Reduction of hydraulic conductivity during the treatment of hydrocarbon polluted soils by using surfactants may be an inconvenience for a good recovery of the pollutant. The purpose of the present research work is to determine the main factor responsible for this reduction and by the same way to give an application solution to this problem. Experimental studies on sand filled laboratory columns have shown that the reduction of hydraulic conductivity can be due neither to the precipitation of the anionic surfactants in the presence of calcium ions nor to the clay minerals present in small proportion in the porous medium. We point out that this phenomenon is essentially due to the agglomeration of micelles and show that addition of 4 wt % of butyl alcohol under specific conditions contributes to improving both the injectability of the surfactant solution and the efficiency of the treatment. The optimized surfactant formulation, containing a mixture of two commercial surfactants and this cosolvent, palliates the reduction of hydraulic conductivity and decreases the interfacial tension by a factor of 100. As a consequence, after three pore volumes of injected surfactant solution, 85% of the trapped oil is removed compared to 11.4% obtained without cosolvent.

**Experimental Section**

**Set up.** Surfactant flow experiments were performed on columns $C_1$ (length $L = 150$ cm, inside diameter $D = 10$ cm) and $C_2$ ($L = 40$ cm, $D = 5$ cm), made of Plexiglas, filled with quartz sand and equipped with piezometric tubes to follow the evolution of hydraulic conductivity $K$ in the different parts of the column. The characteristics of the experimental set up are described in Figure 1. The chosen flow mode is downward. During the experiments, the difference between the water levels in the upstream and downstream tanks was maintained. Flow experiments were carried out at different water head differences ($\Delta h$) in order to study the influence of the hydraulic gradient $\Delta h/L$ on the flow behavior of the solution.

Applying Darcy’s law, the hydraulic conductivity of column zone (i) can be calculated as follows (see Figure 1)

$$K_i = \frac{Q L_i}{S (h_{i-1} - h_i)}$$

where $Q$ is the measured flow rate, $S$ is the cross section of the column, $h_{i-1}$ respectively $h_i$ is the measured piezometric head in section (i-1) respectively section (i), and $L_i$ is the length of the column zone considered. Using a hydraulic gradient of 0.2 corresponds in column $C_1$ to a stationary water flow rate of about 75 mL/min.
The volume of surfactant solution used in the flow experiments varied considerably depending on the applied hydraulic gradient: from 50 up to 300 pore volumes. The infiltration of surfactant solution at the entrance section of the column was stopped when the flow rate was lower than 5% of the initial water flux.

Sand. The porous medium is a uniform and slightly clayey quartz sand H2F (Table 1), which has a specific surface area of 0.5 m²/g and a cationic exchange capacity of 0.34 meq/100 g. Tables 1 and 2 summarize the chemical and physical properties of this medium.

In order to minimize trapped air in the sand columns, the sand was introduced in the set up initially filled with water. The bulk density of the porous medium was about 1.59 g/cm³. Afterwards the sand columns were flushed downward using deaerated water.

Contaminant. The chosen pollutant was a commercial diesel oil. This product contains a wide range of hydrocarbons (67.9% aliphatics and 32.1% aromatics) and, because it is used so widely, is representative of many cases of real-life pollution. Its properties are given in Table 3. A dye (organorub) was added in order to allow visual detection of the pollutant during the experiments. Soil samples are analyzed by infra-red spectrometry after extraction with carbon tetrachloride (CCl₄) for oil quantification.

The volume of surfactant solution used in the flow experiments varied considerably depending on the applied hydraulic gradient: from 50 up to 300 pore volumes. The infiltration of surfactant solution at the entrance section of the column was stopped when the flow rate was lower than 5% of the initial water flux.

**Results and Discussion**

**Study of the Surfactant Flow Behavior.** The plugging phenomenon (dramatic decrease of the hydraulic conductivity K) occurs in the upper zone of the column, while the remainder is spared (Figure 2). If the plugging were due to the precipitation of the anionic surfactants by calcium ions (20), we would have observed a decrease of K in all column zones. Referring to the results (Figure 2), it is possible that filtration of surfactants by fine particles takes place in the upstream part of the column and causes the plugging after injection of seven pore volumes (V = discharged volume; Vp = pore volume of the porous medium).

The role of fine particles is shown in Figure 3. The results of experiments using a porous matrix devoid of clay minerals were obtained by displacement of clay particles present in...
the medium (24). The plugging phenomenon is persistent in spite of the elimination of clay minerals. This proves that fine particles are not responsible for the flow rate decrease of the surfactant solution in the porous medium. Evidently, we have to consider the properties of the surfactant solution in this process. Furthermore, we notice that the first decrease in the flow ratio $Q/Q_0$ (1.0 to 0.8; $Q_0$ is the initial flow rate), observed in Figures 3–6, is due to the difference of viscosity between the water initially used for the saturation of the porous medium and the surfactant solution.

The effect of the applied hydraulic gradient on the surfactant infiltration was also studied. The results obtained are illustrated in Figure 4. The plugging took place whatever value of hydraulic gradient was applied in the experiments. The volume of infiltrated surfactant solution varies in the same way as the hydraulic gradient.

The results of all experiments show a significant decrease in the flow rate after 10 h, and flow essentially ceases at nearly 20 h (Figure 5). The fact that time plays a role in the decrease of the infiltration flow rate induced us to take into account the properties of the surfactant mixture.

This point of view was understood by studying the effect of varying the ripening time of the solution before its injection. Applying the same hydraulic gradient ($\Delta h/L = 0.2$), three experiments were realized as follows: a first test on surfactant injection was conducted with a freshly prepared solution, a second with a solution allowed to stand for 24 h, and a third experiment with a solution 52 h old. The results shown in Figure 6 underscore the characteristic variations of the surfactant solution behavior versus time, which means that the solution should not be allowed to stand for a long time before injection.

**Interpretations.** We have shown that the surfactant solution possesses some kind of instability. The experiment carried out with a high hydraulic gradient allows one to inject a considerable volume of surfactant but does not solve the problem of plugging, which is observed after 20 h of infiltration. Furthermore, a surfactant solution which stands for a long time before its utilization quickly plugs the porous medium.

The main factor responsible for the plugging phenomenon is due only to the properties of the surfactant solution used and is independent of interactions between the aqueous...
solution and the porous matrix (sorption, precipitation, etc.). The filtration of dispersed objects contained in the aqueous medium leads us to assume that the surfactant forms aggregates which, after a certain time, have a size sufficient to be retained at the surface of the porous matrix and cause its plugging. In our case, the surfactant solution concentration to be retained at the surface of the porous matrix and cause aggregates which, after a certain time, have a size sufficient to be injected in the porous medium, the new solution is more effective. The interfacial tension, measured by the spinning drop method, was shown to be reduced by a factor of 100, and the mass balance of the oil recovered from the injection of two pore volumes of surfactant solutions (Table 4).

The pollutant recovery experiments were performed in C2 columns filled with 4% oil-saturated sand using the two surfactant formulations Resol 30 and Resol+. The porous medium was first flooded with water, and then the surfactant solution was injected at a fixed hydraulic gradient (Δh/L = 0.2). The results show a significant difference between the recovery efficiency of the two solutions (Figure 9). In addition to its being well injected in the porous medium, the new solution is more effective. The interfacial tension, measured by the spinning drop method, was shown to be reduced by a factor of 100, and the mass balance of the oil recovered increases from 8% (for the formulation without alcohol (Resol 30)) to 78% (for the formulation with alcohol (Resol+)) after the injection of two pore volumes of surfactants (Table 4).

The influence of the two compounds (nonionic and anionic surfactants) has been studied in additional laboratory experiments. The results of tests 1–3 (Table 5) show clearly that the absence of one of the surfactants affects significantly the recovery of oil initially trapped at residual saturation (4%) in the porous matrix.

The quantity of alcohol to be used seems of great importance since its variation can also affect the oil recovery from the columns. Results given in Table 6 demonstrate that less than 4% (test 5) could be insufficient for disturbing liquid crystal formation. Test 6 confirms that more than 4% of alcohol is not useful; on the contrary, it can decrease the oil recovery.

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