

## **EXTRACTION TECHNOLOGIES FOR NATURAL BITUMEN AND HEAVY OIL**

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### **Summary**

Tar sand (also known as oil sand and bituminous sand) is a sand deposit that is impregnated with dense, viscous petroleum-like material called bitumen. Tar sand deposits are widely distributed throughout the world and the various deposits have been described as belonging to two types: (a) stratigraphic traps; and (b) structural traps although gradations between the types of deposit invariably occur.

Methods for the recovery of bitumen from tar sand are based either on mining combined with some further processing or operation on the tar sands in situ. The mining methods are applicable to shallow deposits, characterized by an overburden ratio less than 2.0, i.e. the overburden depth to thickness of tar-sand deposit is less than 2.0. The Athabasca deposit is mine able within current concepts of the economics and technology of open-pit mining. Because of the chemical and physical properties of the bitumen, non-mining (in situ) recovery techniques have not had the same degree of success as recovery operations. However, heavy oil, which has a varying degree of mobility in the reservoir, can be successfully recovered by use of non-mining secondary and tertiary recovery techniques.

The API gravity of tar sand bitumen varies from 5° API to approximately 10° API depending upon the deposit, viscosity is very high, and volatility is low. On the other

hand, the API gravity of heavy oil is on the order of 10 to 20°. The viscosity of heavy oil is high relative to conventional crude oil but is substantially lower than the viscosity of bitumen. Similarly, a higher proportion of heavy oil is volatile relative to bitumen but the constituents of both heavy oil and bitumen exhibit lower volatility than conventional crude oil.

The lack of mobility of bitumen requires a mining step followed by the hot water process that is, to date, the only successful commercial process to be applied to bitumen recovery from mined tar sand. Many process options have been tested with varying degrees of success and one of these options may even supersede the hot water process at some future date.

Heavy oil, because of this greater mobility under reservoir conditions can be recovered by a variety of enhanced oil recovery techniques.

## **1. Introduction**

Conventional crude oil is produced from the oil-bearing formations by drilling wells into the formation. The oil is driven from the formation up through the wells (production wells) by energy stored in the formation, such as the pressure of dissolved natural gas. If this natural energy of the formation is expended or, as in the case of tar sand deposits, if it was never present, then energy must be injected into the formation in order to stimulate production.

## **2. Enhanced Oil Recovery**

In reservoirs that contain heavy oil, it is desirable to initiate enhanced oil recovery (EOR) operations as early as possible. This may mean considerably abbreviating conventional secondary recovery operations or bypassing them altogether. Thermal floods using steam and controlled in situ combustion methods are also used. Thermal methods of recovery reduce the viscosity of the crude oil by heat so that it flows more easily into the production well. Thus advanced techniques are usually variations of secondary methods with a goal of improving the sweeping action of the invading fluid.

Enhanced oil recovery is defined as the incremental ultimate oil that can be economically recovered from a petroleum reservoir over oil that can be economically recovered by conventional primary and secondary methods. The intent of enhanced oil recovery is to increase the effectiveness of oil removal from pores of the rock (displacement efficiency,) and to increase the volume of rock contacted by injected fluids (sweep efficiency).

To understand the phenomenon of enhanced oil recovery, it is helpful to understand the condition in the reservoir after other recovery operations have been exhausted. The oil remaining after conventional recovery operations is retained in the pore space of reservoir rock at a lower concentration than originally existed. In portions of the reservoir that have been contacted or swept by the injection fluid, the residual oil remains as droplets (or ganglia) trapped in either individual pores or clusters of pores. It

may also remain as films partly coating the pore walls. Entrapment of this residual oil is predominantly due to capillary and surface forces and to pore geometry.

In the pores of those volumes of reservoir rock that were not well swept by displacing fluids, the oil continues to exist at higher concentrations and may exist as a continuous phase. This macroscopic bypassing of the oil occurs because of reservoir heterogeneity, the placement of wells, and the effects of viscous, gravity, and capillary forces, which act simultaneously in the reservoir. The resultant effect depends upon conditions at individual locations.

The higher the mobility of the displacing fluid relative to that of the oil (the higher the mobility ratio), the greater the propensity for the displacing fluid to bypass oil. Because of fluid density differences, gravity forces cause vertical segregation of the fluids in the reservoir so that water tends to under-run, and gas to over-ride, the oil-containing rock. These mechanisms can be controlled or utilized only to a limited extent in primary and secondary recovery operations.

Enhanced oil recovery processes use thermal, chemical, or fluid phase behavior effects to reduce or eliminate the capillary forces that trap oil within pores, to thin the oil or otherwise improve its mobility or to alter the mobility of the displacing fluids. In some cases, the effects of gravity forces, which ordinarily cause vertical segregation of fluids of different densities, can be minimized or even used to advantage. The various processes differ considerably in complexity, the physical mechanisms responsible for oil recovery, and the amount of experience that has been derived from field application. The degree to which the enhanced oil recovery methods are applicable in the future will depend on development of improved process technology. It will also depend on improved understanding of fluid chemistry, phase behavior, and physical properties; and on the accuracy of geology and reservoir engineering in characterizing the physical nature of individual reservoirs.

### **3. Chemical Methods**

Chemical methods include polymer flooding, surfactant (micellar or polymer and micro emulsion) flooding, and alkaline flood processes. Polymer flooding (Polymer augmented water flooding) is water flooding in which organic polymers are injected with the water to improve areas and vertical sweep efficiency. The process is conceptually simple and inexpensive, and its commercial use is increasing despite relatively small potential incremental oil production. Surfactant flooding is complex and requires detailed laboratory testing to support field project design.

The terms micro emulsion and micellar solutions are used to describe concentrated, surfactant-stabilized dispersions of water and hydrocarbons that are used to enhance oil recovery. At concentrations above a certain critical value, the surfactant molecules in solution form aggregates called micelles. These micelles are homogeneous, transparent or translucent, and stable to phase separation and are capable of solubilizing fluids in their cores and are called swollen micelles. The term soluble oil is often used to describe an oil external system having little or no dispersed water.

Although used to describe the process, neither micro emulsion or micellar solution accurately describes all compositions that are used in emulsion flooding. In fact, many systems used do not have an identifiable external or continuous phase and these terms do not always apply.

Micro emulsion flooding (micellar/emulsion flooding) refers to a fluid injection process in which a stable solution of oil, water, and one or more surfactants along with electrolytes of salts is injected into the formation and is displaced by a mobility buffer solution. The mobility buffer is in turn displaced by injecting water. Depending on the reservoir environment, a pre-flood may or may not be used. The micro emulsion is the key to the process. Oil and water are displaced ahead of the micro emulsion slug, and a stabilized oil and water bank develops. The displacement mechanism is the same under secondary and tertiary recovery conditions. In the secondary case, water is the primary produced fluid until the oil bank reaches the well.

In micro emulsion flooding, two approaches have developed to enhance oil recovery. In the first process, a relatively low-concentration surfactant micro emulsion is injected at large pore volumes of 15% to 60% to reduce the interfacial tension between the water and oil, thereby increasing oil recovery. In the second process, a relatively small pore volume, from 3 to 20% of a high-concentration surfactant micro emulsion, is injected. With the high concentration of surfactant in the micro emulsion, the micelles solubilize the oil and water in the displacing micro emulsion. Consequently, the high-concentration system may initially displace the oil in a miscible-like manner. However, as the high-concentration slug moves through the reservoir it is diluted by the formation fluids and the process ultimately or gradually reverts to a low-concentration flood. However, this initial displacement forms an oil bank, which is very important in establishing displacement efficiency. Low-concentration systems typically contain 2% by weight to 4% by weight surfactant, whereas high-concentration systems contain 8% by weight to 12% by weight of the surfactant.

Mobility control is important to the success of the process. The mobility of the micro emulsion can be matched to that of the stabilized water-oil bank by controlling the micro emulsion viscosity. The mobility buffer following the micro emulsion slug prevents rapid slug deterioration from the rear and thus minimizes the slug size required for efficient oil displacement. Water external emulsions and aqueous solutions of high-molecular-weight polymers have been used as mobility buffers.

Micro emulsion flooding can be applied over a wide range of reservoir conditions. Generally, wherever a water flood has been successful, micro emulsion flooding may also be applicable. In some cases in which water flooding was a failure because of poor mobility relationships, micro emulsion flooding might be technically successful because of the required mobility control. Of course, if water flooding was a failure because of certain reservoir conditions, such as fracturing or very high permeability streaks, micro emulsion flooding will most likely also fail.

In micro emulsion flooding, the slug must be designed for specific reservoir conditions of temperature, resident water salinity, and crude oil type. If the temperature is very high, a fluid-handling problem may result in the field because of the increased vapor

pressure of the hydrocarbon in micro emulsion. There is a range of oil field characteristics to which micro emulsion flooding can be applied.

In analyzing the applicability of micro emulsion-polymer flooding to a given reservoir, the need for a thorough understanding of the reservoir and fluid characteristics cannot be overemphasized. As mentioned, such characteristics as the nature of the oil and water content, relative permeability, mobility ratios, formation fractures, and variations in permeability, porosity, formation continuity, and rock mineralogy can have a dramatic effect on the success or failure of the process.

Conventional water flooding can often be improved by the addition of polymers (polymer flooding) to injection water to improve the mobility ratio between the injected and in-place fluids. The polymer solution affects the relative flow rates of oil and water and sweeps a larger fraction of the reservoir than water alone, thus contacting more of the oil and moving it to production wells. Polymers currently in use are produced both synthetically (polyacrylamides) and biologically (polysaccharides). The polymers may also be cross-linked in situ to form highly viscous fluids that will divert the subsequently injected water into different reservoir strata.

Polymer flooding has its greatest utility in heterogeneous reservoirs and those that contain moderately viscous oils. Oil reservoirs with adverse water flood mobility ratios have a potential for increased oil recovery through better areas sweep efficiency. Heterogeneous reservoirs may respond favorably as a result of improved vertical sweep efficiency. Because the microscopic displacement efficiency is not affected, the increase in recovery over water flood will likely be modest and limited to the extent that sweep efficiency is improved, but the incremental cost is also moderate. Currently, polymer flooding is being used in a significant number of commercial field projects. The process may be used to recover oils of higher viscosity than those for which a surfactant flood might be considered.

Polymer solutions must be stable for a prolonged period at reservoir conditions. Mechanical, chemical, thermal, and microbial effects can degrade polymers. However, degradation can be minimized or even prevented totally by using specific equipment or techniques.

Stability problems may occur as a result of oxygen contamination of the polymer solutions. Such contamination can lower the screen factor of polyacrylamide solutions by as much as 30%. In field operations, the loss of mobility reduction due to oxygen may be more serious since control of the reservoir fluid composition can be difficult. Sodium hydrosulfite in low concentrations is an effective oxygen collector for polyacrylamide solutions. However, sodium hydrosulfite tends to catalyze polymer deterioration when free oxygen and decomposed polymers are present. Therefore, the proper use of sodium hydrosulfite is imperative to avoid severe polymer degradation. In addition, caution is necessary to prevent oxygen from re-entering the system once sodium hydrosulfite has been added to the makeup water.

Surfactant flooding is a multiple-slug process involving the addition of surface-active chemicals to water. These chemicals reduce the capillary forces that trap the oil in the

pores of the rock. The surfactant slug displaces the majority of the oil from the reservoir volume contacted, forming a flowing oil-water bank that is propagated ahead of the surfactant slug. The principal factors that influence the surfactant slug design are interfacial properties, slug mobility in relation to the mobility of the oil-water bank, the persistence of acceptable slug properties and slug integrity in the reservoir, and cost.

A slug of water containing polymer in solution follows the surfactant slug. The polymer solution is injected to preserve the integrity of the more costly surfactant slug and to improve the sweep efficiency. Both these goals are achieved by adjusting the polymer solution viscosity in relation to the viscosity of the surfactant slug to obtain a favorable mobility ratio. The polymer solution is then followed by injection of drive water, which continues until the project is completed.

Each reservoir has unique fluid and rock properties, and specific chemical systems must be designed for each individual application. The chemicals used, their concentrations in the slugs, and the slug sizes depend upon the specific properties of the fluids and the rocks involved and upon economic considerations.

Alkaline flooding adds inorganic alkaline chemicals, such as sodium hydroxide, sodium carbonate, or sodium orthosilicates, to the water to enhance oil recovery by one or more of the following mechanisms: interfacial tension reduction, spontaneous emulsification, or wet ability alteration. These mechanisms rely on the in situ formation of surfactants during the neutralization of petroleum acids in the crude oil by the alkaline chemicals in the displacing fluids.

Although emulsification in alkaline flooding processes decreases injection fluid mobility to a certain degree, emulsification alone may not provide adequate sweep efficiency. Sometimes polymer is included as an ancillary mobility control chemical in an alkaline water flood to augment any mobility ratio improvements due to alkaline-generated emulsions.

Other variations on this theme include the use of steam and the means of reducing interfacial tension by the use of various solvents. The solvent approach has had some success when applied to bitumen recovery from mined tar sand, but when applied to non-mined material phenomenal losses of solvent and bitumen are always a major obstacle. This approach should not be rejected out solvent hand since a novel concept may arise that guarantees minimal (acceptable) losses of bitumen and solvent.

Miscible fluid displacement (miscible displacement) is an oil displacement process in which an alcohol, a refined hydrocarbon, a condensed petroleum gas, carbon-dioxide, liquefied natural gas, or even exhaust gas is injected into an oil reservoir, at pressure levels such that the injected gas or alcohol and reservoir oil are miscible; the process may include the concurrent, alternating, or subsequent injection of water.

The procedures for miscible displacement are the same in each case and involve the injection of a slug of solvent that is miscible with the reservoir oil followed by injection of either a liquid or a gas to sweep up any remaining solvent. It must be recognized that

the miscible slug of solvent becomes enriched with oil as it passes through the reservoir and its composition changes, thereby reducing the effective scavenging action.

Microscopic observations of the leading edge of the miscible phase have shown that the displacement takes place at the boundary between the oil and the displacing phase. The small amount of oil that is bypassed is entrained and dissolved in the rest of the slug of miscible fluids; mixing and diffusion occur to permit complete recovery of the remaining oil. If a second miscible fluid is used to displace the first, another zone of displacement and mixing follows. The distance between the leading edge of the miscible slug and the bulk of pure solvent increases with the distance traveled, as mixing and reservoir heterogeneity cause the solvent to be dispersed.

Other parameters affecting the miscible displacement process are reservoir length, injection rate, porosity and permeability of reservoir matrix, size and mobility ratio of miscible phases, gravitational effects, and chemical reactions. Miscible floods using carbon dioxide, nitrogen, or hydrocarbons as miscible solvents have their greatest potential for enhanced recovery of low-viscosity oils. Commercial hydrocarbon-miscible floods have been operated since the 1950s, but carbon-dioxide-miscible flooding on a large scale is relatively recent and is expected to make the most significant contribution to miscible enhanced recovery in the future.

Carbon dioxide is capable of displacing many crude oils, thus permitting recovery of most of the oil from the reservoir rock that is contacted (carbon-dioxide-miscible flooding). The carbon dioxide is not initially miscible with the oil. However, as the carbon dioxide contacts the in situ crude oil, it extracts some of the hydrocarbon constituents of the crude oil into the carbon dioxide and carbon dioxide is also dissolved in the oil. Miscibility is achieved at the displacement front when no interfaces exist between the hydrocarbon-enriched carbon-dioxide mixture and the carbon-dioxide-enriched oil. Thus, by a dynamic (multiple-contact) process involving inter-phase mass transfer, miscible displacement overcomes the capillary forces that otherwise trap oil in pores of the rock.

The reservoir operating pressure must be kept at a level high enough to develop and maintain a mixture of carbon dioxide and extracted hydrocarbons that, at reservoir temperature, will be miscible with the crude oil. Impurities in the carbon-dioxide stream, such as nitrogen or methane, increase the pressure required for miscibility. Mixing due to reservoir heterogeneity and diffusion tends to locally alter and destroy the miscible composition, which must then be regenerated by additional extraction of hydrocarbons. In field applications both miscible and near-miscible displacements may actually proceed simultaneously in different parts of the reservoir.

The volume of carbon dioxide injected is specifically chosen for each application and usually ranges from 20% to 40% of the reservoir pore volume. In the later stages of the injection program, carbon dioxide may be driven through the reservoir by water or a lower cost inert gas. To achieve higher sweep efficiency, water and carbon dioxide are often injected in alternate cycles.

In some applications, particularly in carbonate (limestone, dolomite, and chert) reservoirs where it is likely to be used most frequently, carbon dioxide may prematurely break through to producing wells. When this occurs, remedial action using mechanical controls in injection and production wells may be taken to reduce carbon-dioxide production. However, substantial carbon-dioxide production is considered normal. Generally this produced carbon dioxide is re-injected, often after processing to recover valuable light hydrocarbons.

For some reservoirs, miscibility between the carbon dioxide and the oil cannot be achieved but carbon dioxide can still be used to recover additional oil. The carbon dioxide swells crude oils, thus increasing the volume of pore space occupied by the oil and reducing the quantity of oil trapped in the pores. It also reduces the oil viscosity. Both effects improve the mobility of the oil. Carbon-dioxide-immiscible flooding has been demonstrated in both pilot and commercial projects, but overall it is expected to make a relatively small contribution to enhanced oil recovery.

The solution gas-oil ratio for carbonated crude oil should be measured in the normal way and plotted as gas-oil ratio in volume per volume versus pressure. The greater the solubility of carbon dioxide in the oil, the larger is the increase in the solution gas-oil ratio. In fact, the increase in the gas-oil ratio usually parallels the increase in the oil formation volume factor due to swelling. It should be noted that the gas in any gas-oil ratio experiment is not carbon dioxide but contains hydrocarbons that have vaporized from the liquid phase. Consequently, whether the gas-oil ratio is measured in a pressure-volume-temperature cell or from a slim tube experiment, compositional analysis must be carried out to obtain the composition of the gas as well as that of the equilibrium liquid phase.

The density of crude oil saturated with carbon dioxide can be determined in the laboratory by the use of a hydrometer or a pycnometer. If actual measured values are not available, the correlation developed for crude oil containing dissolved natural gases can be used but give only approximate values at best. The density of pure carbon dioxide is a function of pressure and temperature. In an actual mathematical simulation of flow during carbon dioxide flooding, the density in the mixing zone must be specified as a function of pressure and mixing zone composition.

Hydrocarbon gases and condensates have been used for over 100 commercial and pilot miscible floods. Depending upon the composition of the injected stream and the reservoir crude oil, the mechanism for achieving miscibility with reservoir oil can be similar to that obtained with carbon-dioxide (dynamic or multiple-contact miscibility), or the miscible solvent and in situ oil may be miscible initially (first-contact miscibility). Except in special circumstances, these light hydrocarbons are generally too valuable to be used commercially.

Nitrogen and flue gases have also been used for commercial miscible floods. Minimum miscibility pressures for these gases are usually higher than for carbon dioxide, but in high-pressure, high-temperature reservoirs where miscibility can be achieved these gases may be a cost-effective alternative to carbon dioxide.

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### Biographical Sketch

**Dr. James G. Speight** has a Ph.D. in Organic Chemistry from the University of Manchester, England, and works for CDW Inc. as an Author/Lecturer/Technical and Business Advisor. Previously, he was Chief Executive Officer at the Western Research Institute (1990–1998). Chief Executive Officer. Dr. Speight has thirty years of experience in areas associated with the properties and processing of conventional and synthetic fuels. He has participated in, as well as led, significant research in defining the use of chemistry of heavy oil and coal. He has well over three hundred publications, reports, and presentations detailing these research activities. Dr. Speight is currently editor of the journal *Petroleum Science and Technology* (formerly *Fuel Science and Technology International*), editor of the journal *Energy Sources*, and co-editor of the journal *Reviews in Process Chemistry and Engineering*. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemistry and Adjunct Professor of Chemical Engineering at the University of Wyoming as well as Adjunct Professor of Chemical and Fuels Engineering at the University of Utah. Dr. Speight is the author/editor/compiler of nineteen books and bibliographies related to fossil fuel processing and environmental issues. As a result of his work, Dr. Speight was awarded the Diploma of Honor, National Petroleum Engineering Society, For Outstanding Contributions to the Petroleum Industry in 1995 and the Gold Medal of Russian Academy of Sciences (Natural) for Outstanding Work in the Area of Petroleum Science in 1996. He has also received the Specialist Invitation Program Speakers Award from NEDO (New Energy Development Organization, Government of Japan) in 1987 and again in 1996. Dr. Speight also received the degree of Doctor of Sciences from the Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia For Exceptional Work in Petroleum Science in 1997.