



Libyan Academy

**School of Engineering and Applied Science
Department of Chemical and Petroleum Engineering**

***“Experimental Investigation on Asphaltene Deposition
in Porous Media During Gas Injection”***

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Abstract

The deposition of asphaltene is considered to be one of the most difficult problems during oil production. The presence of asphaltene in crude oil and consequently adsorption and deposition of asphaltene on the surface of the rocks has some effects on the properties of rock such as porosity, permeability and wettability.

Asphaltene can precipitate during primary oil recovery, CO₂ injection, and hydrocarbon gas injection. Asphaltene precipitates may deposit to the surface of pores or plug the pore throat causing permeability reduction, wettability alteration and formation damage.

In this research asphaltene deposition problem during natural depletion and dynamic displacement of oil by CO₂ in two different porous media is experimentally inspected. Two different rock samples (limestone and sandstone) from Libyan reservoirs are used as a representative of porous media.

During oil flood experiments, the results show that the porosity and permeability of the two types of core samples are reduced and their wettability are altered from water-wetting to oil-wetting due to asphaltene depositions on the rock surface. Also the results indicate that the sandstone rock sample is originally more water-wet than the limestone rock sample. This is referred to the amount of deposited asphaltene on the sandstone rock is lower than the amount deposited on the limestone rock.

Dynamic flow experiments show that the asphaltene precipitation increases as the pore volume of CO₂ injection increases which leads to pore plugging, porosity reduction and absolute permeability damage.

Irreducible water measurements showed that CO₂-induced asphaltene change the rock wettability to oil-wet.

In order to investigate the effect of CO₂ injection pressure and concentration on asphaltene precipitation, three limestone core samples were used to represent reservoir formation during displacement test. The results show that by increasing the pore volume of the injected CO₂, asphaltene precipitation increases, also the increase in injection pressure causes less precipitation of asphaltene. It is found that the precipitated asphaltene can reduce permeability, porosity and alter the wettability of the core samples.

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Nomenclature

A	Cross-sectional area of core sample, cm
L	Length of core sample, cm
q	Volumetric flow rate, cm ³ /sec
K _i	Initial Permeability, mD
K	Instantaneous permeability, mD
K _{air}	Air permeability, mD
K _d	Damaged permeability, mD
K _g	Gas permeability, mD
K _l	Liquid permeability, mD
Swi	Initial water saturation, %
W	Asphaltene content of crude oil, wt%

Greek Symbols

ϕ_i	Initial porosity, %
ϕ_d	Damaged porosity, %
ρ_o	Density of crude oil, gm/cm ³
μ_o	Viscosity of crude oil, cp
ΔP	Pressure drop, Psig

Abbreviations

PV	Pore volume of core sample, cm ³
BV	Bulk volume of core sample, cm ³
GV	Grain volume of core sample, cm ³
w	Weight of core sample, gram
API	American Petroleum Institute
GOR	Gas oil ratio, Scf/STB
ADE	Asphaltene deposition envelope
EOR	Enhanced oil recovery
SARA	Saturates, Aromatics, Resins and Asphaltenes

Asphaltene precipitation from reservoir fluids during oil production is a serious problem because it can result in plugging of the formation, wellbore and production facilities. Field conditions conducive to asphaltene precipitation include normal depletion and gas injection for Improved Oil Recovery (IOR).

Heavy organics (asphaltene, resin, etc.) deposition is a common problem in all sections of the oil industry, including oil production, transportation, and processing ^(1, 2). One of the most important aspects of this problem is asphaltene deposition, which causes major difficulties in petroleum mixtures, such as petroleum reservoir fluids.

A petroleum reservoir fluid is a complex polydisperse mixture consisting mostly of light and heavy paraffins, aromatics, resins and asphaltenes. Asphaltene is recognized as the heavy fraction of petroleum fluids, which is insoluble in some species such as paraffins but soluble in polar/aromatic species such as toluene, xylene, etc.) ⁽³⁾.

Asphaltenes are the least understood and the most problematic organic deposits. They are high molecular weight, non-crystalline, polar compounds which exist in crude oil. Asphaltenes consist of polyaromatic condensed rings with short aliphatic chains and heteroatoms such as nitrogen, oxygen, sulfur and various metals. Asphaltene molecules carry a core of stacked, flat sheets of condensed aromatic rings linked at their edges by chains of aliphatic and/or naphthenic-aromatic ring systems. The condensed aromatic rings exist in the form of a non-homogeneous flat sheet. Deposition of these materials may cause a number of difficulties including wettability reversal, permeability reduction, increased pressure drop, well and pipeline plugging and finally production rate reduction ⁽⁴⁾.

Considering pressure drop due to continued production from reservoirs and higher viscosity of depleted reservoirs necessitates the need for pressure maintenance and gas injection. Pressure variation and composition change, like during gas injection, are the major causes of asphaltene deposition ⁽⁴⁾.

Changes in such environmental parameters as pressure, temperature and composition (like during production, depletion, gas injection/addition of solvent or dispersant injection) can change characteristics in an oil mixture so that the oil will become unstable and finally heavy organics will flocculate and deposit. Surface activity and self-association of asphaltene particles and their tendency for growth during deposition, could lead to problems during production, transportation and processing of petroleum.

According to the field experience and experimental observations asphaltene stability depends on a number of factors, including the composition of the surrounding fluid, pressure, and temperature.

The effect of composition and pressure on asphaltene precipitation is generally believed to be stronger than the effect of temperature. Addition of paraffinic compounds shifts the solubility of asphaltenes in the bulk oil because its solvent power affects interactions among asphaltenes and resins. If the paraffinic compounds are good solvents for resins but not for asphaltenes, as the volume of diluent increases both the interaction between resins and asphaltenes and the capacity of the former to stabilize the asphaltene molecules as small aggregates becomes weak, causing asphaltenes to precipitate ^(5, 6).

Pressure depletion alone can destabilize asphaltenes and is likely the major reason for asphaltene deposition in well-bore pipes. As the density of the crude oil decreases because of depressurization, the screening effect on asphaltene interactions arising from the presence of oil components decreases, causing the interactions between asphaltenes to become stronger, which in turn induces the precipitation.

Deposition on the rock surface can take place when asphaltene precipitation occurs inside the reservoir porous medium; i. e. there is no deposition of asphaltene in the porous medium before the onset of asphaltene precipitation. Precipitation and deposition are two different processes and governed by different mechanisms. When precipitation occurs, asphaltene particles come out of solution, are solidified and a new solid phase is generated in the solution, whereas when deposition takes place on the rock, this can severely reduce permeability, cause formation damage and alter wettability.

Carbon dioxide (CO₂) can be used in a process known as EOR to recover more oil. When CO₂ is injected for EOR it contacts oil that cannot be produced conventionally and causes it to swell and becomes less viscous, if the subsurface rock is to be thought as sponge-like with pores containing the oil, and then swelling of the oil helps to push the portion of oil out of pores. The reduced viscosity then improves the flow of oil to the production wells. This technique is called CO₂-EOR is well established. If the CO₂ is used then stored in the oil reservoir, EOR has the potential to become an environmentally attraction option as well as economical.

In a CO₂ miscible displacement process, the injected CO₂ solvent can induce flocculation and deposition of asphaltene and other heavy organic particles. This can cause numerous production

problems with a detrimental effect on oil recovery. Therefore, it is important to understand the behavior of this organic matter under reservoir operating conditions.

The present work focuses on the investigation of asphaltenes deposition effects on porosity reduction, permeability damage and wettability alteration of reservoir rocks during oil flooding and CO₂ gas injection by dynamic flow tests.

Two common rock types (limestone and sandstone) from Libyan hydrocarbon reservoirs are used as porous media rock representative. The oil used in the experiments was taken from Libyan reservoirs.

In this work, the precipitation of asphaltene from Libyan oil reservoir was studied. A series of experiments were designed and carried out to examine the effect of CO₂ injection on asphaltene precipitation. Different injection pressures were used in dynamic flooding experiments in order to investigate the effect of pressure versus pore volume of CO₂ injected. These dynamic displacement tests simulate the reservoir conditions.

One of the most important phenomena in the oil industry is the precipitation and deposition of heavy organic materials such as asphaltene in petroleum reservoirs, which can cause several problems. For instance, asphaltene precipitation in oil reservoirs can cause diffusivity reduction and wettability alteration in reservoir rock and finally affect the oil production and economical efficiency ^(7, 8). In general, the parameters that govern precipitation appear to be composition of the crude, pressure, temperature, and properties of asphaltenes ⁽³⁾. Asphaltene precipitation problems can be categorized as follows:-

- 1- Precipitation and deposition can be caused by the changes in temperature and/or pressure during primary depletion.
- 2- Precipitation and deposition can be caused by blending or commingling of two no compatible reservoir fluid streams (i.e., subsea completions), acid stimulation and/or enhanced recovery injection gases (CO₂, H₂S, or rich gas).

In field situations, when pressure in the reservoir is reduced or when light hydrocarbon or other gaseous injectants are introduced, the colloidal suspension may become destabilized, resulting in asphaltene and resin molecules precipitating out of the oil, so asphaltene will first precipitate then can flocculate and depending on the flow dynamics may or may not deposit in the rock matrix ^(9, 10). Recent research has shown that this precipitation process, whether it is due to pressure depletion or gas injection, is largely reversible. However, there can be significant hysteresis in the redissolution process, that is, the time required for asphaltenes to go back into solution may be considerably longer than the time required for the original precipitate to form ⁽¹⁰⁾.

Asphaltenes can cause problems in oil production, transportation, and processing. Whether or not asphaltenes cause problems is unrelated to the amount of asphaltene in the oil. What is important is the stability of those asphaltenes and stability depends not only on the properties of the asphaltene fraction, but also on how good a solvent the rest of the oil is for its asphaltenes. As recognized, light oils with small amounts of asphaltenes are more likely to cause problems during production than heavy oil with larger amounts of material in the asphaltene fraction. The heavier oil also contains plenty of intermediate components that are good asphaltene solvents whereas the light oil may consist largely of paraffinic materials in which, by definition, asphaltenes have very limited solubility. Because that, oils with significant amounts of asphaltenes often can be produced without any asphaltene related problems, whereas severe asphaltene problems have been reported for some oils with amounts of asphaltenes that are barely measurable.

Asphaltenes in heavier oils can also cause problems if they are destabilized by mixing with another crude oil during transportation or by other steps in oil processing ⁽¹⁰⁾.

Asphaltenes are the n-pentane insoluble fractions of crude oil that remain in solution under reservoir temperature and pressure conditions. They are destabilized and start to precipitate when the pressure, temperature, and/or composition changes occur during primary production or gas injection. The onset point of asphaltene is the point that asphaltene lose its stability ⁽¹⁰⁾. In fact, if the solubility condition in the oil falls below this level then asphaltenes start to precipitation and form separate and visible phase.

Then precipitated asphaltene particles will grow in size, and may start to flocculate and maybe make deposition on surface of rock.

Precipitation occurs above the saturation or bubble-point pressure, reaches a maximum value around the saturation pressure, and decreases as pressure drops further. In other words, further decrease in pressure from the bubble-point pressure gives rise to a decrease in the amount of precipitate. Above the saturation pressure, the precipitation is solely due to pressure, while below the bubble-point pressure both pressure and composition affect the precipitation behavior. As the light components come out of the solution, the solubility of asphaltene in the liquid phase increases. After asphaltene precipitates from the oil, it may flocculate to form much larger size molecules. Flocculated asphaltenes can be suspended with oil flow or can be deposited onto the rock and cause formation damage.

Asphaltene deposition could be explained in terms of adsorption, plugging and entrainment figure (2.1). So, flocculated asphaltenes can be adsorbed onto the rock surface by adsorption.

Also, they may be trapped within the porous media because of their size, blocking the pore throats of the formation by plugging or the deposited flocculated asphaltenes can be flushed away by oil due to shearing effect if the local oil velocity is high by entrainment.

Deposition begins with adsorption of flocculated asphaltene particles onto active sites on the rock surface. Adsorption can be explained in terms of irreversible thermodynamics. Recent investigations show that asphaltene deposition is due to adsorption followed by hydrodynamic retention or trapping process of particles at the pore throats. In addition to adsorption, the deposition also occurs because of mechanical entrapment, this entrapment is similar to the deposition of fines in porous media.

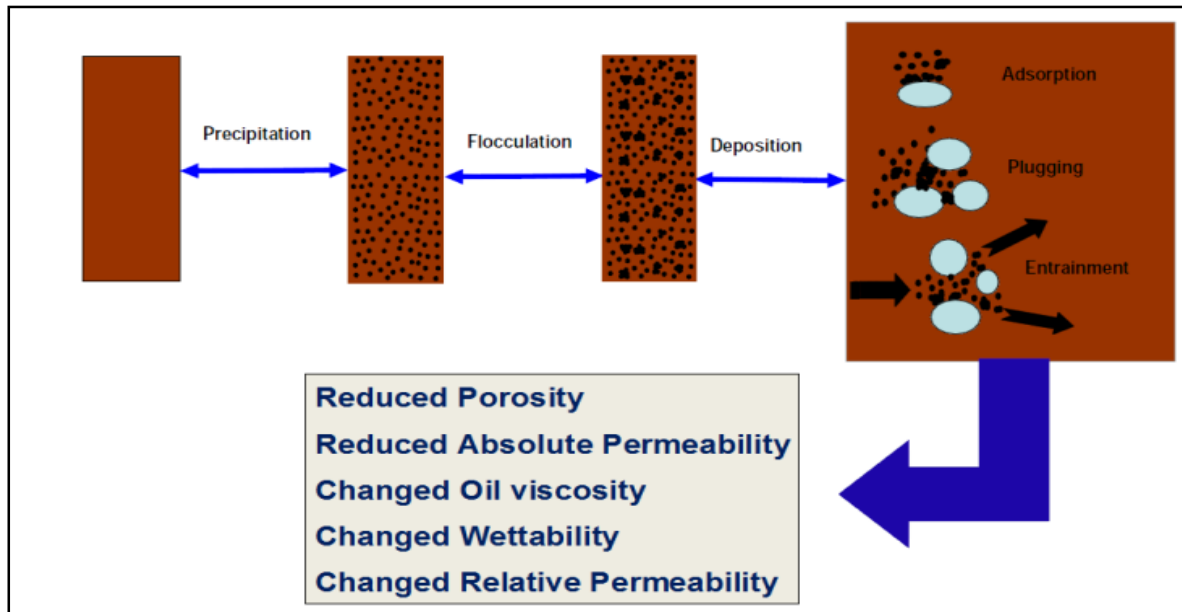


Figure (2.1): Asphaltene Precipitation and Deposition Modeling in Reservoir Conditions ⁽¹⁾.

The deposition process through mechanical entrapment (also called plugging deposit as the deposition plugs the pore throat) is complex. Deposition of solid asphaltenes causes a reduction of the pore space available for fluids, actually, porosity reduction. Other formation damage mechanisms may include absolute permeability reduction and alteration of rock wettability from water-wet to oil-wet. The deposition may induce favorable changes in relative permeabilities, end-point saturations and effects on the displacement efficiency^(11,12,13). For instant, wettability controls the flow and distribution of immiscible fluids in an oil reservoir and thus plays a key role in any oil recovery process. One way that oil components are thought to alter wettability is by coating pore surfaces with precipitated asphaltenes.

The deposited asphaltene may cause alteration of rock wettability from water-wet to oil-wet. Wettability has been shown to affect relative permeabilities, irreducible water saturation, residual oil saturation, capillary pressures, dispersion and electrical properties.

The alteration of relative permeabilities and the end points has the strongest influence on displacement processes⁽¹⁴⁾.

Asphaltene itself is not problematic, but asphaltene precipitation is a big concern. Precipitation may happens during different phases of production specially CO₂ flooding. It is well known that light and medium oil reservoirs are good candidate for CO₂ injection as a tertiary recovery after water flooding⁽¹⁵⁾.

Although wax may deposit just like asphaltene but wax deposition is a reversible process which can be eliminated by thermal treatment methods⁽¹⁶⁾.

Asphaltene content of light oils is not high but the interesting point is that the amount of the asphaltene in crude oil is not the cause of precipitation. Normally in light oil reservoirs, asphaltene solubility is low. Low solubility makes asphaltene very unstable and increases the possibility of precipitation. That is why in some fields with 17 weight percent (wt%) asphaltene (Boscan field in Venezuela) no asphaltene precipitation was observed while other fields with 0.15 wt% asphaltene (Hassi-Masoud in Algeria) has many production problems due to asphaltene precipitation and deposition^(17,18). Usually asphaltene precipitation problems firstly observed in production facilities, then tubing, afterward the asphaltene deposit area can move toward bottom hole and well neighboring formation as reservoir depletion proceeds. However recently in few fields it is observed that well impairment has begun in early stages which cause to draw concern toward reservoir itself⁽¹⁹⁾.

Asphaltene precipitation and deposition may affect large region in the reservoir, it would be started from wellbore and extend over large distances from its origin. In contrast, the reservoir damage due to wax deposition is rather limited to a short distance, maximum 1 foot away from the wellbore. Asphaltene treatment would not be as easy as wax removal, especially if precipitation and deposition happens within the oil reservoir; it can reduce formation permeability and porosity and alter wettability of the rock. Asphaltene stability inside the crude depends on a number of factors including pressure, temperature, and composition of the fluid. So any changes in these three factors may alter the stability and lead to asphaltene precipitation^(18, 19).

The effect of composition and pressure on asphaltene precipitation is generally believed to be stronger than the effect of temperature⁽²³⁾. When CO₂ injected to the oil reservoir it will contribute to the asphaltene precipitation by composition change. Changes in composition normally happen during gas injection processes employed in enhanced oil recovery (EOR). Gas injection includes processes such as miscible flooding with CO₂, N₂ or natural gas⁽¹⁹⁾. Burke⁽²⁰⁾ observed that dissolved gas affect the solubility of asphaltene in live oil.

During production life of a well composition of reservoir fluid will change as the result of pressure depletion. Therefore lighter components will leave the oil phase and gas-oil ratio (GOR) will be reduced and density will increase. In this case lesser asphaltene would precipitate since it goes into

solution with oil. Asphaltene precipitation is different from flocculation and deposition but all three of them may cause serious damage to the formation.

The process of asphaltene precipitation consists of few important steps:-

- First step which is precipitation happens when the solid particles form a distinct phase as they come out of solution, the quantity and size of solid particles at this stage could be quite small.
- At the second step which is called flocculation stage, the small solid particles clump together and grow larger.
- Deposition is the third stage, a point at which the particles are so large that they can no longer be supported by the liquid and therefore settle out on solid surfaces⁽²¹⁾.

Flocculated and deposited asphaltene may lead to formation damage by impairing the permeability by plugging the pore throat and altering wettability through adsorbing on the negatively charged mineral sites⁽²¹⁾. To this point there has been intensive research focus on the formation damage due to unstabilized and flocculated colloidal asphaltene deposition.

Asphaltene flocculates contribute to the formation of organic deposits causing formation damage problem⁽²²⁾. During the last three decades asphaltene problems have been studied intensively, however the majority of these researches deal with static asphaltene precipitation in closed systems. Although these works can help to investigate onset of precipitation with regards to different parameters such as pressure, CO₂ concentration and etc, but absence of a porous medium is a concern. Complex interaction between the fluid and porous medium is playing a very important role in asphaltene precipitation and deposition which should not be ignored⁽²³⁾.

Nowadays lots of researchers have focused on asphaltene precipitation in dynamic manner with resembles, although not fully, but near reservoir condition. It would provide the circumstance for studying the effect of asphaltene on formation properties.

2.1 Asphaltene Deposits in the Oil Industry:-

Asphaltenes are the heaviest constituents of crude oil⁽²⁴⁾. Under initial reservoir fluid conditions, they are believed to be dissolved in the crude oil as colloidal particles. This gives the oil a black-brown coloration⁽²⁵⁾.

Several factors, like changes in reservoir pressure, temperature, and composition, may cause asphaltene to precipitate from the crude oil as a solid. Solid asphaltenes are often found in the form of sticky and deformable deposits⁽²⁶⁾.

Asphaltene rich crude oils are present worldwide⁽²⁷⁾. Locations known to be significantly affected by asphaltenes include the southern and central regions of Alberta, Canada, the West Texas and Alaska, the Norwegian sector of the North Sea, the southern producing regions of Mexico, and Saudi-Arabia^(27,28). The most serious asphaltene deposition problems are associated with oil fields in Venezuela, The Persian Gulf, the Adriatic Sea and the U.S. Gulf of Mexico⁽²⁷⁾.

Asphaltenes are considered to be the least valuable component of the crude oil⁽²⁹⁾. The presence of asphaltenes means additional difficulties related to transport and processing due to the increased crude oil viscosity caused by the asphaltenes.

Asphaltenes have high resistance to cracking and they are therefore often held responsible for decreasing the yield of petroleum distillates.

Because the asphaltenes usually contain heavy metal components, they are very hard to biodegrade; this makes them unpopular from a petroleum waste perspective, but most commonly, asphaltenes represent a significant problem from a production and reservoir management point of view.

Numerous production problems encountered in oil production have been associated with asphaltenes⁽²⁹⁾. At sufficiently low reservoir pressure, asphaltenes can deposit within the formation and block the pore throats, which may reduce the permeability significantly.

Asphaltenes adsorbing onto the rock surface may shift the wettability properties of the rock from water-wet to oil-wet, which may reduce the relative permeability.

Another problem is related to the high viscosity of asphaltene rich crude oils, which can cause problems associated with production rate, pumping energies, and transfer rates. Furthermore, asphaltenes contribute in stabilizing tight water in oil emulsions.

This can also lead to higher viscosity, or even blocking of pore throats. Asphaltenes are also a common nucleation site for paraffin crystallization, and the two substances are often found within the same deposit⁽³⁰⁾.

Deposits of asphaltenes may also lead to wellbore plugging, flow restrictions in tubings, flowlines and production facilities, fouling of downhole safety valves, and solids build-up in storage tanks⁽²⁷⁾.

Well interventions for cleaning out asphaltene restrictions and restore well productivity often constitute significant expenses for the affected oil companies⁽²⁹⁾.

Precipitation of asphaltenes in the formation usually happens near the wellbore because of the significant pressure draw-down generated there⁽²⁴⁾. But theoretically, the precipitation can occur throughout the whole reservoir.

2.2 Description of Asphaltenes

To understand what asphaltenes actually are, some knowledge of the chemical composition of crude oils is required.

2.2.1 Crude Oil Composition

Crude oils have a complex composition and may consist of tens of thousands of different hydrocarbon molecules⁽³¹⁾. This makes it virtually impossible to characterize the crude oils by their individual molecular types. Therefore, it is common to employ a hydrocarbon group type analysis for such purposes.

The SARA-separation is a frequently used group type analysis⁽³¹⁾. It separates the crude oils in four main chemical classes, Saturates, Aromatics, Resins and Asphaltenes, based on differences in solubility and polarity. This is illustrated in figure (2.2).

The saturates (also called aliphatics) are non-polar compounds containing no double bonds⁽³¹⁾. Weakly polar (or non-polar) compounds containing one or more benzene rings make up the aromatics.

Resins and Asphaltenes constitute the two fractions that are comprised of polar molecules their molecules can be regarded as similar except that the asphaltene molecules have higher molecular weight, typically 500-1500 g/mole; both fractions are operationally defined⁽³¹⁾.

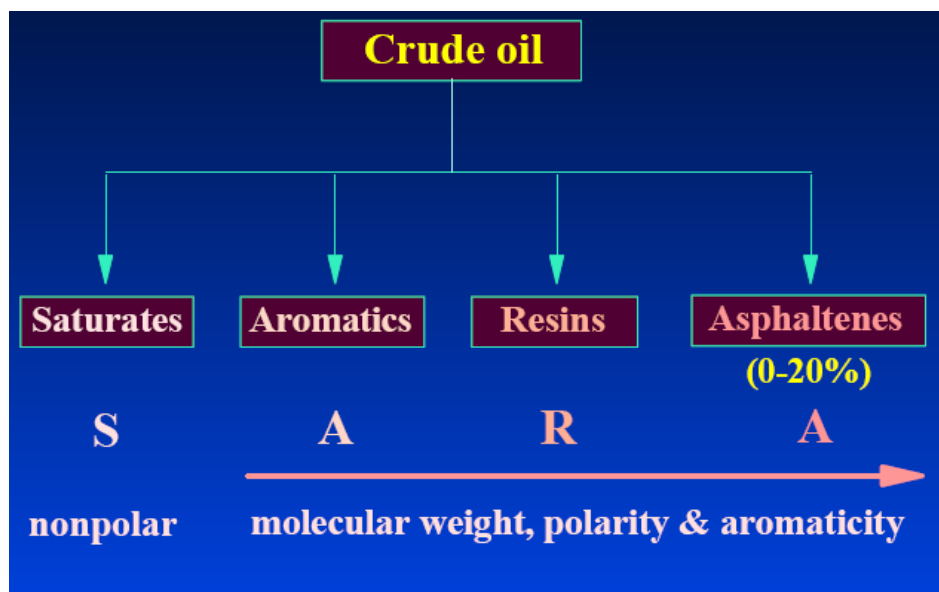


Figure (2.2): SARA Separation ⁽¹⁾

Resins can be defined as the fraction of the crude oil soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane. Asphaltenes are defined as the fraction of the crude oil precipitating in light alkanes (light weight aliphatic hydrocarbons) like pentane, hexane or heptane while the precipitate is soluble in solvents like toluene and benzene. Although these definitions are unsatisfactory to chemists, they are valid in many respects to other professionals such as petroleum engineers ⁽³²⁾.

Another crude oil constituent that should be mentioned is maltene ⁽³²⁾. Asphalts are often divided into three parts, based on solubility and polarity, namely asphaltenes, resins and maltenes ⁽³³⁾. While asphaltenes are aromatic and the most polar and viscous part, the maltenes are made up of aliphatic molecules, and they are non-polar and the least viscous part. The polarity and viscosity of resins is in between that of asphaltenes and maltenes. Despite their aliphatic nature, the maltenes are able to suspend the asphaltene in a similar way as resins ⁽³²⁾.

2.2.2 Chemical Attributes

In terms of chemical structure, asphaltenes are complex multinuclear, aromatic, high molecular weight petroleum components, which include both hydrocarbon and non hydrocarbon groups, such as Nitrogen (N₂), Oxygen (O₂), Sulphur (S), Vanadium (V) and Nickel (Ni) ⁽³¹⁾.

Being aromatic means that the asphaltenes are made up by one or more six-carbon rings characteristic of the benzene series and related organic groups ⁽²⁹⁾. Molecules that are not aromatic are termed aliphatic, and are incompatible with aromatic molecules.

Present non-carbon atoms in a carbon ring are called heteroatoms ⁽³¹⁾. In crude oil, the largest percentage of heteroatoms (O₂, S, N₂) and organometallic constituents (Ni, V, Fe) is found in the asphaltene fraction, but resins often contain heteroatoms as well.

2.3 Mechanisms of asphaltene precipitation

Understanding the mechanism of the heavy organic deposition would result in more economical, environmentally sounder, and speedier oil production, transportation, and processing technologies. The kind and amount of depositions of heavy organics from petroleum fluids vary, depending on the hydrocarbons present in oil and the relative amounts of each family of heavy organics ^(32, 33). Four different effects (mechanisms) are recognized for such depositions. One or more of these mechanisms would describe the organic depositions that may occur during oil production, transportation or processing. Based on these four different mechanisms four models are provided which are detailed by Mansoori ⁽¹⁾.

2.3.1 Polydispersivity effect

The degree of dispersion of heavy organics in oil depends upon the chemical composition of petroleum⁽³³⁾. The ratio of polar/non-polar and light/heavy molecules and particles in petroleum are the factors primarily responsible for maintaining the stability of the polydisperse oil mixture. Deposition of heavy organics can be explained by an upset in the polydisperse balance of oil composition.

Any change in temperature, pressure, and composition, such as addition of a solvent to oil may destabilize the polydisperse oil. For example, upon increase in the aromatic hydrocarbon content of a crude oil (a polar miscible solvent) asphaltene particles form micelle-type aggregates which do not grow in size with increasing concentration. This phenomenon is simply due to packing constraints, resulting from the complicated molecular structure of asphaltene ⁽³⁴⁾. On the other hand, upon increase in the paraffinic hydrocarbon content of a crude oil, asphaltene particles may separate into a solid aggregate phase. Segments of the separated fractions which contain sulfur, nitrogen, oxygen and/or hydrogen bonds could start to flocculate and as a result produce the irreversible heavy organic deposits which may be insoluble in solvents.

2.3.2 Steric colloidal effects

It is demonstrated that some of the components of petroleum, especially asphaltene have a strong tendency for self-association. Upon further increase of the paraffinic hydrocarbon content of a crude oil some of the heavy organics will form colloids, will separate from the oil phase into an aggregate

and then will remain suspended in oil by some peptizing agents, like resins, which will be adsorbed on their surface and keep them afloat. Stability of such steric colloids is considered to be a function of concentration of the peptizing agent in the solution, the fraction of heavy organic particles surface sites occupied by the peptizing agent, and the equilibrium conditions between the peptizing agent in solution and on surface of heavy organic particles.

The amount of peptizing agent adsorbed is primarily a function of its concentration in the oil^(35,36,37).

2.3.3 Aggregation effect

A concentration variation of a peptizing agent (such as resins) in oil will cause its adsorbed amount on the surfaces of heavy organic particles to change. The peptizing agent concentration in oil may drop to a point at which its adsorbed amount would not be high enough to cover the entire surface of heavy organic particles. This may then permit the heavy organic particles to come together (irreversible aggregation), grow in size, and flocculate. The nature and shape of the resulting aggregates will determine their effect on the behavior of the petroleum fluids^(37, 38).

2.3.4 Electrokinetic effect

When the oil is flowing in a conduit (porous medium, well, pipeline, etc.) there is an additional effect (electrokinetic effect) to be considered in the deposition of its colloidal heavy organic constituents⁽³⁶⁾. This is because of the development of an electrical potential difference along the length of the conduit generated by the motion of charged colloidal particles. This electrical potential difference could then cause a change in the charged and colloidal particles further down the conduit, the ultimate result of which is their untimely deposition and plugging of the conduit.

The factors influencing this effect are the electrical, thermal and wettability characteristics of the conduit, flow regime, temperature, pressure, flowing oil properties, characteristics of the polar heavy organics and colloidal particles, and blending of the oil.

Flowing oils containing, both, polar (like asphaltene) and non-polar (like paraffin) macromolecules could have plugging problems which would be a result of the combination of electrokinetic and dynamic pour point effects. Depending on the operation and the kind of heavy organics present in the oil one or more of the effects described above will cause heavy organic depositions^(32, 36).

2.4 Chemical Factors Affecting Asphaltene Precipitation

Recall that asphaltenes are operationally defined as the fraction of crude oil precipitating in light alkanes like pentane, hexane or heptanes⁽³¹⁾. The amount of these hydrocarbons relative to the

amount of solvent constituents present in the oil (the ratio of polar to non polar components and the ratio of high to low molecular weight components) is vital for the solubility of asphaltenes ⁽³⁶⁾. Any action of chemical, mechanical or electrical nature which results in alteration of these ratios may cause the asphaltenes to flocculate.

2.4.1 Solubility and Aggregation Mechanisms

A crude oil's ability to keep asphaltenes in solution depends on several factors. As mentioned, the variety of crude oil constituents is huge, and thus the variety of solvent concentrations and solvent powers in different oils are too huge also.

Becker ⁽³⁹⁾ explains that the solvents form solvation sheaths that surround the complex asphaltene molecules and keep them soluble.

Since the asphaltenes have a high degree of unsaturation and possess a high aromatic character while the surrounding crude is more aliphatic in character, Becker ⁽³⁹⁾ suggests that the solvation sheaths consist of molecules of both aromatic and aliphatic character.

The resins and maltenes are believed to make up the solvation sheaths ⁽³²⁾. The fatty alkyl substituents of these molecules provide buoyancy and insulation for the asphaltene.

Without the stabilizing species to protect it, a bare asphaltene molecule presents an electronegative and solvent-incompatible surface to the bulk fluid⁽³²⁾. In this state, the asphaltenes can begin to separate from the system as a solid. Because a polymer chain from one asphaltene now is able to interact with the polymer chain from another and form chemical bindings called pi-bonds, asphaltene complexes that can grow vastly bigger than the original parent can be created.

One of two mechanisms will occur after the aggregation process, floatation or precipitation ⁽⁴⁶⁾. If the total pull of the liquid surrounding the asphaltene particle balances the apparent weight of the particle, it may float on the surface of the liquid. Further flocculation (e.g. due to the presence or addition of alkane solvents) may cause the particle weight to exceed the upward pull forces, and the asphaltene will precipitate.

There are mainly two ways that asphaltenes are brought out of solution: Aggregation growth with subsequent deposition of asphaltene particles, and adsorption of asphaltenes onto available pipe wall or reservoir rock surfaces ⁽⁴⁴⁾. Both the floatation and precipitation processes may accelerate these mechanisms ⁽⁴⁶⁾.

2.4.2 Resin to Asphaltene Ratio

The ratio of resins to asphaltenes present in the oil is a factor found to be important for the stability of asphaltenes⁽⁴⁴⁾. The stabilizing effect of the resins has already been described. However, the resins may also have a flocculating effect in a colloidal dispersion.

When resins adsorb to asphaltenes, but exist in too small quantities relative to the asphaltenes, the asphaltenes become only partly covered by the resins⁽⁴⁴⁾. In such cases the resins can comprise a bridging function. This happens because a given resin can adsorb on more than one asphaltene particle, and consequently create a flocculation.

In other words, the resins need to be in sufficient amounts in order to adsorb onto the entire asphaltene surfaces and stabilize the dispersion. According to the colloidal theory, the sufficient amount can be expressed as the ratio of resin to asphaltenes present in the oil⁽⁴⁴⁾. It has been found that colloidal asphaltene is stabilized if this ratio is approximately 1.25 or higher. However, precipitation of asphaltenes has been experienced in Hassi-Messaoud oil which has a resin to asphaltene ratio of 22⁽²⁴⁾.

2.4.3 Extended Oil Recovery and Maintenance

Extended oil recovery methods such as water and CO₂ flooding, can generate changes in the crude oil composition that may tilt the delicate ratio of polar to non-polar constituents needed to keep the asphaltenes in solution⁽²⁴⁾. Well stimulation and other well interventions may also cause composition changes. In addition, well interventions can cause critical pressure and temperature changes.

Experiments have also indicated that injection of nitrogen gas can aggravate the asphaltene stability and increase the bulk precipitation amount⁽⁴⁷⁾.

2.4.4 Chemical Effects on the Adsorption Process

The polar components of oil can adsorb on mineral or pipe wall surfaces by several distinct mechanisms. These depend on factors that include brine composition and the solvent quality of the oil for its asphaltenes⁽⁴⁸⁾.

Electrical charges can play a role in asphaltene precipitation processes⁽³²⁾. The surface charge of an oil or solid surface is dependent of the extent of acid/base dissociation reactions which again is dependent on the pH at the surface⁽⁴⁸⁾.

2.5 Physical Factors Affecting Asphaltene Precipitation

Besides crude oil composition, reservoir pressure and temperature are considered to be the most important factors affecting the asphaltene precipitation during primary oil recovery⁽²⁴⁾.

2.5.1 Pressure and Temperature

The pressure effect is the major factor on asphaltene precipitation during the primary oil recovery⁽²⁴⁾. Experiments have demonstrated that the solubility of asphaltenes is at its minimum when the prevailing pressure is at the bubble point.

Asphaltene precipitation can start when the pressure sinks below a certain value, often referred to as the onset pressure⁽²⁴⁾. This pressure can vary significantly between individual reservoirs (crude oils), but it is typically somewhat higher than the bubble point pressure⁽⁴⁹⁾.

The intensity of the precipitation increases as the pressure decreases towards the bubble point pressure, where the precipitation is at its most intense⁽²⁴⁾. The precipitation intensity then decreases, as the pressure continues to decrease below the bubble point, until a point where the precipitation ends.

The pressure and temperature conditions in which asphaltenes can precipitate can be called the asphaltene deposition envelope (ADE)⁽⁴⁹⁾.

Figure (2.3) shows an example of how asphaltene precipitation relates to pressure and temperature.

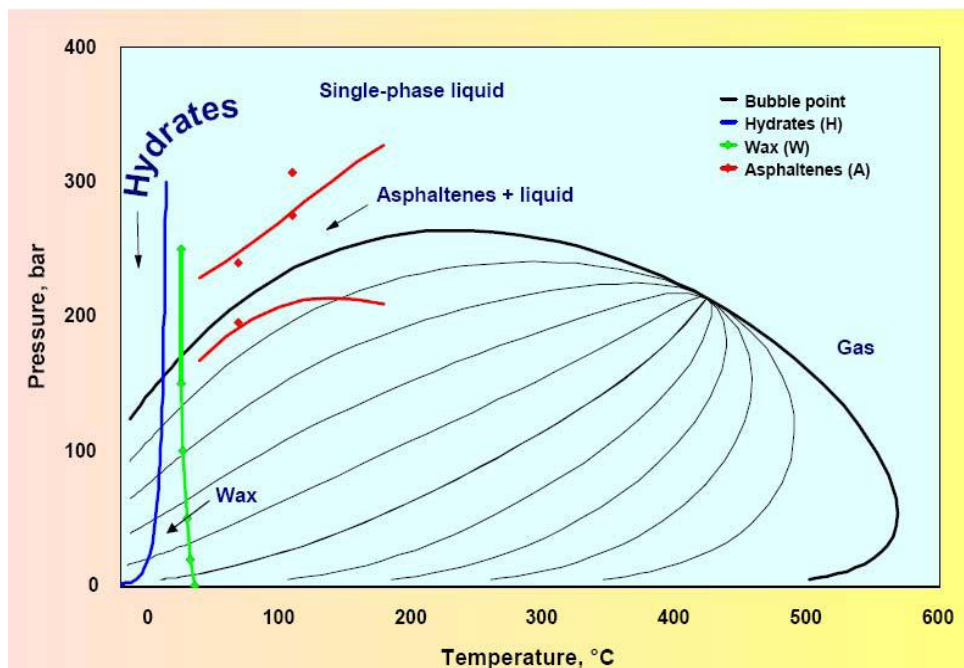


Figure (2.3): Phase behavior with secondary solid and liquid phases⁽³⁾.

Asphaltenes can exist in relatively high temperatures. Unlike waxes, asphaltenes are not crystalline and do not have a specific melting point, thus thermal insulation is not an effective prevention method.

2.5.2 Shear stress

Shear stress can tear apart the protective layer of resins and maltenes from the asphaltenes⁽³²⁾. Both London forces of attraction (between fatty alkyl chains) and pi bonding forces (connecting resins and maltenes with asphaltenes) can be overcome of moderately small shearing forces. The first pi-bonding molecules to be removed are the resins and maltenes. Once these are gone, the asphaltenes are no longer compatible with the bulk crude and may precipitate.

2.5.3 Electrokinetic Effects

After the aggregation process, the asphaltenes may readily interact with other surfaces that attract their electronegative core⁽³²⁾. Electrical charged sites on pipe walls or mineral deposits can act as collection points for the accumulation of these growing aggregates.

A streaming potential may be generated when colloidal liquid mixtures are in transit⁽⁴³⁾. The streaming potential is a voltage difference developed between the ends of a capillary tube or porous medium through which a liquid is forced to flow by an applied pressure difference⁽⁵⁰⁾.

Asphaltenes will flocculate out of solution when placed under the influence of an electrical field⁽⁴³⁾. This has been proven through experiments⁴³. If the streaming potential generated during oil flow through reservoir pores, well tubings or pipes is large enough, it could contribute to flocculating asphaltenes through electrode position⁽⁴³⁾.

In a simplified view, the asphaltenes contained by the oil may be seen as electrical charges in transit⁽⁴³⁾. Then the flow of oil will be equivalent to a streaming current and must therefore involve a potential difference, this potential difference will try to oppose the mechanical transfer of charge. The charged particles can be forced to flow backwards because of this potential difference⁽⁴³⁾. This is primarily attributed to back conduction by ion diffusion and to a small extent to electro osmosis. The total transfer charge due to these mechanisms is called the leaking current. At conditions where the asphaltenes particles remain stationary because of the balance of the two opposing forces that the potential difference is called streaming potential⁽⁴³⁾.

2.5.4 Crude Oil, Brine and Solid Interfaces

Interfaces between crude oil and brine are electrically charged⁽⁴⁸⁾. The oil components available and the composition of the brine, with which they are in contact, are decisive to the electrical charge.

The four main categories of crude oil, brine and solid interactions are identified by:

- Polar interactions,
- Surface precipitations,
- Acid/base interactions, and
- Ion binding or specific interactions between charged sites and higher valency ions.

In the absence of a water film between the oil and solid, the polar interactions predominate. Direct adsorption of asphaltenes from oil onto mineral surfaces has been reported⁽⁴⁸⁾. The adsorption onto clay minerals in the absence of water are dependent of the type of clay and its cation exchange capacity, the nitrogen content of the oil, and the solvent in which the polar compounds are dissolved.

Water has several different ways of influencing oil/solid interactions⁽⁴⁸⁾. Bulk water may shield some surfaces from direct interaction with asphaltenes and thereby reduce adsorption. But in the presence of water, both the solid and oil interfaces become charged. Polar functional groups from both mineral and crude oil phases can act as acids or bases. Acids tend to give away a proton and become negatively charged, while bases tend to gain a proton and obtain a positive charge.

The surface charge will impact interactions between crude oils, brine, and solid surfaces primarily in two ways⁽⁴⁸⁾. One involves the effect of net surface charge on water film stability, and the other involves the influence of ionized acidic or basic sites on adsorption.

If both the oil/water and solid/water interfaces have the same charge, the water film will be stabilized by repulsion forces between the interfaces⁽⁴⁸⁾. Otherwise, the water film will collapse. When the water film has collapsed, crude oil components (such as asphaltenes) at the oil/brine interface can adsorb on the solid surface.

2.6 Fundamentals of asphaltene deposition in porous media

There are three primary sources of fine particles in petroleum bearing formations:

- Invasion of foreign particles carried with the fluids injected for completion, work over, and improved recovery purposes.

- Mobilization of in-situ formation particles due to the incompatibility of the fluids injected into porous media and by various rock-fluid interactions.
- Production of particulates by chemical reactions, and inorganic and organic precipitation.

Fluids injected into petroleum reservoirs usually contain iron colloids produced by oxidation and corrosion of surface equipment, pumps, steel casings, and drilling string ⁽⁵³⁾. Brine injected for water flooding may contain some fine sand and clay particles. Mud fines can invade the formation during overbalanced drilling. These are some examples of the externally introduced particles.

Petroleum bearing formation usually contains various types of clay and other mineral species attached to the pore surface. These species can be released by hydrodynamic shear of the fluid flowing through porous media. Fine particles can also be generated by deformation of rock during compression and dilatation. This is due to variation of the net overburden stress and loss of the integrity of rock grains.

Particulate matter can be produced by various chemical reactions such as the salt formation reactions that occur when the seawater injected for water flooding mixes with the reservoir brine, or the precipitation of asphaltene due to change of the thermodynamic conditions and of the composition of the fluids by dissolution or liberation of light gases⁽⁵⁴⁾. These are typical examples of particle production in porous media.

When fluids are flowing through porous media, the various particles migrate by four primary mechanisms ⁽⁵³⁾:

- Diffusion
- Adsorption
- Sedimentation
- Fluid forces

As the fine particles move along the tortuous flow pathways existing in porous media, they are captured, retained, and deposited within the porous matrix. Consequently, the texture of the matrix is adversely altered to reduce its porosity and permeability. Frequently, this phenomenon is referred to as formation damage measured as the permeability impairment.

Invasion of the near-wellbore formation by high pH filtrate, and injecting low surface tension fluids, such as light paraffins including pentane, hexane, diesel, and gas condensates into reservoirs can cause asphaltene precipitation ⁽⁵⁴⁾.

Asphaltenic/paraffinic sludges can be formed with the spent acid at low pH conditions that can be created during acidizing ⁽⁵⁴⁾.

Waxes, asphaltenes, and resins are the typical sources of organic deposition in wells, pipelines, and reservoir formation during petroleum production. As the wells in asphaltene reservoirs are produced, the organic deposition begins within the upper section of the wells over which the pressure drops to below the asphaltene flocculation pressure, and then the organic deposition zone gradually progresses toward the bottom hole and eventually enters the near wellbore formation ⁽¹⁷⁾. Especially, the reservoir formations containing clays of large specific surfaces, such as Kaolinite, can initially adsorb and retain the polar asphaltenes and resins rapidly ⁽¹⁷⁾. As a result, multi-layer molecular deposits are formed over the pore surface. However, as the asphaltene precipitates suspended in the oil phase combine and form sufficiently large aggregates, these particles cannot pass through and are captured at the pore throats ⁽¹⁷⁾. The pore throat plugging causes severe permeability loss because the gates connecting the pores are closed and/or an in-situ cake is formed by pore filling if the plugged pore throat still allows some flow through the jammed particles.

Asphaltene deposits usually seal the flow constrictions because they are sticky and deformable. Therefore, the conductivity of a flow path may diminish without filling the pore space completely ⁽¹⁶⁾.

Leontarities ⁽¹⁸⁾ stresses that the organic damage in oil reservoirs is primarily caused by asphaltene deposition and that the region of asphaltene deposition may actually extend over considerable distances from the wellbore, especially during miscible recovery. Contrariwise, the organic damage caused by wax deposition is rather limited to a short distance (0 to 1 feet) from the wellbore, because wax deposition in the near wellbore region usually occurs by the cooling of the oil caused by high perforation pressure losses during oil production.

Minssieux ⁽¹⁷⁾ carried out some experiments on core damage from crude asphaltene deposition. Analysis of plugging runs carried out with asphaltene crudes in several types of porous media showed clear similarities with permeability alteration caused by fines migration during brine injection. Hence mechanism and related models applied to solid particles filtration had been shown to help the interpretation of core plugging effects observed in the presence of asphaltenes.

Since the available experimental data of asphaltene deposition in porous rocks are not sufficient in the literature, the study of other particulate processes such as water or polymer injection and the

investigation of mechanisms of deposition involved will be a corner stone for identification of the mechanisms of asphaltene deposition in porous media.

2.7 Deposition mechanisms in porous media

Liquid-solid separation can be accomplished either by solid accumulation in front of a filter medium, or by retention inside a deep porous bed. In the first case, a filter cake is built-up and it stops the suspended particles. In the second case, the suspension flows through the porous medium in which the particles are retained. When flowing through the porous medium, the particles are brought into contact with the possible retention sites where they stop or are carried away by the stream. Herzig et al.⁽⁵⁵⁾ performed a comprehensive study on the subject of flow of suspensions through porous media and the application to deep filtration. They concluded that the deep filtration is the result of several mechanisms as follows:

- The contacting of particles with the retention sites
- The fixing of particles on sites
- The breaking away of previously retained particles

They also stated that the clogging rate, i. e., the number of retained particles per unit of time and per unit of volume of porous medium, is related to the various factors which define the system, namely:

- The carrier fluid (flow rate, viscosity, and density)
- The suspension of particles (concentration, size, and shape of particles)
- The porous medium (porosity, diameter of pores, size and shape of grains, and volume fraction already clogged)

Furthermore, the important problem of the pressure drop of the fluid through the bed has to be studied as well as its change with clogging.

Herzig et al.⁽⁵⁵⁾ considered all parameters which describe the elementary mechanisms of clogging and decolmatage (de-clogging) processes, i. e., the retention sites, the retention forces exerted on the particles retained in these sites, the capture mechanisms which bring the particles into contact with the sites, as well as the decolmatage processes of retained particles.

2.7.1 Retention sites: - It is possible to distinguish several retention sites as depicted in the following figures.

2.7.1.1 Surface sites: - as shown in figure (2.4), the particle stops and is retained on the surface of a porous bed grain.

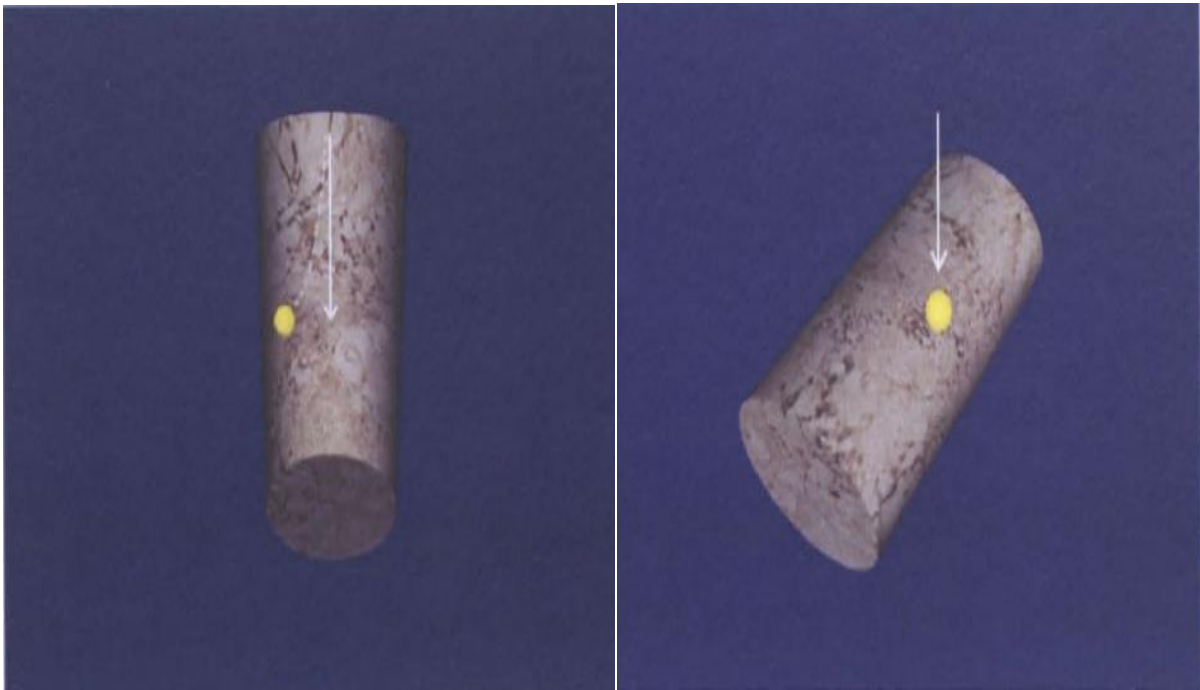


Figure (2.4): Surface sites ⁽⁵⁵⁾

2.7.1.2 Constriction sites:- The particle cannot penetrate into a pore of a smaller size than its own.

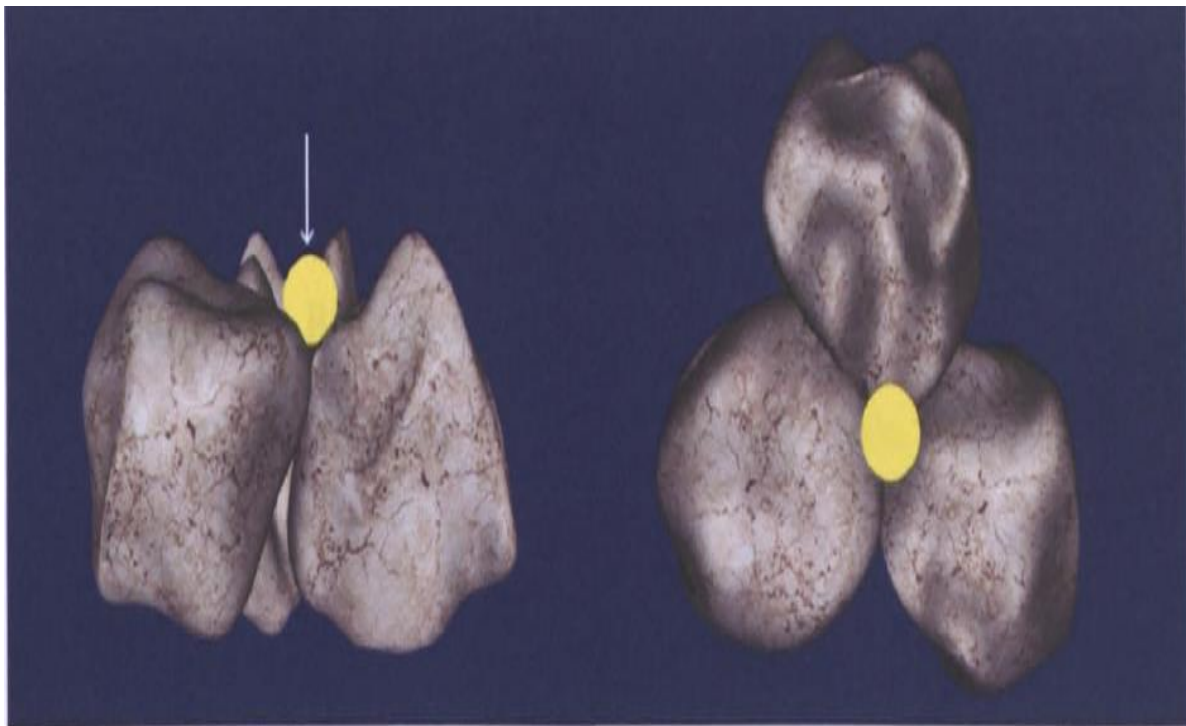


Figure (2.5): Constriction sites ⁽⁵⁵⁾

2.7.1.3 Crevice sites: - The particle becomes wedged between the two convex surfaces of two grains.

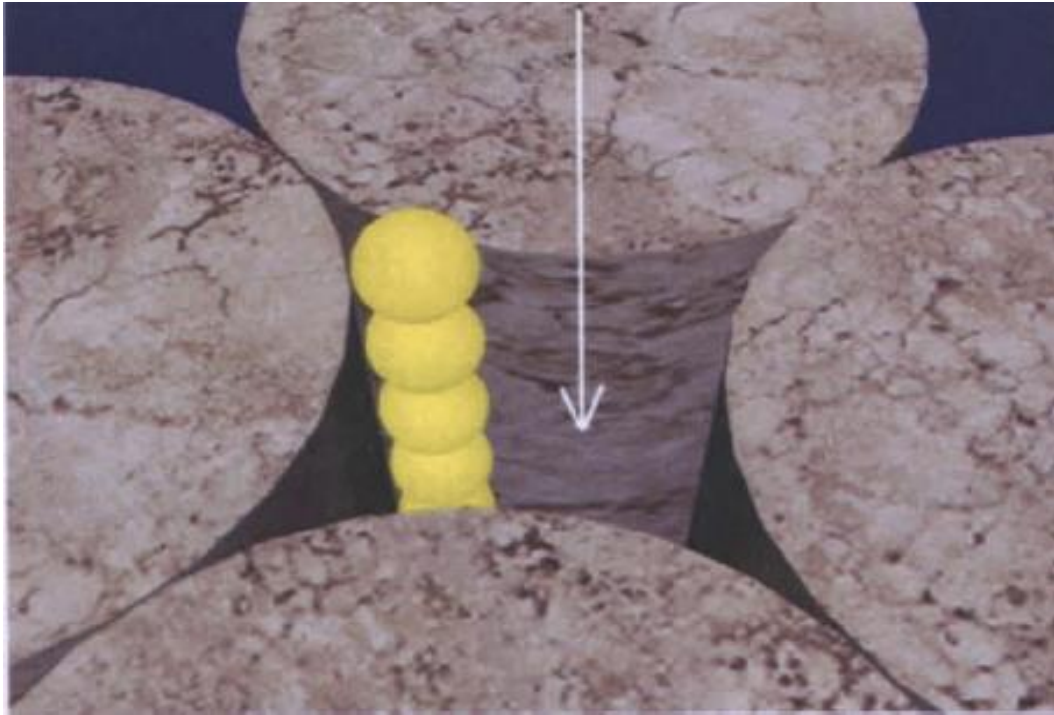


Figure (2.6): Crevice sites ⁽⁵⁵⁾

2.7.1.4 Cavern sites: - The particle is retained in a sheltered area, a small pocket formed by several grains.

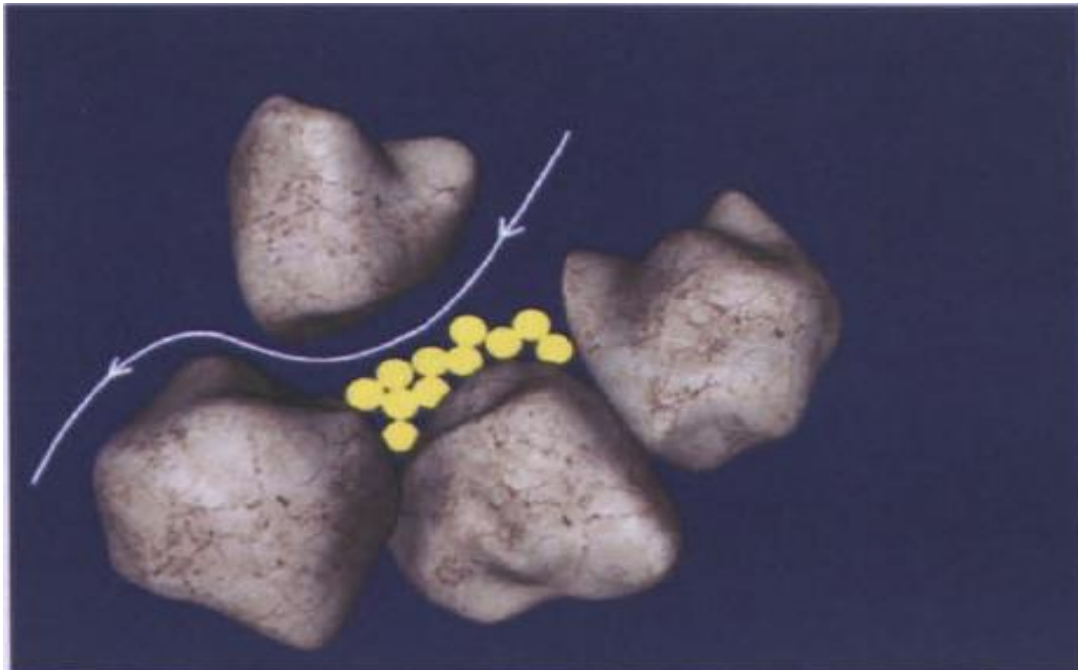


Figure (2.7): Cavern sites ⁽⁵⁵⁾

2.7.2 Retention forces:- The retention forces include:

2.7.2.1 Axial pressure of the fluid:- The fluid pressure may hold an immobilized particle against the opening at a constriction.

2.7.2.2 Friction forces:- A particle wedged in a crevice may have been slightly deformed when stopped, and may remain in place by friction.

2.7.2.3 Surface forces:- These include the Van der Waals forces, which are always attractive, and the electrical forces (electrostatic or electrokinetic) which are either attractive or repulsive according to the physicochemical conditions of the suspension.

2.7.2.4 Chemical forces:- In the case of colloidal particles or in other particular cases, actual chemical bonding may occur.

2.7.3 Capture processes:- The capture processes are as follows:

2.7.3.1 Sedimentation: If the particles have a density different from that of the liquid, they are subjected to gravity and their velocity no longer is that of the fluid; thus, by sedimentation they can meet the filter medium.

2.7.3.2 Inertia: Still owing to their apparent weight, the particles cannot follow the same trajectories as the fluid, they deviate from the streamlines (when the directions of the trajectories change suddenly) and can be brought into contact with the bed grains.

2.7.3.3 Hydrodynamic effects: Owing to the non-uniform shear field and the non sphericity of particles, hydrodynamic effects may occur; these effects cause a lateral migration of suspended particles which may be brought into contact in this way with retention sites.

2.7.3.4 Direct interception: Even with exactly the same density as the fluid, the particles would not be able, owing to their size, to follow the smallest tortuosities of the streamlines of the carrier fluid and they will thus collide with the walls of the convergent areas of the pores.

2.7.3.5 Diffusion by Brownian motion: The particles diffuse and can reach areas which are not normally irrigated by the suspension, and they are retained there.

The permeability damage induced by particle deposition is caused by the additional viscous forces created around the deposited particles. They depend of course on the particle-to-grain size ratio and pore structure, but are mainly sensitive to where deposition occurs. When particles are deposited at a site where fluid velocity is negligible, such as near stagnation points, the permeability change may

be undetectable, while particle bridging at a pore throat where velocity is maximum will cause the maximum change in permeability.

2.7.4 Decolmatage processes

It is necessary to distinguish between the spontaneous decolmatage due to the normal flow of suspension through the clogged bed, and the decolmatage caused by the operator who suddenly changes the flow conditions. Spontaneous decolmatage may occur if local variations in pressure or flow rate change the flow in the neighbourhood of retained particles or if a moving particle collides with a retained particle.

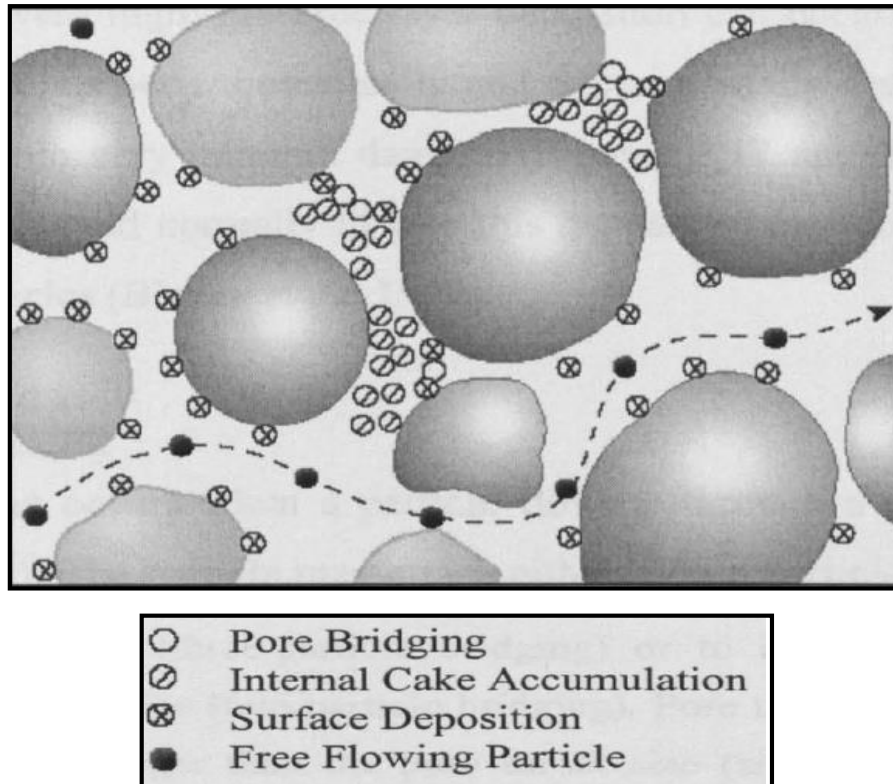
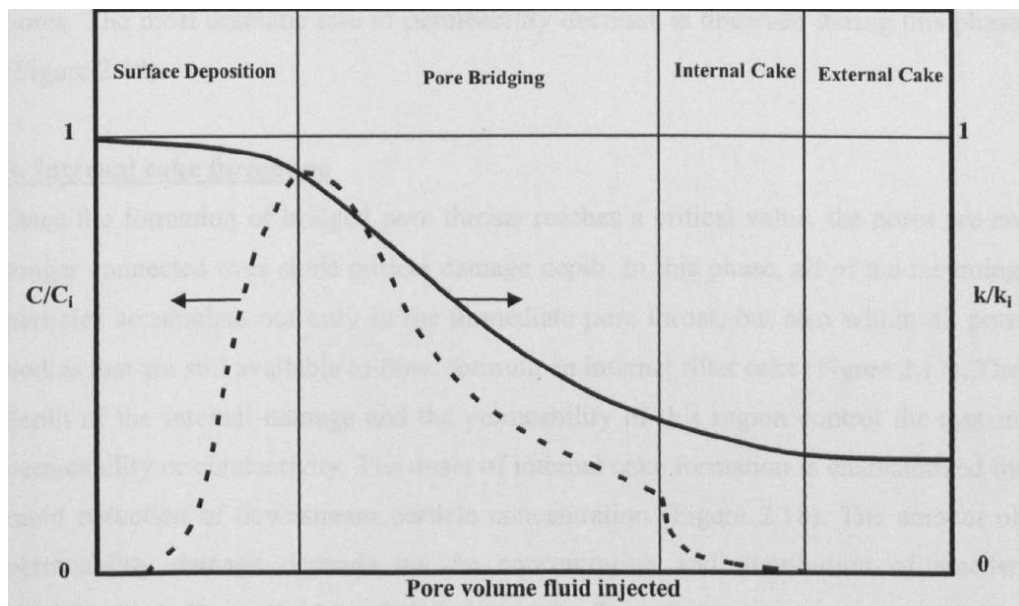
Provoked decolmatage results from impulses, i. e., from sudden variations in pressure or flow rate in the whole bed caused by the operator or by reversal of the flow direction. The processes of spontaneous or provoked decolmatage are similar but the extent of the first is local, whereas the second occurs everywhere in the whole bed.

2.8 The physics of permeability damage

Roque et al.⁽⁵⁶⁾ carried out extensive laboratory experiments with quartzitic sandstone having a well-characterized pore structure and commercial latex microspheres. During these experiments, the main operating parameters, i. e. particle size and concentration, flow rate and porous medium permeability were systematically varied.

A detailed analysis of the obtained results clearly showed that four phases, schematically illustrated in figures (2.8) and (2.9), must be considered to describe the permeability damage process due to the in-depth particle deposition. The dashed line in figure (2.9) represents the ratio of instantaneous concentration of the fines to the initial concentration while the solid line gives the permeability ratio caused as an influence of particle deposition. In each phase, the physics of particle retention and the net effect on permeability are different.

The most significant findings with respect to particle-deposition mechanisms and resulting permeability reduction involve deposition kinetics and the location of particle retention. An important conclusion from this analysis is that interpack conductivity or permeability reduction depends on the specific particle deposition mechanism.

Figure (2.8): Interpack damage mechanisms ⁽⁵⁶⁾Figure (2.9): Phases of fines damage process and relative effects on permeability ⁽⁵⁶⁾

2.8.1 Surface deposition of particles

In this phase, particles deposit on the grain/pore surface. The kinetics of this process depends on physical and chemical factors such as pore-scale hydrodynamics, electrostatic charge differences between particles and pore surfaces, pore-surface texture, and particle composition. The effect of particle deposition on permeability is significant only if it takes place in pore throats.

Thus permeability reduction is not related to the total amount deposited but to the fraction deposited in pore throat areas. Note that surface deposition may be restricted to a monolayer when the flowing suspensions are highly stable, i. e., there are strong repulsive interactions between particles. When the energy barrier opposing aggregation is not very high, multiple layer deposition can occur during this surface deposition phase. It has been theoretically and experimentally demonstrated that this phase alone results in very minimal damage (figures 2.8 and 2.9). Colloidal and clay-sized particles would normally fit into this deposition mechanism in the absence of larger macroparticles ⁽⁵⁷⁾.

2.8.2 Pore throat bridging

Pore throat bridging occurs when a particle flowing through a pore throat forms a bridge (figure 2.9). The particle may attach either to two particles already deposited onto a pore throat surface (three-particle bridging) or to a previously deposited particle and pore throat surface (two-particle bridging). Pore throat bridging can also occur when particles are larger than the pore throat size (single-particle bridging).

Once a bridge is formed and consolidated, the newly arriving particles accumulate upstream from bridged pores, thus decreasing drastically fluid flow through these pores. The most dramatic rate of permeability decrease is observed during this phase (figure 2.9).

2.8.3 Internal cake formation

Once the formation of bridged pore throats reaches a critical value, the pores are no longer connected over some critical damage depth. In this phase, all of the incoming particles accumulate not only in the immediate pore throat, but also within all pore bodies that are still available to flow, forming an internal filter cake (Figure 2.8). The depth of the internal damage and the permeability of this region control the system permeability or conductivity. The onset of internal cake formation is characterized by rapid reduction of downstream particle concentration (Figure 2.9). The amount of permeability damage depends on the concentration and distribution of smaller particles (including colloidal and clay size) in the flow stream.

2.8.4 External cake formation

At the point where internal cake formation is achieved, particles accumulate upstream from the inlet of the porous medium, thus forming an external cake (Figures 2.9 and 2.10). The various particulate processes are schematically depicted in Figure (2.10).

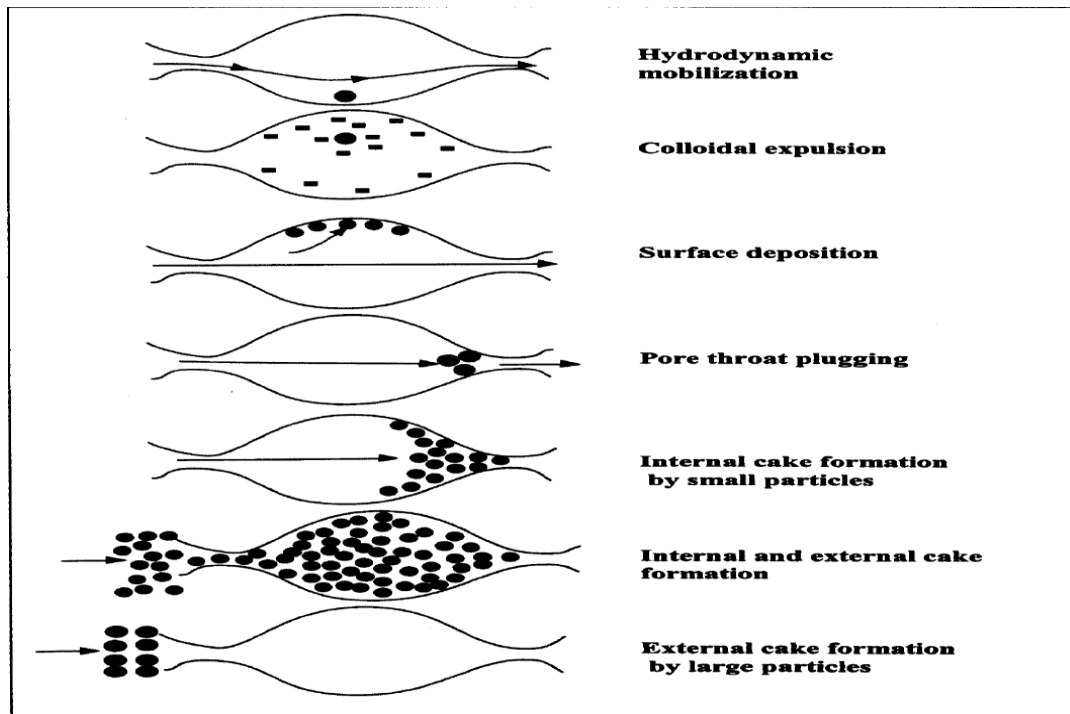


Figure (2.10): Various Particulate processes ⁽¹⁶⁾

2.9 Basic Asphaltene Models

Before the factors that cause asphaltene precipitation are discussed, some basic models and important controversies from the prevailing literature should be known. This is important because there exists several theories and models regarding the stability of asphaltenes which are not completely congruent and thus give rise to different ways of understanding the asphaltene phenomenon and its precipitation mechanisms.

2.9.1 Thermodynamic Model Versus Colloidal Model

The stability of asphaltenes (and thereby also the precipitation mechanisms) is a subject of some controversy in the literature ⁽³¹⁾. Numerous models based on different microscopic theories have been proposed for predicting asphaltene precipitation ⁽⁴⁰⁾.

Essentially, there are two different physical models available for description of asphaltene in crude oil, namely the thermodynamic model (also called the true solution model) and the colloidal model ^(24,41).

The true solution model is based on the assumption that asphaltene precipitation process is thermodynamically reversible. This may happen since it is assumed that the asphaltene particles can

be dispersed and stabilized in the oil. The complete dissolution of asphaltenes in some organic solvents such as toluene supports this assumption⁽⁴²⁾.

The colloidal approach is based on the assumption that asphaltenes are solid particles colloiddally suspended in crude oil and stabilized by the resin molecules⁽⁴²⁾. When the adsorbed resin molecules are dissolved into solution, asphaltene particles may undergo aggregation to form larger flocculations under Van der Waals attraction forces (London forces). This concept is based mainly on titration experiments, which demonstrate that once the adsorption equilibrium of resins between solid (asphaltene) and liquid phases is disturbed by adding paraffinic solvents, the asphaltene particles flocculate irreversibly⁽⁴²⁾. Whether the asphaltene-crude solution is a true solution or a colloidal solution is still debatable, but a number of asphaltene stability models with different assumptions and limitations have evolved from these two views⁽⁴²⁾.

2.9.2 Stability of Colloidal Dispersions

Within the colloidal chemistry, there exists two theories that account for the stability of colloidal dispersions⁽⁴³⁾. They are called the “DLVO Theory” and “The Steric Stabilization Theory”. The DLVO theory (named after its authors) is applicable to electrolytic systems where stabilization is due to an electrical double layer.

The steric stabilization theory is applicable to systems where the dispersed phase is stabilized by repulsive interactions between molecules adsorbed on the surface of the suspended particles⁽⁴³⁾.

2.9.3 Thermodynamic Colloidal Model

The Thermodynamic Colloidal Model is central in most of the literature concerning asphaltene stability and precipitation. It was developed by Leontaritis and Mansoori⁽⁴³⁾ who, based on the nature of asphaltene particles and the other contents of petroleum fluids, believed that asphaltene dispersions in oil corresponded best with the steric stabilization theory. In this model, the asphaltene particles are assumed to be both partly dissolved in the oil and partly in colloidal and/or micellar form⁽⁴³⁾. This depends largely on the other particles present in the oil (e.g. resins, paraffins and aromatics)⁽³⁰⁾. The solid asphaltene particles in colloidal suspension are believed to be stabilized against further aggregation by resins that have adsorbed onto their surface acting like a repulsive barrier. The chemical interaction between asphaltenes and resins creates a soluble particle called micelle⁽⁴⁴⁾. The asphaltenes present in micelles are said to be in micellar form, and the resins then form a protective layer around the asphaltenes.

The forces responsible for creating the repulsive barrier are short ranged intermolecular repulsive forces, called steric forces.

These forces are created between the resin layers. Since the repulsive forces are stronger than the attractive Van der Waals forces responsible for aggregating the asphaltenes, the asphaltenes remains dispersed (stabilized).

Experimental part of this research includes two main parts

PART 1: This part focuses on the investigation of asphaltene deposition effects on porous media properties such as porosity reduction, permeability damage and wettability alteration of reservoir rocks during CO₂ gas injection by dynamic flow tests. In this work two common rock types (limestone and sandstone) from Libyan hydrocarbon reservoirs are used as porous media rock representative. The properties of these porous media are listed in table (3.1).

Table (3.1): Properties of porous media

Property Rock type	Length (L) cm	Diameter (d) cm	Pore volume (PV) cm ³	Porosity (ϕ) %	Permeability (K _{air}) mD	Permeability (K _i) mD
Limestone	5.47	3.81	13.588	21.996	17.599	7.13
Sandstone	5.24	3.83	6.219	10.352	25.858	6.61

PART 2: consists of the investigation of the effect of CO₂ gas injection pressure and CO₂ concentration on asphaltene precipitation and the influence of CO₂ induced asphaltene precipitation on formation properties, three limestone core samples were selected for the experiment. Rock properties tests were conducted for each core sample by Helium gas Porosimeter equipment and nitrogen gas permeameter as it is illustrated in figures (3.1 and 3.2) the results for porosity and permeability measurement are shown in table (3.2).

Table (3.2): Core properties before displacement tests

Core No.	Length (L) cm	Diameter (d) cm	Pore volume (PV) cm ³	Porosity (ϕ) %	Permeability (K _{air}) mD	Permeability (K _i) mD
1	5.40	3.80	13.94	23.40	13.60	5.915
2	5.34	3.75	14.41	24.40	11.28	4.889
3	5.40	3.80	14.65	24.35	12.97	5.502

Dynamic asphaltene precipitation tests were carried out with several runs at different CO₂ injection pressures, Variations in injection pressure makes it possible to assess the effect of carbon dioxide pressure on asphaltene precipitation phenomena.

CO₂ gas with 99.9 % purity was applied for flooding tests.

The effects of asphaltene precipitation were investigated by using core flooding apparatus. These experiments were conducted using actual reservoir liquids, brine and CO₂, flowing through actual cores under similar reservoir conditions of temperature and pressure.

For the core flood experiments synthetic brine was prepared in the laboratory from de-ionized water, 84.30 grams of sodium chloride (NaCl) per liter of water. The prepared solution has a salinity of 80,000 ppm with a density of 1.054 g/cc. The saturation procedure is used to restore the water-wet nature of the rocks.

3.1 Selection and preparation of crude oil

To select the best crude oil for the study, different crude oils from various Libyan oil fields were carefully considered. After analyzing the asphaltene content of the different crude oils, the oil with an asphaltene content of approximately 1.92 wt% was selected; the crude oil under study has an API gravity of 34.06

The crude was stored under laboratory conditions to allow any volatile components to evaporate, in order to provide a stable condition and to obtain crude with relatively fixed composition.

3.2 Crude oil properties determination:

Before determination of the properties of the crude, it was filtered to remove any sand particles, for filtering the crude, a piece of standard filter paper Wattman 42 was placed on a Buckner funnel and the crude poured on it.

3.2.1 Determination of crude oil density and viscosity:

The density and viscosity of the crude oil sample were measured at different temperatures using Anton-Paar SVM 3000 Stabinger Viscometer according to ASTM D7042-04 standard test method, the measuring variables are dynamic viscosity, kinematic viscosity and the density, the temperature ranges from -60 °C to +105 °C, while the asphaltene content of the crude was measured using IP/143 standard method.

The properties of crude oil sample are listed in table (3.3).

Table (3.3): Crude oil properties

Density of crude oil, (ρ_o) at 25 °C, g/cc	0.8566
Density of crude oil (ρ_o) at 90 °C, g/cc	0.8097
Viscosity of crude oil (μ_o) at 25 °C, cp	11.0
Viscosity of crude oil (μ_o) at 90 °C, cp	3.1
Asphaltene content of crude oil, (W), wt%	1.92

3.2.2 Determination of the amount of asphaltene precipitated:

The amount of asphaltene precipitated was determined using the standard method IP/143, this standard specifies a procedure for the determination of the heptanes insoluble asphaltene content of gas oil, diesel fuel, residual fuel, lubricating oil, bitumen and crude petroleum which has been topped to an oil temperature of 260 °C. The procedure for this method is presented in detail in appendix (A) and briefly outlined as follows:

1. Weigh a quantity of sample into a flask of appropriate capacity.
2. Add heptanes to the test portion in the flask at a ratio of 30 ml to each 1 gram of sample.
3. Mix the contents until the test portion has fully dispersed within the heptanes then boil the mixture under reflux for 60 min $\pm$ 5 min, remove the flask and the contents at the end of this period, cool, close with a stopper and store in a dark cupboard for 90 min, calculated from the time of removal from reflux.
4. Place the folded filter paper in the filter funnel using forceps; thereafter handle the filter paper only with forceps. Without agitation, decant the liquid into the filter paper, and then transfer the residue in the flask as completely as possible with successive quantities of hot heptanes, using stirring rod as necessary. Give the flask a final rinse with hot heptanes and pour the rinsings through the filter. Set the flask a side without washing for use again after the next step.
5. Remove the filter paper and the contents from the funnel and place in the reflux extractor. Using a flask different from that used initially, reflux with heptanes at rate of 2 drops/sec to 4 drops/sec from the end of the condenser for an extraction period of not less than 60 min, or until a few drops of heptanes from the bottom of the extractor leave no residue on evaporation on a glass slide.
6. Replace the flask by the one used initially, and to which has been added 30 ml to 60 ml of toluene and continue refluxing until all the asphaltene have been dissolved from the paper.
7. Transfer the contents of the flask to a clean and dry evaporating vessel weighed to the nearest 0.2 mg by tare against a similar dish.
Washout the flask with successive small quantities of toluene to a total not exceeding 30 ml. Remove the toluene by evaporation on a boiling water.
8. Dry the dish and contents in the oven for 30 min. cool in the cooling vessel for 30 min to 60 min and re-weigh by tare against the dish used previously for this purpose, and which has been subjected to the heating and cooling procedure as was the dish containing asphaltenes.

9. Calculate the asphaltene content, A in % (m/m), of petroleum products using the equation:

$$A = 100 \cdot (M/G)$$

Where: M is the mass of asphaltenes, in grams

G is the mass of test portion, in grams

3.3 Selection of porous media:

Two types of porous media (sandstone and limestone) were selected in order to investigate the effect of asphaltene precipitation in porous media. Rock properties tests were conducted for each core sample is shown in Table (1).

3.4 Porous media properties measurements:

Before running the core flood experiments the properties of porous media was measured as follows:

3.4.1 Dean Stark Analysis:-

The equipment as shown in figure (3.1) consisted of a flask, a sample chamber with side arm for collection of water and a condenser with a silica gel filter fitted to the top as an atmospheric water trap. The solvent used for extraction was toluene; this has been previously de-watered by distillation, and refluxed in each extraction unit for at least twelve hours to remove any water in the system. Water if present, accumulated in the trap, was removed from the system and preliminary recycling continued. The core chips were taken from the core, weighed and transferred immediately to clean, pre-weighed tares.



Figure (3.1): Dean stark apparatus

The tares with samples were sealed without delay in distillation apparatus and the system was refluxed for a minimum of 24 hours. Water accumulation in the graduated side arm was recorded,

and when the samples stabilized were removed. Upon removal from extraction apparatus, the samples were tested for fluorescence under ultraviolet light to check for hydrocarbon presence.

The samples were subsequently transferred to a standard oven at 60° C, and dried at constant weight. Once dried and weighed, the samples with tares were placed in individual soxhlets and cleaned with methanol to remove salts.

The methanol in the soxhlet chamber was tested with silver nitrate solution to ensure that the salt derived from formation water had been removed from the sample.

Finally the samples were returned to the oven and again dried to constant weight and subjected to porosity measurements in the manner discussed below.

3.4.2 Porosity, Permeability and Grain Density Measurements:-

The clean, dry samples were subjected to various analyses to determine porosity, permeability and grain density values where possible. The experimental procedures and equipment specifications are discussed below:-

3.4.3 Helium Gas Expansion Porosimeter:-

Core analysis laboratory of Libyan Petroleum Institute use a twin cell helium expansion gas porosimeter for the plug samples grain volume measurement. The porosimeter as shown in figure (3.2) operates using the principle of Boyle's Law.

A sealed reference chamber in the instrument is filled with helium gas at ambient temperature to a pressure of 100 psig. A sample is placed in another sealed chamber, connected to the reference chamber by a two way valve.

This valve when opened allows the gas in the reference chamber to expand into the combined volume of the two chambers. From Boyle's Law, The volume of the sample chamber can be calculated when the volume of the reference chamber, the initial pressure and the final pressure are known.

The instrument must be calibrated before using the porosimeter for analysis. This is done by running a series of stainless steel blanks of known volumes, to build up a graph of blank volume versus the inverse of the final pressure.

The resulted calibration graph has to be entered into a computer program which performs a linear regression, producing an equation relating the grain volume of any sample run to the final pressure reading.

The porosity and the grain density were then calculated by determining the bulk volume, and the weight of the sample.



Figure (3.2): Helium gas expansion porosimeter

The instrument used by our laboratory has the following specifications:-

Pressure indicator with remote pressure transducer

Range	:	0 -100 psi
Resolution	:	0.01 psi
Accuracy	:	$\pm 0.1\%$ of the full scale

Precision Pressure Controller

Range	:	0 -100 psi
Resolution	:	Better than 0.01 psi
Repeatability	:	Better than 0.02 psi

3.4.4 Positive Displacement Pump:-

The positive displacement mercury pump is used to determine the bulk volume of each sample. The unit consists of a stainless steel high pressure pycnometer (sample container); it is attached to the volumetric pump cylinder. As the hand wheel connected to the pump is wound in or out, mercury is

charged or withdrawn from the sample chamber. The volume of mercury displaced is measured linearly by a digital transducer connected to the pump.

In practice, mercury is allowed into the pycnometer to a set reference mark, and the transducer set to zero. This process should be repeated several times to ensure accuracy. The mercury is subsequently released back into the pump and the sample is placed and sealed in the pycnometer.

After that mercury is allowed back into the pycnometer up to the previously determined reference mark, and the display shown on the digital transducer noted. This value is later converted to the actual volume by using a simple correction factor derived from calibration volumes. The mercury is cleaned and the pump reset to zero at least once every four samples, depending on the sample type.

3.4.5 Calculation of Porosity:-

The porosity of a plug sample is calculated by using the following equations:-

Pore volume, (PV), cc = Bulk volume, (BV) - Grain volume, (GV)

Porosity, (ϕ %) = Pore volume, (PV) / Bulk volume, (BV) *100

Grain density, (gm/cc) = Sample weight, (w) / Grain volume, (GV)

3.4.6 Nitrogen Gas Permeability:-

The clean, dry sample is placed in the Hassler-type core holder as shown in figure (3.3), and an overburden pressure of 200 psig is applied to the cell, compressing the rubber sleeve around the sample.

Nitrogen gas pressure is applied to one end face of the sample, whilst the other end face is open to atmospheric pressure, causing the gas to flow through the sample. The flow of gas is measured at the low pressure (downstream) end face of the sample. The flow rate is measured by passing the gas through one of three laminar flow orifices and measuring the differential pressure developed across the orifice.



Figure (3.3): Nitrogen gas permeameter

The transducers and flow orifices are calibrated using a dead weight tester and soap film meter at least once every three months, or when any component is altered or replaced.

The equipment specifications are as follows:-

High pressure precision regulator

Range : 0 - 30 psi

Resolution : Better than 0.01 psi

High pressure transducer and readout (upstream)

Range : 0 - 100 psi

Resolution : 0.01 psi

Accuracy : ± 0.1 % of the full range

Low pressure transducer and readout (upstream)

Range : 0 - 15 psi

Resolution : 0.001 psi

Accuracy : ± 0.1 % of full scale

The length of the sample, upstream and downstream pressures, flow rate, viscosity of nitrogen, barometric pressure and temperature are entered into Darcy's equation for gas permeability, equation (3.1), and the permeability of the sample calculated.

$$K_g = \frac{2000 \times P_b \times Q_g \times \mu_g \times L}{(P_1^2 - P_2^2) \times A} \dots\dots\dots (3.1)$$

Where:

K_g : Gas permeability, mD

P_b : Barometric pressure, atm

P_1 : Upstream pressure, atm

P_2 : Downstream pressure, atm

Q_g : gas flow rate, cc/sec

μ_g : Gas viscosity, cp

L : Sample length, cm

A : Cross-sectional area, sq. cm

Klinkenberg Permeability:-

The Klinkenberg permeability correction is calculated using the mathematical relationship between K_g and K_l as follows:

$$K_l = 0.68 (K_g)^{1.06} \dots\dots\dots \text{(Empirical Correction)}$$

This empirical correction is valid for permeability ranges from 0.01 up to 174 mD and from 175 to 7500 mD using the following table:

(K_g) Permeability range, mD	(K_l) Klinkenberg Permeability, mD
175-299	$K_g - 20$
300-699	$K_g - 30$
700-999	$K_g - 40$
1000-1699	$K_g - 50$
1700-2299	$K_g - 60$
2300-5799	$K_g - 80$
5800-7500	$K_g - 100$

3.5 Experimental work with porous media

To understand the phenomenon of asphaltene deposition at reservoir conditions several experiments were conducted with a reservoir rock porous medium. The experimental setup was designed to conduct these experiments at high pressures and high temperatures matching the reservoir conditions. Details of the experimental equipment and procedures are described in this chapter.

3.5.1 Experimental setup:

The experimental setup is shown in Figure (3.4) schematically. A photograph of the experimental setup is given in Figure (3.5). The experimental setup consists of an oven assembly, control panel, two injection pumps type D series syringe pump, three fluid reservoirs mounted on a rack, nitrogen gas cylinder with a pressure gauge regulator and numerous pieces of glassware.

The reservoir condition core flood equipment was used to carry out all the reservoir condition investigations.

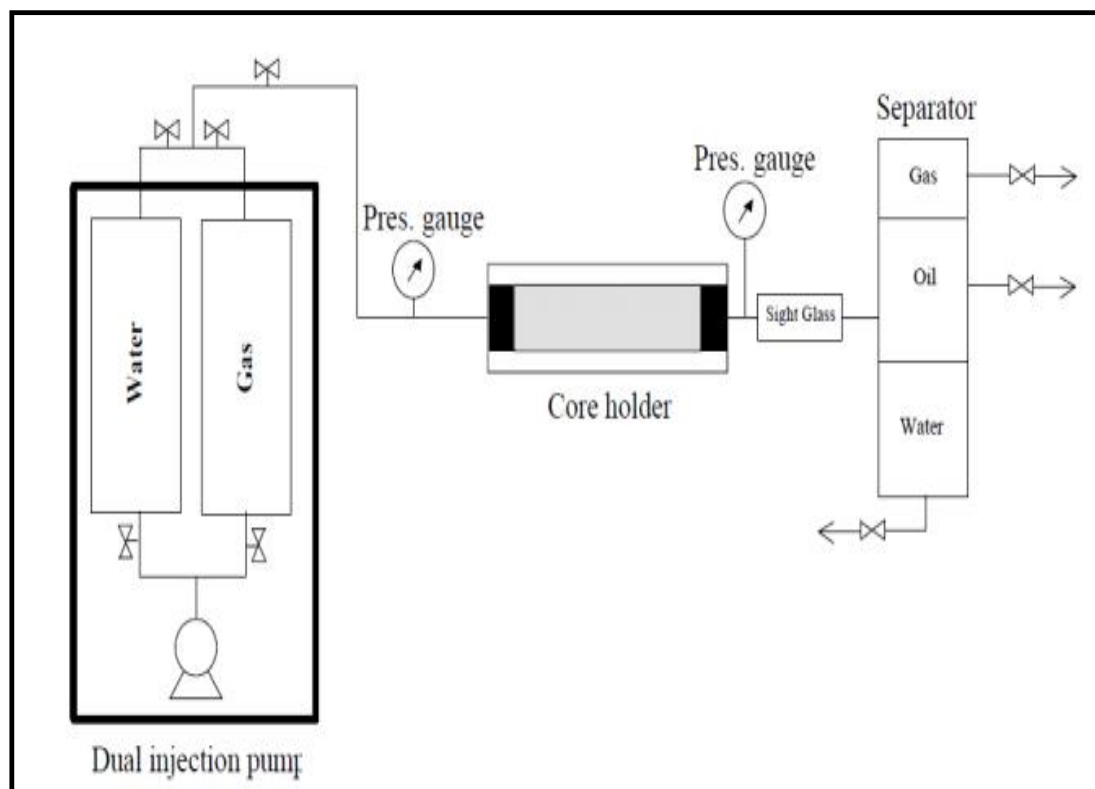


Figure (3.4): Schematic diagram of the experimental setup

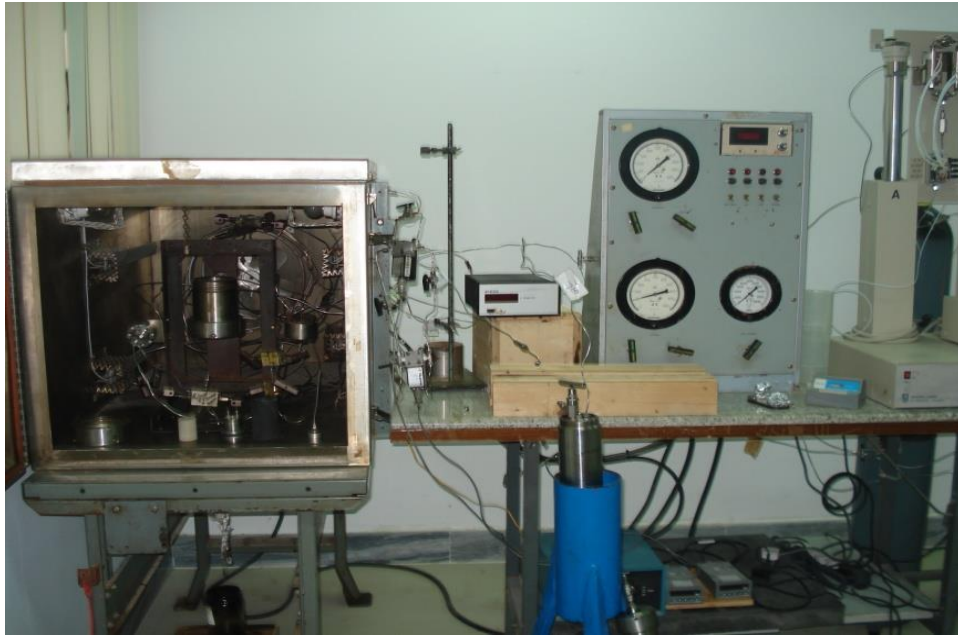


Figure (3.5): Photograph of the core flood equipment

The entire core flooding system consisted of:

1. An oven assembly: This provides temperature during the testing.

Subcomponents contained within the oven include:

- 1.1. The core holder, which is mounted within the oven, is a vessel designed to hold the core sample, subject it to simulated reservoir overburden pressure and allow fluids to pass through it. The core holder utilizes hydrostatic pressure, such that confining pressure is equally applied to all surfaces of the core sample. The core is retained in a neoprene sleeve by two ends plugs, which conform to the ends of the sample and permit fluid flow through the core. This system allows the application of up to 10,000 psig pressure on the sample.
- 1.2. Heater coils for both oil and water.
- 1.3. Heating elements for the air within the oven.
- 1.4. Oil filter.
- 1.5. Thermometer.
- 1.6. An air circulating fan.

The oven has window for observations and hinged doors for internal component access.

2. Control Panel: is the monitor and control unit for the system.

Three 5000 psig gauge monitor: overburden pressure gauge, the confining pressure on the core sample; upstream pressure, the pressure which pushes fluids into and through the core sample;

and back pressure, the pressure which retains fluids in the core sample. Several valves are grouped with these gauges to control the pressures entering the oven assembly and the core holder, a digital transducer monitor is mounted in the control panel and shows the differential pressure between the upstream and downstream flow pressures for fluids passing through the sample.

3. Core rubber sleeve which protects the core in the core holder and applies uniform overburden pressure to the core.
4. Measuring cylinder (separator) to measure the flow rates and fluid volume at the outlet of fluids produced from the core.
5. High pressure injection pumps: The 260D Isco D-Series pump module as shown in figure (3.6) was used in the experiments, and is a syringe pump designed specifically for refilling under high pressure and pressure programming to handle supercritical fluids.

With pressure control to 7,500 psi (517 bars) and a flow rate range from sub-microliter to 100 ml/min, the 260D offers exceptional versatility for almost any type of R&D or method development with supercritical CO₂ and other fluids. Dual-pump systems can provide the capability to meter solvent modifiers into the flow stream, or to deliver non-stop continuous flow.



Figure (3.6): Photograph of the 260D Isco-type high pressure syringe pump

3.5.2 Flooding Experiments:

A series of flooding tests were carried out in order to determine the effect of asphaltene precipitation on porous media properties, the procedures for the flood test is as follows:-

Before running the flooding tests the permeability, porosity, pore volume, length and diameter were measured on the selected clean dry core samples then the clean, dry samples were loaded in a stainless steel pressurized cell and evacuated for 24 hours. A sodium chloride solution of (80,000 ppm) was introduced at the end of the period, followed by pressurizing the system at 2500 psig for 24 hours to assist penetration. Gravimetric checks were made to ensure complete saturation of pore spaces.

3.5.3 System setup and test procedures:-

1. Disassemble, clean and reassemble all oil lines.
2. Fill the high pressure injection pump with water.
3. Clean and fill the high pressure vessel with crude oil.

The high pressure vessel have a circular piston inside which can move easily up and down, the piston divides the cylinder volume into two parts, The upper part is filled with the displaced fluid (crude oil) and the lower part with the displacing fluid (water). The role of the piston is simply to prevent mixing of the two fluids. The vessel has to end caps with a one-way high pressure valves to control the flow of fluids. To fill the vessel with crude oil simply open the upper end cap and pour the crude oil in the vessel and tightly replace the cap. Then pressurize the oil sample in the vessel to the required pressure by connecting a 1/8 “ stainless steel line from the top end of the injection pump to the bottom end of the vessel.

4. Open the core holder by removing the top and bottom end caps.
5. Install the rubber sleeve over the upstream end plug inside the core holder, making certain it is pushed completely on.
6. Insert the prepared core sample into the sleeve.
7. Insert the downstream end plug and stem into the sleeve and push the core sample until it touches the upstream end plug.
8. Replace the end cap on the core holder.
9. Open the overburden valve, connect to injection pump and apply overburden pressure to the core sample and close the valve.
10. Connect a line from the tee connector on the back pressure regulator to the downstream stem on the core holder.

11. Apply gas pressure to the back pressure regulator using nitrogen cylinder.
12. Connect the top end of the high pressure crude oil vessel to the top end of the core holder and open the upstream end plug of the core holder.
13. Turn on the oven heater and set the temperature control to the desired temperature of 90 °C.
14. As the system temperature approaches temperature equilibrium, all connections should be inspected for leaks.
15. Place a receiving tube under the effluent flow of the back pressure regulator. Start flow by reducing the back pressure.
16. When the flow is observed, start the timer. Collect the effluent which should be water in the receiving tube.
17. Continue injecting oil until no more water was produced, the amount of the producing water is measured, difference between the initial water saturation and the produced water will be the amount of the irreducible water.
18. The oil flooding continues and produced oil is collected in a receiving tube for each pore volume injected.
19. The upstream and the downstream pressures and the produced oil volumes, are recorded at each pore volume injected.
20. The instantaneous permeability, porosity and the asphaltene content for the produced oil is measured.
21. The amount of deposited asphaltene in the porous media was measured during oil injection to depict the deposition effect of porous media properties.
22. For determination of CO₂-induced asphaltene precipitation, Core samples were then subjected to Carbon Dioxide (CO₂) gas injection, CO₂ was injected into oil-saturated porous media, the asphaltene content was measured to determine the effects of injected CO₂ on asphaltene precipitation. The amount of produced water was measured to evaluate the change of the irreducible water saturation due to additional asphaltene precipitation.
23. Influence of gas injection pressure on asphaltene precipitation was also examined. Three Limestone core samples with approximately same rock properties were tested for the effect of gas injection pressure. The tests were carried out with several runs at different CO₂ injection pressures, the core holder temperature and pressure were fixed at 90 °C and 2500 Psig, the selected injection pressures were 700, 1300 and 1750 Psig. CO₂ was continuously injected with a flow rate from 0.3 – 0.35 cc/min and the recovered oil was collected at every 10 minutes until there was no more produced oil was observed. The samples collected were

analyzed for asphaltene content and the porous media properties were measured for each pressure injection.

24. The variations of permeability versus pore volumes of fluid injected were measured by applying Darcy's law for single phase flow:

$$K = 14700 (q \mu L / A \Delta P) \dots\dots\dots (3.2)$$

Where:

K = Permeability, mD

q = Flow rate, cc/min

μ = Viscosity, cp

L = Length, cm

A = Cross-sectional area, cm²

ΔP = Pressure difference, Psig

In this chapter, all the experimental observations previously outlined in chapter 3 will be presented. The experiments carried out to fulfill the objectives of this study may be classified into four main categories:

- Porous media effects.
- Influence of CO₂ injection on asphaltene precipitation.
- Effect of gas injection pressure on asphaltene precipitation.
- Influence of CO₂-induced asphaltene precipitation on porous media properties.

4.1 Porous Media Effects:-

In this experiment two core samples (Sandstone and Limestone) were used, the properties of the core samples are shown in table (3.1) in chapter (3).

The samples were cleaned using soxhlet extraction apparatus and dried in a regular oven at temperatures from 50 to 100 °C. Each core sample was then saturated with water of 80,000 PPM salinity.

Dead oil was injected into the porous media at a rate of 1.0 cc/min. The asphaltene content of the produced oil was measured at each pore volume injected during oil flood and the volume of the produced oil was measured.

The oil injection was continued until no more water production is obtained, the irreducible water saturation and maximum oil saturation were determined from material balance.

The original asphaltene content of injected oil was 1.92 % weight. Figures (4.1) and (4.2) depict the effect of pore volume injected on asphaltene deposition during oil injection for limestone and sandstone core samples, respectively.

The asphaltene content of the produced oil at first pore volume of oil injection was reduced from 1.92 wt% to 1.65 wt% for limestone and from 1.92 wt% to 1.79 wt% for sandstone due to the asphaltene adsorption on the clean surface of porous media.

After 2.0 pore volumes of oil injection for limestone and 3.0 pore volume of oil injection for sandstone, the water production was stopped.

During this process the asphaltene content of the produced oil started to increase but remained below the initial value, because the outflow of water in porous media leads to creation the new sites for additional deposition of asphaltene.

Once the water production is stopped, the asphaltene content of the produced oil reached a value near the original value at 3.0 pore volumes of oil injected for limestone and 6.0 pore volumes of oil injected for sandstone. This increase indicates the possible re-dissolution of adsorbed asphaltene on the porous media surface. The fluctuation of asphaltene content of the produced oil around the initial value with additional oil injection was due to slight re-dissolution and tacking-off of the adsorbed asphaltene.

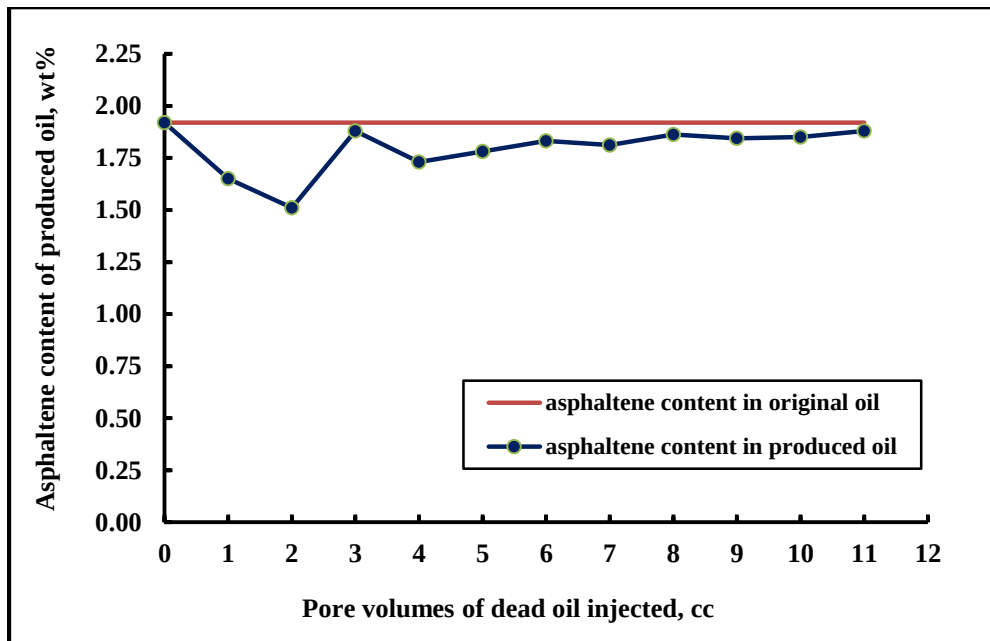


Figure (4.1): Asphaltene content of oil produced during oil flood (Limestone)

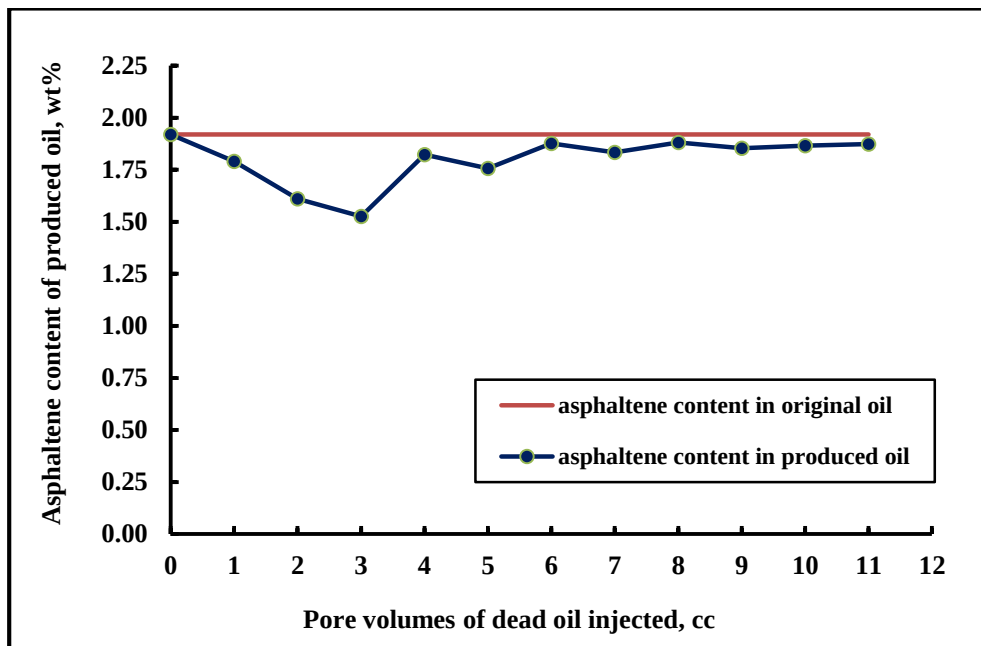


Figure (4.2): Asphaltene content of oil produced during oil flood (Sandstone)

This fluctuation stopped after about 8.0 pore volumes of oil injected for limestone and 9.0 pore volumes of oil injected for sandstone and the asphaltene content of the produced oil almost reached near its initial value. This state may be assumed as the steady state condition. Steady state indicates that the ability of porous media for adsorption of asphaltene has come to the end and the natural gas flooding effects on additional asphaltene deposition can be tested.

Figures (4.1) and (4.2) indicate that the presence of water film on rock surface can reduce or delay the asphaltene deposition process. In strongly water-wet rocks such as sandstone, the presence of water shields more surfaces from direct interaction with asphaltene. As a result the amount of asphaltene deposition onto more water-wet surfaces will be less than the amount deposited onto less water-wet surfaces such as some limestone.

Besides, these figures show that the asphaltene deposition rate on the sandstone surface is less than the deposition rate on limestone media that is, in comparison with the limestone medium it takes more time for the oil in sandstone media to displace water and reach its initial asphaltene content.

Figures (4.3) and (4.4) show the permeability ratio (K_d / K_i) variations as a function of pore volume of dead oil injection into the porous media. From these figures we can find that both the adsorption and desorption of asphaltene through porous media occurred.

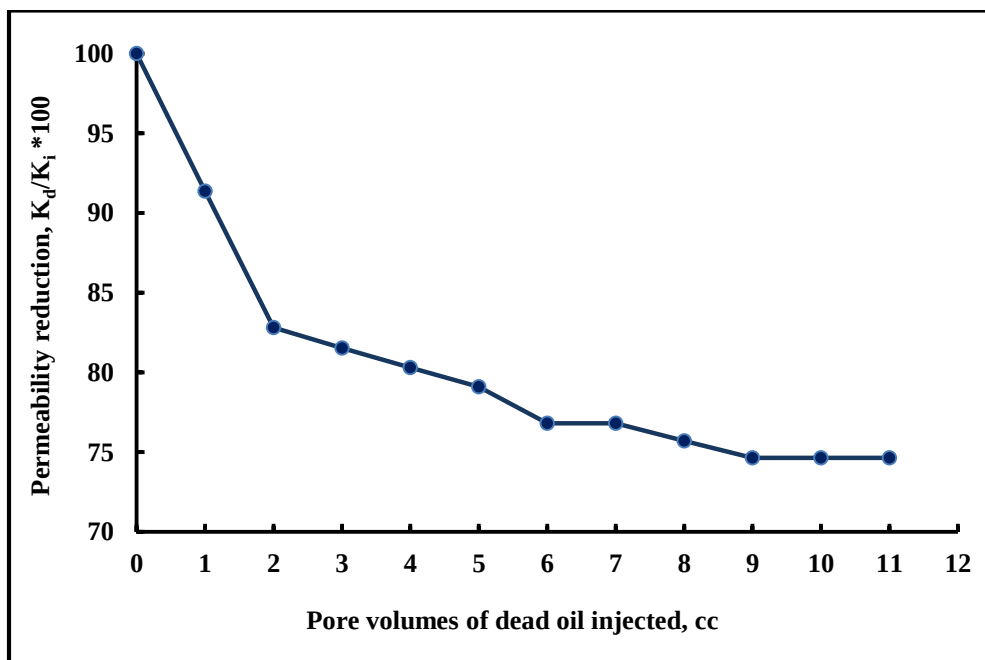


Figure (4.3): Permeability ratio variations during oil injection (Limestone)

At first the high rate of asphaltene adsorption on porous media causes high permeability and pressure drop reduction, then after a certain amount of dead oil flooding almost 2.0 and 3.0 pore volumes for

limestone and sandstone respectively the desorption process starts and the slope of the permeability reduction is decreased.

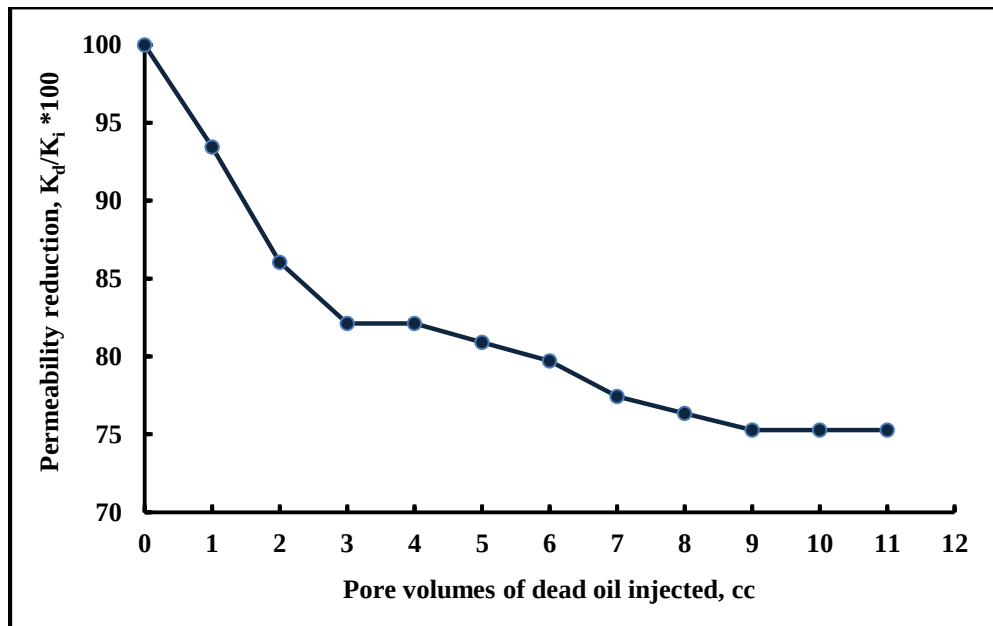


Figure (4.4): Permeability ratio variations during oil injection (Sandstone)

The porosity ratio (ϕ_d / ϕ_i) reduction due to asphaltene deposition during oil injection is shown in figures (4.5) and (4.6). It can be seen that the higher the asphaltene deposition on porous media the greater is the reduction in porosity.

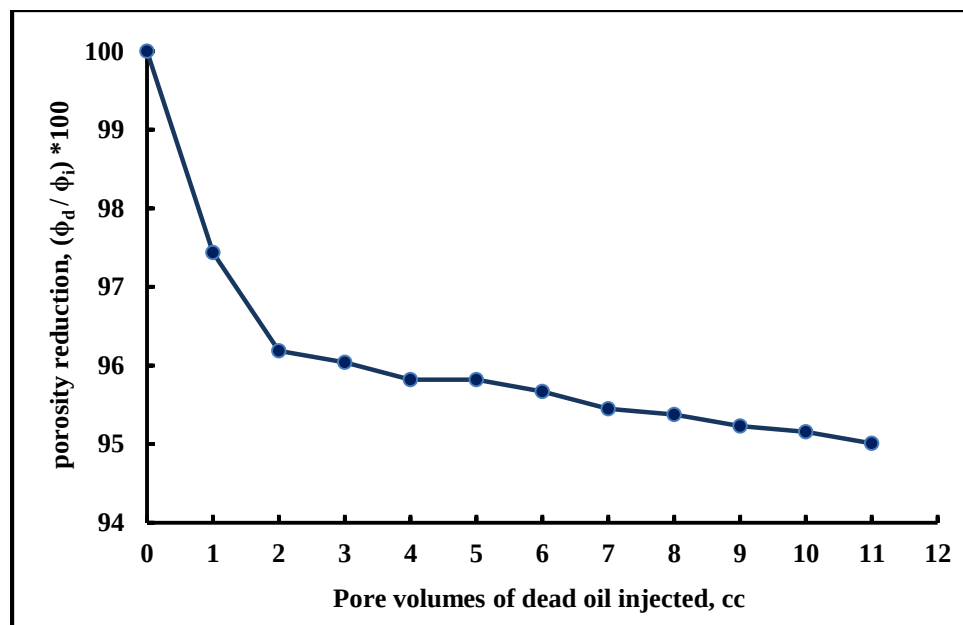


Figure (4.5): Porosity ratio reduction during oil injection (Limestone)

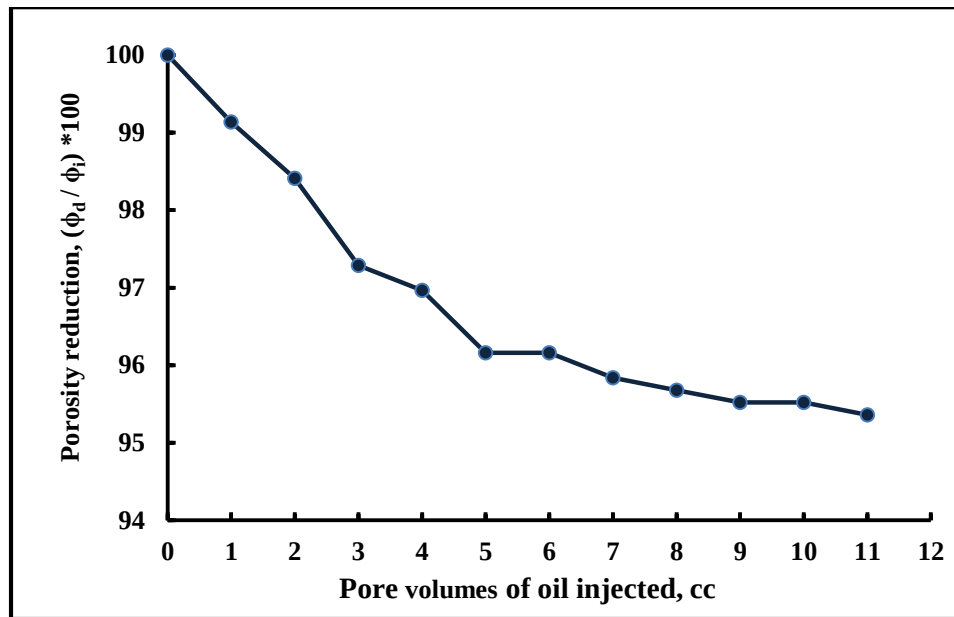


Figure (4.6): Porosity ratio reduction during oil injection (Sandstone)

4.2 Influence of CO₂ injection on asphaltene precipitation:

Carbon Dioxide (CO₂) gas was injected into oil-saturated porous media to determine its effects on asphaltene deposition. The injection rate was 0.355 cc/min. When the injected gas contacted the oil, change in the composition of the oil is observed. Asphaltene instability and its eventual deposition were noticed.

Figures (4.7) and (4.8) show the variations in the asphaltene content of the produced oil with Pore volumes of injected gas for Limestone and sandstone porous media respectively.

The asphaltene content of the produced oil remains unchanged until about 0.43 Pore volume of CO₂ injection. After that the asphaltene content of the oil produced was reduced. This reduction was due to an increase in asphaltene deposition in porous media through CO₂ injection.

Additional injections of CO₂ caused a sharp reduction in the asphaltene content of the produced oil. These results show that additional asphaltene precipitation/adsorption occurs in porous media during CO₂ gas injection. Additional asphaltene deposition in porous media due to CO₂ injection caused further Permeability and porosity reductions.

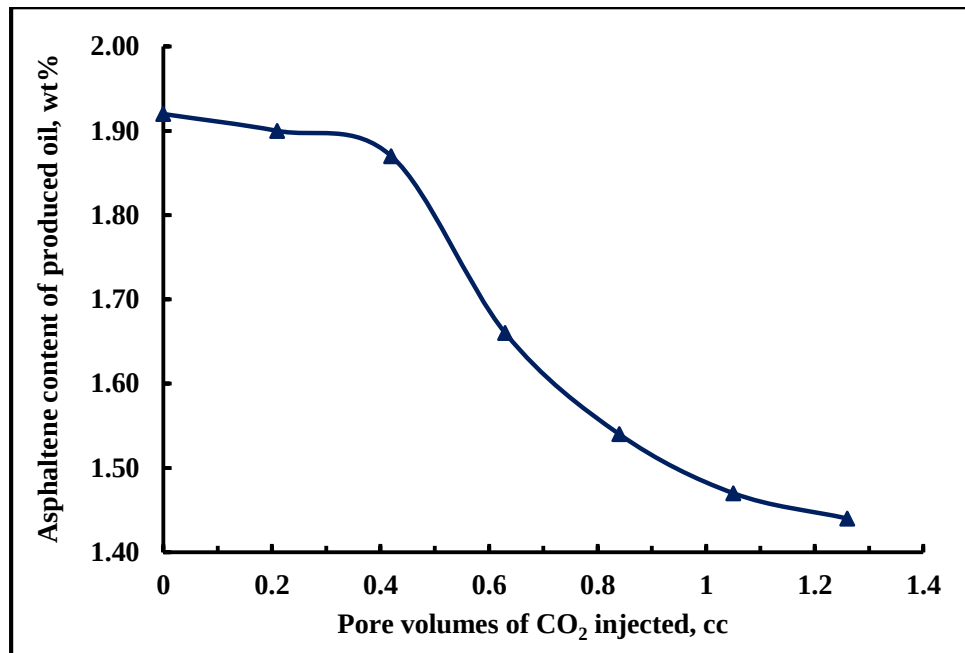


Figure (4.7): Asphaltene content of produced oil during CO₂ injection (Limestone)

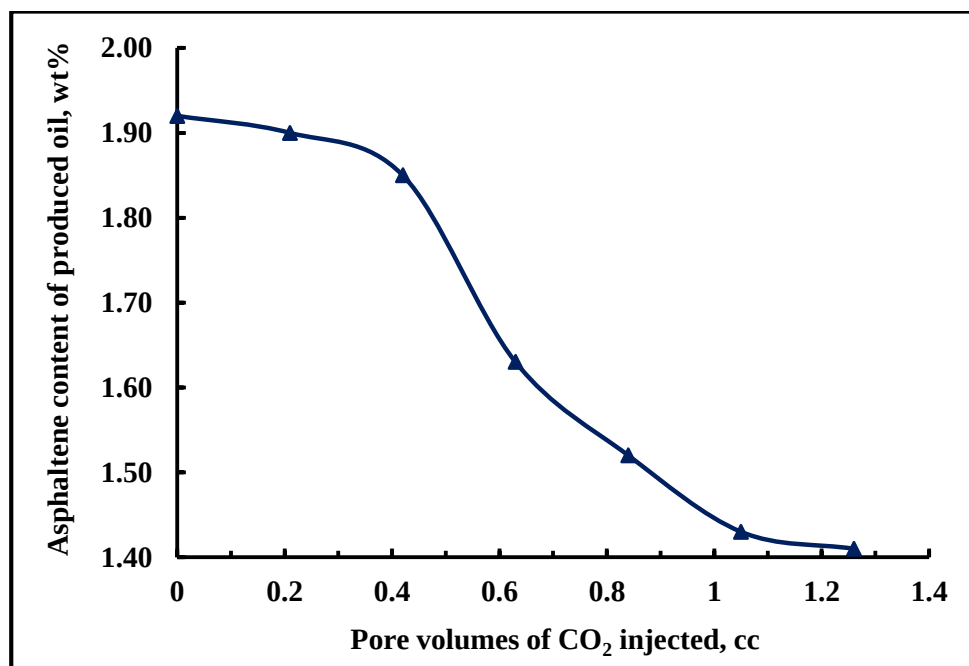


Figure (4.8): Asphaltene content of produced oil during CO₂ injection (Sandstone)

Tables (4.1 and 4.2) show the absolute permeability ratio reductions and the percent reduction of permeability of the porous media after asphaltene deposition to the original absolute permeability before and after gas injection.

The data of table (4.2) are graphically presented in figure (4.9) which indicated that the permeability reduction has increased after CO₂ injection.

Table (4.1): Permeability ratio reductions before and after CO₂ injection

Porous Media	Ratio of Permeability Reductions, K_d / K_i , (%)		Reduction (%)
	Before gas injection	After gas injection	
Limestone	74.65	71.98	2.67
Sandstone	75.28	72.35	2.93

Table (4.2): Percent of permeability reductions before and after CO₂ injection

Porous Media	Permeability Reductions Percent, $(K_i - K_d) / K_i$, (%)	
	Due to oil injection	Due to gas injection
Limestone	25.35	28.02
Sandstone	24.72	27.65

From figure (4.9) the permeability of the Limestone has been reduced about 25.35% during the oil flood process and it was increased to 28.02% after 1.26 pore volume of CO₂ injection, whereas the permeability of Sandstone was reduced about 24.72% during the oil flood and further reduced to 27.65% after 1.26 pore volume of CO₂ injection.

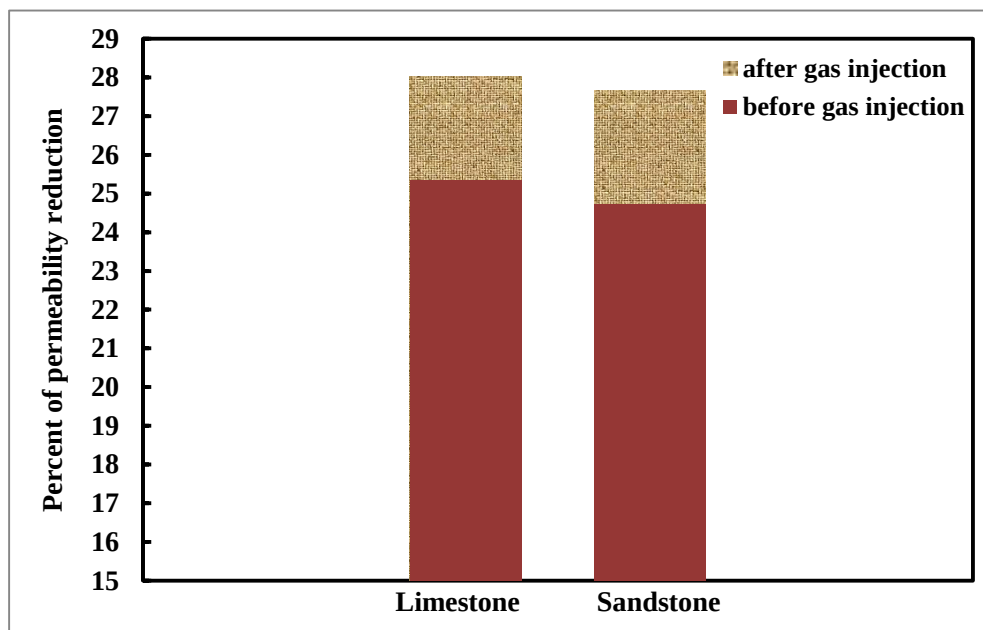


Figure (4.9): Comparison of permeability reductions before and after CO₂ injection for limestone and sandstone porous media

The porosity for the two porous media was also calculated during oil flood and gas injection processes, the porosity reductions in the CO₂ injection process was greater than porosity reduction during saturating porous media by oil injection; these variations indicate that most of asphaltene

depositions occur after CO₂ injection. After injection of about 1.26 pore volume of CO₂, the ratio of porosity reductions of limestone and sandstone rock types was about 1.16% and 1.33% respectively, the results of porosity ratio reductions and the percent of porosity reductions are presented in tables (4.3 and 4.4) and the data of table (4.4) are graphically plotted in figure (4.10).

Table (4.3): Porosity ratio reductions before and after CO₂ injection

Porous Media	Ratio of Porosity Reductions, ϕ_d / ϕ_i , (%)		Reduction (%)
	Before gas injection	After gas injection	
Limestone	95.01	93.85	1.16
Sandstone	95.36	94.03	1.33

Table (4.4): Percent of porosity reductions before and after CO₂ injection

Porous Media	Porosity Reductions Percent, $(\phi_i - \phi_d) / \phi_i$, (%)	
	Due to oil injection	Due to gas injection
Limestone	4.99	6.15
Sandstone	4.64	5.97

From figure (4.10) the percent reductions in porosity for Limestone rock type due to oil injection was 4.99% and further reduced to 6.15% after 1.26 pore volume of CO₂ injection, whereas for sandstone the percent of porosity reduction due to oil injection was 4.64% and after 1.26 pore volume of CO₂ injection, the porosity was further reduced to 5.97%.

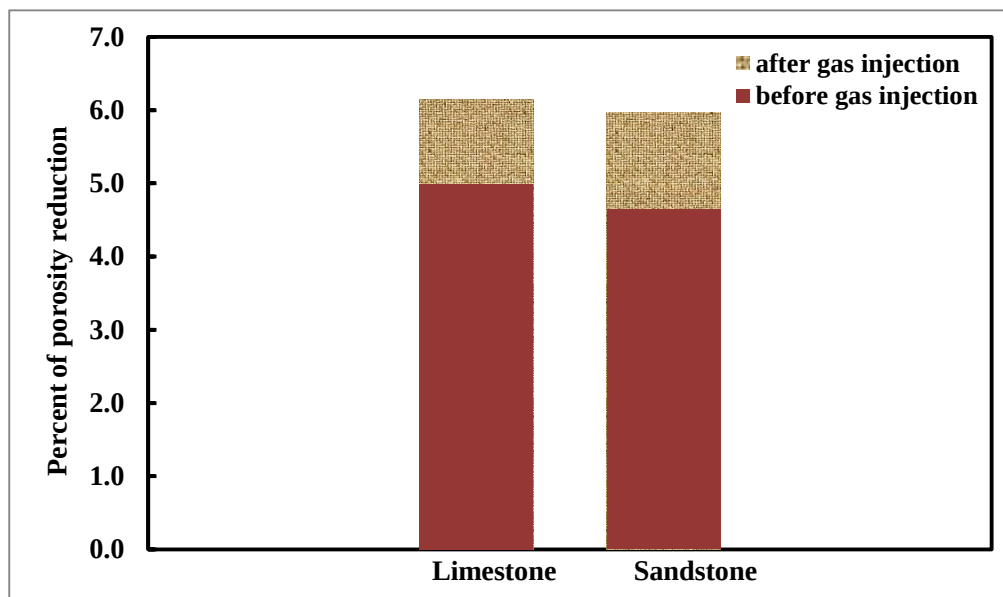


Figure (4.10): Comparison of porosity reductions before and after CO₂ injection for the two porous media

The amount of water production during oil flood and CO₂ injection was also measured to determine the amount of irreducible water saturation (S_{wi}) before and after CO₂ injection, As shown in table (4.5), the irreducible water in porous media was reduced after CO₂ injection.

These results indicate that asphaltene deposition caused changes in the wettability of porous media toward oil-wet; the change in the amount of irreducible water in porous media was used as an indication of porous media wettability alteration.

It has been demonstrated that oil wet formations have much lower irreducible water than water wet formations.

Table (4.5): water saturations before and after CO₂ injection

Porous Media	Irreducible water, (S_{wi} %)	
	Before gas injection	After gas injection
Limestone	19.71	11.32
Sandstone	16.39	10.92

The amount of irreducible water in porous media can be evaluated by measurement of the initial water content of the porous media and the cumulative produced water when there is no more water production. The results show that due to asphaltene depositions on the rock surface, the porosity and permeability of the porous media were reduced and its wettability was altered from water-wetting to oil-wetting. These changes in the content of the irreducible water in porous media have been used as a criterion for wettability alteration.

4.3 Effect of CO₂ injection pressure on asphaltene precipitation:

Three carbonate core samples (Limestone) were selected to investigate the effect of CO₂ injection pressure on asphaltene precipitation, the rock properties tests were conducted for each core sample and the results are shown in table (3.2) in the previous chapter.

Table (4.6) presents properties of the chosen crude oil (34.06 °API) for all the experiment runs. The measured asphaltene content of the crude oil was 0.7 wt %.

Table (4.6): Crude oil properties

Density of crude oil (ρ_o) at 25 °C, g/cc	0.8488
Density of crude oil (ρ_o) at 90 °C, g/cc	0.7959
Viscosity of crude oil (μ_o) at 25 °C, cp	6.6
Viscosity of crude oil (μ_o) at 90 °C, cp	3.55

To determine the effect of CO₂ injection pressure on asphaltene precipitation, Dynamic asphaltene precipitation tests were carried out with several runs at different CO₂ injection pressures where the core holder's temperature and pressure were kept constant, the temperature of the core holder was fixed at 90 °C, and the overburden pressure was set at 2500 psig.

The selected injection pressures was 700, 1300 and 1750 psig and the injection rate was from 0.3 to 0.35 cc/min.

Run No. 1: Injection Pressure 700 Psig

Figure (4.11) shows that the asphaltene started to precipitate after 0.21 pore volumes of CO₂ injected and the amount of asphaltene that already precipitated in the core was 0.06 wt %. At 0.42 pore volumes injected, the amount of asphaltene precipitated in the porous media was 0.14 wt %. Then the asphaltene precipitation increased to 0.29 wt % at 0.63 pore volumes injected, the asphaltene precipitation continued to increase as the pore volume increased and it reached 0.50 wt % after 1.26 pore volumes of CO₂ injected.

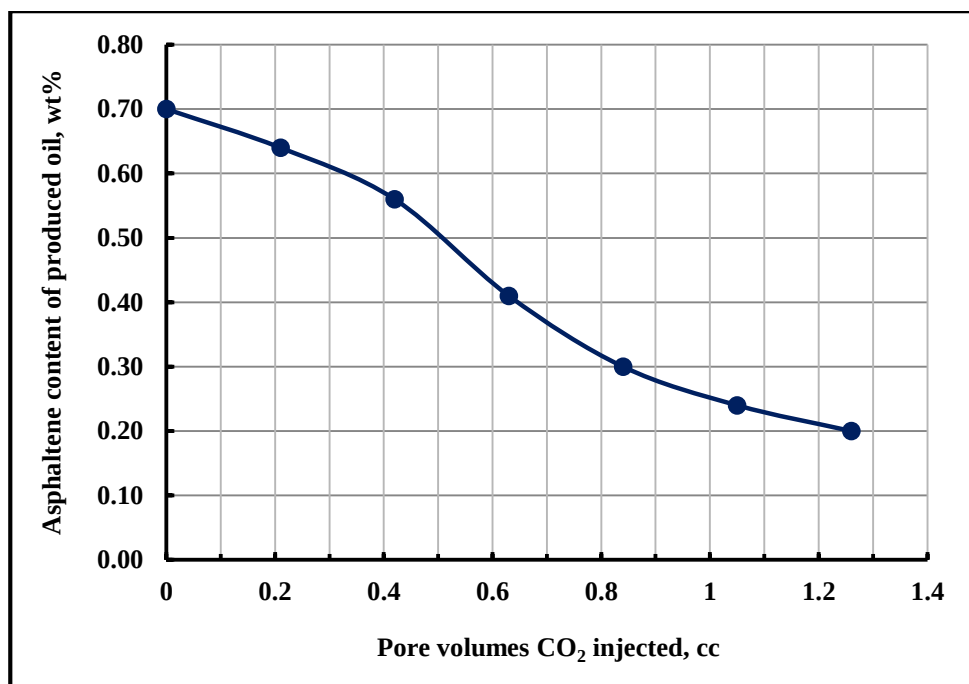


Figure (4.11): Asphaltene content of produced oil during CO₂ injection at 700 Psig

Run No. 2: Injection Pressure 1300 Psig

At this run as shown in figure (4.12) the asphaltene started to precipitate as the CO₂ injection reached 0.42 pore volumes, the amount of asphaltene precipitated was 0.05 wt%, the asphaltene content in

the produced oil continued to decrease as the injected pore volumes increased, the amount of asphaltene precipitated in the core sample was 0.16 wt% at 0.63 pore volumes injected, and increased to 0.27 wt% at 0.84 pore volumes injected then 0.33 wt% at 1.05 pore volumes injected and it reached 0.41 after 1.26 pore volumes of CO₂ injected.

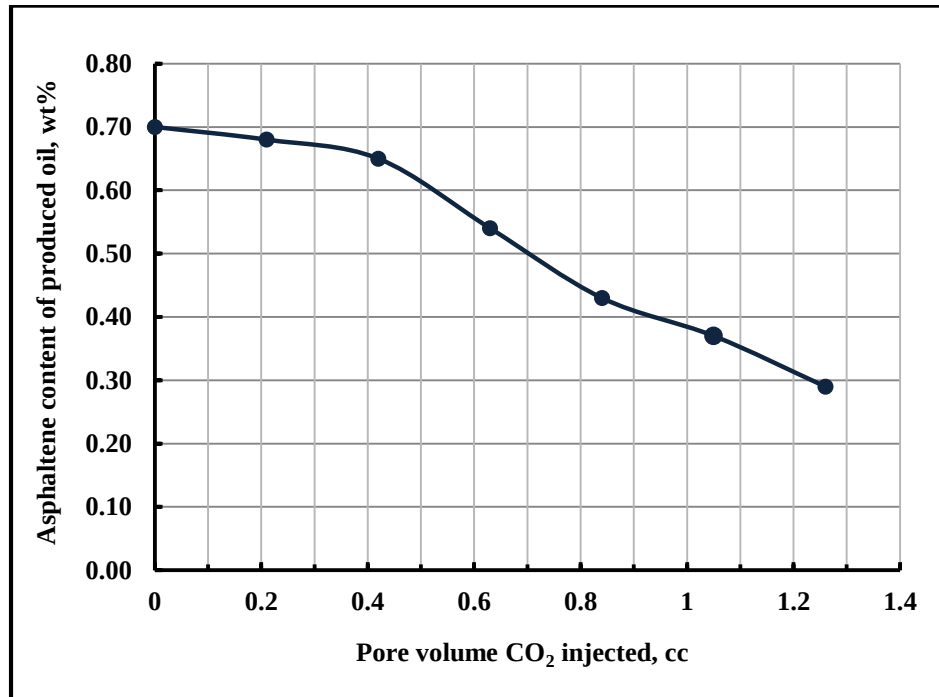


Figure (4.12): Asphaltene content of produced oil during CO₂ injection at 1300 Psig

Run No. 3: Injection Pressure 1750 Psig

As shown in figure (4.13) in this run where pressure was 1750 psig, asphaltene started to precipitate as the injected CO₂ reached 0.63 pore volumes and the amount of asphaltene that already precipitated in the core was 0.05 wt %. At 0.84 pore volume, the amount of asphaltene precipitation in the porous media was 0.18 wt %. Then the asphaltene precipitation increased to 0.26 wt % at 1.05 pore volumes injected, and 0.31 wt % for the 1.26 pore volumes that has been injected by CO₂.

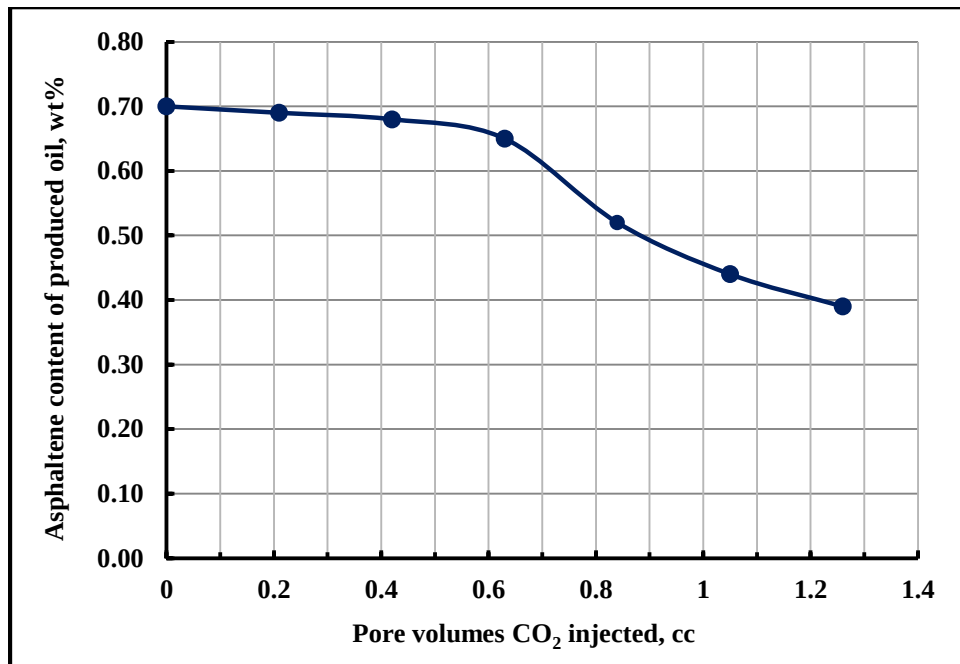


Figure (4.13): Asphaltene content of produced oil during CO₂ injection at 1750 Psig

The results of the experiment runs are compared together to examine the effect of injection pressure on asphaltene precipitation and the effect of the pore volumes injected, from all runs the asphaltene precipitation occurred. Figure (4.14) shows comparison of the results of asphaltene content analysis for the recovered oil versus pore volume of injected CO₂ at different pressures. Figure (4.14) proves that as the pressure increases asphaltene precipitation decreases, this could be due to the difference in solubility of asphaltene in low and high pressure.

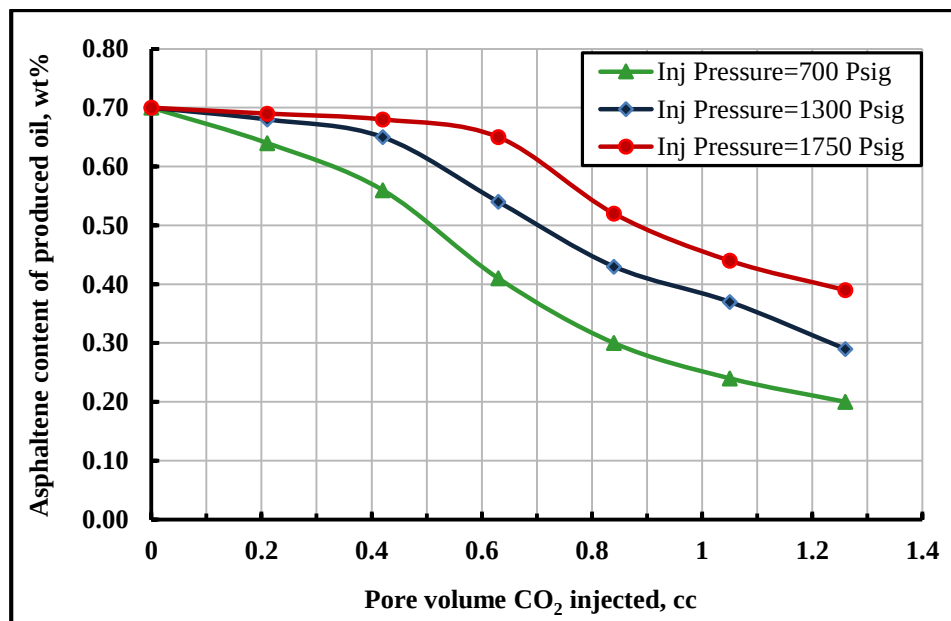


Figure (4.14): Asphaltene content of produced oil during CO₂ injection at different pressures

It seems that when the injection pressure increases asphaltene remains dissolved in the reservoir fluid. However, at low pressure this solubility decreases. Furthermore large distance between asphaltene particles and the particles of the surrounding fluid caused more precipitation of asphaltene at lower pressures, other than that high energy injected gas can desorb the adsorbed asphaltene onto the core. In the meantime some of the precipitated and deposited asphaltene onto core may be carried away by high pressure gas and leave the core with flow of recovered oil.

Moreover it is clear that pore volume of injected CO₂ has major influence on the amount of asphaltene precipitation. As pore volume of injection increases, asphaltene precipitation increases too. This increase explains that when more CO₂ gas is in contact with oil for longer time, asphaltene precipitates more. Addition of CO₂ affects the interaction between resin and asphaltene, other than that during recovery by CO₂, some hydrocarbon molecules can be extracted into gas phase.

During CO₂ flooding some of intermediate hydrocarbon molecules would be extracted by in-situ vaporization from reservoir oil into the injected gas. It suggests that vaporizing drive would extract some of resin molecules, which disturbs the stability of asphaltene and leads to precipitation.

4.4 Influence of CO₂-induced asphaltene precipitation on porous media properties:

The permeability and porosity of the core samples were measured before and after CO₂ injection for all the runs in order to investigate the changes in porous media properties due to asphaltene precipitation. As mentioned in the methodology each core was treated with cyclohexane solvent in such a way that removes residual oil while only asphaltene remain inside the core sample, the results of the permeability reductions and permeability ratio variations after CO₂ injection are illustrated in table (4.7).

Table (4.7): Permeability ratio percent and reductions after 1.26 PV of CO₂ injection

Run Number	Injection Pressure Psig	Percent of Permeability reduction ($K_i - K_d$) / K_i *100	Percent of Permeability ratio (K_d/K_i)*100
1	700	30.8	69.20
2	1300	26.7	73.30
3	1750	21.1	78.90

The effect of CO₂ induced asphaltene precipitation on the permeability of porous media for all experiment runs is shown in figures (4.15 and 4.16).

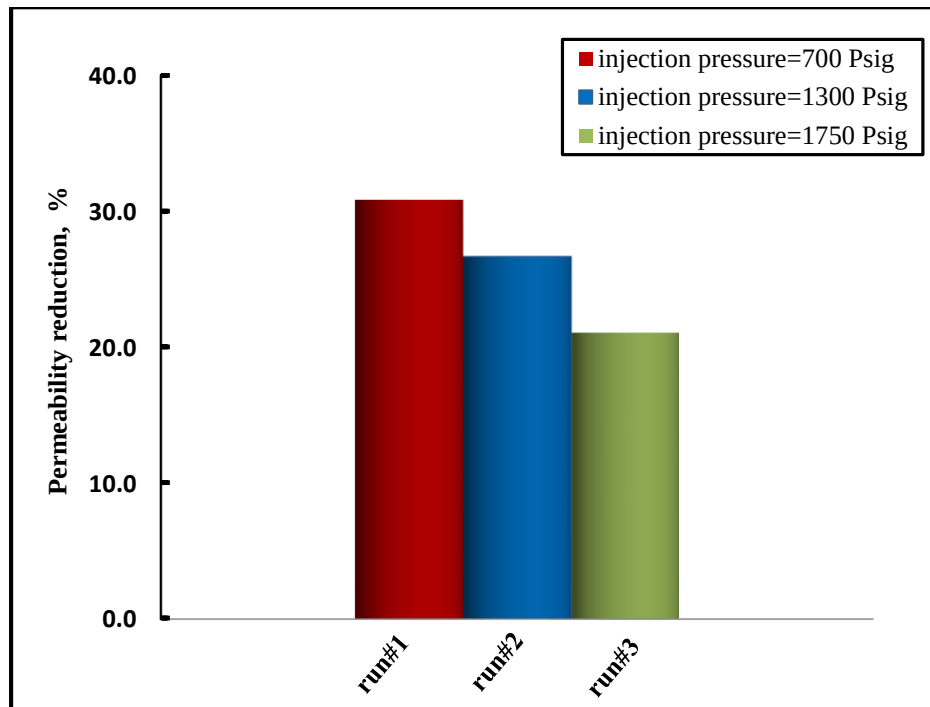


Figure (4.15): Percent of permeability reductions during CO₂ injection

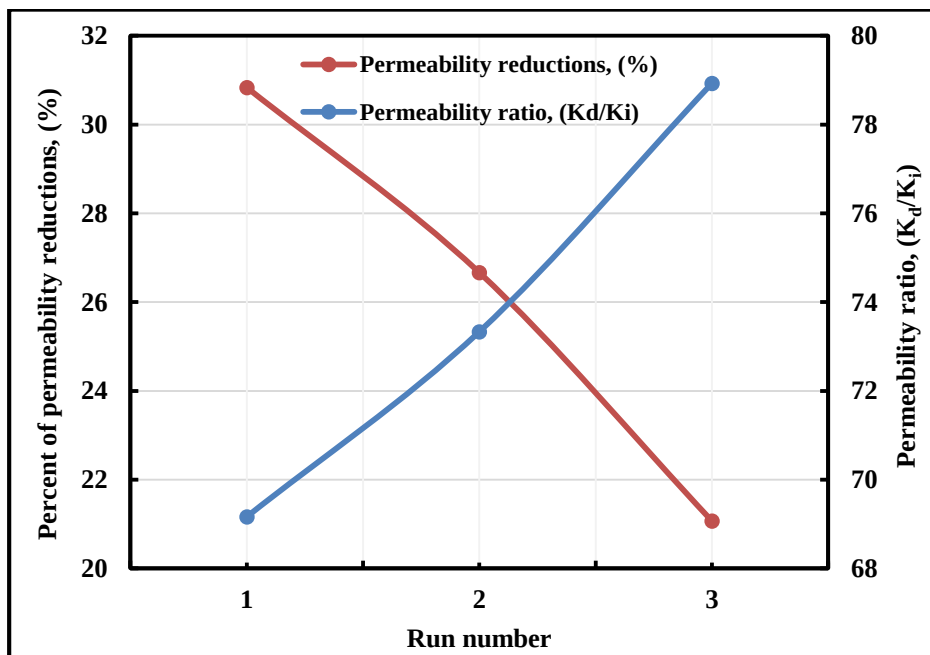


Figure (4.16): Percent of permeability reductions and permeability ratio during CO₂ injection

As shown in from figures (4.15 and 4.16), in run no. 1 where the pressure was 700 psig, with the most asphaltene precipitation, the permeability of the core was reduced by 30.8%, at run no. 2 the permeability was reduced by 26.7%, whereas in run no. 3 with the higher pressure the permeability was decreased to 21.1%.

Additional asphaltene deposition in porous media can cause further porosity reduction, the percent

of porosity ratio data and porosity reductions percent after CO₂ injection for the pressure runs are presented in table (4.8) whereas the percent reduction of the porosity of the porous media are plotted in Figures (4.17 and 4.18).

Table (4.8): Porosity ratio percent and porosity reductions after 1.26 PV of CO₂ injection

Run Number	Injection Pressure, Psig	Percent of porosity reduction $(\phi_i - \phi_d) / \phi_i * 100$	Percent of porosity ratio $(\phi_d / \phi_i) \%$
1	700	5.26	94.74
2	1300	4.82	95.18
3	1750	2.92	97.02

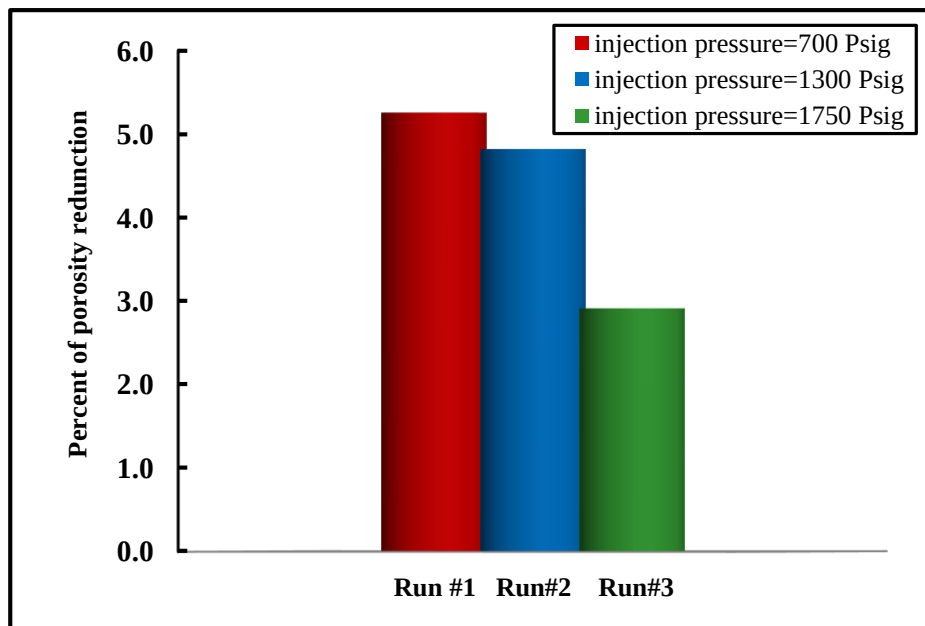


Figure (4.17): Percent of porosity reductions during CO₂ injection

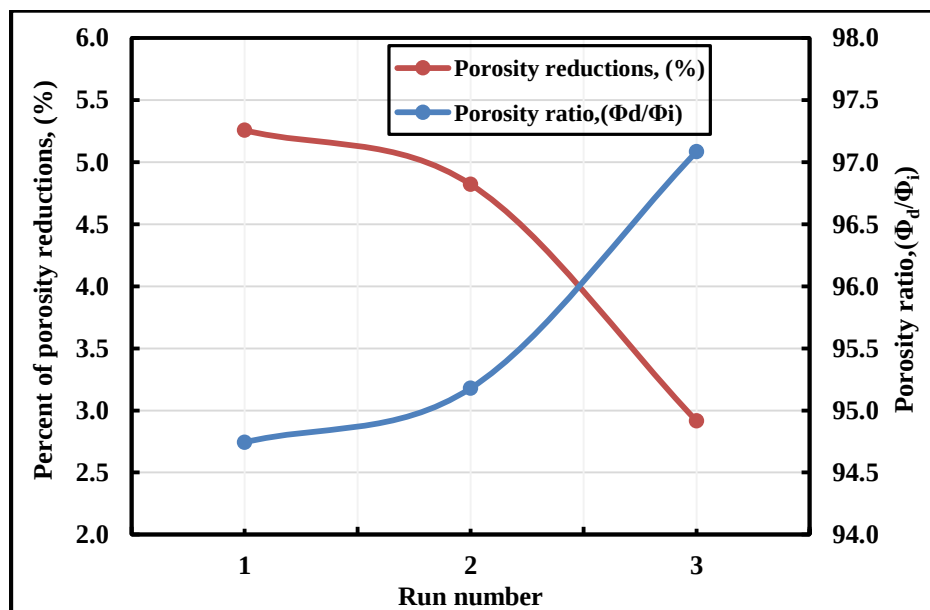


Figure (4.18): Porosity reductions percent and porosity ratio during CO₂ injection

As shown from figures (4.17 and 4.18), the porosity of the porous media in run no. 1 at pressure 700 Psig has been reduced about 5.26%, at run no. 2 the porosity was reduced to 4.82%, in run no.3 as the pressure increases the porosity was reduced to 2.92%.

Figures (4.16) and (4.18) show that there is an obvious reductions in the permeability and porosity of the porous media due to asphaltene precipitation, during continuous CO₂ flooding. Increasing the injected pore volume would result in more asphaltene precipitation, besides that, by increasing the injection pressure of CO₂, less asphaltene would deposit.

The dynamic flow experiments depict that due to the presence of asphaltene inside the core samples, porosity and permeability of the porous media would be reduced, these reduction in values confirm the fact that at highest pressure, as in run no. 3 where the pressure was 1750 Psig, less asphaltene precipitated, because less permeability and porosity reduction was reported. At the same time as in run no. 1, with the lowest injection pressure of 700 psig, demonstrates the most decline in permeability and porosity.

The water saturation of each core sample was measured before and after the CO₂ injection, figures (4.19 and 4.20) show the effect of CO₂ injection pressure on the wettability of the porous media, the reduction in water saturation was observed in all the injection pressures. In run no. 1 with the lowest pressure of 700 Psig which experienced the highest asphaltene precipitation has the most reduction in water saturation. Table (4.9) presents the water saturation results before and after 1.26 pore volumes of CO₂ injection at different pressures.

Table (4.9): Wettability alteration results before and after CO₂ injection

Run Number	Injection Pressure, Psig	Irreducible water, (S_{wi} %)		Wettability change (%)
		Before gas injection	After gas injection	
1	700	28.33	15.36	45.78
2	1300	28.52	15.82	44.53
3	1750	28.05	15.96	43.09

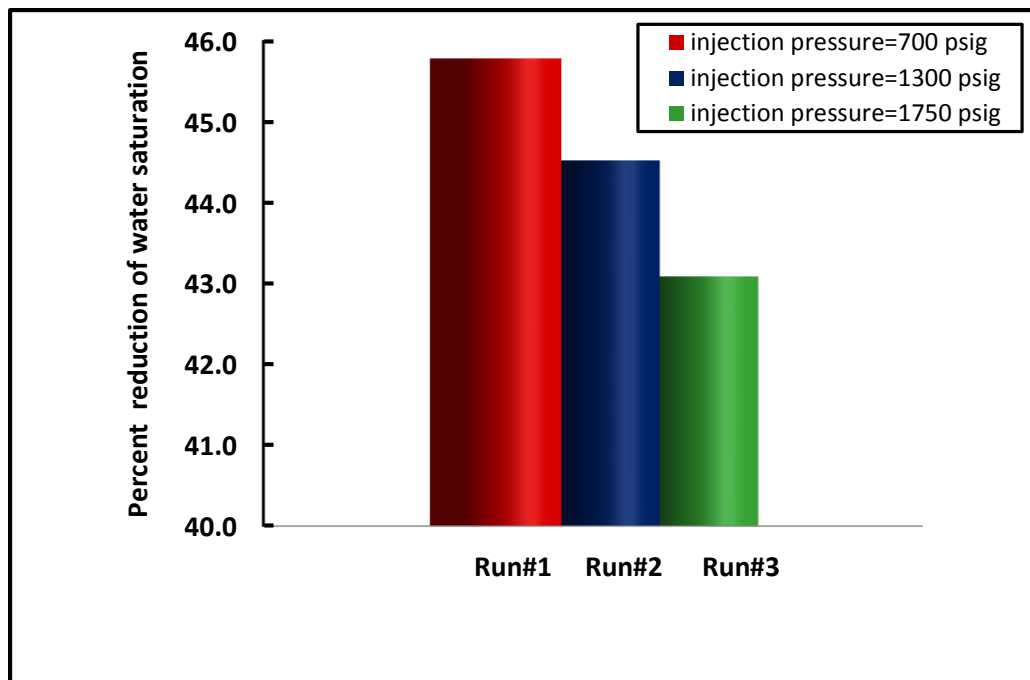


Figure (4.19): Percent reduction of water saturation after CO₂ injection at different pressures

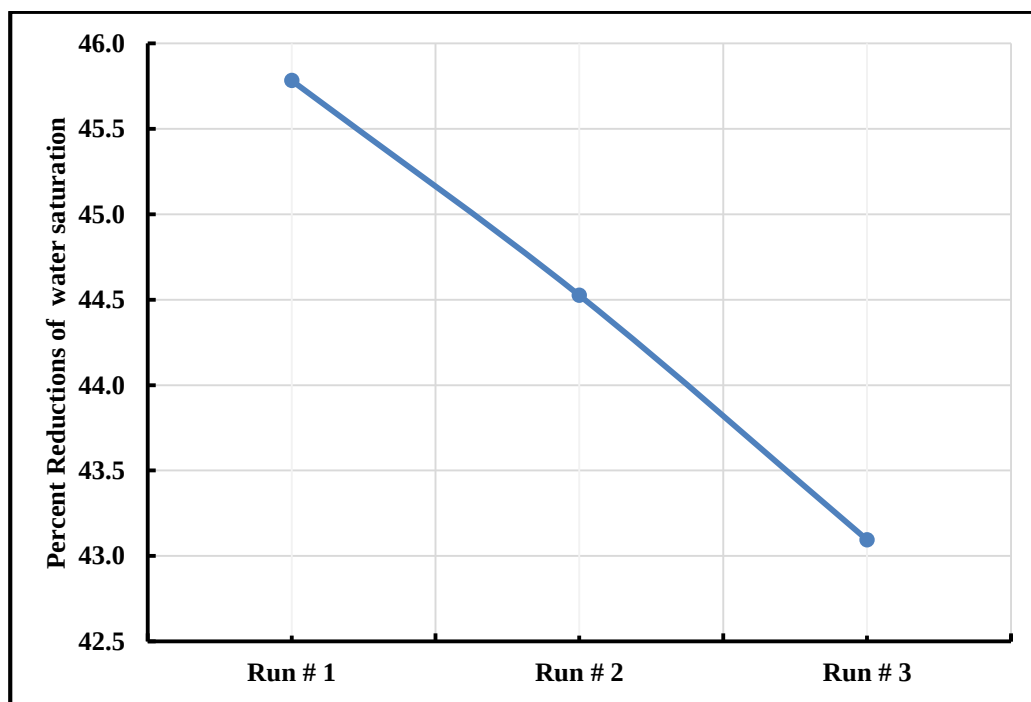


Figure (4.20): Percent reduction of water saturation after CO₂ injection at different pressures

The core sample number (1) of run number (3) at injection pressure of 1750 psig was compared with another core sample number (4) of a higher permeability; table (4.10) to examine the effect of asphaltene precipitation on the properties of the porous media with different permeabilities (high and

low permeabilities). The results show that the core sample with a higher permeability experienced a higher reduction in permeability after 1.26 pore volume of CO₂ injected due to the asphaltene precipitation, the percent reduction was 29.0% in the higher permeability core sample compared with 21.1% reduction in the low permeability core sample.

Table (4.10): Core properties before displacement tests

Core No.	Length cm	Diameter cm	Pore volume cm ³	Porosity %	Permeability K _{air} , mD	Permeability K _i , mD
1	5.40	3.80	13.94	23.40	13.60	5.915
4	5.15	3.72	14.76	26.72	26.41	15.332

The results of the permeability reduction and the percent of the permeability ratio reductions of the two core samples are presented in table (4.11) and graphically plotted in figure (4.20).

Table (4.11): Permeability ratio percent after 1.26 pore volume of CO₂ injection

Core No.	Permeability reduction (K _i - K _d) / K _i , (%)	Percent of Permeability ratio (K _d /K _i) , (%)
1	21.10	78.90
4	29.00	71.00

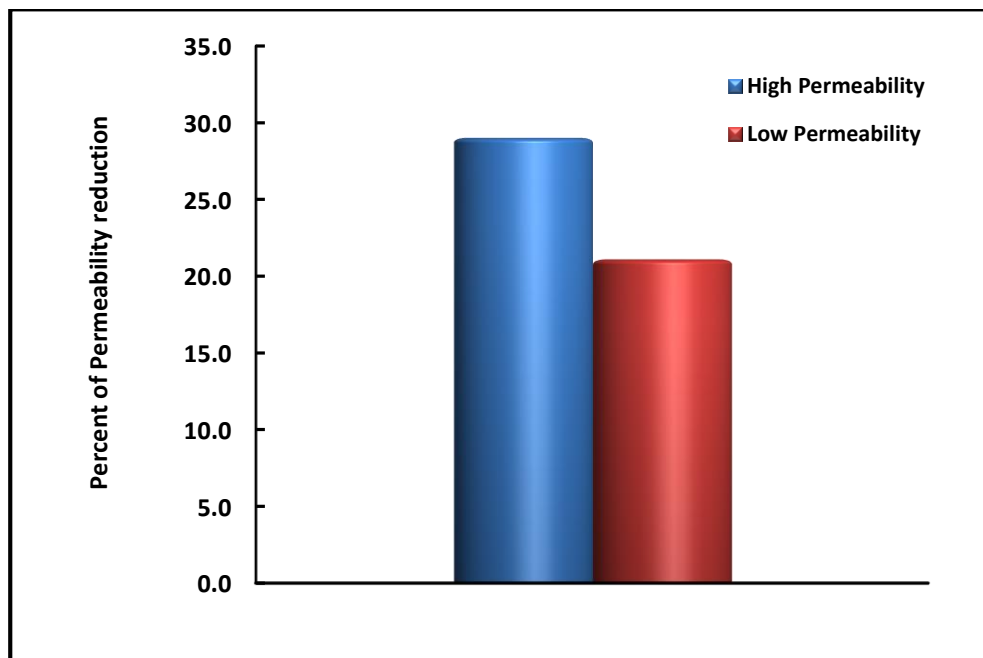


Figure (4.21): Percent reduction of permeability after 1.26 PV CO₂ injection

The asphaltene content of the produced oil was also measured for the two core samples; as shown from figure (4.22), the core sample with the higher permeability shows a low asphaltene content in the produced oil which means that the most of asphaltene was precipitated in the core. Also increasing of CO₂ pore volume injection leads to an increase in asphaltene precipitation. This increment explains that when more CO₂ gas is in contact with oil for longer time, asphaltene precipitates more.

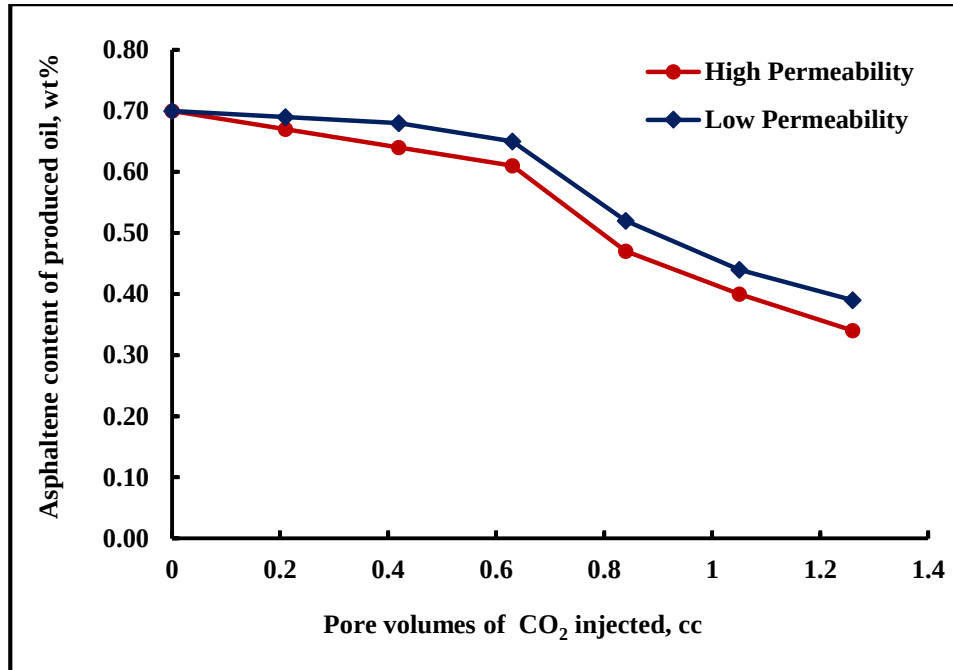


Figure (4.22): Asphaltene content of produced oil during CO₂ injection

The porosity of both core samples was also measured. Table (4.12) shows the results of the percent of porosity reductions and the porosity ratio percent for both core samples. The porosity of core sample number (1) with the lower permeability was reduced from 23.40% to 22.72% whereas the porosity of core sample number (4) with the higher permeability was reduced from 26.72% to 25.93%. The percent reduction of the porosity of the core samples was 2.92% and 2.95% respectively. The results are graphically presented in figure (4.23).

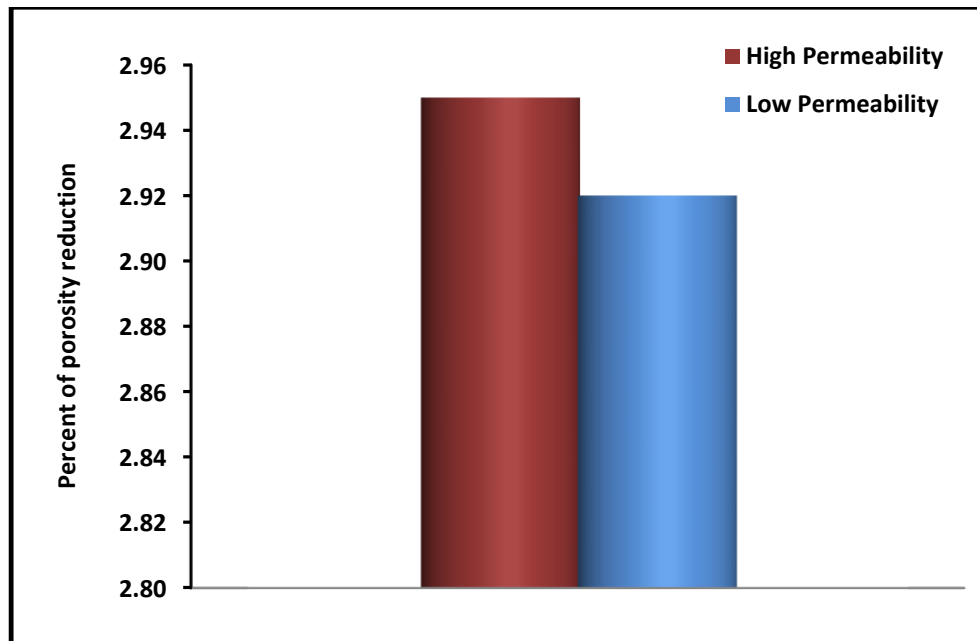
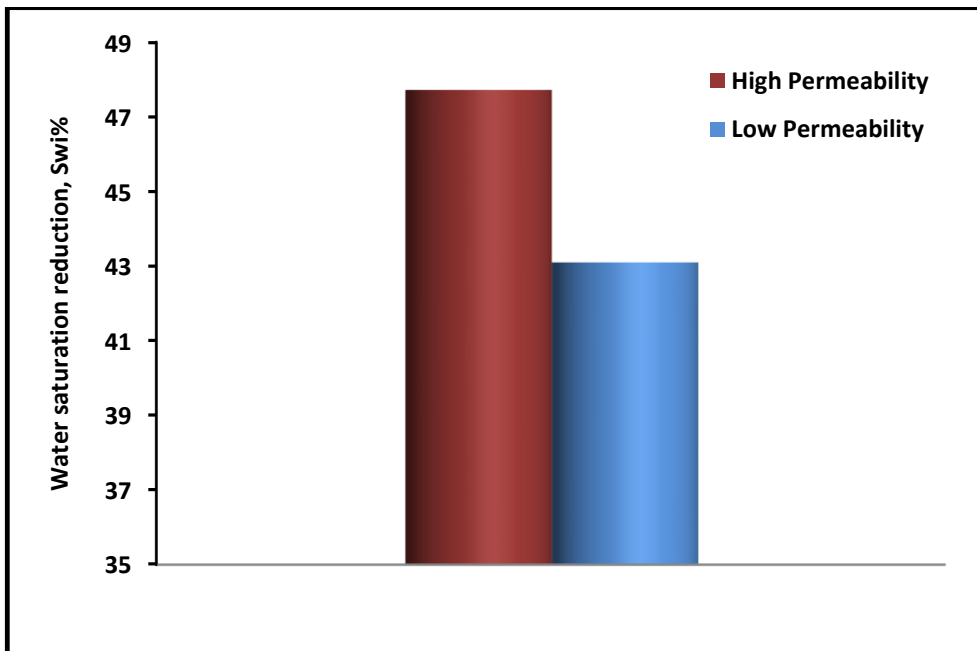
Table (4.12): Porosity reductions after 1.26 PV of CO₂ injected

Core Number	Porosity reduction , $(\phi_i - \phi_d) / \phi_i$, %	Porosity ratio , (ϕ_d / ϕ_i) , %
1	2.92	97.08
4	2.95	97.05

The water saturation was also measured for the two core samples before and after CO₂ injection. Table (4.11) shows a comparison of the saturations and the wettability changes. The results of water saturations are graphically represented in figure (4.24).

Table (4.13): Wettability alteration results before and after CO₂ injection

Core Number	Irreducible water, (S_{wi} %)		Wettability change (%)
	Before gas injection	After gas injection	
1	28.05	15.96	43.09
4	29.13	15.58	47.73

Figure (4.23): Percent reduction of porosity after 1.26 PV CO₂ injectedFigure (4.24): Percent reduction of water saturation after 1.26 PV of CO₂ injected

From figure (4.24), the water saturation ($S_{wi}\%$) of the core sample No. (1) with the lower permeability before CO₂ injection was 28.05% then reduced to 15.96% after CO₂ injection, whereas the water saturation, ($S_{wi}\%$) of the core sample No. (4) with the higher permeability before CO₂ injection was 29.13% then reduced to 15.58% after CO₂ injection, the percent reduction of the water saturations of the two core samples was 43.09% and 47.73% respectively. The core sample with the higher permeability experienced a higher reduction in water saturation.

During the course of this laboratory study, the following conclusions and recommendations have been drawn:

1. Conclusions:

- The deposition of asphaltene is considered to be one of the most difficult problems during oil production. The presence of asphaltene in crude oil and consequently adsorption and deposition of asphaltene on the surface of the rock has some effects on the properties of rock such as porosity, permeability and wettability.
- Asphaltene can precipitate during primary oil recovery, CO₂ injection, and hydrocarbon gas injection. Asphaltene precipitates may deposit to the surface of pores or plug the pore throat causing formation damage.
- During oil flood experiments, the results show that due to asphaltene deposition on the rock surface, the porosity and permeability of the two types of core samples (limestone and sandstone) are reduced and their wettability are altered from water-wetting to oil-wetting.
- Dynamic flow experiments show that the asphaltene precipitation increases as the pore volume of CO₂ injection increases which leads to pore plugging, porosity reduction and absolute permeability damage.
- The results show that, increasing the CO₂ injection pressure causes less precipitation of asphaltene.
- Irreducible water measurements showed that CO₂-induced asphaltene changes the rock wettability to oil-wet.

2. Recommendations:

- It is believed that the properties of the porous medium have significant effects on the phenomenon of asphaltene deposition. Among them, pore size distribution, wettability and permeability of the porous medium are more important than others. Experimental investigations concerning the effect of these crucial factors on asphaltene deposition are strongly recommended.
- Experimental investigation of asphaltene deposition due to miscible and/or immiscible injection in a fractured porous medium is strongly recommended.
- For gaining better understanding it is recommended to study rock composition, heterogeneity and porosity and permeability distribution along with precipitation phenomenon.

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➤ **Crude oil Composition**

➤ **Standard Test Method (IP 143):**

**Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum
and Petroleum Products**

Appendix (A)

Crude Oil Composition

Component	Formula	Molecular weight, g/mol	Mole %
Propane	C ₃ H ₈	44.10	0.24
Iso-Butane	C ₄ H ₁₀	58.12	0.29
n-Butane	C ₄ H ₁₀	58.12	1.02
Iso-Pentane	C ₅ H ₁₂	72.15	1.16
n-Pentane	C ₅ H ₁₂	72.15	1.93
Hexane	C ₆ H ₁₄	86.18	5.05
Heptane	C ₇ H ₁₆	96	9.24
Octane	C ₈ H ₁₈	107	11.79
Nonane	C ₉ H ₂₀	121	10.15
Decane	C ₁₀ H ₂₂	134	9.39
n-Undecane	C ₁₁ H ₂₄	147	7.27
n-Dodecanes	C ₁₂ H ₂₆	161	5.97
n-Tridecanes	C ₁₃ H ₂₈	175	6.00
n-Tetradecanes	C ₁₄ H ₃₀	190	4.45
n-Pentadecanes	C ₁₅ H ₃₂	206	4.59
n-Hexadecanes	C ₁₆ H ₃₄	222	3.17
n-Heptadecanes	C ₁₇ H ₃₆	237	3.67
n-Octadecanes	C ₁₈ H ₃₈	251	2.64
n-Nonadecanes	C ₁₉ H ₄₀	263	2.06
n-Eicosane	C ₂₀ H ₄₂	275	1.76
n-Heneicosane	C ₂₁ H ₄₄	291	1.67
n-Docosane	C ₂₂ H ₄₆	300	1.46
n-Tricosane	C ₂₃ H ₄₈	312	1.31
n-Tetracosane	C ₂₄ H ₅₀	324	0.88
n-Pentacosane	C ₂₅ H ₅₂	337	0.68
n-Hexacosane	C ₂₆ H ₅₄	349	0.51
n-Heptacosane	C ₂₇ H ₅₆	360	0.47
n-Octacosane	C ₂₈ H ₅₈	372	0.34
n-Nonacosane	C ₂₉ H ₆₀	382	0.26
n-Triacontane plus	C ₃₀ H ₆₂ ⁺	413.71	0.60
Total			100.00



Designation: D6560 – 12

Designation: IP 143/01

Standard Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products^{1,2}

This standard is issued under the fixed designation D6560; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers a procedure for the determination of the heptane insoluble asphaltene content of gas oil, diesel fuel, residual fuel oils, lubricating oil, bitumen, and crude petroleum that has been topped to an oil temperature of 260°C (see [A1.2.1.1](#)).

1.2 The precision is applicable to values between 0.50 and 30.0 % m/m. Values outside this range may still be valid but may not give the same precision values.

1.3 Oils containing additives may give erroneous results.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:³

[D86](#) Test Method for Distillation of Petroleum Products at Atmospheric Pressure

[D1298](#) Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

¹ This test method is under the jurisdiction of ASTM Committee [D02](#) on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee [D02.14](#) on Stability and Cleanliness of Liquid Fuels.

Current edition approved April 15, 2012. Published May 2012. Originally approved in 2000. Last previous edition approved in 2005 as D6560-00(2005). DOI: 10.1520/D6560-12.

² This standard is based on material published in the IP *Standard methods for Analysis and Testing of Petroleum and Related Products and British Standard 2000 Parts*, copyright Energy Institute, 61 New Cavendish Street, London, W1M 8AR. Adapted with permission of Energy Institute.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[D4052](#) Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

[D4057](#) Practice for Manual Sampling of Petroleum and Petroleum Products

[D4177](#) Practice for Automatic Sampling of Petroleum and Petroleum Products

2.2 *Energy Institute Standard:*⁴

[Specifications for IP Standard Thermometers](#)

3. Terminology

3.1 Definitions:

3.1.1 *asphaltenes, n*—(rarely used in the singular) — *in petroleum technology*, represent an oil fraction that is soluble in a specified aromatic solvent but separates upon addition of an excess of a specified paraffinic solvent.

3.1.1.1 *Discussion*—In this test method, the aromatic solvent is hot toluene and the paraffinic solvent is heptane.

3.1.1.2 *Discussion*—Historically, benzene was the aromatic solvent, but benzene is not typically used now for health reasons. The precision of this test method when using toluene has been found to be the same as when using benzene.

4. Summary of Test Method

4.1 A test portion of the sample is mixed with heptane and the mixture heated under refl and the precipitated asphaltenes, waxy substances, and inorganic material are collected on a filter paper. The waxy substances are removed by washing with hot heptane in an extractor.

4.2 After removal of the waxy substances, the asphaltenes are separated from the inorganic material by dissolution in hot toluene, the extraction solvent is evaporated, and the asphaltenes weighed.

5. Significance and Use

5.1 Asphaltenes are the organic molecules of highest molecular mass and carbon-hydrogen ratio normally occurring in crude petroleum and petroleum products containing residual

⁴ Available from Energy Institute, 61 New Cavendish St., London, W1M 8AR, UK.

***A Summary of Changes section appears at the end of this standard**

material. They may give problems during storage and handling

if the suspension of asphaltene molecules is disturbed through excess stress or incompatibility. They are also the last molecules in a product to combust completely, and thus may be

one indicator of black smoke propensity. Their composition normally includes a disproportionately high quantity of the sulfur, nitrogen, and metals present in the crude petroleum or petroleum product.

6. Apparatus

6.1 *General*—Ground-glass joints from different sources may have one of two diameter to length ratios. For the purposes of this test method, either is suitable, and for some applications, the diameter itself can be one of two. However, it is critical that the male and female parts of each joint are from the same series to avoid recession or protuberance.

6.2 *Condenser*, with a coil or double surface, fitted with a 34/45 or 34/35 ground-glass joint at the bottom to fit the top of the extractor. Minimum length is 300 mm.

6.3 *Reflux Extractor*, conforming to the dimensions given in Fig. 1. Tolerances are 61 mm on the height and outer diameter (OD) of the extractor body and 60.5 mm on all other dimensions. The female ground-glass joint at the top shall match the male at the bottom of the condenser, and the male ground-glass joint at the bottom shall match the female of the conical flask.

6.4 *Conical Flasks*, of borosilicate glass of appropriate capacity (see 11.2 and Table 1), with ground-glass joints to fit the bottom of the extractor.

NOTE 1—Sizes 24/39, 24/29, 29/43, or 29/32 are suitable.

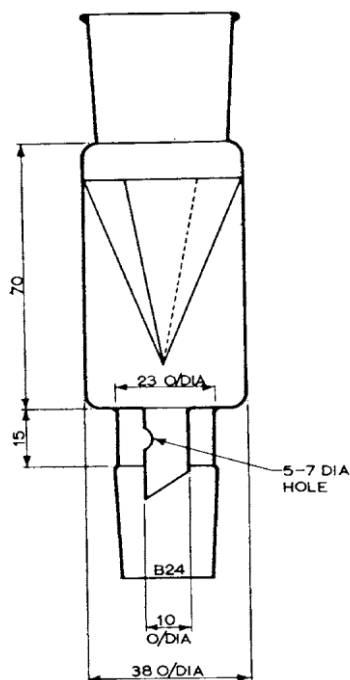


FIG. 1 Extractor

TABLE 1 Test Portion Size, Flask, and Heptane Volumes

Estimated Asphaltene Content % m/m	Test Portion Size g	Flask Volume mL	Heptane Volume mL
300 ± 60	1000	10 ± 2	Less than 0.5
240 ± 60	500	8 ± 2	0.5 to 2.0
120 ± 30	250	4 ± 1	Over 2.0 to 5.0
60 ± 15	150	2 ± 1	Over 5.0 to 10.0
25 to 30	100	0.8 ± 0.2	Over 10.0 to 25.0
25 ± 1	100	0.5 ± 0.2	Over 25.0

6.5 *Stopper*, of borosilicate glass of a size to fit the conical flask.

6.6 *Evaporating Vessel*, of borosilicate glass. Either a hemispherical dish of approximately 90 mm diameter, or another suitable vessel used in conjunction with a rotovapor.

NOTE 2—A rotovapor in conjunction with a nitrogen atmosphere reduces the hazard of toluene evaporation (see 11.7).

6.7 *Filter Funnel*, of borosilicate glass, approximately 100 mm diameter.

6.8 *Filter Papers*, Whatman⁵ Grade 42, 110 or 125-mm diameter.

6.9 *Analytical Balance*, capable of weighing with an accuracy of 0.1 mg.

6.10 *Forceps*, of stainless steel, spade ended.

6.11 *Timing Device*, electronic or manual, accurate to 1.0 s.

6.12 *Oven*, capable of maintaining a temperature from 100 to 110°C.

6.13 *Graduated Cylinders*, of 50 and 100 mL capacity.

6.14 *Stirring Rods*, of glass or polytetrafluoroethylene (PTFE), 150 by 3-mm diameter.

6.15 *Cooling Vessel*, consisting of either a desiccator without desiccant, or another suitable tightly-stoppered vessel.

6.16 *Mixer*, high-speed, nonaerating.

7. Reagents

7.1 *Toluene (methylbenzene)* [C₆H₅CH₃], analytical reagent or nitration grade.

7.2 *Heptane* [C₇H₁₆], analytical reagent grade.

8. Sampling

8.1 Unless otherwise specified, take samples by the procedures described in Practice D4057 or D4177.

9. Test Portion Preparation

9.1 Test portions from the laboratory samples shall be drawn after thorough mixing and subdivision. Heat viscous samples of residual fuels to a temperature that renders the

⁵ The sole source of supply of the filter papers known to the committee at this time is Whatman Int. Ltd., Maidstone, UK. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

sample liquid, but not above 80°C, and homogenize, using the mixer (see 6.16) as necessary.

9.2 Heat samples of penetration grade bitumens to a temperature not exceeding 120°C, and stir well before taking an aliquot.

9.3 Samples of hard bitumens shall be ground to a powder before an aliquot is taken.

9.4 Samples of crude petroleum shall be prepared in accordance with the procedure described in the Annex A1, unless it is known that the crude petroleum contains negligible quantities of material boiling below 80°C.

10. Apparatus Preparation

10.1 Clean all glass flasks (see 6.4) and dishes (see 6.6) by a means that matches the cleanliness obtained by the use of a strongly oxidizing agent, such as chromosulfuric acid, ammonium peroxydisulfate in concentrated sulfuric acid at approximately 8 g/L, or sulfuric acid itself, soaking for at least 12 h, followed by rinses in tap water, distilled water, and then acetone, using forceps only for handling. (**Warning**—Chromosulfuric acid is a health hazard. It is toxic, a recognized carcinogen as it contains Cr (VI) compounds, which are highly corrosive and potentially hazardous in contact with organic materials. When using chromosulfuric acid cleaning solution, eye protection and protective clothing are essential. Never pipette the cleaning solution by mouth. After use, do not pour cleaning solution down the drain, but neutralize it with great care, owing to the concentrated sulfuric acid present, and dispose of it in accordance with standard procedures for toxic laboratory waste (chromium is highly dangerous to the environment). Nonchromium containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium, which has its own special disposal problems.)

10.2 For routine analysis, use a proprietary laboratory detergent to clean the glassware, followed by the rinses described in 10.1. When the detergent cleaning no longer matches the cleanliness required based on visual appearance, use a strong oxidizing agent.

10.3 After rinsing, place the glassware in the oven (see 6.12) for 30 min, and cool in the cooling vessel (see 6.15) for 30 min before weighing.

11. Procedure

11.1 Estimate the asphaltene content of the sample, or residue obtained from the procedure in Annex A1, and weigh the quantity, to the nearest 1 mg for masses above 1 g and to the nearest 0.1 mg for masses of 1 g and below (see Table 1), into a flask (see 6.4) of appropriate capacity (see Table 1).

11.2 Add heptane (see 7.2) to the test portion in the flask at a ratio of 30 mL to each 1 g of sample if the expected asphaltene content is below 25 % m/m. For samples with an expected asphaltene content of above 25 % m/m, a minimum heptane volume of 25 mL shall be used (see Table 1).

11.3 Boil the mixture under reflux for 60 ± 5 min. Remove the flask and contents at the end of this period, cool, close with

a stopper (see 6.5), and store in a dark cupboard for 90 to 150 min, calculated from the time of removal from reflux.

11.4 Place the filter paper, folded as shown in Fig. 2 (so as to prevent loss of asphaltenes by creeping), in the filter funnel, using forceps. Thereafter, handle the filter paper only with forceps. Without agitation, decant the liquid into the filter paper, and then transfer the residue in the flask as completely as possible with successive quantities of hot heptane, using the stirring rod (see 6.14) as necessary. Give the flask a final rinse with hot heptane, and pour the rinsings through the filter. Set the flask aside, without washing, for use as specified in 11.6.

11.5 Remove the filter paper and contents from the funnel, and place in the reflux extractor (see 6.3). Using a flask different from that used initially, reflux with heptane (see 7.2) at a rate of 2 drops/s to 4 drops/s from the end of the condenser for an extraction period of not less than 60 min, or until a few drops of heptane from the bottom of the extractor leave no residue on evaporation on a glass slide.

11.6 Replace the flask by the one used initially, and to which has been added 30 to 60 mL of toluene (see 7.1), and continue refluxing until all the asphaltenes have been dissolved from the paper.

11.7 Transfer the contents of the flask to a clean and dry (see Section 10) evaporating vessel (see 6.6), weighed to the nearest 0.2 mg by tare against a similar dish. Wash out the flask with successive small quantities of toluene to a total not exceeding 30 mL. Remove the toluene by evaporation on a boiling water bath, or by evaporation in a rotovapor under an atmosphere of nitrogen. (**Warning**—Perform the evaporation in a fume hood.)

11.8 Dry the dish and contents in the oven (see 6.12) at 100 to 110°C for 30 min. Cool in the cooling vessel (see 6.15) for 30 to 60 min and reweigh by tare against the dish used previously for this purpose, and which has been subjected to the same heating and cooling procedure as was the dish containing asphaltenes.

NOTE 3—Asphaltenes are very susceptible to oxidation, and it is important that the procedure specified in the final drying stage is adhered to exactly as regards to temperature and time 61 min.

12. Calculation

12.1 Calculate the asphaltene content, A , in % m/m, of petroleum products as follows:

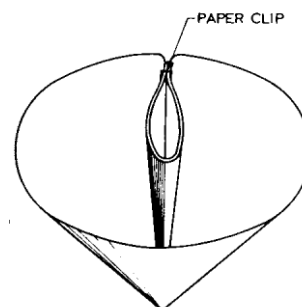


FIG. 2 Filter Paper

$$A = 100 (M/G) \quad (1)$$

where:

M = is the mass of asphaltenes, in grams, and
 G = is the mass of test portion, in grams.

12.2 Calculate the asphaltene content, C , in % m/m, of crude petroleum prepared in the manner described in the Annex, as follows:

$$C = 100 (MR/GD) \quad (2)$$

where:

M = is the mass of asphaltenes, in grams,
 R = is the mass of the residue from distillation, in grams,
 G = is the mass of the residue aliquot, in grams, and
 D = is the mass of crude petroleum sample distilled, in grams.

13. Report

13.1 Report the following information:

13.1.1 The heptane insoluble asphaltene content of values less than 1.00 % m/m, to the nearest 0.05 % m/m, by Test Method D6560.

13.1.2 The heptane insoluble asphaltene content of values of 1.0 % m/m and greater, to the nearest 0.1 % m/m, by Test Method D6560.

14. Precision and Bias

14.1 *Precision*—The precision values were determined in an interlaboratory program, using benzene as solvent, in 1956. A second interlaboratory program, using toluene as solvent, was carried out in 1975 to confirm the precision. No data from the 1956 evaluation program can be found.

NOTE 4—A recent (1998) interlaboratory program in France on four samples with asphaltene contents in the range from 0.50 to 22.0 % m/m resulted in estimated precision values very similar to those given in 14.2

and 14.3, except for the reproducibility at very low levels (<2.0 % m/m), which was significantly worse.

14.2 *Repeatability*—The difference between two successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the value below in only 1 case in 20.

$$r = 0.1 A \quad (3)$$

where A is the average result, in % m/m.

14.3 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the value below in only 1 case in 20.

$$R = 0.2 A \quad (4)$$

where A is the average result, in % m/m.

14.4 *Bias*—Since heptane insoluble asphaltenes are defined by this test method, no bias can be assigned. The term asphaltenes may be associated with other similar procedures using alkanes as precipitating agents other than heptane. In general, lighter alkanes will give higher results and heavier alkanes will give lower results than heptane, but no consistent ratio can be assigned.

15. Keywords

15.1 asphaltenes; bitumen; crude petroleum; diesel fuel; gas oil; heptane insoluble residues; lubricating oil; residual fuel oils

ANNEX

(Mandatory Information)

A1. PREPARATION OF CRUDE PETROLEUM RESIDUE BY DISTILLATION

A1.1. Scope

A1.1.1 This annex covers a procedure for the preparation of a crude petroleum residue (topped to an oil temperature of 260°C) suitable for the determination of asphaltene content (see 9.4).

A1.2. Terminology

A1.2.1 *Definitions*:

A1.2.1.1 *crude petroleum residue, n*—residue from distillation to an oil temperature of 260°C carried out under conditions of this specified preparatory procedure.

A1.3. Summary of Test Method

A1.3.1 A weighed test portion of the crude petroleum sample is distilled in specified glass apparatus under specified

conditions of heat input and rate of distillation. The distillation is stopped at an oil temperature of 260°C and the mass of the residue determined.

A1.4. Apparatus

A1.4.1 *Distillation Apparatus*:

A1.4.1.1 *Residue Distillation Apparatus*, conforming to the requirements of Test Method D86, with the exception of the temperature sensor. The temperature sensor shall be a liquid-in-glass thermometer of total immersion type of total length 300 to 320 mm, with a temperature range from −4 to 360°C, and a maximum scale error of 2°C, or an alternative temperature measurement device or system of at least equivalent accuracy. A transparent bath, maintained at 15 ± 3°C, is mandatory for the receiver.

NOTE A1.1—A suitable thermometer is an IP 4C, as specified in

Appendix A of Specifications for IP Standard Thermometers.

A1.4.1.2 *Drying Distillation Apparatus*, conforming to A1.4.1.1, with the exception of a 500-mL distillation flask instead of the flask specified, and a 200-mL separating funnel immersed in broken ice instead of the receiver.

A1.4.2 *Drying Apparatus*, consisting of one of the following:

A1.4.2.1 *Centrifuge*.

A1.4.2.2 *Filter Apparatus*, operating at increased pressure.

A1.4.2.3 *Steel Container*, capable of withstanding 1000 kPa pressure and of being heated to 200°C.

A1.4.2.4 *Cottrell-type Electrostatic Separator*.

A1.5. Sample Preparation

A1.5.1 If the crude petroleum contains sufficient water to cause difficulties in distillation (excessive foaming), dry the sample by a method that avoids the loss of volatile components. The methods given in A1.5.1.1 – A1.5.1.5 are suitable.

A1.5.1.1 Separate the water by gravity or by centrifuging in a closed container at the lowest practicable temperature.

A1.5.1.2 Filter the sample at the lowest practicable temperature and applied pressure, through anhydrous calcium chloride, sodium sulfate, or other suitable drying agent, in a closed vessel.

A1.5.1.3 Heat the sample in a closed steel container (see A1.4.2.3) fitted with a temperature sensor and pressure sensor. Fill the container to approximately 70 % capacity, and heat it until the oil reaches a temperature of 200°C, or until the pressure reaches 700 kPa. Allow the container to cool to ambient temperature, and then decant the oil from the separated water.

A1.5.1.4 Construct a Cottrell-type separator from a tall glass beaker with a brass gauze cylinder, lined with flannel that has been saturated with water, and then squeezed out to leave it damp, fitted tightly inside. A brass gauze cylinder mounted on the glass spindle of a laboratory stirrer, rotated at approximately 30 rev/min, forms the central electrode. Pour the sample into the beaker, and apply a voltage to the electrodes. Interrupt the water precipitation at intervals to prevent the loss of volatile components, and allow the oil to cool. Separate the oil from the water that has coalesced and run down the flannel lining.

A1.5.1.5 Distil off the water with the more volatile hydrocarbons in the apparatus described in A1.4.1.2. Charge the flask with 300 mL of sample, and place the temperature sensor such that the sensing point (bulb) is immersed in the sample. Heat the flask gently so that the oil temperature rises slowly to

150°C, vaporizing into the condenser by means of a small gas flame any drops of water that collect on the walls of the flask. Stop the distillation when no more water passes over in the distillate. Allow the residue to cool, run off the water collected in the separating funnel, and add the oily distillate back to the residue and mix thoroughly. If visible water is still present, filter by the method described in A1.5.1.2.

A1.6. Procedure

A1.6.1 Determine the density at 15°C of the crude petroleum by Test Method D1298 or D4052.

A1.6.2 Weigh the distillation flask to the nearest 0.1 g, and charge it with a mass equivalent to 100 mL of sample at 15°C to within 0.1 g, ensuring that no oil flows down the vapor tube during this operation. Record the mass of oil (*D*). Place the liquid-in-glass thermometer so that the bottom of the bulb is 2.0 ± 0.5 mm from the bottom of the flask, or the alternative temperature sensor to a position established to give identical temperature readings.

NOTE A1.2—The position of the temperature sensor in the holder may be premarked before addition of the test portion to the flask.

A1.6.3 Swab out the condenser tube, and assemble the apparatus with the vapor tube of the flask extending into the condenser tube a distance of between 25 and 50 mm. Make the connection between flask and condenser tight by means of a stopper or bung through which the vapor tube passes.

A1.6.4 Place a clean dry receiver at the outlet of the condenser such that the condenser tube or adaptor extends into it at least 25 mm, but not below the 100-mL mark. Immerse the receiver up to the 100-mL mark in the transparent bath (see A1.4.1.1). Cover the top of the receiver closely during the distillation with a piece of paper weighted to restrict volatile losses and also to overcome the buoyancy of the receiver in the water bath. Circulate ice-cold (below 4°C) water through the condenser.

A1.6.5 Apply heat to the flask, and distil the crude petroleum at a rate not exceeding 2.5 mL/min until it ceases to foam, after which keep the rate of distillation constant at 2.0 to 2.5 mL/min (approximately 1 drop/s). Continue the distillation without interruption to 260°C. Remove the heat, and allow the condenser to drain into the receiver.

A1.6.6 Allow the residue in the flask to cool, remove the temperature sensor, and weigh the flask and residue. Record the mass of the residue (*R*).

A1.6.7 Use this residue to carry out the procedure (see Section 11) for the determination of asphaltene content.

SUMMARY OF CHANGES

Subcommittee D02.14 has identified the location of selected changes to this standard since the last issue (D6560–00(2005)) that may impact the use of this standard.

(1) Updated 3.1.1.

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