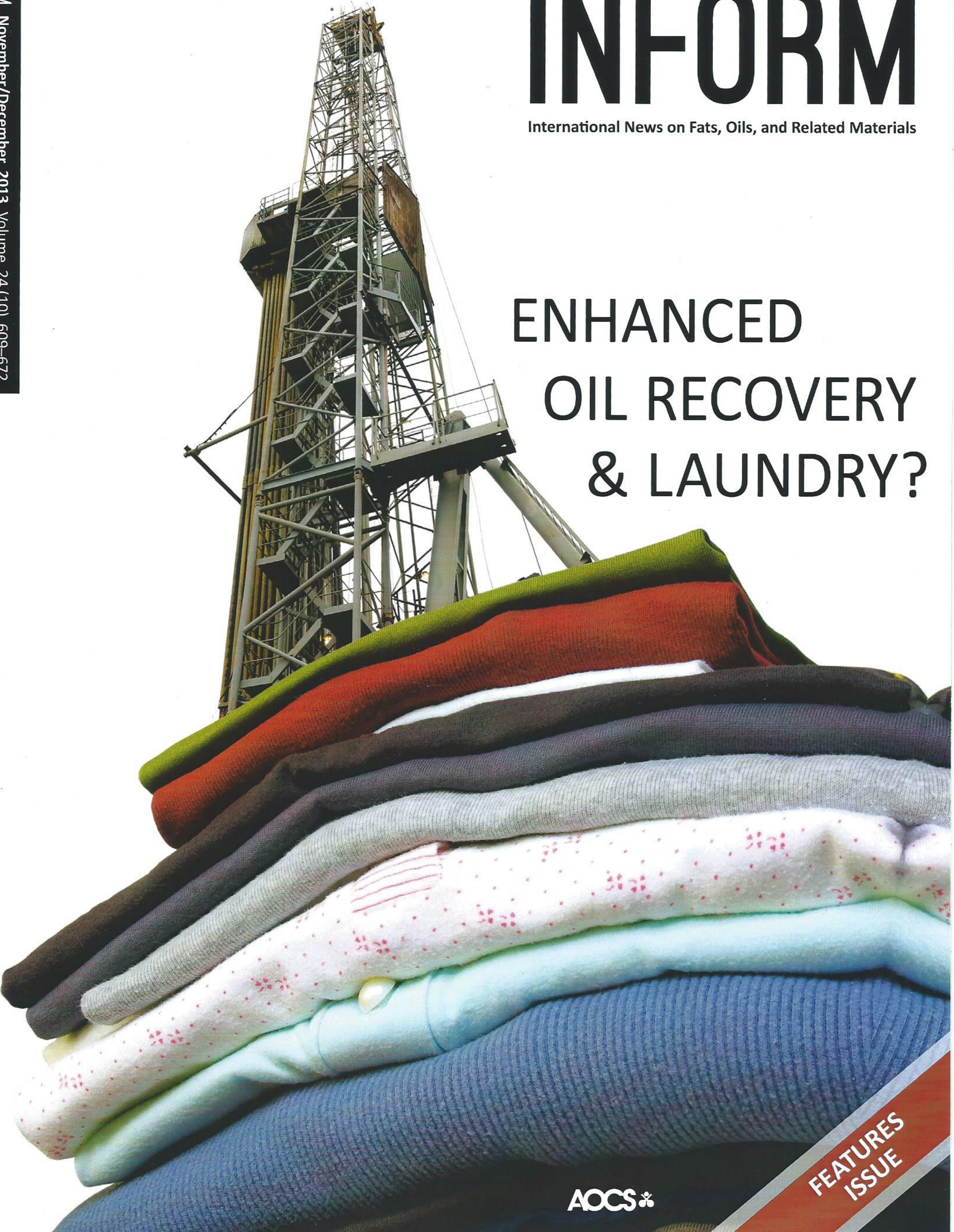
INFORM November/December 2013 Volume 24 (10) 609–672

INFORM

International News on Fats, Oils, and Related Materials



ENHANCED OIL RECOVERY & LAUNDRY?

FEATURES ISSUE

AOCS

ENHANCED OIL RECOVERY & HOUSEHOLD LAUNDRY—

more alike than you might think

Kirk H. Raney

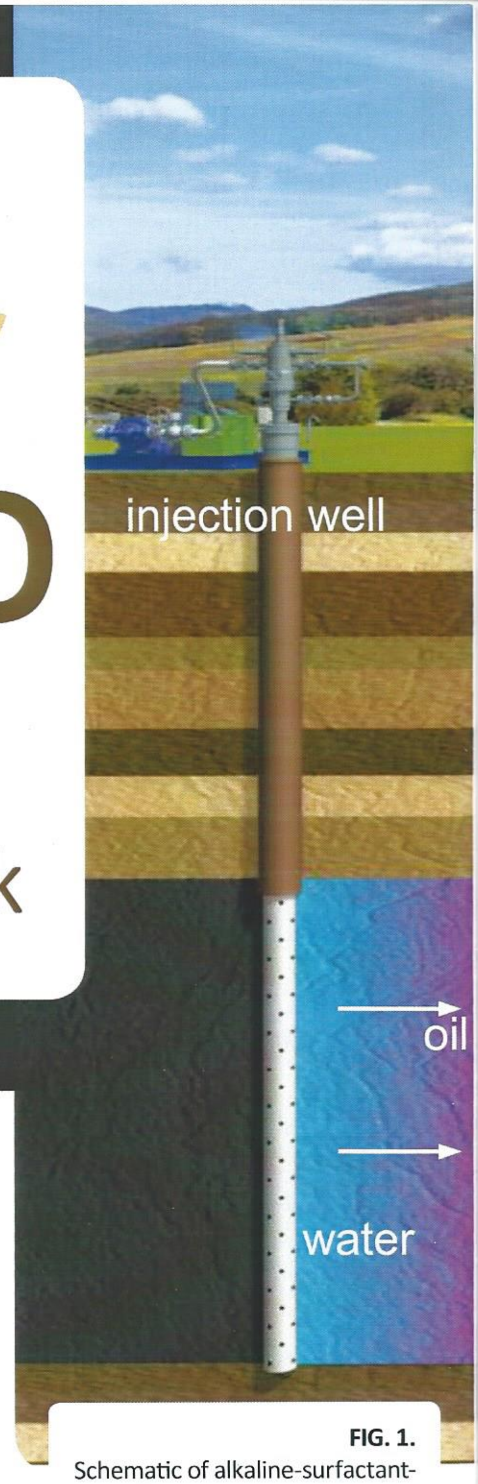
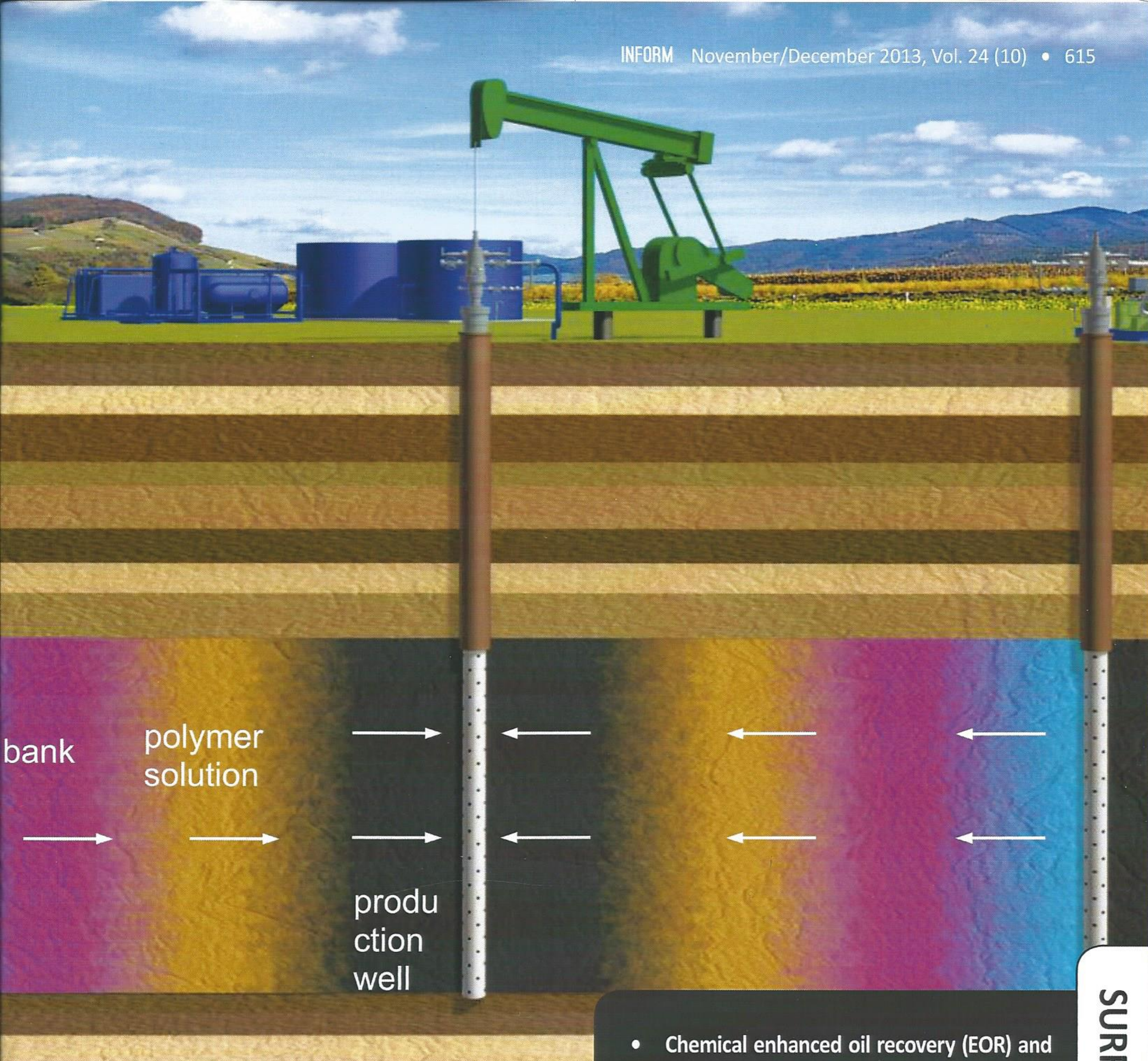


FIG. 1.
Schematic of alkaline-surfactant-polymer oil recovery process.

Over the course of my career, I have worked on a variety of applications of surfactants, for both consumer and industrial uses. I have spent considerable time studying household laundry and chemical enhanced oil recovery (EOR) surfactants. On the surface, these are two very dissimilar uses of surfactants. However, I have also noted some striking similarities between them. As one use (i.e., household laundering) will continue to be a huge market for surfactants and the other (EOR) has tremendous growth potential and hence could compete for surfactant supply, I will describe some of these similarities, as well as some subtle differences, in this article.

This cover story is based on a presentation by Kirk H. Raney, winner of the 2013 Samuel Rosen Memorial Award given by AOCS in recognition of significant advancement, cumulative advancements, or application of the principles of surfactant chemistry.

Of primary importance when comparing household laundering and EOR is to recognize that both are aqueous-based detergency processes for "cleaning" porous media. Professor Milton Rosen has defined detergency in the following manner: "The term detergency, when applied to a surface-active agent, means the special property it has of enhancing the cleaning power of a liquid" (Rosen and Kunjappu, 2012). In home laundry, surfactant solutions are used to clean porous fabric substrates whereas aqueous surfactant slugs are used in chemical EOR to remove crude oil from porous rock such as sandstone or limestone.



- Chemical enhanced oil recovery (EOR) and household laundering are detergency processes that differ greatly in scale but share many similarities in mechanisms and technical requirements.
- The implementation onset of surfactant-based EOR projects will cause significant growth in surfactant consumption with some overlap and competition with laundry markets.
- The oil industry can learn much from the detergent industry with regard to surfactant product formulations, chemical logistics, environmental requirements, and legislation.

WHY CHEMICAL EOR?

During production of crude oil, 60–70% of the oil remains in the reservoir rock due to capillary forces, after conventional primary pressure-driven processes. In fact, up to 300 billion barrels of trapped oil are estimated to exist in the United States at this time (Henthorne, Walsh, and Llano, 2013). Future energy supply scenarios show that crude oil will continue to be the major source of the world's energy requirements, particularly for transportation. A recent study predicts that crude oil will still provide about one-quarter of the global energy demand in 2050 (Kramer and Haigh, 2009). Therefore, recovery of this

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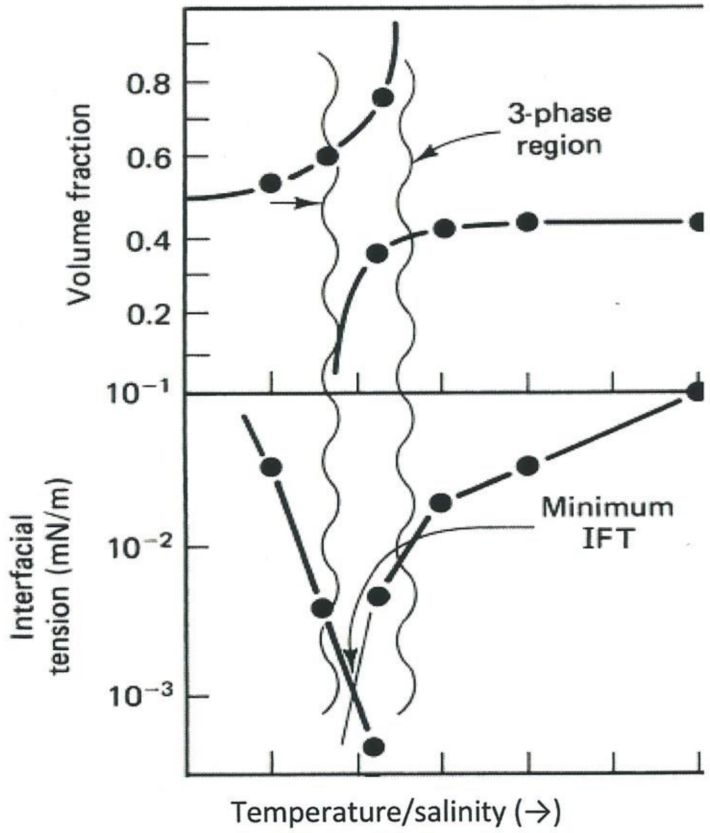

FIG. 2. Correlation of Winsor III phase behavior with ultralow oil-water interfacial tension (IFT) found at optimum salinity or the phase inversion temperature.

known trapped oil will be critical for several decades. Surfactant-based chemical EOR will be one way to recover some of this oil. Currently, there are about 40 surfactant-based EOR projects around the world, mostly at the pilot stage of production.

The alkaline-surfactant-polymer (ASP) EOR process works by pushing a slug of ASP "cocktail" through the reservoir rock, effectively "cleaning the rock" of valuable crude oil as it flows through it. The surfactant plays the key role of releasing the oil from the rock pores, while the alkalinity (in this case, sodium carbonate) protects the surfactant from water hardness ions, produces soap from the crude oil, and minimizes surfactant adsorption on the rock. The polymer, typically a hydrolyzed high-molecular-weight polyacrylamide, provides viscosity to the ASP slug to prevent fingering of the ASP solution through the oil and maintain plug flow and efficient oil displacement in the reservoir. Figure 1 (page 615) is a schematic diagram showing the flow of ASP fluids and the formation of an oil bank in the oil reservoir.

Due to the large pore volume of the reservoirs containing the trapped crude oil, a single chemical EOR application of 100,000 barrels injected/day would require about 100 million pounds (45,000 metric tons) of surfactant/year for several years. This amount of surfactant for one ASP flood is 2–3% of the approximately four billion pounds (1.8 million metric tons) of surfactants consumed annually for

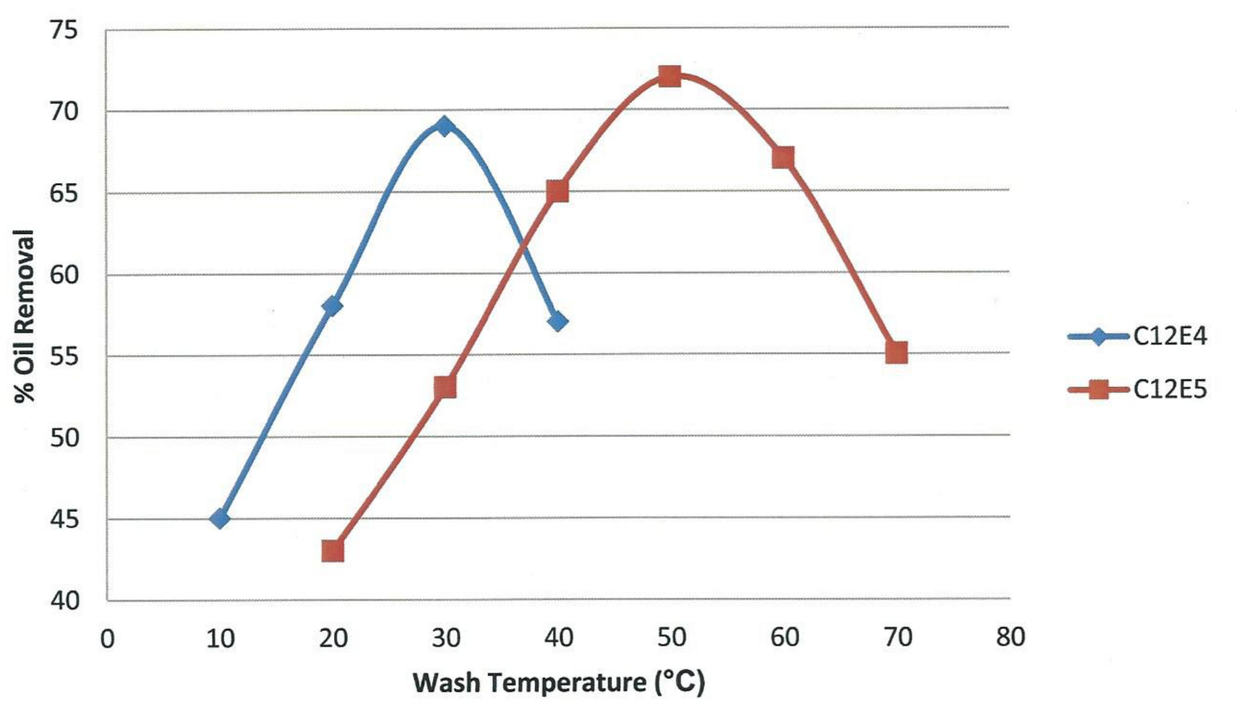

FIG. 3. Correlation of optimum nonpolar soil removal by specific alcohol ethoxylate surfactants from 65:35 polyester/cotton fabric with the oil-water-surfactant phase inversion temperature (PIT). Adapted from Miller and Raney (1993).

household laundering in the United States. In contrast to oil production, household laundering requires only a few grams of surfactant per washload, but billions of washloads are performed per year leading to the large overall surfactant consumption for this process.

MECHANISTIC COMPARISON

The removal of oil from a porous substrate by an aqueous medium can be related to the dimensionless capillary number, the ratio of viscous forces to the interfacial forces holding the oil in the pores:

$$N_c = \mu v/\gamma \qquad [1]$$

where N_c is capillary number, μ = viscosity of the flowing phase, v = velocity of flowing phase, and γ = interfacial tension between oil and water. As N_c increases, oil mobility increases. For chemical EOR, interfacial forces dominate as the flow rate through the rock is only about one foot (30 cm)/day. Therefore, ultralow interfacial tensions on the order of 10^{-3} dyne/cm are required to release significant quantities of the crude oil from the rock. Similarly, ultralow interfacial tensions are often present when oily soil detergency from fabric is optimized. However, the flow of washing solution through the fabric, as represented by v in Equation 1, also contributes significantly to efficient laundering, unlike in the chemical EOR process.

Surfactant systems for EOR are designed to provide the so-called Winsor III behavior, where surfactant solubility is balanced between oil and water, a middle-phase microemulsion is formed in a three-phase region, and oil-water interfacial tension is ultralow (see Fig. 2). For the anionic surfactants commonly used in EOR, this phase behavior occurs at the so-called optimum salinity for a given reservoir and temperature. In an analogous manner, optimum detergency of oily soils from synthetic fabrics using nonionic surfactants has been shown to occur at the phase inversion temperature (PIT), where phase and interfacial tension behavior identical to that found at optimum salinity is noted (Miller and Raney, 1993). Hence, surfactants for EOR and oily-soil detergency applications can be initially screened for effectiveness and optimized using the same indirect phase behavior and interfacial tension measurements.

Laboratory-scale performance screenings of surfactant systems for detergency and for EOR are similar in other ways. Washing soiled fabric swatches provides qualitative and/or quantitative measurements of detergency performance. Within Shell Chemicals R&D, radiotracer detergency techniques measuring oil levels in water have been used to identify and quantify optimized nonpolar oil removal at the PIT (see Fig. 3). For chemical EOR, separated efflu-

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FIG. 4. Sandstone core after alkaline surfactant polymer injection at left end (upper) and (lower) core cross sections showing residual oil after flooding (lower). Cross sections from top left to bottom right progress from inlet to outlet and show more residual oil near the outlet.

ents from core floods are typically used to quantify removal of crude oil from sandstone or carbonate cores. At the end of the core floods, the cores can be sectioned to qualitatively indicate the "cleanliness" of the rock after flooding with a controlled amount of surfactant solution. I have often noted that these qualitative observations of cross-sectioned rock samples, such as those in Figure 4, are very similar to observations of stained fabric swatches after laboratory detergency tests.

SURFACTANT REQUIREMENTS

The surfactants used in EOR and home laundering are generally different: Anionic surfactants for chemical EOR are typically high molecular weight anionic surfactants (e.g., having C_{20}–C_{24} hydrocarbon tails), whereas blends of anionic and nonionic surfactants with shorter, predominantly linear hydrophobes (e.g., C_{12}–C_{16}) are most commonly active ingredients in laundry detergents (Rosen and Kunjappu, 2012). In the last few years, branched anionic surfactants have gained favor for ASP processes due to their reduced tendency to form viscous liquid crystalline and microemulsion phases in the oil reservoir as compared to their linear analogs (Barnes *et al.*, 2008).

With regard to the formulations themselves, however, great similarities exist between the two applications. Typical formulations for a laundry powder and an ASP process are shown in Table 1. In addition to similar ingredients, it is quite interesting that the ratios of the three major ingredients are nearly the same—a 3:1 weight ratio of sodium carbonate to surfactant with a much lower level of polymer. Variations can occur, however, because chemical EOR is applied to reservoirs with wide differences in reservoir rock, crude oil, and formation water properties, the latter affecting the salinity of the water used in the formulation.

Despite their structural differences, surfactants for either application are prepared from the same feedstocks including olefins, alcohols, and alkylene oxides. As a result, direct competition for these feedstocks and the process units to make the surfactants will inevitably occur as full-scale ASP processes are initiated around the world and the volume of surfactants used for EOR approaches the amounts currently used for detergent applications.

PRODUCT FORMS

The shipment and storage of surfactant during commercial field operations is a huge problem for application of surfactant EOR. For a typical 100,000 bbl (16 million liters)/day injection, storage requirements for an offshore project to ensure uninterrupted supply

TABLE 1. Comparison of ingredients and dosage levels of a typical laundry detergent powder and alkaline-surfactant-polymer (ASP) enhanced oil recovery formulation

Ingredient	Example laundry powder	Typical ASP formulation
Surfactants	0.2 grams/liter	5 grams/liter
Soda ash	0.6 grams/liter	15 grams/liter
Polymer (acrylate-based)	0.01grams/liter (anti-redeposition–low MW)	1 gram/liter (viscosifying–high MW)
Other ingredients	Enzymes, fragrance, etc.	Co-solvent (optional for solubility enhancement)

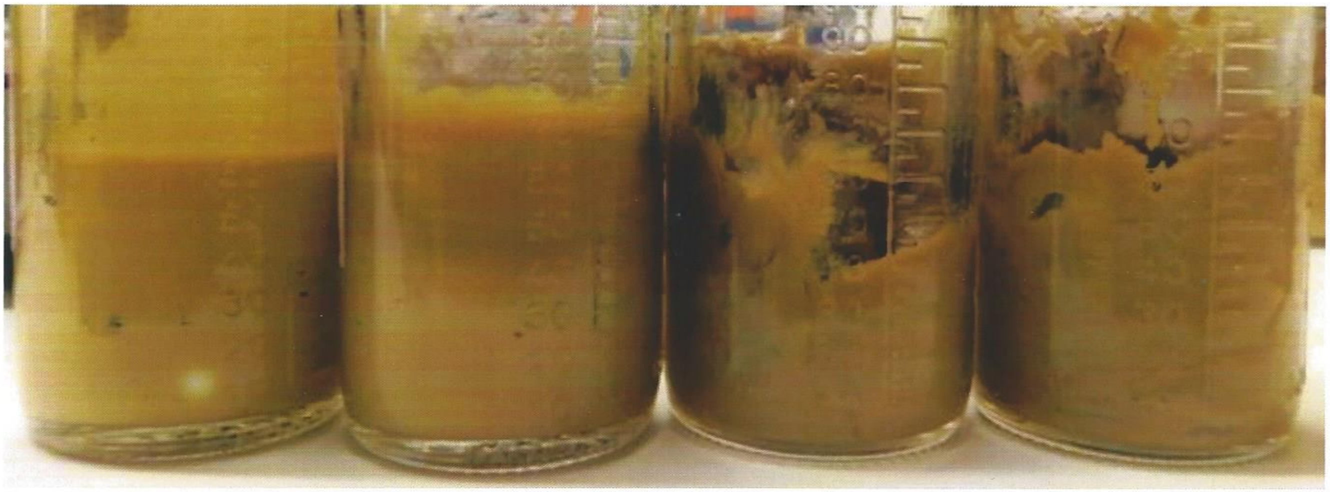

FIG. 5. Change in product consistency as water content is reduced from 80% to 30% (left to right) in an internal olefin sulfonate surfactant used for EOR.

of chemicals to the wells would be 7 million pounds (3,200 metric tons) of active surfactant and 17 million pounds (7,700 metric tons) of soda ash. Unfortunately, storage space is at a premium, particularly on deepwater production platforms, such as those found in the Gulf of Mexico (Raney *et al.*, 2012).

New concentrated surfactant forms would be useful to improve transportability and compactness of EOR surfactants. However, reducing water content from 70–80% to 20–30% for an EOR surfactant product typically converts the product form from a flowable liquid to very viscous pastes and gels (see Fig. 5). I believe technical advancements made by the laundry detergent industry, such as inclusion of small quantities of non-flammable solvents to produce flowable and easily dilutable compact heavy-duty laundry liquids, can be applied to this situation (Barnes *et al.*,2008). Similarly, technologies to produce compact laundry detergents containing sodium carbonate, surfactant, and polymer could be used to produce space-efficient powder forms for use in chemical EOR (Raney *et al.*, 2012; Barnes *et al.*, 2012). As already noted, the ratios of those three ingredients are quite similar for both powder laundry detergents and ASP EOR applications, making transfer of technologies fairly straightforward.

It is interesting to use Figure 5 to point out that two important surfactant characteristics for household detergent usage, color and odor, are of little consequence in EOR product forms.

ENVIRONMENTAL CONSIDERATIONS

Fresh water is a valuable resource around the world. In this regard, new low water-usage washing machines are important components of home laundering processes. In addition, past research between Shell and the Institute for Applied Surfactant Research (University of Oklahoma, Norman, USA) has

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For more information on EOR see *Inform 20*:682–685 (2009).

looked at the possibility of reusing both wash and rinse water for washing home laundry at an industrial scale (Scamehorn *et al.*, 2007). In initial studies, rinse and wash water were filtered through a 0.1 µm filter to remove oily and particulate soils and recirculated back to serve as a portion of the wash and rinse water for sequential washes in a home washing machine. Ninety percent water reuse and 40% surfactant recovery were achieved with little degradation in cleaning observed over the subsequent wash cycles.

Now, similar concepts are being used to allow reuse of water for chemical EOR. This process is specifically referred to as produced water reinjection (Raney *et al.*, 2012). Microfiltration of produced water removes the produced solids and residual oil droplets to a sufficient degree to allow reinjection of the water along with makeup chemicals without plugging the injection wells.

Fate of laundry detergent ingredients in municipal wastewater treatment facilities has been widely studied (Rosen and Kunjappu, 2012). Specific concerns about aquatic toxicity of surfactants and slow biodegradation of antiredeposition polymers are two key issues that have been mostly resolved by the detergent industry.

Produced water at offshore oil production facilities is commonly released into the ocean. Without additional expensive piping and pumps, produced water reinjection will not be an option in these situations, and the chemical EOR produced water will require not only removal of dispersed oil but also removal or degradation of produced surfactant and polymer (hundreds of parts per million) to allow its disposal into the ocean, that is, overboarding (Raney *et al.*, 2012). This need for environmentally benign water disposal is a major technology gap that must be addressed before widespread offshore chemical EOR can take place. What the detergent industry has learned regarding the aquatic fate and effects of surfactants and polymers will be quite helpful to understand the extent of treatment required for successful overboarding of offshore-produced water from chemical EOR processes.

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