Research note

Surfactant Remediation of LNAPL Contaminated Soil; Effects of adding alkaline and foam producing substances

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Abstract

Uncontrolled release of light non aqueous phase liquids (LNAPL) such as diesel, gasoline, fuel oils and lubricating oils from transporting vehicles, pipeline and underground storage tanks (UST) could lead to the migration of contaminants to the subsurface soil and ground water. There is a high interfacial tension (IFT) between LNAPL molecules and water molecules that makes water a non-efficient cleaning material for removing LNAPL from the soil. Nowadays, surfactants (surface active agents) can promote the enhanced removal of LNAPL from the subsurface through mobilization and solubilization. Encouraging results were achieved from laboratory and field results. The aim of this study is to improve the clean up efficiency of surfactant-flooding for two different surfactants; Triton X-100 and Sodium Dodecyl Sulfate which are known as mobilizing and solubilizing surfactants, respectively, by adding alkaline (increasing pH) and foam producing substances. It is shown here that adding alkaline improves the performance of Triton X-100 in removing LNAPL from the contaminated soil by about 8 percent, but spoils the remediating capability of Sodium Dodecyl Sulfate by about 3 percent. Also, adding a foaming agent helps the surfactant solution in removing the LNAPLs out of the soil by more than 5 percent.

Keywords: LNAPL, Surfactant, Remediation, Alkaline, Foam

Introduction

Today, for many countries around the world groundwater is an important source of drinking water. It is more pleasing than surface water as it is greater in quantity, better in quality, less vulnerable to contamination, and more economical in distribution. However, groundwater quality has generally deteriorated owing to human activities. The land disposal of solid wastes and waste water from domestic, municipal, and industrial uses contain very high amounts of organic compounds in both liquid and dissolved forms. Landfills and impound- ments are designed to minimize the adverse effects of these wastes. However, different organic liquids can be released to the subsurface from landfills and impoundments, owing to their poor design and deterioration. In addition, in many regions, especially in developing countries, there is still the illegal discharge of waste directly into the ground. This will ultimately result in the contamina- tion of groundwater by organic compounds [1]. Usually, these organic liquids are immiscible with water: so called non- aqueous phase liquids (NAPLs). Once released to the subsurface, NAPLs infiltrate

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downwards owing to gravity. NAPLs that are less dense than water, called light NAPLs or LNAPLs, accumulate on the water table and form a lens, whereas NAPLs which are denser than water, termed dense NAPLs or DNAPLs, continue to migrate through the saturated zone [2]. Upon reaching an impermeable layer, they will accumulate on the surface of that layer as a mobile phase. In moving downward, a portion of LNAPLs will be retained within the soil pores as immobile residual LNAPLs as a result of capillary forces. Improper disposal, accidental spills and leaked LNAPLs such as gasoline, fuel oil and creosote are persistent pollutants in the subsurface environment [3]. The tendency of NAPL contaminants to tightly bind onto the soil particles and the existence of high IFT between NAPL and water molecules, make it difficult to remediate and treat the NAPL contaminants. Thus, leaching from the soil ultimately becomes a continuous source of the groundwater contamination [4]. Removing the free phase LNAPL by pumping is referred to as primary remediation, and can only be utilized if a region of high LNAPL saturation exists. After primary pumping, a significant portion of LNAPL will remain within the soil as capillary forces overcome viscous and buoyancy forces. This discontinuous LNAPL is referred to as trapped residual LNAPL. Trapping may also occur during plume migration or seasonal water table fluctuations. Because of the high contacting area between trapped residual LNAPL and soil or water, the contamination becomes more dangerous when trapping occurrs. Remediation of trapped residual LNAPL is referred to as secondary or tertiary remediation [5]. As most organic compounds are only slightly soluble in water, they may exist in the subsurface for 100 years or more. On the other hand, the solubilities of LNAPLs are very small, but are sufficiently high enough to cause significant con-tamination of groundwater. For example, the maximum contamination level (MCL)

proposed by the US Environmental Protection Agency for trichloroethylene (TCE) is 5 mg/l. The solubility limit concentration of TCE is 1100000 mg/l, which is more than five orders of magnitude higher than the proposed MCL. Thus, residual LNAPLs represent a long-term source of soil and groundwater con-tamination [2]. In order to minimize the adverse effect of hazardous waste materials on the quality of groundwater, control measures regarding soil contamination should be considered before any serious deterioration occurs. These measures can be divided into preventive and remedial approaches. Preventive measures aim to manage and control the sources of contamination. These consist of hazardous waste management, by which risks associated with waste disposal and remediation should be minimized. However, even with preventive methods, accidental spillage or leakage of the organic liquids to the subsurface can occur. In addition, many inactive and (or) abandoned hazardous waste sites still exist and require remediation [2]. In this research the ability of surfactants to remediate the LNAPL contaminated soil is investigated. Nowadays, Surfactant-Flooding is an important technique in oil recovery processes as an EOR (Enhanced Oil Recovery) method and many aspects of this method are used in many countries to extract residual oil from oil fields.

Surfactants
Surface-active agents (abbreviated as surfactant) are substances that reduce the surface tension of a solvent and form aggregates like micelles in aqueous media. The change of surface tension by the dissolution of some compounds originates from the concentration of the surfactant at the surface of the solution. A surface active molecule consists of two parts with opposing characters. One part is hydrophilic (polar part or water attracting) and the other end is hydrophobic (non-polar or water repelling).
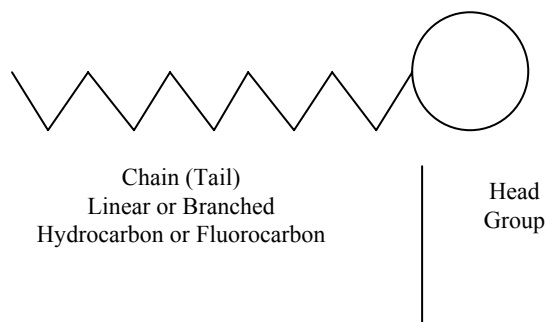
A surfactant molecule represented as in Figure 1.

Chain (Tail)
Linear or Branched
Hydrocarbon or Fluorocarbon

Head
Group

Figure 1. A schematic of a surfactant molecule

Surfactants are classified according to their hydrophilic group. Anionic, cationic, amphoteric, and nonionic surfactants contain negative, positive, positive and negative and neutral charges as their hydrophilic group respectively. A phenomenon unique to surfactants is the self-assembly of molecules into dynamic micelles (Figure 2). Micelle formation occurs above a critical concentration of surfactant monomers, referred to as the critical micelle concentration (CMC), which is different for every surfactant. The CMC is a function of the surfactant's structure, the temperature of the surfactant solution, the concentration of added electrolytes, and the concentration of solutes. The average number of surfactant molecules in a micelle is called the aggregation number [6].

Surfactants show significant potential for enhancing the remediation of soil and groundwater contaminated with organic compounds [7]. Surfactants enhance organic contaminant removal in soil washing/ flooding through two different mechanisms, solubilization and mobilization. Surfactants can have characteristic hydrophobic structural groups that have a strong desirability for LNAPL together with a hydrophilic group, which has a strong attraction for water. Surfactants are delivered into the subsurface environment through the aqueous phase. They are primarily used to either enhance the dissolution of LNAPL into the aqueous phase or to reduce the interfacial tension between LNAPL and the aqueous phase. For surfactant-enhanced solubility of LNAPL, the design approach is based in part on the recovery of a contaminated aqueous phase. However, when surfactants are used to reduce interfacial tension, LNAPL is mobilized. Hence, the design strategy is based on the recovery of free phase LNAPL [2, 7].
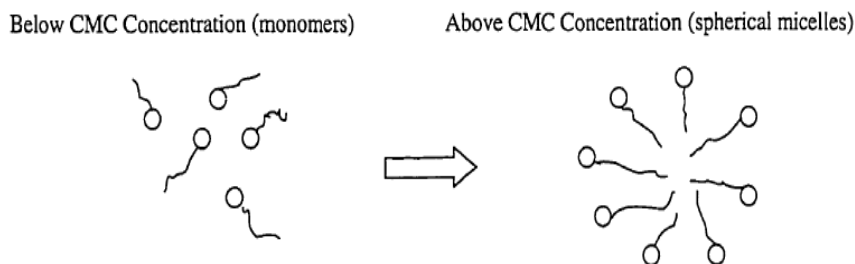

Figure 2. Schematic of CMC concentration of a surfactant solution

Proposed Method

The clean up efficiency of LNAPL by water is very low due to high IFT that exists between the organic materials and water. This mechanism is already known to petroleum engineers during the waterflooding of an oil reservoir as a secondary oil recovery process. Surfactants have been used in the oil industry to enhance waterflooding efficiency. In the same manner, the LNAPL molecules make a strong connection with soil molecules, making them difficult to be removed completely. Therefore, there is a need for chemicals to be added to water to reduce the interfacial tension and enhance the water-flooding process as it is already known to petroleum engineers for enhanced oil recovery.

Using the surfactants to remediate the contaminated soils in some cases may have two major problems or restrictions. First, the surfactant itself is an expensive material that increases clean up costs. This is not a major problem for the oil industry as the produced oil compensates the high cost of surfactant flooding. However, in the environmental clean up process, the cost is so critical that industries must use the chemicals carefully. This restriction motivated us to investigate the effects of additives to enhance the clean up efficiency using surfactants. The second concern in some cases is the nature of the surfactant itself. The surfactant residuals may be toxic, and the migration of the fluids containing dissolved contaminants will probably lead to the spreading of the contaminated zone and further contamination of the ground water. The ability to control the migration of contaminant-laden fluids can be improved by using foam. Using the foaming agents could increase the contact area between the solution and soil and the remediation can take place more efficiently. In this study, alkaline materials (such as NaOH, KOH or Na_2CO_3) in small amounts are added to the surfactant solution, enhancing the surfactant flooding. The

foaming agent, along with air injection, could lead to a more efficient clean up process. Using these additives (Alkaline materials to increase the PH and foaming agents) results in a dramatic reduction in the amount of surfactants used for the clean up process. The improved recovery factor in the presence of alkalis is still attributed to the reduced interfacial tension, wettability alteration, elimination of rigid films at oil-water interfaces, initiation phase inversion in dispersed systems and the precipitation of multivalent cations from the formation water which may also influence the ion-exchange processes in the contaminated soil. A generally accepted conclusion is that the crude oil must contain acidic components which react with the alkaline materials in the interface. The "soaps" or surfactant-like materials that formed under normal con-ditions might then decrease the interfacial tension by several orders of magnitude, implying a correlation could exist between the reduced interfacial-tension and the acid number of oils. On the other hand, the positive effect significantly depends on the pre-adsorption mechanism of naturally occurring surfactants present in oils. Therefore, adding alkaline to the surfactant solution is effective only when LNAPL contaminants are made of hydrocarbons [8, 9, and 10].

Conversely, the foaming agents added to the surfactants reduce the amount of chemicals needed and therefore, by a specified amount of surfactant solution, a larger area could be cleaned out, decreasing the operation costs significantly. As the foam usually contains 70-80% air, it provides considerable amounts of oxygen to the soil which could enhance the remediation process via LNAPL volatilization. This would also increase the oxygen content of soil to improve the living conditions for both microorganisms and plants [5, 11, 12 and 13]. In this study, a collection of surfactant, water, alkaline and a foaming agent is used to clean up contaminated soils that are infected or

polluted by engine oil.

Materials and Methods
Experimental Model

To mimic the polluted soil a sand packed column was employed in this study. A stainless steel pipe with an inside diameter of 3.5 cm and outside diameter of 4 cm was used as the sand pack holder. Two stainless steel meshed distributors were positioned on both ends of the column. The entrance and exit parts of the model were equipped with stainless steel flanges and two stainless steel check valves to control the flooding rate. Silicate sand with a mesh number of 50 was selected as the soil environment. First, the sand was washed and allowed to dry in free air for 2 days. Then, it was poured into the sand pack gradually and was packed well by shaking and then hitting the steel sand pack by a plastic hammer. Also, the steel sand pack was connected to earth (grounded) by an electrical wire to evacuate the probable static electricity that repelled the sand particles. When the sand pack holder became full, the end flange was closed and the packed column was connected to a CO_2 storage tank; the CO_2 gas was allowed to flow through the sand pack for about 15 minutes to completely expel the entrapped air. Then it was flooded with water and during water-flooding the permeability of the sand pack was measured using the Falling Water method [14]. The water-flooded sand pack was then flooded with a kind of heavy refined oil and about 4 to 5 pore volumes of the oil were allowed to pass through it. At this time, the sand pack represented a soil that was polluted with LNAPL that have connate water and were ready to be remediated.

To visually see the effect of adding foam to the surfactant solution, a glass sand pack model was also used. This glass model is made of two square flat 1 cm thick, 20*25 cm wide pieces of glass having a space of about 1-cm between them, while 3 sides (bottom, right and left sides) are sealed with aquarium glue and an aluminum bar. The top side was left open for filling the bed and then was sealed with a cap. The procedure for preparing the sand pack is the same as for the steel tube model.

For injecting the surfactant solution into the sand packed bed, a low flow rate, high pressure pump is used. The flow rates were controlled with a high pressure stainless steel needle valve. The out coming fluid from the bed is collected, water and oil is separated and the amount of oil that is remediated from the sand pack is recorded. To compare the results better and find the effect of surfactant solution in remediating the soil, more experiments were done individually using water, surfactant solution, surfactant solution enriched with alkaline (pH around 11) and surfactant solution enhanced with foaming agent.

Materials

Heavy refined oil provided by Behran Jonoub Motor Oil Company was used in the experiments as contaminant fluid. Properties of this oil are reported in Table 1.

Two surfactants, Triton X-100 (T-X100) and Sodium Dodecyl Sulfate (SDS) (we will refer to as surfactants A and B, respectively) were used. Surfactant A is non-anionic with CMC of 0.1262 g/L, and surfactant B is anionic with CMC of 2.4 g/L.

Surfactant A is of a type that decreases the interfacial tension (IFT) between water and oil and removes the oil from the soil by mobilizing it. Surfactant B is of a type that dissolves the oil molecules and removes the oil by solubilization process.

To modify the pH of the surfactant solution, the 2N solution of NaOH is used. For generating foam in the surfactant solutions, foaming agent AA, along with an air injecting pump are used.

Experiments

Three sets of experiments were done in order to investigate the effects of surfactant flooding in comparison to waterflooding in

remediating the silica sand packed, contaminated with LNAPL. First, the contaminated soil was remediated by waterflooding alone and then by surfactant flooding to compare water and surfactant flooding performances. Then, by adding alkaline (NaOH) to surfactant solutions and increasing the pH, the effect of adding alkaline was checked. Finally, by adding a foaming agent assisted by an air pump, the effects of foam production in the surfactant solution in the remediating process was tested.

Table 1. Oil Properties

Property	Value
Brand Name	Behran Jonoub Motor Oil
Standards	SAE-50, Mono Grade
Dynamic viscosity @ 20° C	811.9 cP
Dynamic viscosity @ 30 °C	591.2 cP
Flash point	250° C
Pour point	-9° C
°API at 20° C	21
Asphaltene content, %wt	<0.2
Resin acid content, %wt	<0.3
Sulfur content, %wt	≈0
Salts, %wt	≈0

Experiments set 1. First, waterflooding was used to remediate the contaminated soil. When no more oil was produced under the waterflooding process, the surfactant flooding was started. Surfactant A at concentrations of 0.01, 0.1 and 1 weight percent (%wt.) and surfactant B at concentrations of 0.01, 0.1 and 1 %wt. are used to remediate the contaminated packed bed in 6 different experiments.

Experiments set 2. Surfactant A and surfactant B at a concentration of 0.01 %wt. and pH of 11~11.5 were used to remediate the contaminated soil in two different experiments to check the effect of adding alkaline.

Experiments set 3. Traces of foaming agent were added to the solution of surfactant A at concentrations of 0.01 and 1 %wt., to be used for the remediation of contaminated soil and to investigate the effect of adding a foaming agent.

Results and Discussion
Results
Figures 3-6 show the remediation process with respect to time as a sample of surfactant flooding, alkaline-surfactant flooding and foam-surfactant flooding respectively and the graphs for all experiments are not included here. The whole experimental results for ten different tests are shown in Table 2.

Figures 3 and 4 reveal the rate of contaminant removal during waterflooding, followed by surfactant flooding for surfactants A and B at a concentration of 0.1%wt.

Figure 5 shows the rate of contaminant removal for waterflooding, followed by alkaline-surfactant flooding for surfactant A at a concentration of 0.01 %wt.

Figure 6 shows the rate of contaminant removal for waterflooding, followed by surfactant-foam flooding for surfactant A at a concentration of 0.01 %wt.

Table 2 shows the sand packed physical

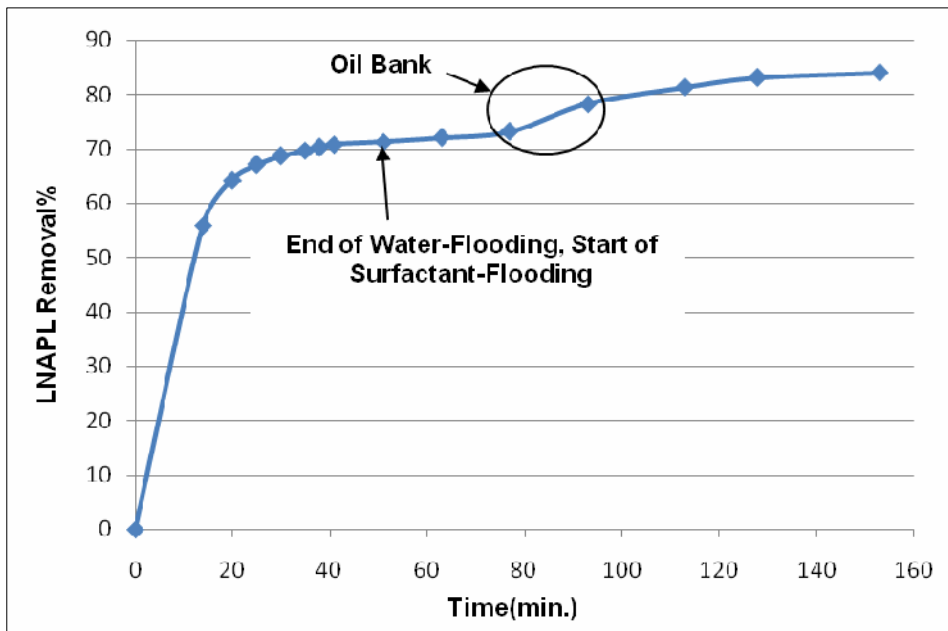properties such as porosity and permeability, along with LNAPL removal results for each experiment.

Figure 3. Rate of removing LNAPL by 0.1 %wt. solution of surfactant A
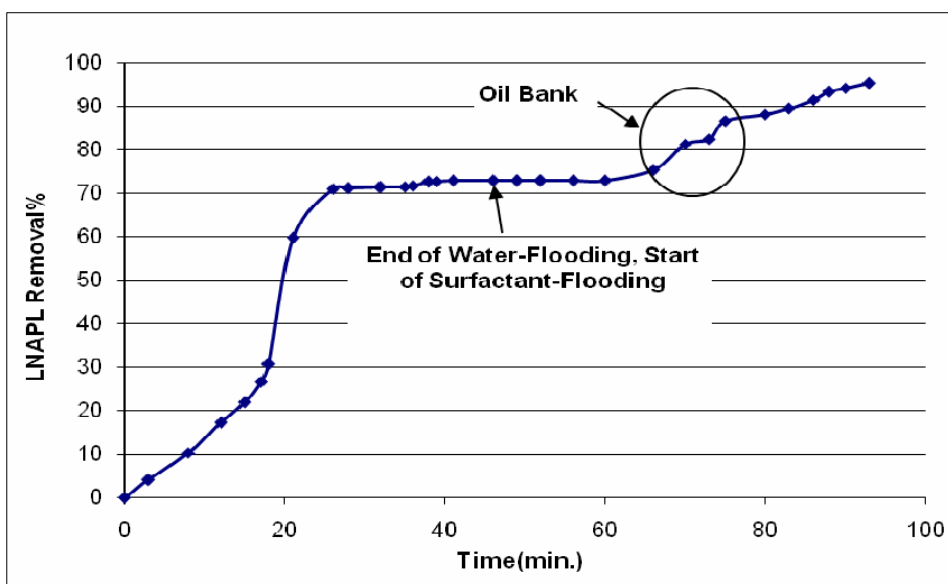

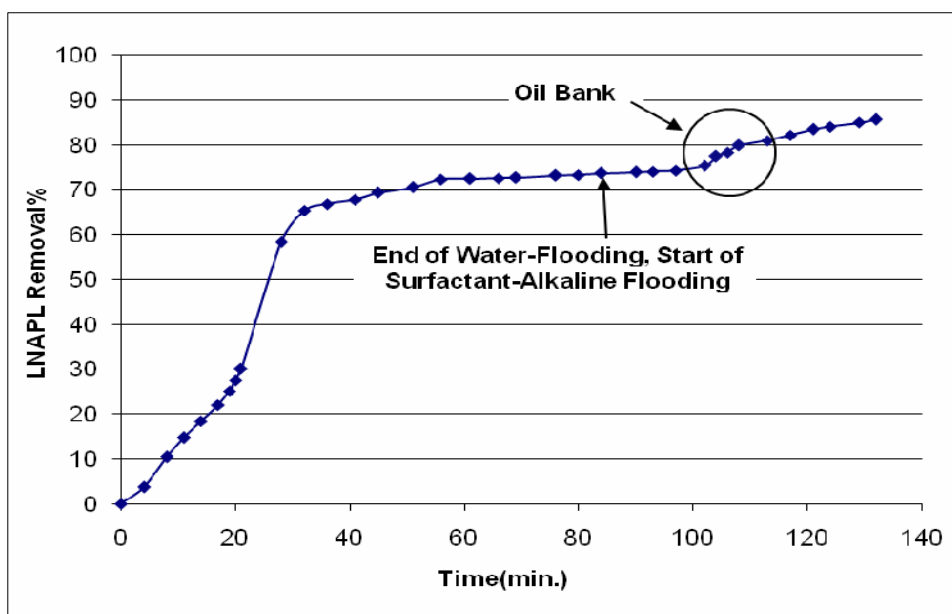**Figure 4.** Rate of removing LNAPL by 0.1 %wt. solution of surfactant B

Figure 5. Rate of removing LNAPL by 0.01 %wt. solution of surfactant A with pH=11
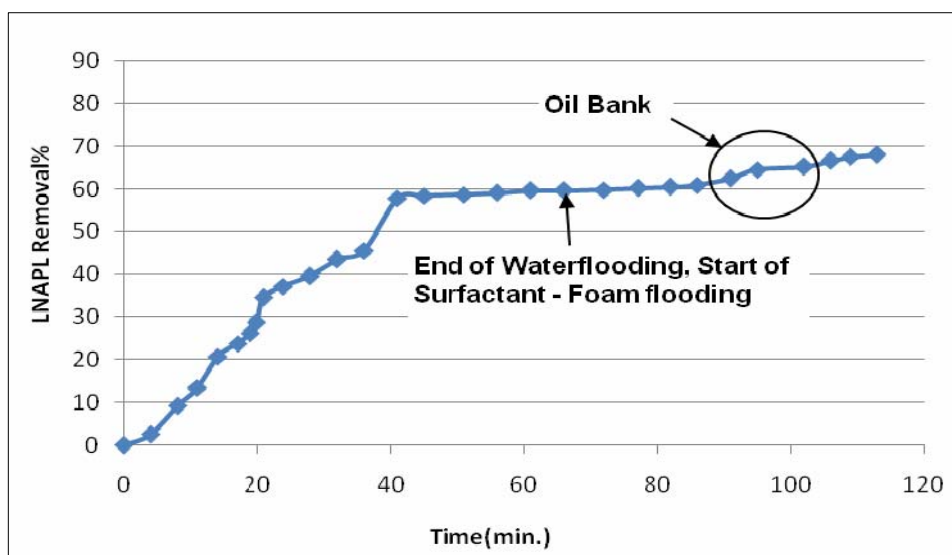

Figure 6. Rate of removing LNAPL by 0.01 %wt. solution of surfactant A with foaming agent

Table 2. Sand packed physical properties and LNAPL removal recoveries.

Exp. No.	φ (%)	K_{abs} (Darcy)	S_{oi}	Surfactant Type	Concentration (%wt.)	Exp. Type*	pH	W LNAPL Removal** (%)	S LNAPL Removal** (%)	S LNAPL Removal*** (%)	Ultimate LNAPL Removal** (%)
1	30.0	83.0	82.0	A	0.01	W, S	7	55.9	5.9	13.5	61.8
2	37.1	80.0	83.0	A	0.1	W, S	7	69.6	13.3	49.4	82.9
3	20.1	67.8	91.0	A	1	W, S	7	71.0	15.7	32.1	86.7
4	32.6	58.6	90.8	B	0.01	W, S	7	45.1	12.8	23.3	57.9
5	31.4	74.1	89.8	B	0.1	W, S	7	72.8	22.5	82.7	95.3
6	35.7	63.4	85.0	B	1	W, S	7	52.3	27.4	57.5	79.7
7	23.0	61.7	88.0	A	0.01	W, SA	11	73.4	13.1	49.4	86.5
8	36.4	70.4	87.0	B	0.01	W, SA	11	49.1	10.0	19.6	59.1
9	34.0	66.6	88.0	A	0.01	W, SF	7	59.6	11.2	27.7	70.8
10	31.0	62.3	91.0	A	1	W, SF	7	61.0	17.3	44.0	78.3

* (W=Water-flood, S=Surfactant-flood, SA=Surfactant Alkaline-flood, SF=Surfactant Foam-flood)
** Based on Originally Oil in Place (OOIP)
*** Based on Initially Oil in Place after waterflooding (IOIP)

A comparison between the ultimate LNAPL removals for different types of experiments is shown in Figure 7. The white part of each bar shows the waterflooding LNAPL removal efficiency and the dark part demonstrates the effect of surfactant, alkaline and foam flooding on the LNAPL removal efficiency.
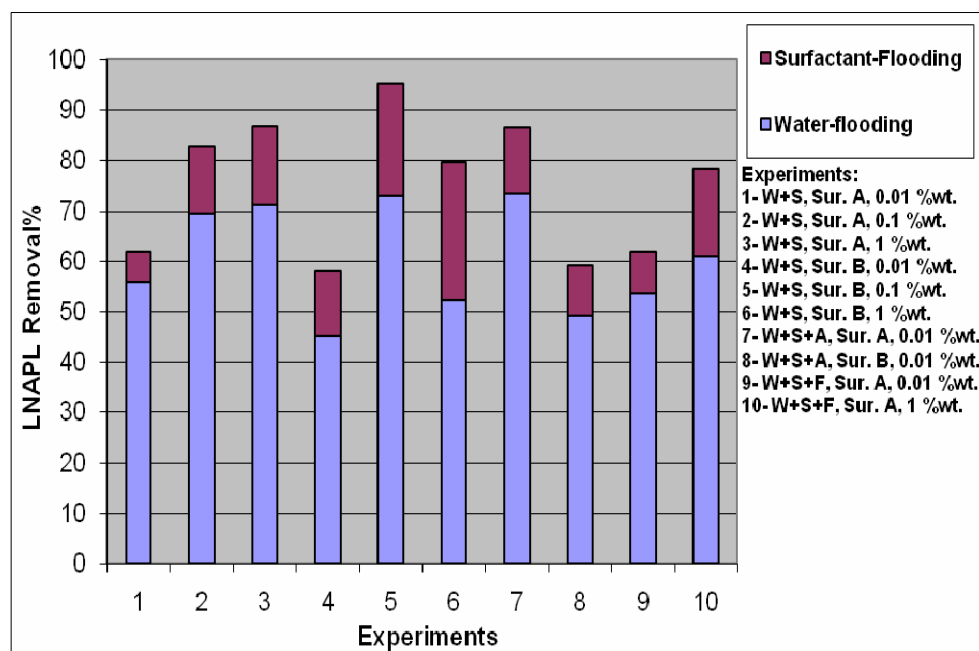

Figure 7. Water and Surfactant flooding LNAPL removal results for different experiments.

Discussion

- Because of high interfacial tension, the existence of adhesive forces between LNAPL molecules and soil particles, and

the high capillary pressure that traps LNAPL molecules in the pores, the remediation of LNAPL contaminant is so difficult in many areas. The use of water, which is not expensive and is also available in many places, as a cleaning agent to wash the LNAPLs out of soil was started late in the 1960s. However, it is clear that waterflooding bypasses the contaminants in the soil up to 50%. This fact is shown in Figures 3-6 and Table 2. It is recommended here to enhance the water-flooding process using surfactant additives which could improve the clean up efficiency up to 27% on the top water-flooding.

- The results indicate that increasing the surfactant concentration from 0.01 to 0.1 and from 0.1 to 1%wt. improves the LNAPL removal by about 8 and 2 percent respectively (Experiments 1-3). For surfactant B, increasing the surfactant concentration from 0.01 to 0.1 and from 0.1 to 1%wt. improves the LNAPL removal by about 10 and 5 percent respectively (Experiments 4-6). Since the surfactant materials are expensive, it is recommended here to use 0.1 %wt. solution to remediate the contaminated soil, although the 1 %wt. solution has higher LNAPL removal.

- As stated before, surfactant A is a mobilizing surfactant agent, while surfactant B is a solubilizing one. To remove this kind of LNAPL, surfactant B shows better results than surfactant A. Therefore, it is better to use solubilizing surfactants to remediate soil contaminated with organic compounds such as oil, gasoline, etc. Table 2 shows the results of contaminant removal for both surfactants A, B.

- Adding alkaline (increasing pH up to about 11) seems to enhance the action of surfactant flooding by creating the in-situ surfactant from the oil [10]. The results in Table 2 for experiments 7 and 8 prove that

adding alkaline to the solution of surfactant A improves LNAPL removal by about 8 percent. However, surfactant B shows different results as stated in Table 2. It was found that adding alkaline agents spoil the ability of this surfactant in LNAPL removal process by about 3 percent.

- The results of experiments number 9 and 10 show that the addition of a foaming agent to the surfactant solution improves the performance of the surfactant solution, up to 3 percent, which is not as effective as alkaline enrichment. However, it is known that the foaming agent along with air injection could improve the areal sweep efficiency considerably. Furthermore, many surfactant solutions have the capability of creating foam or bubbles only by injecting air through the solution and therefore, foaming agents are no longer needed.

- The experimental results show that an oil bank was formed during the experiments as the surfactant was injected into the model and start to move from injection to exteraction point. The creation of the oil bank could improve the sweep efficiency significantly as it collects the discontinuous oil blobs in the field when it moves further to the production well. It is shown in Figures 3-6 that LNAPL removal increases suddenly as the oil bank found its way out of the contaminated sand.

Conclusion

1. In almost all cases where we deal with cleaning the organic materials out of soil, surfactant-flooding is much better than water-flooding.

2. The best concentration (from the economical point of view) to use for these two surfactants in this research is 0.1 %wt.

3. Since the recovery of oil is not important in soil remediation and only the cleaning

process is significant, it is recommended to use the solubilizing surfactants rather than mobilizing ones. Creation of oil banks during the cleaning process, is a key factor to increase the rate of oil removal.

4. In contrast to surfactant A, it is better not to use the alkaline material, NaOH, with surfactant B.

5. Needs of high areal sweep efficiency and injection of air into the soil encourage us to use foaming agents along with surfactants.

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