of the recombined subfractions of maltene exhibited low interfacial tensions, thus difficulties arise in attempting to recreate the parent material by simple remixing of its constituents.

6. RECOMMENDATIONS

Based on the conclusions formulated in this work, the following related topics are suggested as possible future research endeavours:

1. The research could be extended to reconstitution of samples as similar as possible to mined oil sand (i.e. unaltered bitumen would be employed). Parallel experiments at high temperature would permit direct comparison of results obtained using mined and reconstituted oil sand samples having the same composition. To achieve satisfactory mixing during reconstitution, the tumbling would have to be performed at an elevated temperature to lower the bitumen viscosity. Precautions would thus have to be taken to preclude the evaporation of significant amounts of water under those conditions.

2. A scaled physical model could be developed to test the findings of the present research. The results from a scaled model are more likely to be applicable in a reservoir situation than the results from an elemental model. The results of the present work would ideally be incorporated into the design of such a scaled model.

NOTATION

A	empirical constant (Section 2)
	Hamaker constant (Appendix 1)
B	empirical constant
d	characteristic dimension of a porous medium
D	dielectric constant
e	electron charge
f	weight fraction
g	gravitational constant
h	water layer thickness
k	absolute permeability (Section 2)
	Boltzmann constant (Appendix 1)
k_i	effective permeability to ith fluid
k_{ri}	relative permeability to ith fluid
L	liquidity
M	mass (Section 2.6)
	mobility ratio (Section 2.7)
n	empirical constant (Section 2)
	number of counterions per unit volume (Appendix 1)
N_b	Bond number
N_{ca}	capillary number
o	(subscript) pertaining to the oil phase
p	static pressure
p_c	capillary pressure
P	combined static and gravitational pressure
q	linear velocity
r	radius
R	principal radius of curvature
Re	Reynold's number
S	saturation
t	temperature, °C
T	absolute temperature
V	volume fraction (Section 2.6)
	absolute volume (Section 2.7)
w	(subscript) pertaining to the aqueous phase

y	reduced surface potential
z	counterion valence
β	specific surface area
γ	interfacial tension
ϵ	permittivity of the aqueous phase
ϵ_o	permittivity of a vacuum
θ	contact angle
κ	Debye-Huckel reciprocal double layer thickness
λ	London wavelength
η	viscosity
ν	kinematic viscosity
ρ	density
ψ	surface potential
ϕ	porosity
$\Delta\rho$	density difference
$\underline{\nabla}$	del operator

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APPENDIX 1: Calculation of disjoining pressure

The disjoining pressure is a composite of three interactions: the electrical double layer forces, van der Waals attraction and hydration forces. The hydration forces only become significant at very close approach and hence are ignored. The calculation is based on a model of a charged sand surface and a parallel charged surface of bitumen, with an aqueous conductor in between them. Since the bitumen and sand surfaces are both negatively charged, the double layer force is repulsive. The disjoining pressure as a function of the separation between the surfaces (the water layer thickness), h, is:

$$P_d(h) = P_r(h) + P_a(h) \qquad \text{(A1-1)}$$

where P_r and P_a are the repulsive and attractive pressures, respectively. Both are functions of the separation distance. The repulsive component is calculated from:

$$P_r(h) = n\ k\ T\ (C_1/C_2) \qquad \text{(A1-2)}$$

$$C_1 = y_1^2 + y_2^2 + 2\ y_1\ y_2 \cosh\ (\kappa h) \qquad \text{(A1-3)}$$

$$C_2 = \sinh^2\ (\kappa h) \qquad \text{(A1-4)}$$

where n is the number of counterions per unit volume, k is the Boltzmann constant and T is the absolute temperature. The subscript 1 refers to the bitumen and 2 refers to the sand. The reduced surface potential, y, is calculated from:

$$y_i = z\ e\ \psi_i \ / \ k\ T \qquad \text{(A1-5)}$$

where z is the counterion valency, e is the electron charge and ψ is the surface potential. The surface potential has been approximated by the zeta potential as measured from electrophoretic mobilities. The Debye-Huckel reciprocal double layer thickness, κ , is obtained from:

$$\kappa^2 = 2\ e^2\ n\ z^2 \ / \ \epsilon\ k\ T \qquad \text{(A1-6)}$$

where ϵ is the permittivity of the aqueous phase. It is calculated from:

$$\epsilon = D\ \epsilon_o \qquad \text{(A1-7)}$$

where D is the dielectric constant of water and ϵ_o is the permittivity of a vacuum.

Equation A1-2, as written, is valid if constant charge density is assumed. If constant potential is assumed then the 2 y_1 y_2 term should be preceded by a negative sign. Determining the appropriate condition is largely a matter of trial-and-error curve fitting of the data to both variations of the equation to see which performs better.

The attractive component is obtained from:

$$P_a(h) = (-A \ / \ 12\ \pi\ h^3)\ C_3 \qquad \text{(A1-8)}$$

$$C_3 = [15.96(h/\lambda) + 2]/[1 + 5.32(h/\lambda)]^2 \quad \text{(A1-9)}$$

where A is the Hamaker constant (approximated to be 10^{-20} J) and λ is the London wavelength (approximated to be 100 nm).

APPENDIX 2: Dean Stark oil sand analysis

The Dean Stark analysis is a procedure for determining the amounts of sand, aqueous phase and organic phase present in a given sample of oil sand. The apparatus is represented in Figure A2-1. It is comprised of a 1000 mL round-bottomed flask, a still head with a side-arm water trap, a thimble support which is suspended from the still head, a condenser, a heating mantle and a variac to control the rate of heating.

The detailed procedure used in this research is as follows. Whatman 43 x 123 mm, single thickness, cellulose extraction thimbles are stored in an oven at 90°C. The reason being that they are hygroscopic. If no precautions are taken, the amount of absorbed water will vary depending upon ambient conditions, thus introducing an erratic source of error when weighing the empty thimble. To avoid this problem, the thimble is taken from the oven and weighed immediately to the nearest 0.01 g. Table A2-1 shows that prolonged standing can lead to an appreciable weight gain due to water absorption. The oil sand to be analyzed is added to the thimble, quantitatively only when an overall mass balance is to be performed. In the course of analyzing most displacement runs it was only the weights of the sand and oil which were important so the oil sand weight initially was not needed. The thimble plus oil sand is placed in a wire basket underneath a solvent distributor and the entire assembly suspended from the still head. Approximately 300 mL of reagent grade

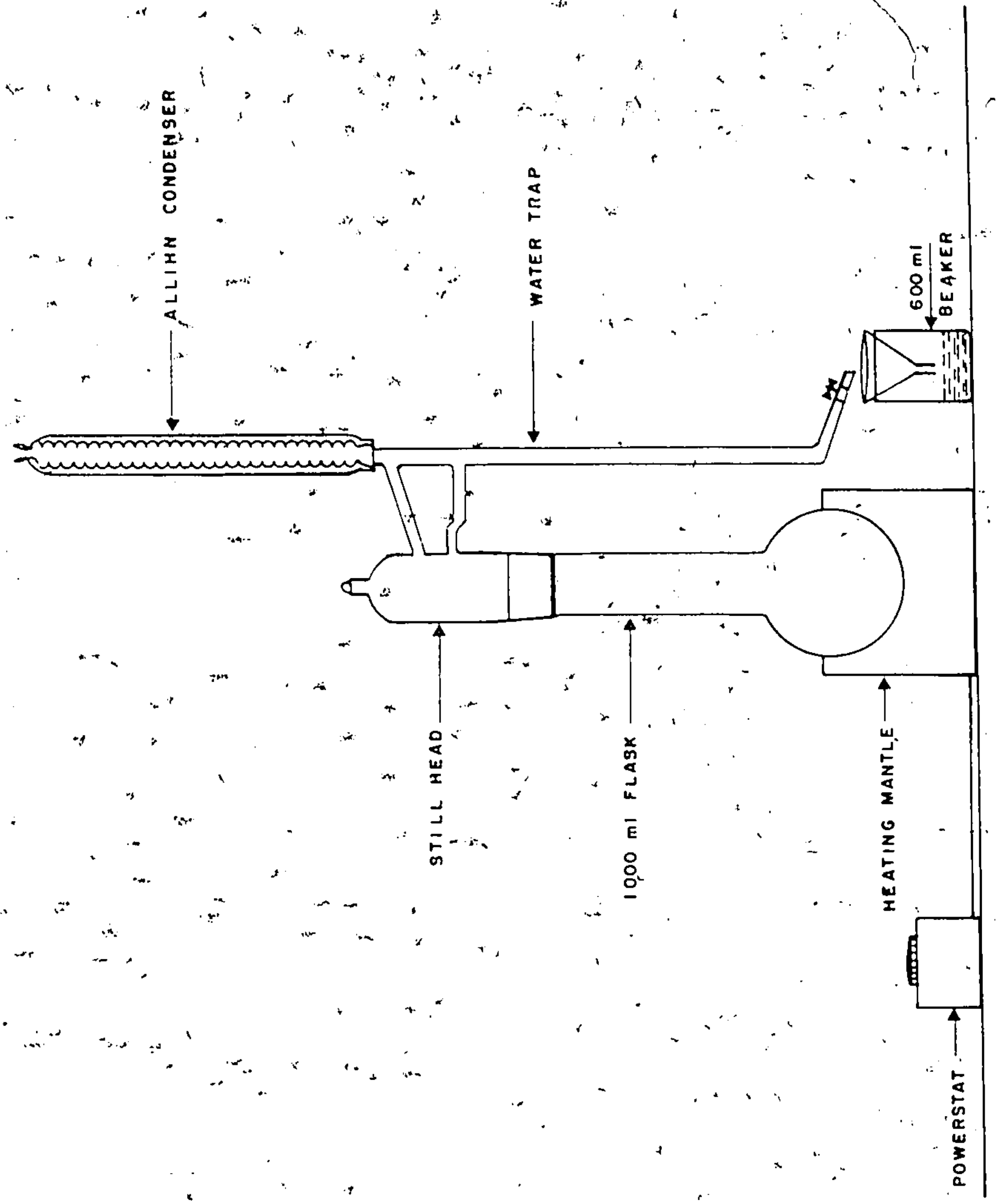

Figure A2-1. Dean Stark solvent extraction apparatus.

TABLE A2-1. Increase in extraction thimble weight with time out of 90°C oven.

Time, min	Weight, g
0	7.25
1	7.29
2	7.30
3	7.32
4	7.32
5	7.34
10	7.36
20	7.40
66	7.50

toluene (Anachemia) is added to the flask and the connections between the still head and the flask, and the side-arm and the condenser made. The exposed part of the flask and the still head are wrapped with fibreglass tape insulation and the power turned on. During reflux, the water in the oil sand is azeotropically distilled with the toluene. Upon condensation the heavier water collects in the side-arm trap while the lighter toluene refluxes back into the still head. The bitumen (or the oil being analyzed) is solubilized by the toluene and collects in the still pot. The reflux is continued until the droplets of toluene falling from the thimble assembly are colourless, indicating that all of the bitumen has been stripped from the sand. This normally takes from 2 to 3 hours. Once completed, the stopcock at the bottom of the side-arm is opened. If the amount of water is to be measured, the contents of the trap are passed through Whatman 1 PS phase separating filter paper. The toluene passes through the paper while the water is retained. Once all of the water has been collected and freed of toluene, it is poured into a tared bottle and weighed. The stopcock is left open to permit the distillation of additional toluene until only 150 to 200 mL of solution remains in the pot. At that time, the power is shut off, the insulation removed and the system left to cool. Once cooled, the contents of the pot are quantitatively transferred to a tared aluminum pan. The thimble plus sand is placed in a vented oven overnight at 90°C to remove the toluene. The toluene-oil mixture is placed in a fume hood with the door drawn down sufficiently to generate a moderate rate of air flow over the liquid surface. The next day, the thimble is removed from the oven and weighed immediately. It is important to note that the initial thimble weighing procedure and the procedure for weighing the thimble plus sand are identical, thus minimizing any error attributable to differing amounts of absorbed water. The aluminum pan plus extracted oil is weighed to determine the weight of oil. Both of these weighing steps are repeated until successive readings taken an hour or more apart agree to within 1%. This was never a problem with the thimble plus sand, it had always reached its completely dried weight by the time the first measurement was made. With the toluene-oil mixture however, it was sometimes necessary to perform several drying-weighing cycles to achieve the desired accuracy. At the end, all of the components of the oil sand have been independently weighed. If a mass balance is being performed, the sum of the three weights can be compared to the initial weight of oil sand to get a measure of the precision of the method.

APPENDIX 3: Factorial design of pack density variables

The coding technique was used so that each of the variables in Table 4-9 had a value of +1 at its upper level and a value of -1 at its lower level. The 16 experiments and the resulting pack densities are shown in Table A3-1. The parameters are ordered in the same way as they appear in Table 4-9. The defining relation for this fractional design is:

$$I = x_1x_2x_3x_4x_5$$

The calculated parameter estimates are listed in Table A3-2. From 3 centrepoint repeats, the standard deviation of these measurements was calculated to be 0.0058. Therefore, the 95% confidence interval is:

$$\pm\, t_{2,0.025}\, s / (n)^{0.5}$$

$$= \pm\, (4.303)\ (0.0058)\ /\ (16)^{0.5}$$

$$= \pm\, 0.0062$$

From inspection of the data the significant variables are: the packing pressure, the sand mass and the number of compaction steps. Although the compaction and release time main effects appeared to be insignificant, their interaction term does seem to be significant, hence these parameters were also held constant.

Table A3-1. Experimental conditions and results.

Test	x_1	x_2	x_3	x_4	x_5	Density, g/cm^3
1	-1	-1	-1	-1	1	2.009
2	1	-1	-1	-1	-1	2.019
3	-1	1	-1	-1	-1	1.938
4	1	1	-1	-1	1	2.049
5	-1	-1	1	-1	-1	2.019
6	1	-1	1	-1	1	2.122
7	-1	1	1	-1	1	1.983
8	1	1	1	-1	-1	2.035
9	-1	-1	-1	1	-1	1.999
10	1	-1	-1	1	1	2.151
11	-1	1	-1	1	1	1.997
12	1	1	-1	1	-1	2.000
13	-1	-1	1	1	1	1.983
14	1	-1	1	1	-1	2.035
15	-1	1	1	1	-1	1.960
16	1	1	1	1	1	2.103

Table A3-2. Parameter estimates.

Variable	Coefficient
average effect	2.025
x_1	0.0391
x_2	-0.0170
x_3	0.0049
x_4	0.0034
x_5	0.0245
x_1x_2	-0.0005
x_1x_3	0.0046
x_1x_4	0.0046
x_1x_5	0.0175
x_2x_3	0.0073
x_2x_4	0.0035
x_2x_5	0.0004
x_3x_4	-0.0131
x_3x_5	-0.0068
x_4x_5	0.0055

APPENDIX 4. Factorial design of operational parameters

The experimental conditions and displacement results are listed in Table A4-1. The defining relation is:

$$I = x_1x_2x_3x_4x_5$$

The calculated parameter estimates are listed in Table A4-2. Repeat experiments were performed at the centrepoints of the first 4 variables using both water and caustic displacing phases. The standard deviation of 5 repeats using water was 4.4, and the standard deviation of 4 repeats using caustic was 6.2. The F-test was used to see if these values were significantly different. They were not, so a pooled standard deviation of 5.2 with 7 degrees of freedom was used to calculate the 95% confidence interval for the parameter estimates. The confidence interval is:

$$\pm t_{7,0.025}\ s\ /\ (n)^{0.5}$$

$$= \pm 3.10$$

The only parameter significant at this level is the nature of the displacing phase.

Table A4-1. Experimental conditions and recovery results.

Test	x_1	x_2	x_3	x_4	x_5	Recovery, %
1	-1	-1	-1	-1	1	57.1
2	1	-1	-1	-1	-1	47.4
3	-1	1	-1	-1	-1	42.6
4	1	1	-1	-1	1	60.4
5	-1	-1	1	-1	-1	36.3
6	1	-1	1	-1	1	58.4
7	-1	1	1	-1	1	53.4
8	1	1	1	-1	-1	44.4
9	-1	-1	-1	1	-1	46.2
10	1	-1	-1	1	1	61.1
11	-1	1	-1	1	1	61.5
12	1	1	-1	1	-1	41.7
13	-1	-1	1	1	1	53.4
14	1	-1	1	1	-1	42.6
15	-1	1	1	1	-1	44.5
16	1	1	1	1	1	69.6

Table A4-2. Parameter estimates.

Variable	Coefficient
average effect	51.3
x_1	1.91
x_2	0.975
x_3	-0.963
x_4	1.29
x_5	8.08
x_1x_2	-0.150
x_1x_3	1.51
x_1x_4	-0.738
x_1x_5	1.10
x_2x_3	1.68
x_2x_4	0.775
x_2x_5	0.888
x_3x_4	0.913
x_3x_5	0.300
x_4x_5	0.750

APPENDIX 5. Factorial design of compositional variables

The experimental conditions are shown in Table A5-1. The defining relations are:

$$I = x_1x_2x_3x_5 = x_1x_2x_4x_6 = x_2x_3x_4x_7 = x_3x_4x_5x_6$$
$$= x_1x_4x_5x_7 = x_1x_3x_6x_7 = x_2x_5x_6x_7$$

The normalization procedure for the water displacement results was to multiply the observed recovery by an appropriate factor taken from Figure 4-9. For example, to normalize the recovery observed in the first experiment to a density of 2.10 the procedure is as follows:

From Fig. 4-9: (recovery at 2.10)/(recovery at 2.00) = 1.16

Therefore, normalized recovery = (1.16) (7.4) = 8.6

The observed and normalized recoveries are presented in Table A5-2. The calculated parameter estimates for each set of recovery data are shown in Table A5-3. Information about the standard deviation was not obtained in these experiments. If it is assumed that these measurements were drawn from a population having the same variance as the data in Appendix 4, the same 95% confidence interval can be applied. Alternatively, one could simply compare the relative magnitudes of the parameter estimates to determine which exert the strongest effect on recovery. From inspection of the data, the strongest main effects were the nature of the displacing phase and the water saturation, with the former exerting the stronger influence. If the confidence interval of ± 3.10 from the design of operational variables is applied, then both of the mentioned variables were significant at the 95% level, independent of the normalization procedure used.

Table A5-1. Experimental conditions.

Test	x_1	x_2	x_3	x_4	x_5	x_6	x_7
1	-1	-1	-1	-1	-1	-1	-1
2	1	-1	-1	-1	1	1	-1
3	-1	1	-1	-1	1	1	1
4	1	1	-1	-1	-1	-1	1
5	-1	-1	1	-1	1	-1	1
6	1	-1	1	-1	-1	1	1
7	-1	1	1	-1	-1	1	-1
8	1	1	1	-1	1	-1	-1
9	-1	-1	-1	1	-1	1	1
10	1	-1	-1	1	1	-1	1
11	-1	1	-1	1	1	-1	-1
12	1	1	-1	1	-1	1	-1
13	-1	-1	1	1	1	1	-1
14	1	-1	1	1	-1	-1	-1
15	-1	1	1	1	-1	-1	1
16	1	1	1	1	1	1	1

Table A5-2. Observed and normalized recoveries.

Test	Density, g/cm3	Recovery, %	Recovery (2.00), %	Recovery (2.10), %
1	2.00	7.4	7.4	8.6
2	1.92	19.1	25.6	29.6
3	1.87	38.3	38.3	38.3
4	1.94	46.0	46.0	46.0
5	2.01	36.1	36.1	36.1
6	2.07	51.2	51.2	51.2
7	1.98	0.0	0.0	0.0
8	1.95	6.8	8.0	9.3
9	2.01	32.0	32.0	32.0
10	1.92	51.3	51.3	51.3
11	1.87	21.9	39.6	46.0
12	1.91	3.1	4.3	5.0
13	1.99	12.1	12.6	14.4
14	2.04	0.0	0.0	0.0
15	1.97	48.8	48.8	48.8
16	1.93	57.7	57.7	57.7

Table A5-3. Parameter estimates for each set of recovery data.

Variable	Parameter estimates using:		
	Recovery	Recovery (2.00)	Recovery (2.10)
average	27.0	28.7	29.6
x_1	2.41	1.83	1.62
x_2	0.84	1.66	1.74
x_3	-0.40	-1.88	-2.46
x_4	1.38	2.11	2.26
x_5	3.43	4.97	5.69
x_6	-0.30	-0.97	-1.12
x_7	18.19	16.49	15.53
$x_1x_2+x_3x_5+x_4x_6$	-1.84	-3.17	-3.51
$x_1x_3+x_2x_5+x_6x_7$	-0.08	0.59	0.74
$x_1x_4+x_2x_6+x_5x_7$	-2.75	-4.29	-5.02
$x_1x_5+x_2x_3+x_4x_7$	0.90	0.17	0.02
$x_1x_6+x_2x_4+x_3x_7$	3.68	5.17	5.73
$x_1x_7+x_4x_5+x_3x_6$	3.96	4.54	4.76
$x_2x_7+x_3x_4+x_5x_6$	1.69	0.87	0.78
third order terms	-0.39	0.94	1.28

APPENDIX 6: Calculation of flow parameters

Reynolds number. A Reynolds number calculation must be performed to determine whether the displacement experiments were conducted in the seepage velocity domain. The form of the Reynolds number for flow in a porous medium is:

$$Re = q\ d\ \rho / \eta \qquad (2.7\text{-}3)$$

The highest flowrate attainable using the Ruska pump was 288 cm^3/h and the cross-sectional area of the cell was 5.067 cm^2, so the maximum value for the linear velocity was:

$$\begin{aligned} q &= (288) / [(5.067)\ (3600)] \\ &= 0.0158 \text{ cm/s} \end{aligned}$$

Although the flow was two-phase, in this calculation it is assumed that only water was flowing. This will yield a maximal value for the ratio ρ/η. At 45°C, for example:

$$\rho = 0.990 \text{ g/cm}^3$$

$$\eta = 0.596 \text{ cp}$$

The characteristic pore diameter is a vague parameter. The value of 15×10^{-4} cm suggested by Hall et al. (43) has been used. The value for the Reynolds number is thus:

$$Re_{max} = (0.0158)\ (0.990)\ (0.0015)\ /\ (0.00596)$$
$$= 0.0039$$

Since this upper bound on the Reynolds number is in the seepage velocity domain, all of the displacement experiments were in the Darcy-type flow region.

Pressure drop in glass bead sections. The displacement cell had an inside diameter of 2.54 cm and an inside length of 38.10 cm. A typical oil sand pellet weighing 40 g and packed to a density of 2.00 g/cm^3 occupied 3.95 cm of the cell length. The remaining 34.15 cm was filled with glass beads. The inlet and outlet side pressures were measured at the entrance and exit points of the cell. Therefore, the measured pressure drop across the cell was a sum of the pressure drops across the oil sand pellet and the glass bead sections. The glass beads were 5 mm spheres packed to a porosity of 42%. The permeability of the bead sections is calculated using the Kozeny-Carman relation, Equation 2.7-4. The equation should work well in this idealized porous medium. Its form is:

$$k = \phi^3 / [5\ \beta^2\ (1-\phi)^2] \qquad (2.7\text{-}4)$$

β = surface area of a sphere / volume of a sphere
= $3/r$

where r is the radius of the sphere. Therefore, the permeability is:

$$k = (0.42)^3 / [5\ (3/0.25)^2\ (0.58)^2]$$

$$= 3.06\times10^{-4}\ \mathrm{cm}^2$$

The simplified form of Darcy's law assuming a linear pressure drop is:

$$q = -k\ \Delta p\ / \eta\ \Delta x$$

Substituting the following values:

$$q = 0.0113\ \mathrm{cm/s}$$

$$\eta(\mathrm{water},\ 45^{\circ}\mathrm{C}) = 0.596\ \mathrm{cp}$$

$$\Delta x = 34.15\ \mathrm{cm}$$

the pressure drop across the glass bead sections was:

$$p = (0.0113)\ (0.00596)\ (34.15)\ /\ (3.06\mathrm{x}10^{-4})$$

$$= 7.52\ \mathrm{g/cm\ s}^2$$

$$= 0.752\ \mathrm{Pa}$$

Compared to measured pressure drops of 100 kPa and greater, the pressure drop across the glass beads was insignificant. Therefore, essentially all of the measured pressure drop occurred across the oil sand pellet.

Permeability of oil sand pellet. The effective permeability to water can be calculated from the pressure drop history of a displacement test. Typical pressure drop behaviour during water displacement experiments is shown in Table A6-1. The pressure drop during alkaline flooding was not as consistent from experiment to experiment. The effective permeability at the beginning of a displacement test (after 1 min) can be calculated by rearrangement of Equation 2.7-4 as follows:

$$\begin{aligned} k_w &= q_w \eta_w \Delta x / \Delta p_w \qquad \text{(A6-1)} \\ &= (0.0113)\ (0.00596)\ (3.95)\ /\ (6.89 \times 10^5) \\ &= 3.86 \times 10^{-10}\ \mathrm{cm}^2 \end{aligned}$$

At the end of a test (20 min) only the pressure drop changed, thus the effective permeability decreased to 1.93×10^{-10} cm^2. The saturation conditions within the oil sand pellet were known at the beginning and end of an experiment only. The initial saturations in an oil sand composed of: 84% by weight sand, 3.4% water and 12.6% of a mixture of 20% hexadecane in bitumen are shown in Table 4-3. Since the system was evacuated and filled with displacing liquid prior to an experiment, the listed water and air saturations are summed to yield the overall water saturation. For a pack density of 2.00 g/cm3, the total initial water saturation was 26.6%. Assuming a recovery efficiency of 40%, the final oil saturation would be 44.0%, hence the final water saturation would be 56.0%. The relative permeability to water at each of these saturation conditions can be estimated using:

$$k_{rw} = S_w^3 \qquad (2.7\text{-}8)$$

For water saturations of 26.6 and 56.0% the relative permeabilities to water are calculated to be 0.0188 and 0.176 respectively. From Equation 2.7-7, the absolute permeabilities at the beginning and end of a water displacement experiment are estimated to be 2.05×10^{-8} and 1.10×10^{-9} cm^2 respectively.

Table A6-1. Pressure drop vs. time during a typical water displacement experiment.

Time, min	Pressure drop, kPa
1	68.9
5	68.9
10	103
15	103
20	138