



Historical perspective

## Wettability alteration: A comprehensive review of materials/methods and testing the selected ones on heavy-oil containing oil-wet systems



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### ABSTRACT

Changing the wetting state of materials is a growing field of research in many areas of engineering and science. In the oil industry, the term wettability alteration usually refers to the process of making the reservoir rock more water-wet. This is of particular importance in naturally hydrophobic carbonates, fractured formations, and heavy-oil systems. This shift in wettability enhances oil recovery in oil-wet and weakly water-wet reservoirs and eventually increases the ultimate oil recovery.

For wettability alteration, two methods have been traditionally used: Thermal and chemical. Although many attempts have been made on reviewing the advancement of research in certain aspects of wettability, a comprehensive review of these techniques, especially in terms of the classification of the chemicals used, has been ignored. In this paper, we begin with this review and provide the past experience of wettability alteration in sandstone and carbonate reservoirs. More than 100 papers were reviewed extensively with an in-depth analysis of different methods suggested in literature. The areas of controversy and contradicted observations are discussed. The limitations and the applicability of each method were analyzed. Concerns on up-scaling laboratory findings to field scale are also addressed. The most promising potential methods are identified and their critical conditions highlighted.

At the end, a selection of reviewed methods is validated experimentally for one of the most challenging cases: Extra heavy-oil and bitumen recovery from fractured-strongly-oil-wet carbonates. Berea sandstone (aged to be oil-wet) and Indiana limestone samples were saturated with heavy oil (3600 cp). Next, the process was initiated by soaking the cores into solvent (heptane or diluent oil) and the oil recovery was estimated using refractive index measurements. Note that solvent was selected to dilute the oil and recover a considerable amount of oil as any chemical or thermal methods yielded inefficiently low recoveries. After the solvent phase, the samples were exposed to wettability alteration through selected chemicals at different temperature conditions through spontaneous imbibition tests to recover more oil and retrieve the solvent diffuse into the sample back. The most promising wettability alteration agents for each type of rock were marked and optimal application conditions (temperatures, injection sequence) were identified. Selected wettability alteration chemicals were finally tested on the bitumen (5–9° API-1,600,000 cp) containing Grosmont carbonate sample from Alberta, Canada. It is hoped that this review fills in the gap in the area of wettability alteration processes by summarizing, critically analyzing, and testing the methods suggested in the literature.

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## 1. Why wettability alteration?

Wettability of surfaces is preferred to be hydrophilic or hydrophobic depending on the type of the application. Self-cleaning surfaces, for example, are designed to be hydrophobic. This can be achieved using different techniques such as increasing the roughness of these surfaces [92]. Another methodology to modify surface wettability is coating these surfaces with low surface energy materials that can be used to render them super-hydrophobic [33]. In petroleum reservoirs, the term wettability alteration usually refers to the process of restoring the original reservoir wettability, which is presumed to be water-wet. The target of this restoration treatment is the unrecoverable oil by conventional waterflooding. An early study showed that altering the wettability toward more water-wet increases enhanced oil recovery [111]. In gas condensate reservoirs, wettability alteration induces a shift in relative gas permeability, which can increase gas well deliverability [57].

The great role of reservoir wettability on primary oil recovery methods such as water drive was recognized by early research [24]. Secondary recovery by waterflooding is directly related to wettability of oil reservoir as well. Wagner and Leach [111], for example, stated that oil recovery during water flooding for an oil-wet reservoir can be less by 15% compared with water-wet reservoir. Most of reservoirs, on the other hand, exhibit some degree of oil-wetness and it is rare to find a strongly water-wet reservoir. If reservoir has similar affinity to oil and water, the wettability is defined as neutral, and when some parts of the reservoir exhibit a different wettability than other parts, the term mixed-wet is used [83].

Jadhunandan and Morrow [48] tested the effect of wettability on oil recovery during water injection and concluded that ultimate oil recovery reaches its maximum near the neutral-wet state and not at a strongly water-wet state. Salathiel [83] showed that reservoirs with mixed wettability can display a higher oil recovery during water flooding than water-wet reservoir. He referred to a field scale experience where a mixed-wet reservoir had an exceptionally high oil recovery compared to water-wet reservoirs. Although there is a general

agreement that wettability alteration of strongly oil-wet reservoir is favorable, no conclusive statements can be made about the extent of the alteration that would lead to the optimum oil recovery.

In the following discussion, we analyze the balance of capillary and gravitational forces during the wettability alteration. Consider a porous medium wettability that is altering from strongly oil-wet state to neutral-wet state and then to strongly water-wet state. This shift in wettability may enhance oil recovery by different mechanisms:

1. While the wettability of reservoir is shifting from strongly oil-wet to neutral wet state, capillary forces that retain oil in porous medium are reduced and then eliminated. The gravitational forces may start playing a role on recovery at this stage. In this range, water contact angle decreases but does not drop below 90°. While wettability alteration may not have a direct impact on oil recovery at this stage, it reduces negative capillary forces, which, in turn, enhance the oil recovery by gravity forces.
2. Alteration of wettability from neutral-wet state toward strongly water-wet state induces capillary imbibition. Both gravity and capillary forces are expected to contribute in oil recovery in this range. Water contact angle needs to be brought below 90°.

## 2. The mechanisms of wettability alteration by enhanced oil recovery (EOR)

As previously explained, a reservoir responds differently to water flooding based on its wettability. The recovery rate becomes lower as the rock behaves more oil-wet. Many of the succeeding enhanced oil recovery (EOR) applications target improving oil recovery by altering the wettability to more water-wet. Several chemical and thermal EOR process were reported to alter the wettability of a reservoir toward water-wetness. The degree of water-wetness that can achieve by EOR immensely depends on how it affects crude oil/brine/rock properties. On the other hand, the mechanisms of crude oil interaction with rock and brine for each petroleum reservoir are different depending on crude oil and brine composition, rock mineralogy, and other reservoir

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