Interfacial Mechanism of Soil Removal

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Abstract

A previously recognized interface-activated mechanism of soil removal appears to be related to the Marangoni effect. This mechanism, which may be the most powerful cleaning mechanism in a system, is due to surface motion created by local variations in the surface tension. The effects of several variables on this mechanism of soil removal were investigated and are discussed.

Introduction

IN STUDIES OF THE REMOVAL of homogeneous soils from hard surfaces, Bourne and Jennings (4) observed what they reported as a "time-independent" cleaning mechanism, as opposed to the classical "flow-mechanism," and which they suggested was due to the passage of the air-solution interface over the soiled surface. Because the forces most probably associated with this interfacial mechanism were those first described by Dupré, they termed this the Dupré mechanism.

Sternling and Scriven (8) studied the spontaneous agitation of the interface between two unequilibrated liquids, and explained this interfacial turbulence in terms of the coupled mass and momentum transport processes for both the bulk and surface phases. They related this to the Marangoni effect (2) in which movement of an interface is caused by spatial variations of interfacial tension.

This study was designed to determine whether the Marangoni effect could account for the Dupré mechanism, and to help explain the forces initiating and propagating this soil-removal mechanism. The results indicate that under the conditions studied, both the rate of dissolution at the soil-air-water boundary line (i.e., the "three phase boundary line") and the rate of transport from this boundary line by surface motion are distinct and important steps in this soil removal process.

Methods and Procedure

Test Strips

Test strips were of type 302 annealed 22 gauge stainless steel with 2_B finish, and measured 6.4 × 225 mm. They were cleaned by a rigorous procedure first suggested by Anderson et al. (1).

Soil

A solution containing 5 mg tristearin/ml was prepared by dissolving in CCl_4 equal weights of carboxyl-labeled C^{14} (Tracerlab, Inc.) and inactive (Eastman Kodak) tristearin. 0.2 ml. of this solution, containing 1 mg tristearin, was spread on one side of a cleaned test strip. The solvent was allowed to evaporate, and the strip baked 10 min in a hot air oven at 125C. While still hot, the surface was then wiped with the edge of a Teflon strip to even out, as far as possible, the deposited soil. This resulted in counts of 25,000 to 32,000/min (see below).

Evaluation of Soil Removal

Previous work has established that in these thin films of radiolabeled tristearin, absorption is not a problem and the radioactivity is a linear function of the amount of soil present (5,6). Counting was achieved by placing the test strip in a track driven at constant speed by a synchronous motor under a thin-window Geiger tube. The window area was decreased by a lead shield, with a 4 × 25 mm window aligned longitudinally with the test strip. Fourteen-minute counts were taken through the central area of the strip, excluding approximately 10 mm at each end, and (by virtue of the lead window) the extreme edges.

Interfacial Cleaning

The cleaning apparatus (Fig. 1) was designed to pass the test strip through the air-solution interface with minimum agitation and under closely controlled conditions. The entire assembly was mounted in a glass-doored constant temperature oven. The test strip was placed on edge in stainless steel wire supports silver-soldered to the stainless steel cradle. The tension of the nylon support yolk suspended over the glass rod eliminated cradle sway.

The cradle, suspended on the nylon support yoke, could be attached to different diameter spindles to control the speed of descent and ascent. With the yoke thread long enough that the immersed test strip would just clear the bottom of the test pan when fully extended the thread was wrapped around the appropriate spool several times, in the direction opposite

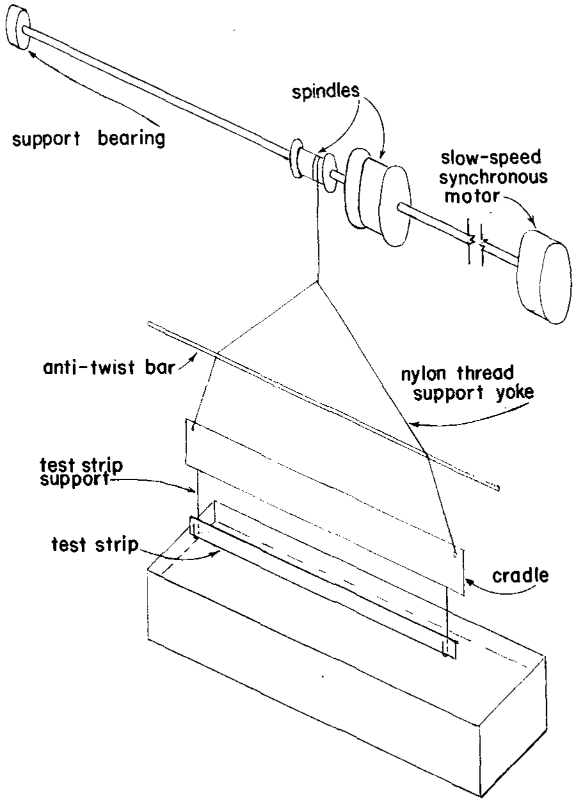

FIG. 1. Immersion apparatus designed for minimum flow generated turbulence.

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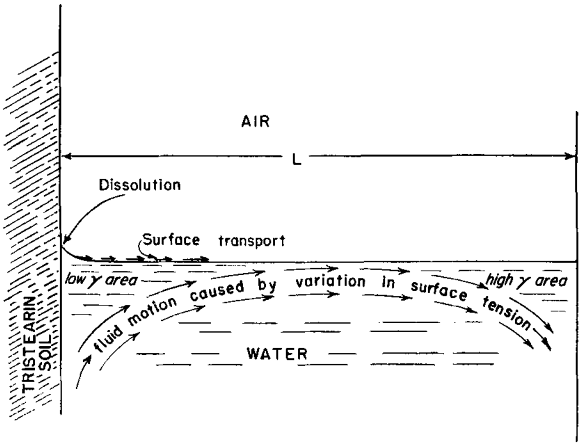

FIG. 2. Schematic representation of the interfacial cleaning mechanism.

to its normal rotation. The entire assembly was brought up to temperature, the test strip inserted in its supports, and the drive motor started. The unwinding thread lowered the test strip through the interface, reached its extremity with the test strip fully immersed but clear of the bottom, and rewound to withdraw the test strip at the same rate of speed. Stainless steel pans of different dimensions were used to attain variable depths of immersion in the water and variable surface areas of the water-air interface. Fresh double-distilled water maintained in a constant temperature water bath, was used as the cleaning medium. At first this water was changed after every third immersion, but when it became apparent that a convective surface mass transport phenomenon was occurring, the solution was changed after each immersion. Figures and data from the first procedure are not used in this report.

Mechanism of Soil Removal

It is believed that the soil removal mechanism studied is a two-step process. A kinetic step governs the dissolution of the soil at the soil-air-water boundary line and a surface removal step governs the transport of the removed soil. This process is illustrated in Figure 2. The dissolution process may be represented in terms of forward and reverse steps as

$$\begin{pmatrix}\text{net rate of}\\ \text{removal}\end{pmatrix} = \begin{pmatrix}\text{rate of}\\ \text{dissolution}\end{pmatrix} - \begin{pmatrix}\text{rate of}\\ \text{adsorption}\end{pmatrix} \quad [1]$$

Certainly these rates could be expressed in terms of the number of moles of soil adsorbed on the steel strip, m, and the concentration of the soil on the air-water interface, γ

$$\begin{pmatrix}\text{net rate of}\\ \text{dissolution}\end{pmatrix} = \frac{dm}{dt} = f\,(m) - g\,(\gamma) \quad [2]$$

Here the functions f and g are unknown, but their existence is assured. If the activity of the soil on the steel strip is a constant, the forward rate will also be a constant; however this is a special case with which we need not be concerned.

The rate of surface removal will also depend upon γ, but in quite a different manner. The variations in γ over the air-water surface give rise to variations in surface tension which in turn generate the fluid motion illustrated in Figure 2. Qualitatively this mechanism is described as follows: If the surface concentration of tristearin is high at the three phase boundary line, the surface tension will be low and a large tangential surface stress will exist. This gives rise to the fluid motion which transports the soil away from the triple boundary. The process is somewhat analogous to an engine which converts the configurational energy of the soil in its pure state into fluid motion which is subsequently dissipated to internal energy by viscous effects. As the air-water surface becomes saturated with soil the tangential surface stress disappears and the fluid motion ceases.

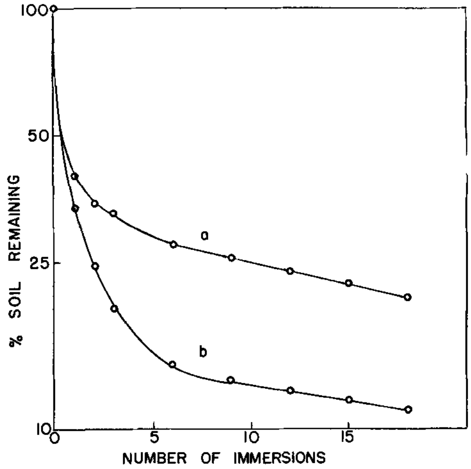

FIG. 3. Per cent soil remaining as a function of the number of immersions. 72C; *a*, 2.1 cm/min; *b*, 14.9 cm/min. Slopes of linear portions (K); *a*, 2.47×10^{-2} immersions^{-1}; *b*, 1.78×10^{-2} immersions^{-1}.

Results and Discussion

There are two extreme cases which might occur in an experimental study of soil removal. One represents a kinetically controlled rate of removal, and the other represents a surface saturation controlling mechanism. In the latter case the kinetics noted in Eq. 2 may be thought of as infinitely fast, and the amount of soil removed depends only on the saturation value of γ and the area of the air-water surface. Under such conditions the amount of soil removed per immersion would be a constant. Figure 3 shows that this is not the case, and that the amount of soil removed depends upon the speed of immersion.

If the rate of removal were kinetically controlled, Eq. 2 would reduce to

$$dn/dt = -f\,(n) \quad [3]$$

Even though the function f (n) is unknown, it is

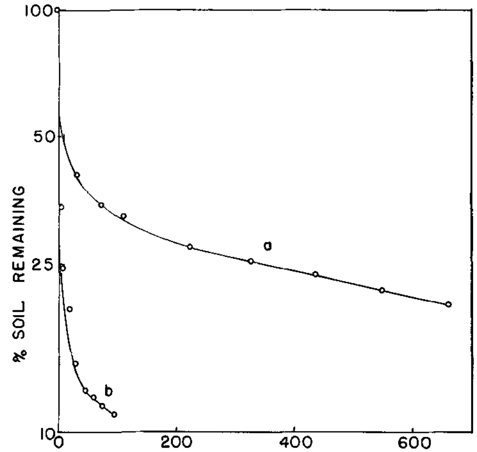

FIG. 4. Per cent soil remaining as a function of time. 72C; *a*, 2.1 cm/min; *b*, 14.9 cm/min. Slopes of linear portions (K'); *a*, 7.22×10^{-4} sec^{-1}; *b*, 3.75×10^{-3} sec^{-1}.

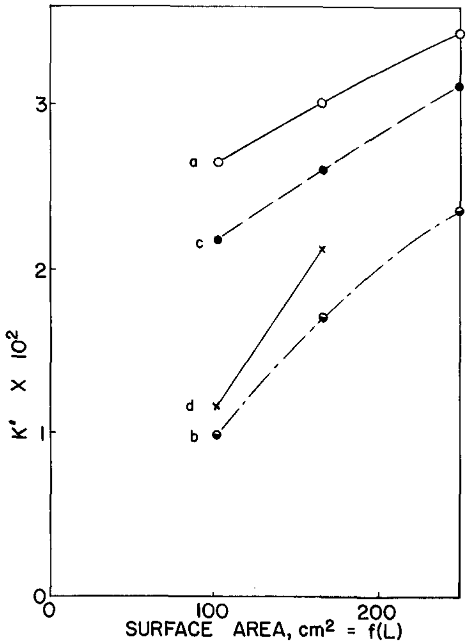

FIG. 5. Effect of surface area [A = f(L)] on rates of soil removal. *a*; 72C, 2.1 cm/min. *b*; 72C, 14.9 cm/min. *c*; 75C, 2.1 cm/min. *d*; 75C, 14.9 cm/min.

reasonable to assume that it can be integrated:

$$\int_{\zeta = n_o}^{\zeta = n} d\zeta/f(\zeta) = G\ (n, n_o) = \int_{o}^{t} d\zeta = t \qquad [4]$$

where ζ and δ are dummy variables of integration. While the function G (n, n_o) is unknown it must have an inverse, and Eq. 4 can be expressed as

$$n/n_o = G'\ (t) \qquad [5]$$

indicating that n is a unique function of time. Here we have presumed that a linear dependence on n_o exists.

Figure 4 shows the percent soil remaining as a function of time, and indicates that two different curves are obtained for the two different speeds of immersion. Thus n/n_o is not a unique function of time and it may be concluded that the removal process is not kinetically controlled. On the basis of these experiments it appears that both the kinetics of dissolution and the surface transport play a significant role in the soil removal process.

Because the percent soil remaining on the strip is an exponential function of the number of immersions in the latter stages of cleaning, the rate of removal of the soil may be conveniently expressed in terms of a first order rate constant, K, defined by

$$K = -\ln\ (Sn/100)/n \qquad [6]$$

where n represents the number of immersions, and Sn is the percent soil remaining after n immersions.

TABLE I

Effect of Surface Area on Rate Constants at Two Velocities

		K × 10²	
	Surface area, cm²	2.12 cm/min	14.9 cm/min
	102	2.09	0.77
	102	2.36	1.21
	102	1.77	1.05
	102	2.45	0.90
Ave.	102	2.17	0.98
	166	2.74	1.74
	166	3.00	1.78
	166	2.47	2.09
	166	2.17	1.38
Ave.	166	2.56	1.75
	250	2.63	2.45
	250	3.09	2.56
	250	3.12	2.04
	250	2.78	2.36
Ave.	250	2.91	2.35

Conditions: Strips lowered 5 cm below surface and withdrawn at the indicated velocities. Solution temperature 72 ± 2C.

The values of K are listed in Table I. In addition to indicating that K depends upon the speed of the immersion, these results show that increased cleaning rates are obtained when the distance L (see Fig. 2 and 5) is increased. This is in accord with the contention that the Marangoni effect plays an important part in the removal process.

To prove that the removal process was primarily, if not entirely, a surface effect, the depth was varied 2½ fold while keeping all other factors constant. This provided a longer contact time between the soil and the bulk phase. No changes in the rate of removal were observed, indicating that tristearin is essentially insoluble in the bulk phase. The soil, insoluble in the bulk phase and nonvolatile must be removed, therefore, by the air-water interface, and most probably by the Marangoni effect. The spreading of oils on water by the Marangoni effect has been characterized previously by Bikerman (3).

Sternling and Scriven (8) established that interfacial transport was inhibited by the presence of surface active materials. Bourne and Jennings (7) reported that the interfacial mechanism of cleaning shows a decrease in effect with decreased surface tension.

Finally, an attempt was made to observe the dissolution of the tristearin onto the air-water interface. Powdered carbon was dusted onto the air-water interface and a soiled and unsoiled stainless steel strip lowered through it. The unsoiled strip failed to disturb the carbon on the surface, whereas the soiled strip dispersed the carbon with explosive violence.

ACKNOWLEDGMENT

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