Impact of surfactant solutions on conventional technologies efficiency for gasoline contaminated aquifer remediation

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ABSTRACT

By coupling vacuum extraction and in situ chemical oxidation (ISCO) with soil washing, it may be possible to improve global aquifer remediation efficiency to reach environmental standards. Vacuum extraction comes to its efficiency limit when gasoline reaches residual saturation. A first surfactant solution injection allows mobilizing gasoline through a vacuum extraction (slurping) system that is used to recover gasoline as a free phase. A second surfactant solution injection before ISCO allows dissolving remaining gasoline adsorbed on soil particles or trapped into the porous media and makes gasoline available for ISCO destruction. The main goal of this research is: (1) to find promising surfactant solutions allowing mobilization of residual gasoline and dissolution of the remaining gasoline, and (2) to test their efficiency on contaminated sediments in laboratory columns, in a $4m^3$ triangular sand tank and on site at the pilot test scale. This paper presents the physical and chemical properties of the studied gasoline and identifies the promising washing solutions with the help of pseudo-ternary phase diagrams. Results from phase diagrams show that surfactant and alcohol mixtures are more efficient than both ingredients used individually. The observed gasoline recovery mechanism in phase diagrams and anticipated in the porous media is mainly dissolution. These solutions should be adapted to mobilize gasoline.

RÉSUMÉ

En combinant l’extraction sous vacuum et l’oxydation chimique avec la technologie de lavage de sol aux solutions tensioactives, il serait possible d’améliorer le rendement global de la réhabilitation afin d’atteindre les critères environnementaux. L’extraction sous vacuum atteint sa limite d’efficacité lorsque l’essence atteint sa saturation résiduelle. L’injection d’une solution tensioactive permet la mobilisation de l’essence par un système d’extraction sous vide, utilisé pour récupérer l’essence en phase mobile. L’injection d’une solution tensioactive précédant l’oxydation chimique permet de solubiliser l’essence restante, adsorbée aux particules de sol ou prise dans le milieu poreux, et rend l’essence disponible pour la destruction in-situ par oxydation chimique. Le but principal de cette étude est donc d’identifier des solutions tensioactives prometteuses permettant la mobilisation de l’essence résiduelle et la solubilisation de l’essence restante, et de tester leur efficacité sur des sédiments contaminés par la suite en petites colonnes de sable, en bac de sable triangulaire de 4 m^3 et in situ à une échelle d’essai pilote. Le présent article porte sur les propriétés physico-chimiques de l’essence à l’étude et l’identification des solutions tensioactives prometteuses à l’aide de la construction de diagrammes de phases pseudo-ternaires. Les résultats obtenus en diagrammes de phases montrent qu’un mélange composé d’un tensioactif et un alcool est plus efficace que chacun pris individuellement. Le mécanisme de récupération de l’essence observé dans les diagrammes de phases et anticipé dans le milieu poreux est principalement la solubilisation. Ces solutions devront être adaptées pour mobiliser l’essence.

1 INTRODUCTION

Aquifer contamination by petroleum hydrocarbons (PH) is a plague that is spread all over the world, and particularly in industrialized countries like Canada. In Canada, PH like gasoline are the most spread contaminants and contaminated sites containing PH are counted by tens of thousands (CCME, 2001). Besides their toxicity and mobility, PH are persistent contaminants in soil because of their low water solubility and their high interfacial tensions (IFT) with water. Because of their persistence in soil, existing remediation technologies are not efficient enough to reach environmental standards for groundwater and soils quality.

According to Bradner and Slotboom, 1975, three forces act on PH behavior in the saturated zone: capillary forces, gravity forces and viscous forces. Capillary forces are defined by Young-Laplace equation: $P_c = 2\sigma\cos\theta / R$ and depend on PH-water IFT (σ), soil particles-PH-water contact angle (θ) and soil pore radius (R). Gravity forces are defined by the following equation: $F_g = \Delta\rho gh$ and depend on density difference between water and gasoline ($\Delta\rho$), gravitational acceleration (g) and on gasoline droplets size (h). Viscous forces are governed by the following equation: $F_v = v\mu = k(dp/dx)$ and are a function of displacing fluid velocity (v), dynamic viscosity (μ), porous media permeability (k) and pressure variation in the displacing fluid for an horizontal flow (dp/dx). To improve gasoline recovery in aquifers, among other possibilities, capillary forces can be decreased through wettability changes and IFT decreasing.

In situ recovery technologies were developed in the last decades to improve aquifer remediation like vacuum extraction (slurping), in situ chemical oxidation (ISCO) and soil washing. These technologies, when used alone, have efficiency limits. For vacuum extraction, when gasoline comes to residual saturation, the remaining gasoline exists as a discontinuous phase which is immobile and unrecoverable. For the chemical oxidation, it is adsorbed gasoline on soil particles or trapped into pore spaces that resists to oxidation. Finally, the soil washing technology generates huge washing solutions volumes that have to be treated/disposed off and the high initial active matter cost make this technology non economic.

Washing solutions are composed of a combination of surfactant and alcohol. Surfactant is an amphiphilic molecule, i.e. having two different polarity parts, one hydrophilic and one lipophilic. Four types of surfactant exist: anionic having the hydrophilic part negatively charged, cationic having the hydrophilic part positively charged, amphoteric having both charges and non ionic having no charge. Surfactant solutions can recover gasoline by two main mechanisms: dissolution and mobilization. Dissolution happens when the active matter (surfactant and alcohol) partitions preferentially in the aqueous phase, so gasoline is “dissolved” into it. Mobilization happens when the active matter partitions preferentially in the oily phase (gasoline), this way the gasoline volume is increased and can be mobilized via an oil bank.

To overcome these limitations, a technology train is proposed. By coupling vacuum extraction and ISCO with the soil washing technology, it may be possible to improve global aquifer remediation efficiency in order to reach environmental standards. This technology train starts with vacuum extraction to recover the mobile part of the gasoline floating free phase until it comes to residual saturation. By injecting a surfactant solution to mobilize gasoline at residual saturation in an oil bank (by reconnecting isolated blobs), gasoline can be recovered by vacuum extraction. By injecting a second type of surfactant solution able to dissolve remaining adsorbed gasoline on soil particles and trapped into porous media, it makes gasoline available in the aqueous phase and can be oxidized with the ISCO technology. Finally, by injecting an acclimated bacteria population to polish the cleaning process.

To accomplish such a technology sequence, laboratory experiments and a characterization of the porous media and the contaminant (gasoline) have to be done. The plan is to characterize at first the gasoline and its relation with the porous media, after that pseudo-ternary phase diagrams will be made to identify promising surfactant solutions. The best washing solutions will be tested in small sand columns experiments, in a $4m^3$ triangular sand tank experiment and on the field with a pilot test. This paper presents the initial phase of this project: characterization of contaminant physical and chemical properties and characterization of soil grain size and mineralogy; identification of promising washing solutions with the help of pseudo-ternary phase diagrams and their dominant recovery mechanism with tie lines solutions.

2 EXPERIMENTAL METHODS

2.1 Characterization of gasoline and geological materials from the contaminated site

A composite sample of weathered gasoline was obtained from observation wells located in the zone of interest at the site. Physical and chemical properties of gasoline such as density, viscosity, water content and chemical composition were respectively measured by a DMA 35N density meter (Anton Paar, Austria), an uncalibrated viscometer size 50 (Cannon Instrument Company, USA), an Aquastar V-200 titrator for Karl Fisher titration method (EM science, USA) and a Clarus 500 GCMS (Perkin Elmer, USA). Grain size analyses were done with conventional sieves and an Analysette 22 laser particle sizer (Fritsch, Germany). For mineralogy, thin sections of coarse fraction (> 2mm) were observed with a microscope under polarized light (Zeiss, Germany). X-ray diffraction analyses were done on the fine fraction with a D5000 x-ray diffractometer (Siemens, Germany). Pending drop method was used with a FTA200 apparatus (First Ten Angstrom, USA), to measure water-gasoline interfacial tension, mineral-water-gasoline contact angle (with quartz, calcite and feldspath) and gasoline surface tension at the ambient temperature (20°C).

2.2 Phase diagrams

Phase diagrams were carried out to evaluate the efficiency of different mixtures of surfactant and alcohol for the gasoline dissolution/mobilization. Pseudo-ternary diagrams have the three following poles: water at the down left, gasoline at the down right and active matter at the center top (Figure 1). The phase diagram shows for different concentrations of each element, if the mixture consists of only one phase, or separated in two or even three phases. The initial aqueous surfactant solution has to show only one phase before its injection in aquifers.

The boundaries of the one/multiple phase zones are determined with the cloud point method (Martel et al, 1993), consisting of adding one of the three element with a gas tight syringe to bring the resulting solution from clear (one phase) to cloudy (two or three phases). A miscibility curve is obtained by connecting all the cloud points. *MS Excel 2007* is used to compile every cloud point and to trace down the miscibility curves in diagrams. The lower the position of the curve in the diagram, the more efficient is the active matter of the solution because it dissolves the same quantity of gasoline at a lower concentration level. However, other considerations such as adsorption on soil particles, overall viscosity or density, or even cost and availability of the chemicals have to be considered also. The construction of diagrams is realized at groundwater temperature at the site, i.e. 8°C. For that, a refrigerated circulator (VWR International, USA), is used to cool down the 40 ml vial wherein the liquids are added to make the phase diagrams.

To find promising solutions, 7 alcohols and 18 surfactants were tested (Table 1). Previous studies showed that using a combination of alcohol and surfactant was more efficient than using a single component (Martel et al., 1993, Saint-Pierre et al. 2004). In order to simplify the number of possible combinations of alcohol and surfactant, all variables, i.e. alcohol, surfactant and their ratio are considered independents. The optimal ratio between the alcohol and the surfactant is first found by choosing one surfactant and one alcohol that are combined at various ratios (0.5, 1.0, 2.0, and 3.0) to make phase diagrams. When the alcohol: surfactant ratio is fixed by the lower miscibility curve, the alcohol type is changed to find the best alcohol. Seven alcohols were tested. With a fixed ratio and a fixed alcohol, 18 other curves were traced to find to best surfactant. Finally, the ultimate step is to readjust the ratio as precisely as possible with the alcohol and the surfactant selected. Also, alcohols were tested alone, to check which one is the most performing when used alone.

Table 1. Surfactants tested in phase diagrams, with their water content and hydrophilic charge type

Identification	Type	% H_2O
Surfactant A	Amphoteric	50,000
Surfactant B	Anionic	27,200
Surfactant C	Anionic	0,248
Surfactant D	Anionic	29,000
Surfactant E	Anionic	69,000
Surfactant F	Anionic	55,200
Surfactant G	Anionic	46,900
Surfactant H	Anionic	8,170
Surfactant I	Anionic	4,740
Surfactant J	Anionic	56,400
Surfactant K	Anionic	2,154
Surfactant L	Anionic	3,340
Surfactant M	-	3,510
Surfactant N	-	3,670
Surfactant O	-	11,800
Surfactant P	Non ionic	2,260
Surfactant Q	Non ionic	1,010
Surfactant R	Non ionic	0,796

A straight line (tie line) relates the compositions of the aqueous phase and the oily phase to the overall composition of all compounds in the system. Tie lines indicate the recovery mechanism involved with each solution. Experimentally, they are determined by preparing mixtures with proportions of the three poles under the miscibility curve, so the three elements in solutions get separated in two phases, an aqueous and an oily one. By preparing four mixtures under the miscibility curve with the same proportion of water and gasoline and an increasing active matter proportion, it is possible to check in which phase (aqueous or oily) the active matter partitions preferentially (Figure 1). If the aqueous phase increases proportionally with the active matter, then dissolution is the principal recovery mechanism. If the oily phase increases proportionally with the active matter, then mobilization is the principal recovery mechanism. To quantify the proportion of all components in all phases, chemical analyses are necessary. Tie lines are carried out for all seven alcohols tested alone and for every promising alcohol/surfactant solutions.

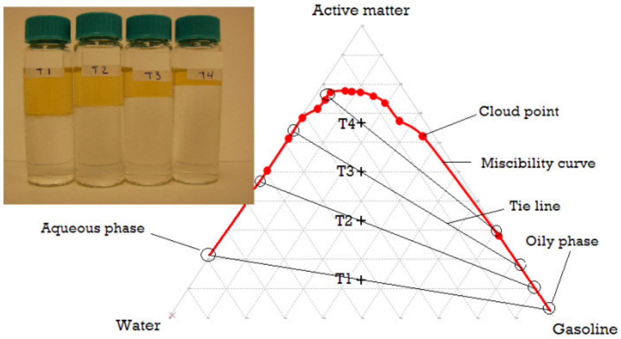

Figure 1. Phase diagram showing cloud points on the miscibility curve, model tie lines and corresponding initial mixtures for their construction (Alcohol III)

3 RESULTS

3.1 Characterization of gasoline and geological materials

Mineralogical analyses of soil particles show that main minerals in the fine fraction (< 63 microns) by x-ray diffraction are in order of importance: quartz (51%), feldspaths (26%) (albite, orthoclase and microcline) and calcite (22%). Thin sections observation on the coarse fraction are planned to check if the same proportion of minerals is observed. Grain size of soil particles is distributed with coarse sand (33%), medium sand (19%), fine sand (18%), fine gravel (17%), coarse gravel (10%) and silt (3%) (see grain size curve on Figure 2).

The mean gasoline surface tension was evaluated from 12 measurements at 20,6 mN/m with a measured range of 17-24 mN/m. The mean interfacial tension was evaluated from 10 measurements at 28,1 mN/m with a measured range of 27-30 mN/m. Based on mineralogical analyses, three different minerals (quartz, calcite and feldspath) were chosen for the measurement of mineral-water-gasoline contact angle. On quartz, the mean contact angle was evaluated from 10 measurements at 68° with a measured range of 43-83°. With feldspath, 8 measurements were done for a mean value of 87° with a measured range of 68-128°. With calcite, the mean value was 47° with a measured range of 36-55°, evaluated from 10 measurements. Mean gasoline density is 0,788 g/cm^3 and viscosity is 689 µPa-S at 8°C. The chemical composition of the weathered gasoline is 36% xylene, 28% toluene, 16% 1,2,4 trimethylbenzene, 10% ethylbenzene and 10% compounds of the methyl ethylbenzene family. Table 2 summarizes all physical and chemical properties of gasoline and geological materials.

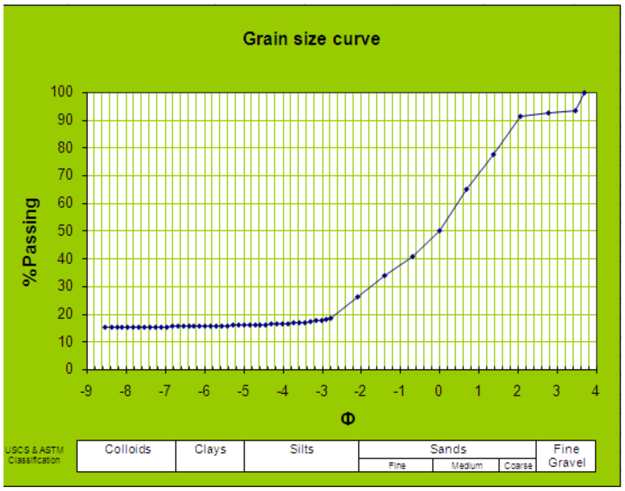

Figure 2. Grain size curve for the studied soil particles

Table 2. Physical and chemical properties of gasoline and geological materials

Properties	Values
Gasoline	
Surface tension - 20°C (mN/m)	20,6
IFT with water - 20°C(mN/m)	28,1
Contact angle - 20°C (°)	
Quartz	68,4
Feldspath	86,7
Calcite	46,6
Density - 8°C (g/cm3)	0,788
Viscosity - 8°C (µPa-S)	689
Chemical composition (%)	
Xylene	36
Toluene	28
1,2,4 Trimethylbenzene	16
Ethylbenzene	10
Methyl ethylbenzene family	10
Geological materials	
Minerals (%)	
Quartz	51
Feldspath	26
Calcite	22
Grain size distribution (%)	
Fine gravel	17
Coarse sand	34
Medium sand	22
Fine sand	25
Silt	2

3.2 Phase diagrams

Used alone, alcohols IV and V seem to be the best ones (Figure 3). Alcohol V and Surfactant L (75% pure) have been selected for determination of the optimal alcohol/surfactant mass ratio. Results show that the best alcohol/surfactant mass ratio was 1.0 (Figure 4), confirming previous experiments for gasoline (Martel et al, 1993). From seven tested alcohols, Alcohol II showed the lowest miscibility curve in the water-rich zone with the Surfactant B (Figure 5). Therefore, Alcohol II was selected to evaluate the efficiency of 18 surfactants at a fixed mass ratio of 1.0 (Figure 6). Four surfactants (Surfactants L, M, N, O) were not compatible with Alcohol II and further tests will be carried out especially for these surfactants. From the 14 remaining, five were selected based on the low position of their miscibility curve in the water-rich zone (Figure 7). Surfactant R seems to be the most promising at this point. Further diagrams will be done to optimize the ratio with these five most promising alcohol/surfactant solutions. These optimized solutions will then be used for sand columns experiments.

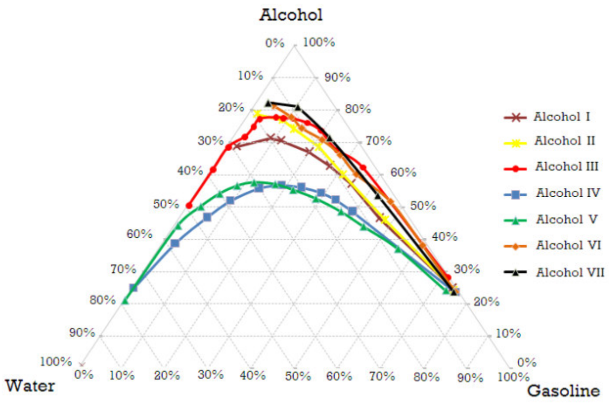

Figure 3. Phase diagram with miscibility curves for alcohols alone

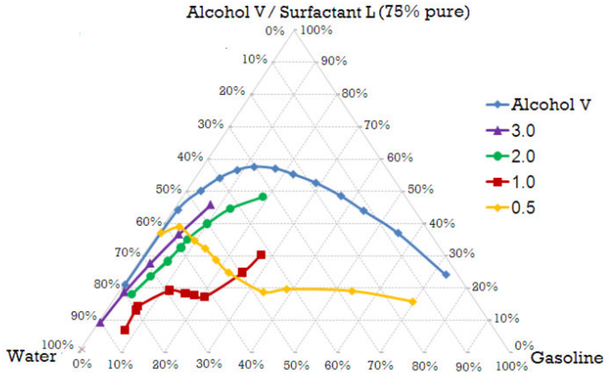

Figure 4. Phase diagrams with miscibility curves for different Alcohol V / Surfactant L (75% pure) ratios

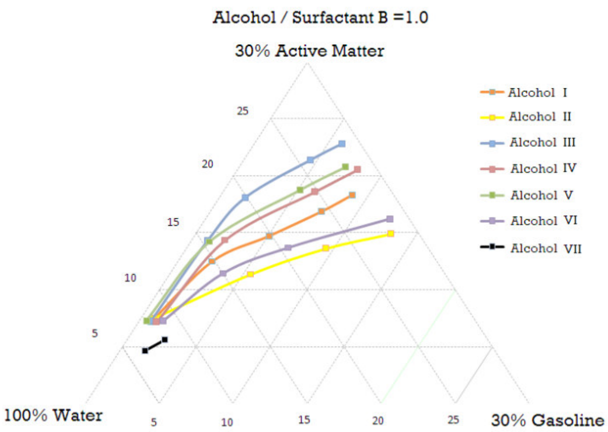

Figure 5. Phase diagram with miscibility curves for different alcohols at a ratio of 1.0

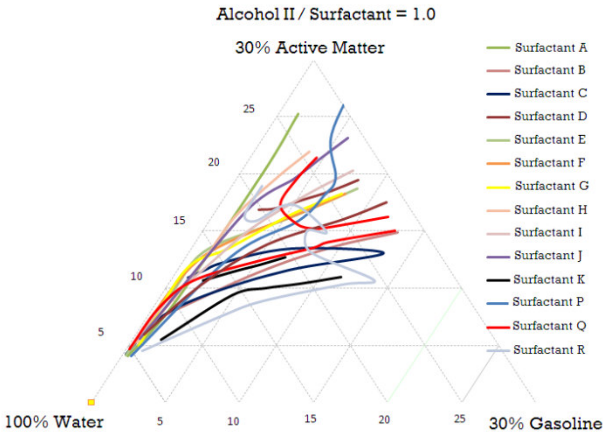

Figure 6. Phase diagram with miscibility curves for all surfactants at a ratio of 1.0

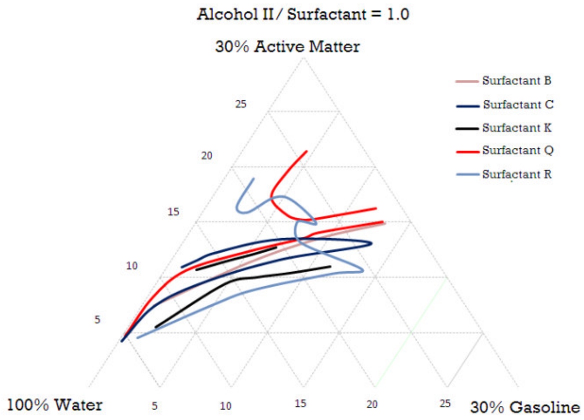

Figure 7. Phase diagram with miscibility curves for best surfactants at a ratio of 1

3.3 Prediction of the dominant recovery mechanism through tie lines

Tie lines have been prepared for alcohols alone and for Alcohol/Surfactant B = 1.0 solutions. Chemical analyses will be carried out with these solutions to identify the main recovery mechanism. Visual interpretation on apparent volumes of the corresponding initial mixture for tie lines construction allows the prediction of the dominant recovery mechanism in a qualitative way. For alcohols, mobilization is the dominant recovery mechanism for 5 of 7 alcohols (alcohols I, II, IV, VI and VII) and dissolution is the main mechanism for alcohols III and V (Figure 8). For Alcohol/Surfactant B = 1.0 solutions, dissolution becomes the dominant recovery mechanism for all alcohol types (Figure 9). Because the Alcohol/Surfactant B solutions are prepared in the water-rich zone, the oily phase is less present in the corresponding initial mixtures for tie lines construction. Figure 9 is a zoom on the oily phase section to see the recovery mechanism. However, because of a shortage of solution, some Alcohol/Surfactant B solutions are represented by only three tie lines points instead of four. Alcohol VII is not shown because of its incompatibility with Surfactant B (see Figure 5). On Figures 8 and 9, the aqueous phase is clear and the oily phase is yellowish.

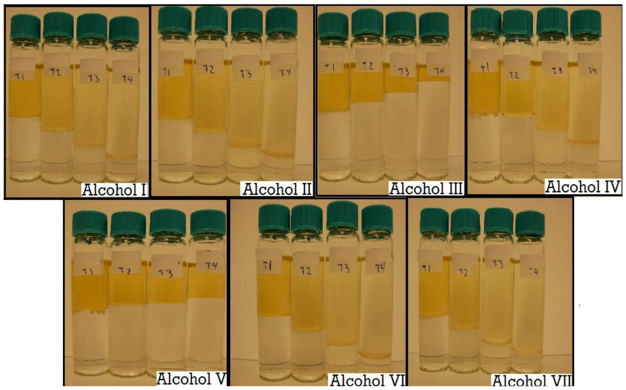

Figure 8. Initial mixtures for tie lines construction for alcohols types

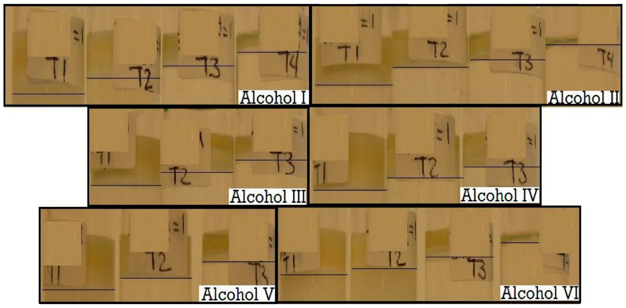

Figure 9. Zoom on initial mixtures for tie lines construction for Alcohol/Surfactant B = 1.0

4 DISCUSSION

4.1 Phase diagrams

Phase diagrams on Figures 3 and 5 show that the performance of an alcohol used alone is not a good indicator to predict its performance when used in combination with a surfactant. Indeed, when used alone, alcohols IV and V are the most promising, while they are poorly performing with the Surfactant B compared to other alcohols. Phase diagram on Figure 4 show that adding surfactant to an alcohol solution increases its dissolution power until it reaches an alcohol/surfactant critical ratio, which is 1.0 in the present study. Phase diagram on Figure 7 reveals that the combination of alcohol and anionic surfactant is as good as a combination of alcohol and non ionic surfactant. Effectively, for five surfactants retained for further tests, three are anionic and 2 are non ionic, which means that both types of surfactant have similar behavior when used with an alcohol.

4.2 Tie lines solutions

Tie lines prepared for alcohols and for Alcohol/Surfactant B on Figures 8 and 9 reveal that the dissolution power of the surfactant, at an alcohol/surfactant ratio of 1.0, can change the dominant recovery mechanism from mobilization to dissolution (alcohols I, II, IV, VI). By increasing the alcohol/surfactant ratio at values greater than 1.0, it could be possible to change gradually the dominant recovery mechanism from dissolution to mobilization. This way, only one surfactant could be used for the technology train and the recovery mechanism could switch from mobilization (for bioslurping) to dissolution (for chemical oxidation) by changing the alcohol/surfactant ratio.

4.3 Future work

Further tests will include column experiments with on-site soil, followed by adsorption tests and compatibility tests with oxidants. A larger scale test (4 m^3 sand tank) will also be conducted prior to implement the technology train on-site. During all these tests, a numerical model will be used to better understand and to predict the phase behavior (UTCHEM) (Delshad et al, 1996).

5 CONCLUSION

This paper was about characterization of physical and chemical properties of gasoline and soil from the studied site. Identification of promising washing solutions with pseudo-ternary phase diagrams and their dominant recovery mechanism with tie lines solutions was carried out. The most performing alcohol used with a surfactant at an optimal alcohol/surfactant ratio of 1.0 is Alcohol II and most promising surfactants are surfactants B, C, K, Q and R. These 5 combinations give the lowest miscibility curves in the water-rich zone. Tie lines show that the recovery mechanism can be changed by changing surfactant, alcohol or alcohol/surfactant ratio. This way, only one surfactant could be used for the technology train with a recovery mechanism that can switch from mobilization (for bioslurping) to dissolution (for chemical oxidation) by changing the alcohol/surfactant ratio.

ACKNOWLEDGMENTS

This project is funded through grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) CRD program with TechnoRem as the industrial partner. Special thanks to Richard Levesque for his help in laboratory experiments.

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