NOVELENHANCED OIL RECOVERY TECHNIQUE

Lakshmana Naik[1] R & Dr. P Justin [2]
[1]Assistant Professor, Department Of Chemical Engineering, AP IIIT, RGUKT, RK Valley.
[2]Assistant Professor, Department Of Chemistry, AP IIIT, RGUKT, RK Valley

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ABSTRACT: *Most of the studies and reviews show that the amount of oil that can be extracted with primary drive mechanisms is about 20 30% and by secondary can reach up to 40% but using modern enhanced oil recovery(EOR) techniques ,recovery can reach upto 60 65%. These techniques of Enhanced Oil Recovery(EOR) are essentially designed to recover oil commonly described as residual oil.The oil that cannot be extracted by produced from the primary recovery.According to the Energy Department the amount of oil produced world wide is only one third of the total oil available.So by using the EOR techniques we will be able to produce more oil as the demand increases while having a shortage in the supply.The project is research and experiment based on the advancement in enhanced oil recovery techniques, it aims reviewing the currently used techniques such as direct carbondioxide injection,Waginjection and the advancements in these techniques that result in better production of oil.The new EOR technique is Combination of citric acid and sodium bicarbonate injection,Acetic acid and sodium bicarbonate injection may drastically benefit enhanced the oil recovery when comparison with existing techniques(*CO_2*injection).*

Key Words: : *Enhanced oi lrecovery,direct carbondioxide injection,Waginjection,*CO_2 *flooding, Aceticacid and sodium bicarbonate injectionandcitricacidandsodiumbicarbonateinjection.*

INTRODUCTION

1.1 Petroleum/Crude Oil:

Petroleum or crude oil is defined as a mixture of hydrocarbons that exists in liquid phase in natural underground reservoirs and remains liquid at atmospheric pressure.In addition to carbon and hydrogen, crude oil may also contain small amounts of oxygen, nitrogen, sulphur and traces of metals. The chemical composition of crude oil may vary between 83-87% carbon, 11-16% hydrogen, 0-7% oxygen and nitrogen combined, and up to 4% sulphur, depending on the oilfield. The composition of crude oil determines the fraction of low hydrocarbons, which are the most useful compounds for the production of liquid fuels for transport[1]. Furthermore, the composition influences the physical and chemical properties of crude oil, including the specific gravity and viscosity, which in turn affect oil extraction processes, as discussed below [2].

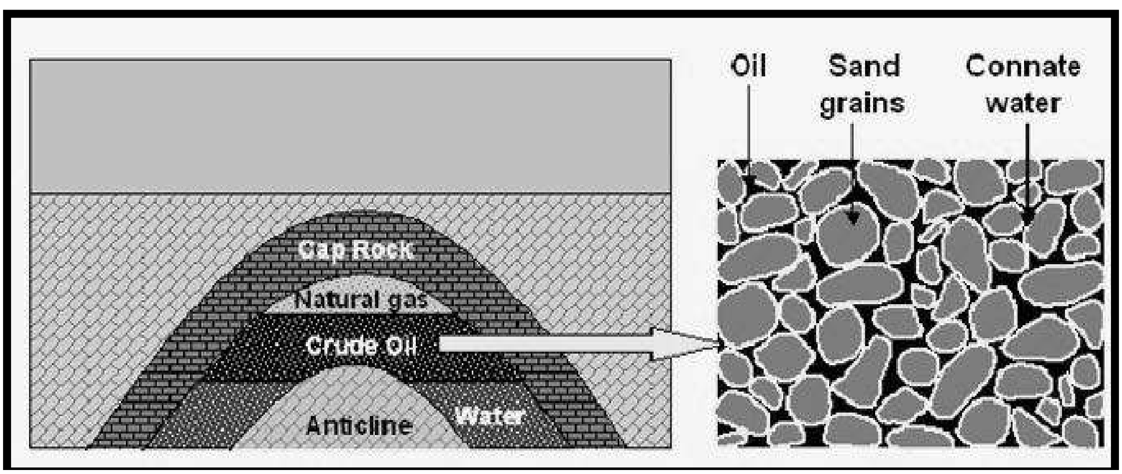

Figure:A typical 'anticline' oil reservoir resulting from the upward folding of geologic strata (left) and a schematic of an oil occurrence within the reservoir (right) [2]

Petroleum is formed in deep geologic formations called source rocks. Upon their formation, the hydrocarbon species that constitute the crude oil migrate upwards, through porous geologic strata. The crude oil either reaches the surface, or is accumulated underground when its upward migration is confined by an impermeable rock, called the cap rock[1]. The geological 'trap' formed by the cap rock is known as the oil reservoir as shown in Figure 1. The oil that is contained beneath the cap rock is in the reservoir rock, which is a porous and permeable geological formation that has the capacity to store and transmit fluids. Typically, the pores between the grains of the reservoir rock form an interconnected network that gives the rock its storage space and its permeability. The typical porosity of a reservoir rock is about 20%, but varying between 3 and 40%, depending on the arrangement of its grains, the depth and the type of rock. Oil and natural gas are found dispersed within the pores of the reservoir rock, together with water trapped in the sediment during its formation, called connate water as shown in ffigure 1. The porosity of the reservoir rock (i.e. the magnitude, interconnectivity, the pore size and shape) and the viscosity and gravity of the crude oil influence the flow of oil within the reservoir in the application of a pressure, which in turn affects oil recovery operations.

1.2Distinguishing Of Hydrocarbons

Generally, hydrocarbons are divided into four groups such as Paraffin's,Olefins,NaphthenesandAromatics.Paraffin's are also called alkanes and have the general formula of C_nH_{2n+2}, where 'n' is the number of carbon atoms. Paraffin's from C1 to C40 usually appeared in crude oil and represent up to 20% of crude by volume. Since paraffin's are fully saturated (no double bond), they are stable and remain unchanged over long periods of geological time. Olefins are another series of noncyclic hydrocarbons but they are unsaturated and have at least one double bond between carbon-carbon atoms. Compounds with one double bond are called mono olefinsor alkenes. Mono olefins have a general formula of C_nH_{2n}.Olefinsare uncommon in crude oils due to their reactivity with hydrogen that makes them saturated; however, they can be produced in refineries through cracking reactions[2].Naphthenes or Cycloalkanesare ring or cyclic saturated hydrocarbons with the general formula of C_nH_{2n}.Cyclopentane (C_5H_{10}), cyclohexane (C_6H_{12}), and their derivatives such as n-alkyl cyclopentanes are normally found in crude oils. Thermodynamic studies show that naphthene rings with five and six carbon atoms are the most stable naphthenic hydrocarbons. The content of cycloparaffin's in petroleum may vary up to 60%.Aromatics are an important series of hydrocarbons found in almost every petroleum mixture from any part of the world. Aromatics are cyclic but unsaturated hydrocarbons that begin with benzene molecule (C_6H_6) and contain carbon-carbon double bonds. Some of the common aromatics found in petroleum and crude oils are benzene and its derivatives with attached methyl, ethyl, propyl, or higher alkyl groups. This series of aromatics is called alkyl benzenes and have a general formula of C_nH_{2n-6}(where $n \geq 6$)[3].

1.3Oil Recovery Techniques

1.3.1Primary recovery

Oil recovery techniques have traditionally been grouped into three categories, based on when they are likely to be implemented in a typical oilfield: primary, secondary and tertiary oil recovery.

Thesetechniques are typically applied during the initial production phase of an oilfield, exploiting the pressure within the reservoir and using pumps to drive the oil to the surface. The pressure difference developed between the reservoir and the bottom of the oil producing well forces oil to flow towards the well which is called reservoir drive. Reservoir drive is the result of the combination of a number of physical mechanisms.Natural water drives resulting from the rise of the water layer below the oil column in the reservoir, displacing oil upward into the well [4]. The root cause of this is the inflow of water into the reservoir from adjacent aquifers. Gas-cap drives resulting from the expansion of the natural gas at the top of the reservoir, above the oil column, which displaces the oil downward in the direction of the producing wells. Dissolved gas drive that results from the dissolution and expansion of gas initially dissolved in the crude oil. Gravity drainage resulting from the movement of oil within the reservoir from the upper to the lower parts where the wells are located, driven by gravitational forces. After reservoir drive diminishes as a result of oil and gas extraction, pumping is used to maintain oil production. The primary recovery stage is completed either when the reservoir pressure is too low to maintain economical production rates, or when the ratio of gas (or water) to oil extraction is high. The primary oil recovery factor (i.e. the ratio between the oil produced during primary recovery and the original oil in place -OOIP-) depends on such factors as the geological characteristics of each reservoir, the viscosity of oil, and the reservoir pressure. It typically ranges between 5-15% of OOIP[5].

1.3.2Secondary recovery

When production by primary recovery methods is no longer viable, methods are applied. They rely on the supply of external energy into the reservoir in the form of injecting fluids to increase reservoir pressure, hence replacing or increasing the natural reservoir drive with an artificial drive .This is typically achieved by injecting water (water-flooding) in the reservoir using a number of injection wells. Although water flooding is used so extensively that this term has become synonymous to secondary oil recovery, other fluids, i.e.

liquids or gases may also be injected into the reservoir to achieve the same goal. Natural gas can be injected either in the gas-cap to increase the volume of gas within the reservoir, hence increasing reservoir pressure and displacing oil downward to the production wells, or into the oil bank to displace oil, however, without mixing with it (a process called immiscible displacement). In this context, CO_2 has also found a very limited number of applications worldwide. Many authors, however, include CO_2 displacement in the family of enhanced oil recovery operations .This is further discussed in subsequent sections of this Chapter. Immiscible gas displacement is not as efficient as water flooding; hence it is used less frequently today. Furthermore, the re-injection of natural gas into an oilfield can compromise the economics of such a project since the sales of the gas may be more profitable. Both the re-injection of natural gas, extracted during oil recovery, back to the oil reservoir and the injection of water have been practiced successfully in the North Sea. The end of the secondary oil recovery process is dictated by economic criteria .A typical recovery factor from water-flood operations is about 30%, depending on the properties of oil and the characteristics of the reservoir rock. On average, the recovery factor after primary and secondary oil recovery operations is between 30 and 50%. The oil recovery factor in the North Sea after primary and secondary recovery currently ranges between 45 and 55% while in some fields it has approached 70% [6].

1.3.3Tertiary oil recovery

It refers to a number of sophisticated operations that are typically done towards the end of life of an oilfield, to maintain oil production and produce an additional 5-15% OOIP. This is achieved by altering the flow properties of crude oil and the rock-fluid interactions in the reservoir to improve oil flow. One of these techniques is CO_2-EOR. With the evolution of knowledge on oil recovery, operations have, however, lost their traditional order of application. In an increasing number of reservoirs, operations otherwise named as 'tertiary' are performed first, such as for the extraction of heavy viscous oils, or they replace traditional secondary oil recovery operations. Hence, the term 'tertiary oil recovery' has recently been disfavored in the literature and substituted by the term enhanced oil recovery or EOR. The term improved oil recovery (IOR) is also frequently used in the same context; however it refers to a broader range of processes that lead to increased recovery, such as improved reservoir characterization and management, advanced drilling techniques [7].

2.Results and Discussion

2.1New MethodologyofChemicalFlood-Method1:

Citric Acid: Citric acid is a weak organic acid with the formula $C_6H_8O_7$. It is a natural preservative which occurs naturally in citrus fruits and is also used to add an acidic or sour taste to foods and drinks. In biochemistry, the conjugate base of citric acid, citrate, is important as an intermediate in the citric acid cycle, which occurs in the metabolism of all aerobic organisms. It consists of 3 carboxyl (R-COOH) groups.Citric acid is a commodity chemical, and more than a million tons are produced every year by fermentation. It is used mainly as an acidifier, as a flavoring, and as a chelating agent.

Sodium Bicarbonate: Sodium bicarbonate (IUPAC name: sodium hydrogen carbonate) is the chemical compound with the formula $NaHCO_3$. Sodium bicarbonate is a white solid that is crystalline but often appears as a fine powder. It has a slightly salty, alkaline taste resembling that of washing soda (sodium carbonate). The natural mineral form is nahcolite. It is a component of the mineral natron and is found dissolved in many mineral springs. It is among the food additives encoded by European Union, identified by the initials E 500. Since it has long been known and is widely used, the salt has many related names such as baking soda, bread soda, cooking soda, and bicarbonate of soda. The word saleratus, from Latin salertus meaning aerated salt, was widely used in the 19th century for both sodium bicarbonate and potassium bicarbonate. The term has now fallen out of common usage.

Properties of chemicals:

Chemical Name	Citric Acid	Sodium Bicarbonate	Sodium Citrate
Molecular Formula	$C_6H_8O_7$	$NaHCO_3$	$Na_3C_6H_5O_7$
Molar Mass (g/mol)	192.12352	84.007	258.06
Melting Point (^0C)	153	50	>300
Boiling Point (^0C)	Decomposes	851	Decomposes
Density (g/cm^3)	1.665	2.20	1.7
IUPAC ID	Citri Acid	Sodium Hydrogen Carbonate	Tri Sodium Citrate
Solubility in Water	Complete	Complete	Complete

Chemistry behind the Reaction:

The process of creating inside pressure by Citric Acid and Sodium Carbonateis a new technique by using chemicals and the chemicals which are used are citric acid ($H_3C_6H_5O_7$) and sodium bicarbonate ($NaHCO_3$). At the present of water the reaction is going to be happening between these two chemicals and this reaction is fizziness.

CITRIC ACID + SODIUM BICARBONATE → SODIUM CITRATE + WATER +CARBON DIOXIDE

From the above fuzziness reaction the output products are sodium citrate, water and carbon dioxide(co_2) will be forms as a result of these products the oil in the dead well are moving in the way of co_2 gas and after that the produced water also carries some of the oil to the movement of the of the co_2 gas to the outside of the well due to the high pressure created by the reaction inside of the well otherwise we can get that oil by using pumps. After the reaction is happened the produced carbon Dioxide will reduce the viscosity as well as oil density, promote swelling and vaporizes and thus extracts portions of oil.And the produced water increases the inside pressure. The products which are produced in this process are recycled for the same. As illustrated in the below Figure2.1. The chemical equation of the reaction is

$$H_3C_6H_5O_7(aq) + 3NaHCO_3(aq) + \ Na_3C_6H_5O_7(aq) + 3CO_2(g) + 3H_2O(l)$$

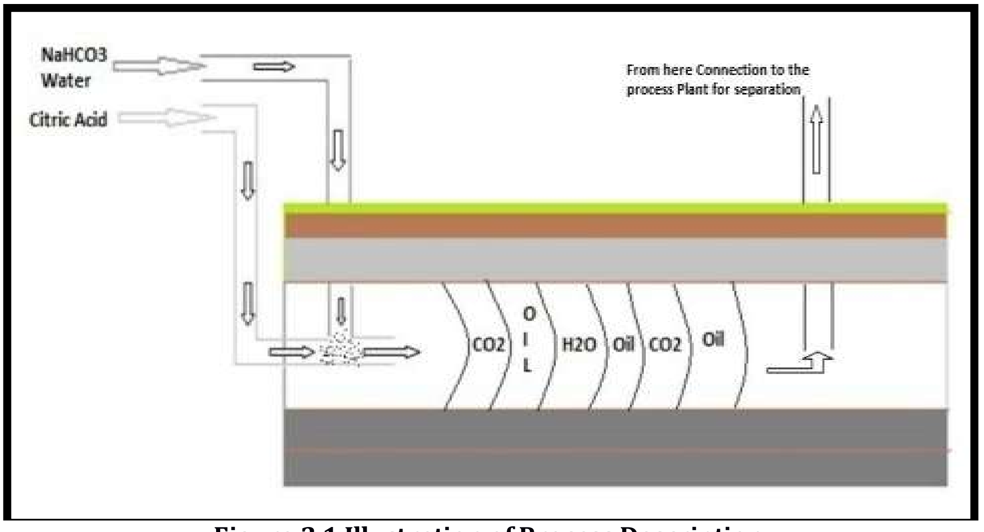

Figure 2.1 Illustration of Process Description

Effect of products on Oil Recovery

Effect of produced CO_2on Oil Recovery: Carbon dioxide is used in EOR techniques due to the combination of solution gas drive, swelling of the oil, reduction of its viscosity and the miscible effects resulting from the extraction of hydrocarbon from the oil. Carbon dioxide is highly soluble in hydrocarbons and this solubility causes the oil to swell, but for reservoirs containing methane a smaller amount of the carbon dioxide dissolves in the crude oil causing a less oil swelling. When reservoir oil is saturated with carbon dioxide at elevated pressures that will result in a substantial decrease in oil viscosity in the reservoir, the water in the formation is also affected by carbon dioxide, some expansion occurs for the water as well causing the density to decrease, so it means after injecting carbon dioxide both the densities of oil and water decreases moving their values near to each other which reduces the effect of gravity segregation [8].

Impact on project efficiency: The efficiency of a CO_2-EOR project can suffer from scale formation in the producer wells through deposition of contaminants that are present in the produced CO_2/water/oil mixture. In the project of the carbonate Dollarhide Devonian unit, scale formation in the producer wells was initially caused by deposition of leached calcium sulphate from the carbonate reservoir, followed by deposition of leached calcium carbonate and then by heavy asphaltenes which were present in the crude oil.Produced CO_2 can make scaling through calcium carbonate worse, as there is a greater concentration of bicarbonate ions in the water from the producer wells causing the deposition of calcite deposits in the pore sand on the sides of the tubing as the pressure drops. Also, when high pressure CO_2reaches the production wells it can expand. The resulting cooling can lead to increased deposition of asphaltenes in the production wells reducing injectivity. The effects are reservoir specific, depending on reservoir and well temperatures and pressures. However there is significant international experience on the use of inhibitors to effectively deal with scaling problems should they arise. Also, due to the small number of carbonate reservoirs in the North Sea, scaling from calcium carbonate should not be significant. On the other hand, in some formations, the produced CO_2 also will dissolve minerals increasing the permeability in sandstones. It is claimed that if dissolution is severe, channels will be created affecting sweep efficiency both on the micro and the macro level, with unpredictable effects in the overall efficiency of the project. This is important for sandstones, because these minerals contribute to the cementation of the rock.

Impact on oil quality:

It is reported that a miscible displacement process will tend to produce lighter crude than the original crude in the reservoir. It has also been suggested that the injection of CO_2may increase the sulphur content of oil. This depends on the levels of sulphur contained in the injected CO_2. The SACROC unit in West Texas utilises some $CO_2$for EOR that has been captured from natural gas processing plants. This is sour CO_2, containing around 2% sulphur. Similarly the CO_2captured from the Dakota Gasification Plant, which is used at Wey burn, contains around 0.9% hydrogen sulphide. Although there is no threshold limit, use of such impure CO_2may increase the sulphur content in the produced oil. After the reaction is completed produced CO_2 can be used in oil recovery process and the oil which is recovered from the well is filled in the storage tanks that contains not only oil it is mixed with CO_2 gas we can separate oil and gas. However, it is possible to design new CO_2 capture plant to provide low levels of sulphur in the CO_2. Coal typically contains 0.6-2.5% sulphur. In a coal IGCC plant, a two stage physical solvent process can be used to remove any H_2S in the gas. The first stage can remove over 99.5% of the sulphur, and the second stage can be used to capture high purity CO_2. If this high purity $CO_2$is used for CO_2-EOR, then there is no increase in the sulphur content of the produced oil through impurities in the produced CO2.

Some of the aspects why CO_2 used for oil recovery &how it increasing the recovery factorare itPromotes swelling,Reduces viscosity,Decreases oil density,Vaporizes and thus extracts portions of oil. CO_2-EOR is a commercial technology, implemented onshore in other parts of the world. However, such projects are not implemented in Europe.CO_2-EOR can increase considerably the European oil production and hence improve the security of oil supply within the EU. However, competing EOR methods may limit the application of the technique. Hence, the benefit would be restricted to a liming number of countries, mainly around the North Sea. The knowledge gained by the implementation of CO_2-EOR projects in the North Sea could be beneficial for other CO_2geological storage projects at the pan-European level, a prerequisite for the development of decarbonised fossil fuel power plants[9].

Effect of produced Water on Oil Recovery:

Typical oil recovery associated with primary pressure depletion is 10-20% of the original oil in place(OOIP).Secondary recovery is the process of injecting fluid, via so-called injection wells, to maintain reservoir pressure and drive additional reservoir fluids toward production wells. The produced water which is produced in reaction drive the reservoir oil towards the production wells by creating pressure. So along with CO_2 the water also useful to increase the recovery rate of the oil.

Some of the advantages are its new technique by using chemical reactions to enhance the oil recovery, the reaction takes place at the point where we require energy to push the oil from dead wells, and it's a process which produces CO_2 as well as H_2O simultaneously and CO_2 and H_2O will be recycled for the further process.

2.2New Methodology of ChemicalFlood-Method 2

Acetic Acid: Acetic acid, systematically named ethanoic acid, is an organic compound with the chemical formula CH_3COOH (also written as CH_3CO_2H or $C_2H_4O_2$). It is a colorless liquid that when undiluted is also called glacial acetic acid. Vinegar is roughly 3 %-9 % acetic acid by volume, making acetic acid the main component of vinegar apart from water. Acetic acid has a distinctive sour taste and pungent smell. Besides its production as household vinegar, it is mainly produced as a precursor to polyvinyl acetate and cellulose acetate. Although it is classified as a weak acid, concentrated acetic acid is corrosive and can attack the skin. Acetic acid is the second simplest carboxylic acid (after formic acid) and is an important chemical reagent and industrial chemical, mainly used in the production of cellulose acetate for photographic film and polyvinyl acetate for wood glue, as well as synthetic fibers and fabrics. In households, diluted acetic acid is often used in descaling agents. In the food industry, acetic acid is used under the food additive code E260 as an acidity regulator and as a condiment. The global demand of acetic acid is around 6.5 million tons per year (Mt/a), of which approximately 1.5 Mt/a is met by recycling; the remainder is manufactured from petrochemical feedstock. As a chemical reagent, biological sources of acetic acid are of interest but generally uncompetitive. Vinegar is dilute acetic acid, often produced by fermentation and subsequent oxidation of ethanol.

Sodium Bicarbonate: Sodium bicarbonate (IUPAC name: sodium hydrogen carbonate) is the chemical compound with the formula $NaHCO_3$. Sodium bicarbonate is a white solid that is crystalline but often appears as a fine powder. It has a slightly salty, alkaline taste resembling that of washing soda (sodium carbonate). The natural mineral form is nahcolite. It is a component of the mineral natron and is found dissolved in many mineral springs. It is among the food additives encoded by European Union, identified by the initials E 500. Since it has long been known and is widely used, the salt has many related names such as baking soda, bread soda, cooking soda, and bicarbonate of soda. The word saleratus, from Latin salæratus meaning aerated salt, was widely used in the 19th century for both sodium bicarbonate and potassium bicarbonate. The term has now fallen out of common usage[10].

Properties of chemicals [13]:

Chemical Name	Acetic Acid	Sodium Bicarbonate	Sodium Acetate
Molecular Formula	CH_3COOH	$NaHCO_3$	$NaCH_3COO$
Molar Mass (g/mol)	60.05	84.007	82.0343
Melting Point (^{0}C)	16	50	324
Boiling Point (^{0}C)	118	851	881.4
Density (g/cm^3)	1.05	2.20	1.53
IUPAC ID	Acetic Acid	Sodium Hydrogen Carbonate	Sodium Acetate
Solubility in Water	Complete	Complete	Complete

Chemistrybehind the Reaction:

The chemical name for baking soda is sodium bicarbonate. Its chemical formula is $NaHCO_3$, meaning it's made of one sodium atom, one hydrogen atom, one carbon atom, and three oxygen atoms. Vinegar is a mixture of acetic acid and water. Dilute acetic acid is the chemical name for vinegar, and its chemical formula is CH_3COOH. From here on out I will write the chemical formulas in parentheses. Baking soda is a base, and vinegar is an acid. An acid is a chemical that wants to get rid of a proton, or a positively charged hydrogen atom. A base is a chemical that wants a proton. When you mix an acid with base exciting things can happen because the acid is ready to give away its proton and the base is right there to receive it! Water is often added to acids and bases to tone down the intensity of this exchange. Water also acts as host in which the acid and base can break apart and react. In water, baking soda breaks apart into a positively-charged sodium ion ($Na+$) and a negatively charged bicarbonate ion (HCO_{3-}). An ion is a charged atom or molecule. Acetic acid doesn't break apart on its own in water as much as sodium bicarbonate; it's mostly diluted so it's not as strong. When we mix baking soda and acetic acid in water together, acetic acid gives its proton to the broken-apart baking soda and together they form sodium acetate (CH_3COONa), water (H_2O), and carbon dioxide (CO_2). These products are created quickly, and the carbon dioxide comes out as a gas, so the whole event is spectacular as you've seen! By reacting with each other, the acidic acetic acid and the basic sodium bicarbonate give up a lot of their energy and create things that have a lower energy relative to each other. The universe favours things at their lowest energy, and so we see a lot of exciting reactions involving acids and bases [11].

The process of creating inside pressure by Acetic Acid and Sodium Carbonate:

It is also a novel technique by using chemicals and the chemicals which are used are AceticAcid (CH_3COOH) and sodium bicarbonate ($NaHCO_3$). At the present of water the reaction is going to be happening between these two chemicals and this reaction is fizziness.

ACETIC ACID + SODIUM BICARBONATE SODIUM ACETATE + WATER +CARBON DIOXIDE

From the above fuzziness reaction the output products are sodium Acetate, water and carbon dioxide(co_2) will be forms as a result of these products the oil in the dead well are moving in the way of co_2 gas and after that the produced water also carries some of the oil to the movement of the of the co_2 gas to the outside of the well due to the high pressure created by the reaction inside of the well otherwise we can get that oil by using pumps. After the reaction is happened the produced carbon Dioxide will reduce the viscosity as well as oil density, promote swelling and vaporizes and thus extracts portions of oil.And the produced water increases the inside pressure. The products which are produced in this process are recycled for the same. As illustrated in the below Figure, the chemical equation of the reaction is

$$CH_3COOH(aq) + 3NaHCO_3(aq) \; Na_3COO(aq) + 3CO_2(g) + 3H_2O(l)$$

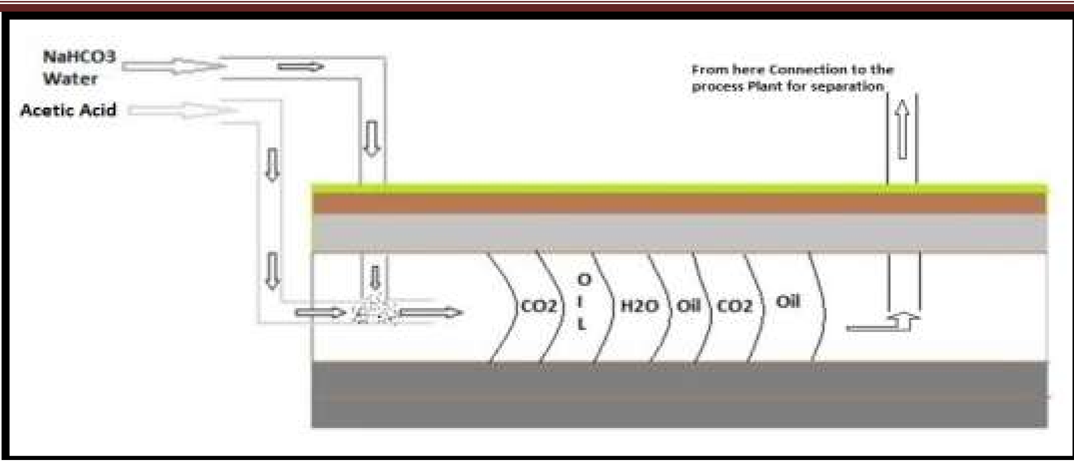

Figure2.2Illustration of Process Description

The effect of products on Oil Recovery, Effect of produced CO_2 on Oil Recovery, Impact on project efficiency, Impact on oil quality and Effect of produced Water on Oil Recovery are same mentioned in Method 1 i.e EOR citiric acid and sodium bicarbonate.

Some of the advantages are its new technique by using chemical reactions to enhance the oil recovery, The reaction takes place at the point where we require energy to push the oil from dead wells, It's a process which produces CO_2 as well as H_2O simultaneously, It's Cheaper than Citric Acid and it is a exothermic reaction so It can melt the solid forms of oil [12].

Conclusions

Method 1 is possible when the oil is in fluid (less viscous) nature, it is little bit high cost process than method 2 and it takes time for reaction to be happened than method 2. Method 2 is possible when the oil is in fluid (high viscous as well as low viscous) nature, It is low cost process and spontaneous reaction than method 1. In this new Methods, Capital and operating cost are not expenses for the Construction and operation because of a small a CO_2 pipeline network compare with CO_2 flooding method. WhenCO_2 is transport into the well there may besmall losses but in this novel method the CO_2 is produced at point of need so there is no transportation and no losses so fully it can utilizes the producedCO_2.Purchase of CO_2 is very expensive compare with our production of CO_2 and as well as we producing water so it is useful to create additional pressure in the well. In Wag injection method alternation of gas and water going to be send but here there are simultaneous production of CO_2 gas and water, the novel methods increases the recovery rate compare with wag injection method. For the water flooding ultimate oil recovery can be increased to 30-35% and other manual techniques like chemical flooding, polymers,tertiary flooding, CO_2 flooding, thermal recovery and the high pressure superheated steam techniques will be 35-40%. The methods discussed gives more than 40% of recovery due lack of losses and simultaneous production CO_2 and water. The percentage of oil recovery depends on properties of oil and characteristics of rocks. This is cheap and novel method by using chemicals. Water flooding is primary technique and CO_2 is secondary technique but this novel technique produces CO_2as well as water simultaneously.

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