Scaled model studies of petroleum contaminant removal from soils using surfactant solutions

N.S. Sundaram, M.R. Islam*

Department of Geology and Geological Engineering, South Dakota School of Mines and Technology, Rapid City, SD 57701, USA

Abstract

This paper presents scaled physical model studies for petroleum contaminant removal using surfactant solutions. Scaling criteria are selected in such a way that a realistic representation of the decontamination process is possible. The proposed scaling approach meets all important requirements of this decontamination process which uses surfactant solutions. This approach scales more accurately where aquifer geometry, viscous forces, and the ratio of the gravitational forces to viscous forces are important. Experimental runs were conducted to investigate the effects of surfactant concentration, contaminant type, and interfacial tension. The optimum surfactant concentration was identified for one of the contaminants used. It was found that the optimum concentration in the field is not necessarily the same as the one which gives rise to the minimum interfacial tension in a spinning drop tensiometer. This aspect of optimum concentration could not be identified in an unscaled physical model. The only factor that was not modelled is heterogeneity. Scaling criteria or proper characterization of a heterogeneous medium is not yet available. However, the scaled physical model, as presented in this paper, provides a realistic approach to modelling a field remediation process enabling one to design a pilot test for further studies. Experimental results are scaled up to field values. Experimental results indicate that the proposed method of decontamination may recover up to 93% of the contaminant originally in place. The clean-up method is effective for a wide range of permeability of the soil. Also, the effect of a vadose zone was studied for a range of surfactant concentrations. Results indicated that the clean-up method has to be planned according to the soils as well as the contaminant.

1. Introduction

Petroleum hydrocarbons are some of the most common ground-water contaminants. The process of in situ soil cleaning using an aqueous surfactant solution is

---

** Corresponding author.

an effective method of removing petroleum contaminants from soils. Several studies using aqueous surfactant solution to remove oily contaminants have been reported in recent years. The American Petroleum Institute (API) conducted studies [1,2] to demonstrate the effectiveness of a non-ionic and an anionic surfactant in water using one-, two-, and three-dimensional laboratory models. Nash and Traver [3] used surfactant solutions to remove petroleum contaminants. Aqueous surfactant solutions removed more than 90%, 85%, and 50% of contaminants from soils in batch, column, and field site experiments, respectively. While these studies demonstrated the potential effectiveness of surfactant solutions for soil cleaning, the laboratory studies did not permit direct interpretation of the results to predict field performance of this process. Scaled model experiments can be used to predict the field performance of surfactant cleaning processes. These models provide a means of answering questions including the effects of injection rate, aquifer heterogeneities, pressure drop, etc. Scaled model experiments can also be used to calibrate numerical models as the relative influence of many of the mechanisms is similar to that expected in the field. The objectives of this work were to select and apply suitable scaling techniques for this process and study the conditions that govern this decontamination process (e.g. effect of interfacial tension, surfactant concentration, etc.).

2. Scaling of in situ surfactant injection

In ground water hydrology, scaled physical models are new and not yet properly tested. While ground water hydrologists continue to use numerical simulation of decontamination processes, scaled physical models have the unique advantage of capturing all physical phenomena occurring in a particular process. A recent review by Farouq Ali et al. [4] indicates that this advantage of scaling approaches puts physical modeling in a more desirable position than numerical simulation which provides results of an established mathematical description of the model.

The first step in modeling surfactant injection processes is the development of scaling parameters. The scaling parameters [5] are generally obtained by casting the governing equations of fluid flow and mass transfer in a dimensionless form. A set of similarity parameters are determined by inspectional analysis. These similarity parameters are combined, or modified based on engineering judgement, to obtain a set of scaling parameters which can generally be matched between a scaled model and the field proto-type. Lozada and Farouq Ali [6] presented six sets of scaling approaches. They also presented the complete set of scaling criteria and realized that all scaling criteria could not be satisfied simultaneously. Therefore, some of the similarity groups had to be relaxed in order to satisfy most scaling requirements involving the important parameters of a specific process. Types of rock/fluid systems, model geometry, pressure drop, flow rate, etc. were different depending on the approaches used.

For the present study, Approach 4, as presented by Lozada and Farouq Ali [6], was chosen. This approach scales more accurately, situations where geometry, viscous forces, and the ratio of the gravitational forces to viscous forces are important. This scaling approach has been found to be appropriate by several researchers [7–9] for

Table 1
Scaling groups satisfied in the present study

$$\frac{\phi_R S_{cR} \mu_{cR}}{t_R K_{cR} p_{cR}} \frac{L^2}{}, \frac{H}{L}, \frac{W}{L}, \frac{\rho_{cR} g_R z_R}{p_{cR}}, \frac{\rho_{gR}}{\rho_{cR}}, \frac{\rho_{sR}}{\rho_{cR}}, \frac{\mu_{cR} K_{gR}}{\mu_{gR} K_{cR}}, \phi_R, S_{cR}, \frac{S_{ci}}{S_{oR}}, \frac{S_{sR}}{S_{cR}}, \frac{S_{gR}}{S_{cR}}, \frac{p_{ci}}{p_{cR}},$$

$$\frac{W_{gR} \mu_{gR}}{L \rho_{gR} K_{gR} p_g{}^R}, \frac{W_c \rho_g}{W_g \rho_w}, \frac{A_{inj}}{LH}, \frac{h_{lR}}{h_{aR}}, \frac{T_{lR}}{T_{aR}}, \frac{\rho_{rR} h_{rR}}{\rho_{wR} h_{wR} w_R}, \frac{h_{gR}}{h_{aR}},$$

Table 2
Laboratory and field parameters

| Parameters	Laboratory model	Field
Contaminated sand thickness	0.6 in	5 ft
Porosity	34%	34%
Permeability	0.14–2 darcy	0.14–2 darcy
Length	3 ft	300 ft
Width	1 ft	100 ft
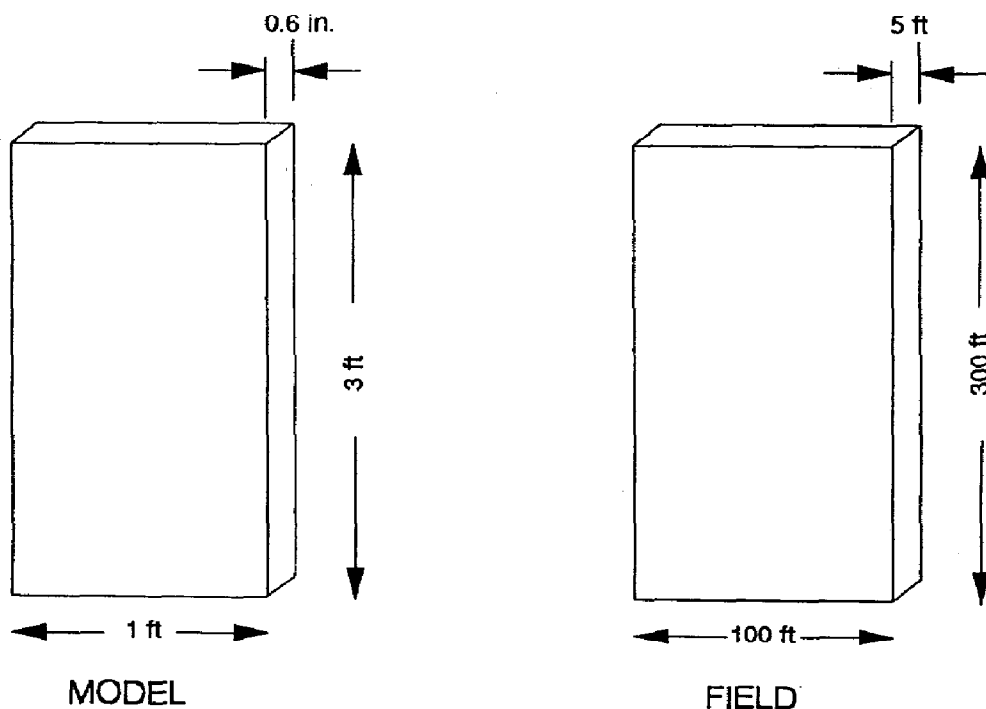
Scaling Factor, a=100
Field Flow Rate = Laboratory Flow Rate x 100^2
Field Pressure Drop = Laboratory Pressure Drop x 100
Field Permeability = Laboratory Permeability

Fig. 1. Schematic of the model and the prototype.

scaled physical modeling of surfactant injection in porous media when above-mentioned properties are considered important. This approach uses the same porous media in the model as in the field. However, the pressure drop in the field is scaled down by a factor of a, where a is the scaling factor. The influence of various variables such as porosity, permeability is satisfied in this approach. This approach can model the average pressure of the porous media and average properties [10], even though pressure-dependent terms are not satisfied. However, pressure itself is not important in this process, considering that the actual pressure is usually small in the field. Effects of fluid properties and capillarity are not satisfied in this approach. Scaling groups satisfied in this approach are shown in Table 1. Scaled and field parameters are listed in Table 2. Fig. 1 shows the schematic of model and field dimensions. This figure also indicates how other parameters are scaled.

3. Experimental apparatus

The experimental apparatus consists of a sand pack holder in the shape of a rectangular box of 90.5 cm × 30.48 cm × 0.635 cm dimensions. This apparatus, made of two Plexiglas plates, was held together by an aluminum frame. A series of holes in the aluminum frame allowed one to insert threaded bolts which were used to tighten the frame until a seal was reached against an o'ring which runs around the sand pack. The injection well consisted of a steel tube connected to a T-joint with a pressure gauge and micro-processor controlled pumpdrive (Masterflex, model 7518-50) for the surfactant solution injection. The recovery well was placed 83.5 cm away from the injection well. This well was also equipped with a pressure gauge and was used to let the fluid out through the bottom section of the model. Fig. 2 shows the schematic of the experimental set-up.
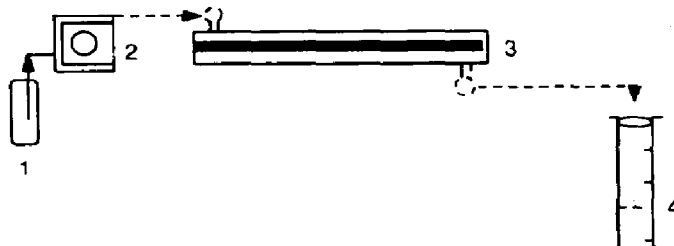
1. SURFACTANT SOLUTION FLASK
2. INJECTION PUMP
3. CROSS SECTION OF EXPERIMENTAL CELL
4. CONTAMINANT AND SURFACTANT FRACTIONS
   COLLECTION FLASK

Fig. 2. Schematic of the experimental setup.

4. Materials

The materials used for conducting different tests are listed below:

(a) *Porous media*: 80–110 mesh fine silica sands (Unimin Co.) were used for most of the experimental runs. In order to investigate the effect of the composition of soils and the presence of clay, several runs were conducted with a mixture of 80–110 mesh, sand and clay (at 15% concentration).

(b) *Oil phase and contaminant*: Kerosene (NAPA Co.) and motor oil (Chevron 10W40) were used as contaminants. Kerosene had a dynamic viscosity of 0.73 mPa s, as measured with a Baroid electronic viscometer, and a density of 0.809 g/ml. The motor oil was an engine oil with a viscosity of 1.24 mPa s and density of 1.6 g/ml.

(c) *Surfactant*: A Chevron Chaser XP-100 anionic alkyl aromatic sulfonate surfactant was used in surfactant cleaning tests. XP-100 is thermally stable. Sundaram and Islam [11] conducted several laboratory experiments to determine biodegradability of XP-100 surfactant in the presence of petroleum contaminants. Their study indicated that XP-100 surfactant in aqueous solutions with concentration ranging from 1% to 5% biodegraded completely in 14 days. They also found that the presence of petroleum contaminants enhanced dispersions of contaminant/surfactant complexes and resulting in increased solubilization rate for petroleum contaminants.

5. Experimental procedure

The selected contaminant (kerosene or motor oil) was injected through the injection well. The silica sand was packed under dry conditions for all experimental runs. The contaminant saturation in the saturated zone was established by injecting petroleum contaminants into a water-saturated packed model, then displacing the contaminant by water flooding. The vadose zone was modeled by initially water saturating the de-aired sand packed model, followed by contaminant injection. For this case, the contaminant injection was followed until first drop of contaminant was produced. Finally, the contaminant was allowed to drain through the recovery well with gravity drainage while allowing air through the injection well. This process was continued for 24 h in order to have a simulated stable vadose zone. The porous medium was replaced with fresh ones after every run was completed. Surfactant concentrations of 1%, 2%, 3%, 4%, and 5% were used in aqueous solutions for various experimental runs. The injection rate was 3 ml per minute for all the runs and 1.6 to 2.2 pore volumes of surfactant solution was injected during experimental runs. This rate corresponds to a field rate of 10 to 12 cubic meters/per day.

6. Results and discussion

Fourteen experimental runs were conducted in this study. The characteristics and results of different runs are summarized in Table 3. Initially, base vadose and saturated zone water injection runs were conducted in order to be able to compare

performance of different experimental runs. Kerosene and motor oil were the two contaminants used throughout the study. Note that final recoveries are defined to be those which are recovered after 500 min laboratory time or 32 days of field time.

6.1. Effect of surfactant concentration

The importance of surfactant concentration can be deduced from different surfactant runs with differing concentrations. The major cost component for in situ surfactant

Table 3
Summary of different experimental runs

Run no.	Aquifer zone	Contaminant	Nature of soils	Cleaning process	Stabilized pressure (psi)	Initial concentration (% PV)	Cumulative removal (% initial volume)
1	Vadose	Kerosene	Sands	Cold water	0.3	47.8	30.3
1a	Saturated	Kerosene	Sands	Cold water	0.4	100	39.0
2	Vadose	Kerosene	Sands	Surfactant solution, 1%	—	43.7	50.3
3	Vadose	Kerosene	Sands	Surfactant solution, 2%	—	49.0	61.7
4	Vadose	Kerosene	Sands	Surfactant solution, 3%	—	47.2	85.2
5	Vadose	Kerosene	Sands	Surfactant solution, 4%	0.34	47.0	93.5
6	Vadose	Kerosene	Sands	Surfactant solution, 5%	0.45	57.0	86.6
7	Vadose	Motor oil	Sands	Surfactant solution, 1%	0.52	54.3	41.0
8	Vadose	Motor oil	Sands	Surfactant solution, 2%	0.50	58.6	56.0
9	Vadose	Motor oil	Sands	Surfactant solution, 3%	0.50	52.0	69.0
10	Vadose	Motor oil	Sands	Surfactant solution, 4%	0.49	56.0	83.0
11	Vadose	Motor oil	Sands	Surfactant solution, 5%	0.51	53.0	84.4
12	Saturated	Motor oil	Sands	Surfactant solution, 4%	0.42	100	86.8
13	Saturated	Motor oil	Sands	Surfactant solution, 5%	0.53	100	89.0
14	Vadose	Kerosene	Sands + 15% clay	Surfactant solution, 4%	0.51	53.2	85.0
15	Saturated	Kerosene	Sands + 15% clay	Surfactant solution, 5%	0.40	100	86.2
16	Vadose	Motor oil	Sands + 15% clay	Surfactant solution, 4%	0.55	56.5	76.8
17	Saturated	Motor oil	Sands + 15% clay	Surfactant solution, 5%	0.50	100	79.0

cleaning of contaminated soils and ground water systems is expected to be for the surfactant. Consequently, an optimum surfactant concentration that gives the highest recovery and uses less surfactant is desirable. The contaminant recovery graph for 4% surfactant concentration used for cleaning of kerosene is shown in Fig. 3. The 4% surfactant concentration gives the best performance in recovering kerosene. The existence of an optimum is further clarified in Fig. 4 which plots recoveries for different runs. A sharp increase in recovery is observed when the concentration is increased from 1% to 5% with a step of 1%. This trend is suddenly changed when the concentration is increased from 4% to 5%. A 5% surfactant concentration yields lower recovery than a 3% concentration. One interesting feature is that the 5% surfactant concentration recovers more oil during the early stages of the clean-up process. When a high-concentration surfactant front comes in contact with the residual oil, the actual interfacial tension between surfactant front and residual oil might have been altered due to the presence of air in the system (vadose zone). The presence of trapped air in pore spaces changes surfactant/oil interfacial tension relationship into surfactant/oil/air relationship. This might have led to high contaminant recovery during the early stages of the clean-up process. As more air is displaced during later stages of the surfactant injection and the removal rate declines, the frontal interfacial tension changes and the oil removal rate declines.
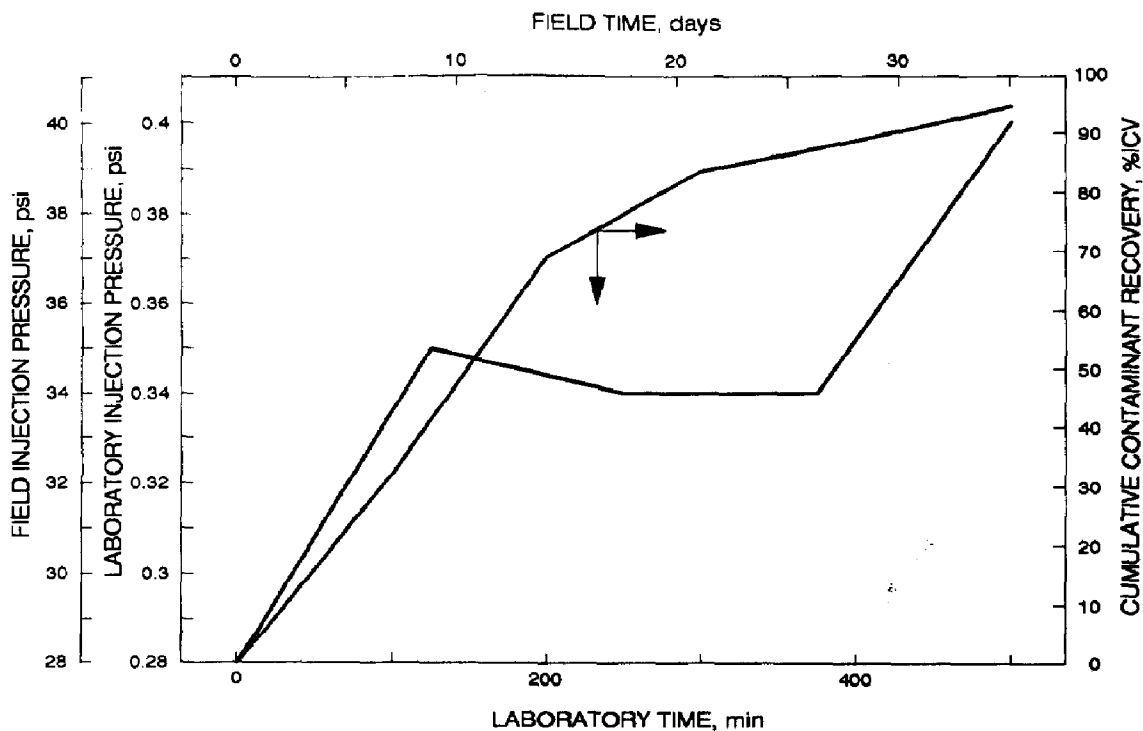

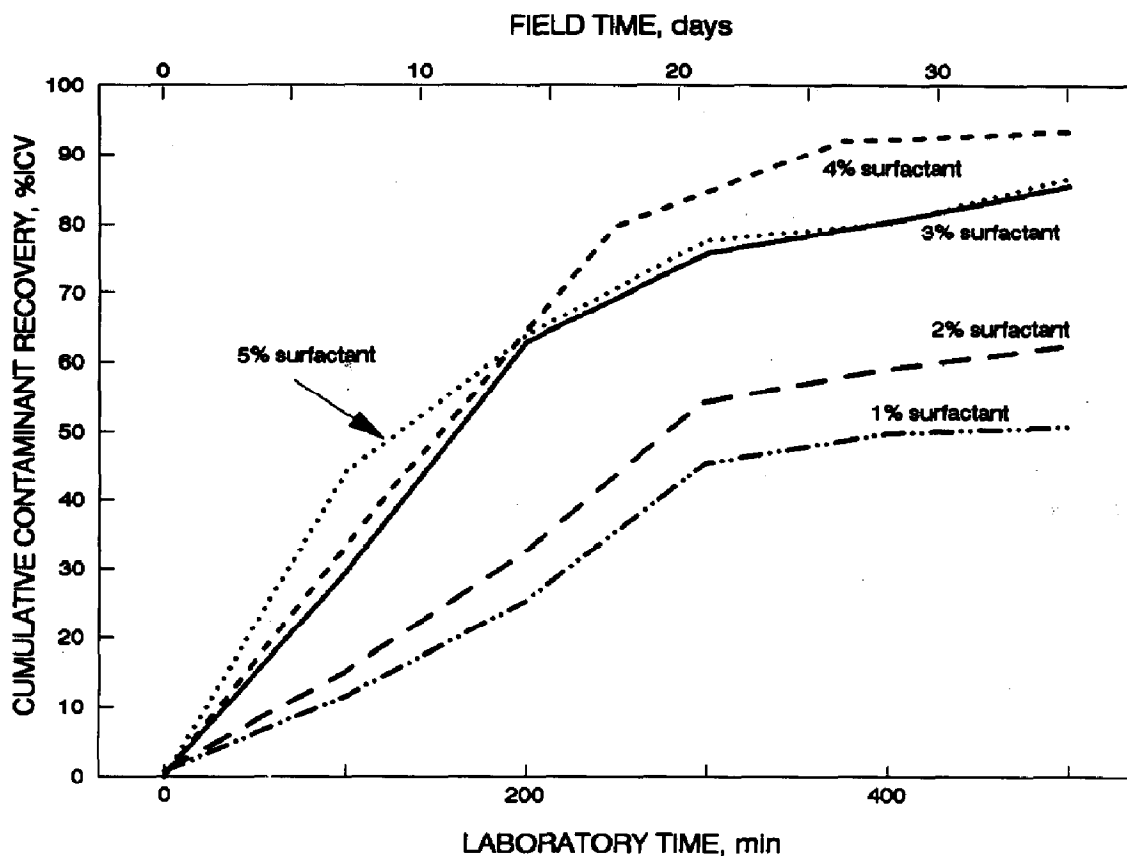Fig. 3. Contaminant removal performance with 4% surfactant solution.

FIELD TIME, days

Fig. 4. Effect of surfactant concentration on kerosene runs (2–6).

The optimum concentration, as observed for kerosene runs, does not hold for the motor oil. The motor oil, which is denser and more viscous than kerosene, shows (Fig. 5) a linear increase in contaminant recovery for the surfactant concentration range of 1–4%. Even though a 5% concentration does not show as much improvement, the recovery does not decline below that of 3% or 4% as evidenced before with kerosene, indicating that an optimum was not reached. Determination of optimum concentration is important not only from economical point of view but also from mechanistic point of view. Operating under non-optimum concentration may foil an otherwise effective process. The economic aspect is evident from considering the amount of contaminant recovered for a given amount of surfactant. The 5% concentration appears to be much more effective when this aspect is considered.

6.2. Effect of contaminant and soil type on surfactant cleaning

Two different types of contaminants were used in this study. One of them, the motor oil, was significantly more viscous and denser than the other contaminant, kerosene.
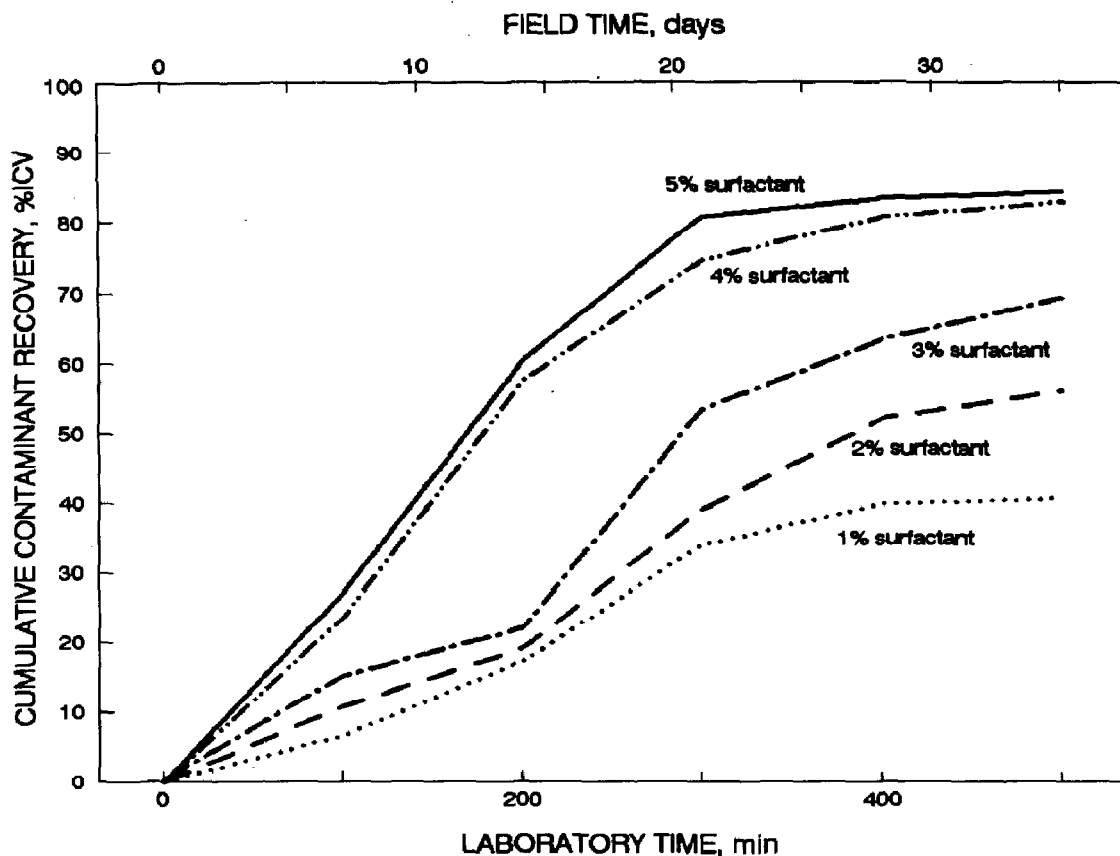
Fig. 5. Effect of surfactant concentration on motor oil runs (runs 7–11).

A 4% surfactant concentration yielded maximum recovery for kerosene in Run 5. This run is compared with corresponding motor oil run (Run 10) for which a concentration of 4% was used as well. Contaminant recovery is consistently higher for the kerosene recovery run. A high-viscosity contaminant is likely to be less effective candidate for surfactant cleaning.

A series of experimental runs was conducted by adding 15% clay to sands. This reduced the permeability of the sand significantly, but added an additional adsorption site for the surfactant. Figures 6 and 7 compare recovery curves for different soil types as applied to kerosene and motor oil, respectively. Song and Islam [12] conducted experimental adsorption studies using the same surfactant, porous media and physical model. They found that high adsorption of surfactant would lead to a lower level of available surfactant for the cleaning front. This might, in turn, require a different optimum concentration for clayey sands. Besides being less permeable, the clayey sand is also highly adsorptive to surfactant. Figs. 6 and 7 indicate that the low permeability affects adversely the clean up of viscous contaminants. From the permeability and pore throat size considerations only, low permeability should decrease recovery.
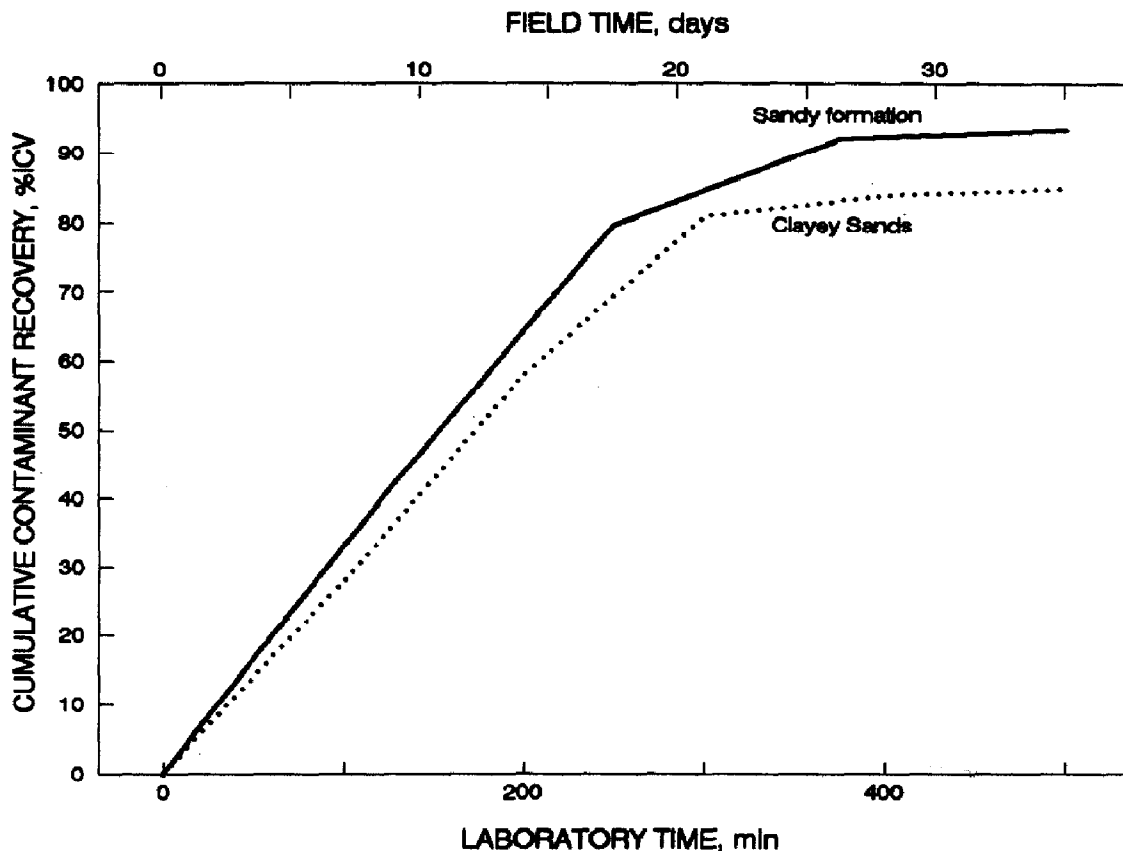
FIELD TIME, days

Fig. 6. Effect of soil type on surfactant cleaning (kerosene).

6.3. Interfacial tension studies

As pointed out earlier, cumulative recovery of contaminants using surfactants depends on many factors, such as, interfacial tension (IFT) between contaminant and surfactant solution. Interfacial tension between petroleum hydrocarbons and surfactants were measured using the Spinning drop tensiometer. When it was not possible to obtain a spinning drop reading for samples due to high interfacial tension, IFTs were measured by a Ring tensiometer. The spinning drop device has been widely used in recent years to measure low interfacial tensions in liquid–liquid systems. Table 4 shows interfacial tension measurements for different concentrations of surfactant solution with kerosene and motor oil. The interfacial tension is the lowest for 3% surfactant solution (Fig. 8) with kerosene as contaminant. The optimum behavior at 4% surfactant concentration did not correspond to a minimum in interfacial tension as shown in Table 4, for kerosene as contaminant. Adsorption studies [13] have indicated that in order to maintain a certain concentration in the core, it is necessary to inject surfactant at a higher concentration. This will explain why recovery was not the highest when surfactant concentration corresponds to the lowest interfacial tension measurement. The optimum concentration as observed for kerosene runs,
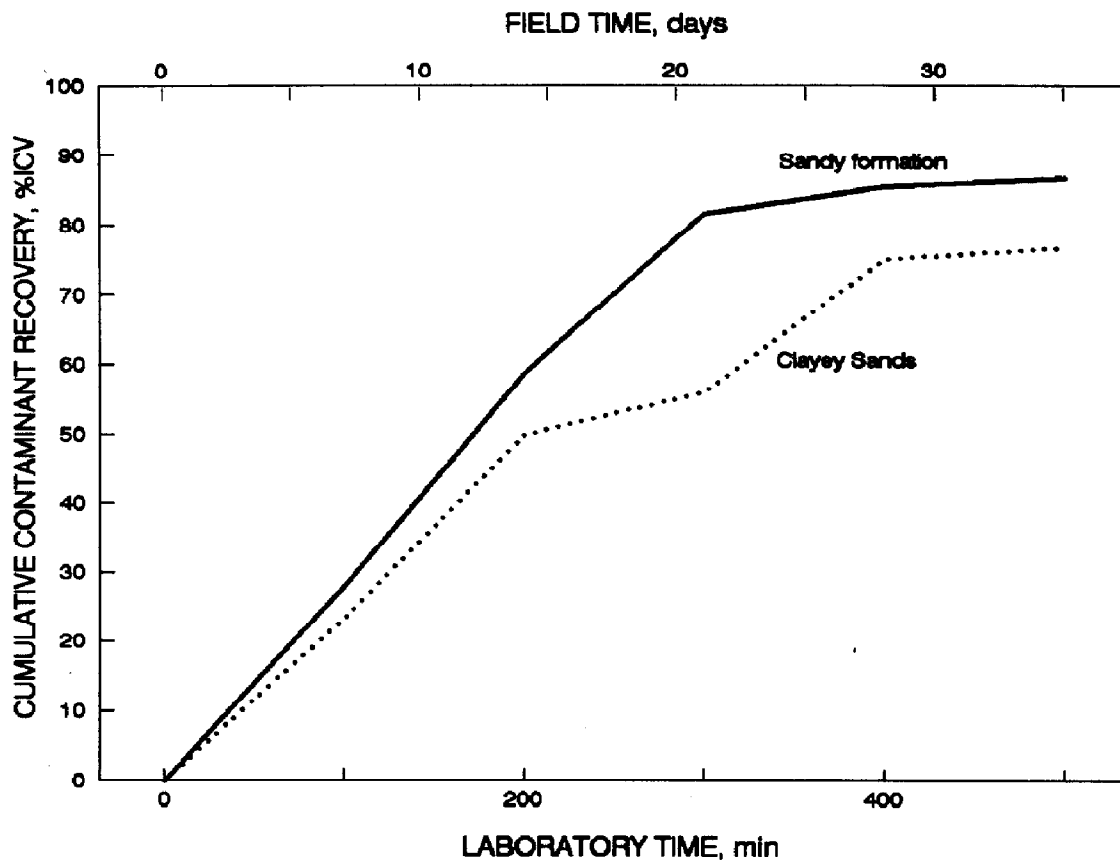
FIELD TIME, days

Fig. 7. Effect of formation type on surfactant cleaning (motor oil).

Table 4
Summary of interfacial tension (IFT) measurements

Surfactant (%)	Hydrocarbon	D1 (g/ccm)	D2 (g/ccm)	Reading	IFT (dyn/sq .cm)	Remarks
1.0	Kerosene	1.0739	0.8767	2.9	2.51	SD
2.0	Kerosene	1.0743	0.8767	2.8	2.42	SD
3.0	Kerosene	1.0751	0.8767	2.0	1.72	SD
4.0	Kerosene	1.0757	0.8767	3.9	3.41	SD
5.0	Kerosene	1.0757	0.8767	4.2	3.68	SD
0.0	Water	1.0732	0.9359	–	14.5[a]	RT
1.0	Motor oil	1.0739	0.9359	–	3.9[a]	RT
3.0	Motor oil	1.0751	0.9359	–	2.2[a]	RT
5.0	Motor oil	1.0757	0.9359	4.8	4.28	SD
6.0	Motor oil	1.0749	0.9359	4.2	3.72	SD
7.0	Motor oil	1.0757	0.9359	2.2	1.91	SD

SD: Measured by spinning drop tensiometer.
RT: Measured by ring tensiometer.
[a] Interfacial tensions obtained by the ring tensiometer do not carry our full confidence, as the apparatus was not used for a long time.
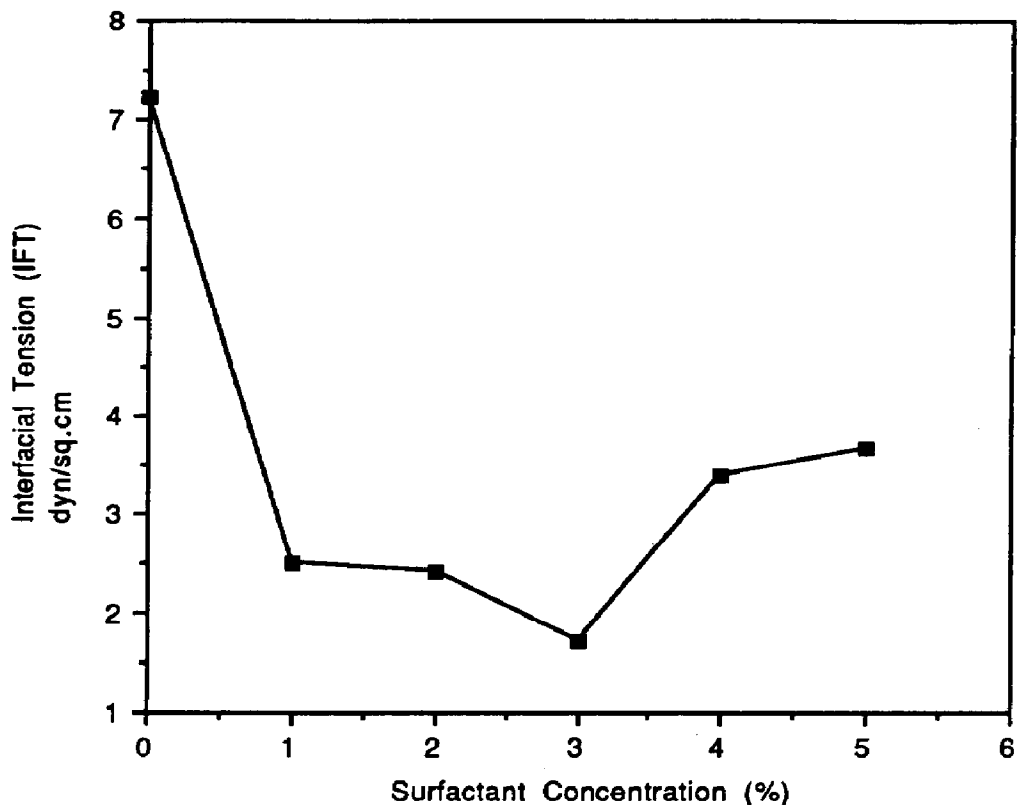
Fig. 8. Interfacial tension versus surfactant concentration for kerosene runs.

does not hold for the motor oil. The motor oil which is denser and more viscous than kerosene, has also higher interfacial tension (Fig. 9) with surfactant solutions. The IFT continues to decline with increasing surfactant concentration in the presence of motor oil.

7. Conclusions

Based on the experimental results presented herein, the following conclusions may be drawn:

(1) Surfactant cleaning of a number of organic contaminants, such as, kerosene, motor oil can be performed effectively in a relatively short-time period, for a scaled physical model.

(2) An optimum surfactant concentration is identified for one of the contaminants used. Such investigation is recommended for each clean-up operation.

(3) The effect of interfacial tension on contaminant recovery was investigated through a series of experimental runs. Recovery of contaminant was achieved by gradual reduction in interfacial tension.
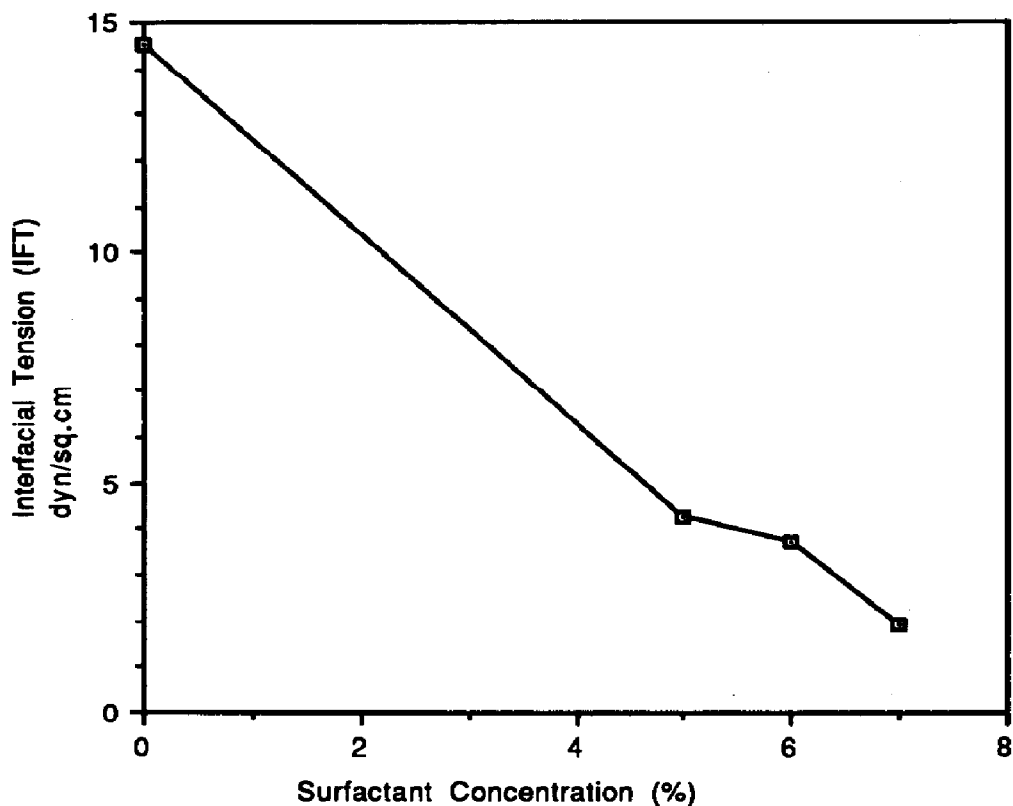
Fig. 9. Interfacial tension versus surfactant concentration for motor oil runs.

Acknowledgements

Nomenclature

A_{inj}	area open for flow through wells
a	scaling factor
b	thickness of the porous medium
c	contaminant
g	gas or steam phase
H	thickness of the model or field
h	enthalpy
ICV	intial contaminant volume
K_{cR}	relative permeability of contaminant phase
K_{gR}	relative permeability of gas phase
L	length
M	mobility ratio

N_c	capillary number
S_c	saturation of the contaminant phase
T_i	temperature of phase i
t	time
v	velocity
W	width of the model
W_c	mass production rate of contaminant
W_g	mass injection rate of cleaning agent
z	thickness of the contaminated zone
ϕ	porosity
ρ	density
μ	viscosity
σ	interfacial tension

Subscripts

g	gas or steam phase
c	contaminant
R	reference quantity
s	surfactant or water phase
w	water phase

References

[1] American Petroleum Institute, Underground movement of gasoline on ground water and enhanced recovery by surfactants, API Report No. 4317, 1979.

[2] American Petroleum Institute, Test results of surfactant enhanced gasoline recovery in a large scale model aquifer, API Report No. 4390, 1985.

[3] J. Nash and J.P. Traver, Field evaluation of in-situ washing of contaminated soils with water/surfactants, Proc. 12th Ann. Research Symp., EPA/600/9-86/022, 1986.

[4] S.M. Farouq Ali, D.A. Redford and M.R. Islam, Scaling criteria for enhanced oil recovery experiments, Paper No. 9, In: Proc. China–Canada Heavy Oil Conference, China, 1987.

[5] R.L. Nielsen and M.R. Tek, Evaluation of scale-up laws for two-phase flow through porous media, Soc. Petrol. Eng. J. (1963) 164–176.

[6] L. Lozada and S.M. Farouq Ali, Experimental design for non-equilibrium immiscible carbon dioxide flood, Proc. 4th UNITRA/UNDP Int. Conf. Heavy Crude and Tar Sands, 4 (1988) 275–296.

[7] M.R. Islam and S.M. Farouq Ali, New scaling criteria for chemical flooding experiments, J. Can. Petrol. Tech., 29(1) (1990) 29–36.

[8] A. Bansal and M.R. Islam, Scaled model studies of heavy oil recovery from an Alaskan reservoir using gravity-assisted gas injection, J. Can. Petrol. Tech. (1994), in press.

[9] M.R. Islam, A. Chakma and K.N. Jha, Heavy oil recovery by inert gas injection with horizontal wells, J. Petrol. Sci. Eng. (1994), in press.

[10] G. Rojas, and S.M. Farouq Ali, Scaled model studies of carbon dioxide/brine injection strategies for heavy oil recovery from thin reservoirs, J. Can. Petrol. Tech. (1986) 85–94.

[11] N.S. Sundaram and M.R. Islam, Surfactant injection followed by steam injection, a novel technique for in situ remediation of petroleum contaminants from soils, J. Contaminant Hydrology, in press.

[12] F. Song and M.R. Islam, Effect of salinity and rock type on sorption behavior of surfactants as applied in cleaning of petroleum contaminants, J. Petrol. Sci. Eng. (1994), in press.

[13] N.S. Sundaram, M. Sarwar, S.S. Bang and M.R. Islam, Biodegradation of anionic surfactants in the presence of petroleum contaminants, Proc. 3rd Int. Ground Water Symp., Environment Canada, Quebec, Canada, 1993.