An Environment-Friendly Alkaline Solution for Enhanced Oil Recovery

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Abstract: The injection of alkali and alkali/polymer solutions is a well-known enhanced oil recovery technique. This article demonstrates how wood ash can be used as a source of low-cost alkali instead of synthetic alkali that is also environmentally friendly. From the experimental studies, it is found that the pH value of 6% wood ash extracted solution is very close to the pH value of 0.5% synthetic NaOH or of 0.75% Na2SiO3 solution. A preliminary microscopic study of oil/oil droplets interaction in natural alkaline solution was carried out in order to understand the oil/water interface changes with time and its effect on oil/oil droplet coalescence. Also, interfacial tension (IFT) was measured for both synthetic and natural alkaline solutions. The IFT values in the presence of acidic crude oil show comparable results.

Keywords: crude oil, interfacial tension, organic acid, pH, wood ash

INTRODUCTION

The history of chemical flooding dates back to the early 1920s, with roots in the disciplines of reservoir engineering and chemistry. Alkaline or caustic flooding began in 1925 with the injection of a sodium carbonate solution in the Bradford area of Pennsylvania (Nultine et al., 1927; Mayer et al., 1983). The alkaline flooding process is simple when compared to other chemical floods, yet it is sufficiently complex to require detailed laboratory evaluation and careful selection of a reservoir for field applications. Caustic flooding is an economical option because the cost of caustic chemicals is low compared to other enhanced oil recovery (EOR) schemes.

Alkaline water flooding is an old recovery process in which pH of the injected water is increased by the addition of relatively inexpensive chemicals. Many crude oils naturally contain a certain amount of organic
An Environment-Friendly Alkaline Solution for EOR

acids (Thibodeau et al., 2003; Zhang, 2004). When this acidic oil is displaced by an alkaline solution, chemical reactions will occur at the interface. These reactions produce surface-active agents, which will in turn reduce the interfacial tension (IFT) between the two fluids and emulsify oil and water (Cooke et al., 1974; Islam and Farouq Ali, 1990). The reduction in interfacial tension between acidic oil and alkaline water depends on the pH of the water, the concentration and type of organic acids in the oil, and the concentration and type of salts in solution (Ramakrishnan and Wasan, 1983; Elkamel et al., 2002).

Mechanisms of Alkaline Flooding

Some researchers (Johnson, 1976; deZabala et al., 1980; Islam and Farouq Ali, 1989; Turksoy and Bagci, 2000) reported that there are four common mechanisms that contribute to the improved oil recovery with chemical methods. These mechanisms are (1) emulsification and entrainment, (2) wettability reversal water-wet to oil-wet, (3) wettability reversal oil-wet to water-wet, and (4) emulsification and entrapment. Other related mechanisms include emulsification with coalescence, wettability gradients, oil-phase swelling, disruption of rigid films, and improved sweep resulting from precipitates altering flow. All the postulated mechanisms have some superficial similarities (Campbell, 1982). Laboratory experiments (Subkow, 1942; Robinson et al., 1977) and field trials (Emery et al., 1970; Cooke et al., 1974) have shown that alkaline flooding performance will depend on (1) water composition, (2) rock oil composition, (3) rock type and reactivity, and (4) alkaline concentration, especially how it interacts with the previously mentioned parameters.

Alkaline Chemicals

The chemicals most commonly used for alkaline flooding are sodium hydroxide (NaOH), sodium orthosilicate (Na₄SiO₄), sodium metasilicate (Na₂SiO₃), sodium carbonate (Na₂CO₃), ammonium hydroxide (NH₄OH), and ammonium carbonate (NH₄)₂CO₃ (Jennings, 1975; Novosad et al., 1981; Larrondo et al., 1985; Burk et al., 1987; Taylor and Nasr-El-Din, 1996; Almalik et al., 1997). Due to reservoir heterogeneity and the mineral compositions of rock and reservoir fluids, the same alkaline solution might induce a different mechanism. A good number of laboratory investigations dealing with the interaction of alkaline solutions with reservoir fluids and reservoir rocks have been reported in the literature (Ehrlich and Wygal, 1977; Campbell and Krumrine, 1979; Ramakrishnan and Wasan, 1983; Trujillo, 1983; Sharma and Yen, 1983). Due to its higher pH values, sodium hydroxide is considered to be the most useful alkaline chemical for oil recovery schemes (Campbell, 1977). The price comparison of the most common synthetic alkaline substances between 1982 to 2006 is shown in Table 1. It shows that alkaline price has
Table 1. Comparison of price and physical properties of most common alkalis (Mayer et al., 1983; Chemistry Store, 2005; ClearTech, 2006)

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<tbody>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>40</td>
<td>13.15</td>
<td>0.775</td>
<td>42</td>
<td>347</td>
<td>285–335</td>
<td>830</td>
<td>285–335</td>
</tr>
<tr>
<td>Sodium orthosilicate</td>
<td>Na₄SiO₄</td>
<td>184</td>
<td>12.92</td>
<td>0.674</td>
<td>15</td>
<td>56</td>
<td>300–385</td>
<td>1,385</td>
<td>300–385</td>
</tr>
<tr>
<td>Sodium metasilicate</td>
<td>Na₂SiO₃</td>
<td>122</td>
<td>12.60</td>
<td>0.508</td>
<td>19</td>
<td>91</td>
<td>310–415</td>
<td>1,340</td>
<td>310–415</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>17</td>
<td>11.45</td>
<td>—</td>
<td>89</td>
<td>7.4</td>
<td>190–205</td>
<td>1,920</td>
<td>190–205</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>106</td>
<td>11.37</td>
<td>0.985</td>
<td>7.1</td>
<td>45.5</td>
<td>90–95</td>
<td>1,460</td>
<td>90–95</td>
</tr>
</tbody>
</table>

increased 5–12 times during the last 15 years. The biggest challenge of any novel recovery technique is to be able to produce under attractive economic and environmental conditions (Islam, 1996; Khan and Islam, 2007). Due to the high cost of synthetic alkaline substances and the environmental impact, the alkaline flooding has lost its popularity. This is reflected in Figures 1 and 2. These graphs have been generated using data reported by Moritis (2004). However, cost-effective alkali might recover its popularity in the recovery scheme. It has become a research challenge for the petroleum industry to explore the use of low-cost natural alkaline solutions for EOR during chemical flooding. In this article, wood ash extracted solution is used as a low-cost natural alkaline solution. Several experiments have been conducted to test the feasibility of that natural alkaline solution. This validation must be developed by laboratory-scale studies, scaling them up to field level applications.

Toxicity of Alkalis

Alkali is one of the most commonly used chemicals for various applications. It has a wide range of applications in different industries, such as
petroleum refinery, pulp and paper mills, battery manufacturer, cosmetics, soap and detergent, leather processing industry, metal processing industry, water treatment plants, etc. The estimated worldwide demand of sodium hydroxide was 44 million tons expressed as 100% NaOH in 1999. The global demand is expected to grow 3.1% per year (SAL, 2006). In Figure 3, Chemical Market Associates Inc. (CMAI, 2005) reported that 62 million tons of alkali were produced in 2005. Alkalis are raw commercial products, and when they are transferred to other parts of the manufacturing plant for use in further chemical processing, there is always the risk of leakage. Each year huge amounts of synthetic alkalis are produced, and all of these alkalis are considered responsible for direct or indirect pollution of the environment. These alkalis also have significant adverse effects on human health (EPA, 1992). Inhalation of dust, mist, or aerosol of sodium hydroxide and other alkalis may cause irritation of the mucous membranes of the nose, throat, and respiratory tract. Exposure to the alkalis in solid or solution can cause skin and eye irritation. Direct contact with the solid or with concentrated solutions causes thermal and chemical burns leading to deep tissue injuries.
and also permanent damage to tissue (MSDS, 2006; ATSDR, 2006). Haynes et al. (1976) reported that a dose of 1.95 g sodium hydroxide can cause death.

The Chemistry of Wood Ash

Wood ash is a by-product of combustion in wood-fired power plants, paper mills, and other wood-burning facilities. A huge amount of wood ash is produced every year worldwide, and approximately 3 million tons of wood ash is produced annually in the United States alone (SAL, 2006). Wood ash is a complex heterogeneous mixture of all the nonflammable, nonvolatile minerals that remain after the wood and charcoal have burned away. Because of the presence of carbon dioxide in the fire gases, many of these minerals will have been converted to carbonates (Dunn, 2003). The major components of wood ash are potassium carbonate, “potash,” and sodium carbonate, “soda ash.” From a chemical standpoint, these two compounds are very similar. From the 1700s through the early 1900s, wood was burned in the United States to produce ash for chemical extraction. Wood ash was mainly used to produce potash for fertilizer and alkali for the industry. On an average, the burning of wood results in about 6–10% ashes. Ash is an alkaline material with a pH ranging from 9–13, and due to its high alkalinity characteristics, wood ash has various applications in different sectors as an environmentally friendly alkaline substance. Rahman et al. (2004) reported that wood ash was found to be effective arsenic adsorbent from contaminated aqueous streams at lower concentration levels.

MATERIALS AND METHODS

For our laboratory tests, wood ash samples were collected from wood furnaces, and the ash samples were sifted with a #30 size sieve to remove as much of the charcoal as possible. Screened wood ash samples and synthetic sodium hydroxide were taken in different amounts and placed in beakers. Different concentrated alkaline solutions were prepared for laboratory testing, and alkalinity of the solutions was measured by a pH meter (Thermo Electron Corporation, Beverly, MA).

Natural alkaline solutions at different concentrations were placed on microscopic slides, and crude oil droplets were added with the help of a needle tip. The properties of the crude oil are given in Table 2. The processes of coalescences and flocculation of the oil droplets were observed with the Carl Zeiss light microscope attached with Axiovision 4.0 software and Axiocam (Carl Zeiss MicroImaging GmbH, Göttingen, Germany) digital camera in the petroleum laboratory of the Civil and Resource Engineering Department, Dalhousie University, Canada. Microscopic digital images of the crude oil were captured after every 5 sec, and the images of the oil droplets were analyzed using an image processing software.
Table 2. Physical properties of the crude oil

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Physical properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>01.</td>
<td>Specific gravity</td>
<td>0.7–0.95</td>
</tr>
<tr>
<td>02.</td>
<td>Vapor pressure</td>
<td>&gt;0.36 KPa at 20°C</td>
</tr>
<tr>
<td>03.</td>
<td>Vapor density</td>
<td>3–5 (approx)</td>
</tr>
<tr>
<td>04.</td>
<td>Freezing point</td>
<td>−60°C to −20°C</td>
</tr>
<tr>
<td>05.</td>
<td>Viscosity</td>
<td>&lt;15 centistokes at 20°C</td>
</tr>
<tr>
<td>06.</td>
<td>Solubility</td>
<td>Insoluble</td>
</tr>
<tr>
<td>07.</td>
<td>Coefficient of water/oil distribution</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

IFT Measurement Using Du Nouy Ring Method

The interaction of the alkali in floodwater and the acids in reservoir crude oil results in the in situ formation of surfactants that cause the lowering of IFT. A reduction in IFT assists the oil recovery process by mobilizing residual oil. IFT is an important physical property and has wide applications in many industries (Alguacil et al., 2006). The value of IFT can be determined by different methods (Lecomte Du Nouy, 1919; Couper, 1993). In this study, IFT values measured using the Du Nouy ring method.

RESULTS AND DISCUSSION

The prepared wood ash extracted solution was filtered by Whatman-113 filter paper. As a result, the solution became clear (Figure 4b). The pH value of the natural alkaline solutions at different percentages (1, 2, 4, 6, and 8%) are presented in Table 3. It is found that the alkalinity of 6% wood ash solution is close to 0.5% synthetic sodium hydroxide solution. This value is also very close to the pH of 0.75% Na$_2$SiO$_3$ solution (Green and Willhite, 1998). It is well known that the alkaline solution of pH range 12–14 is treated as a strong base. During alkaline flooding, the pH value of the synthetic alkaline is maintained in the range of 11.5–13.5 as a common practice. Therefore, it is proposed that the natural alkaline solution extracted from the 6% wood ash can be used instead of 0.5% synthetic sodium hydroxide solution or 0.75% synthetic sodium metasilicate solution during the chemical flooding scheme in an acidic reservoir. Burk (1987) reported that Na$_2$CO$_3$ solutions are less corrosive to sandstone than NaOH or Na$_4$SiO$_4$. The buffering action of sodium carbonate (Na$_2$CO$_3$) can reduce alkali retention in the rock formation. The main composition of wood ash is carbonate slats (Na$_2$CO$_3$ or soda ash and K$_2$CO$_3$ or potash). Carbonate slats offer an additional advantage upon contact with hard water. The resulting carbonate precipitations do not adversely affect
Figure 4. (a) Before filtration of alkaline solution (6% wood ash). (b) After filtration of natural alkaline solution (6% wood ash).
An Environment-Friendly Alkaline Solution for EOR

Table 3. Comparison of alkalinity between natural alkaline solution extracted from wood ash and synthetic sodium hydroxide solution at different concentrations

<table>
<thead>
<tr>
<th>Synthetic sodium hydroxide solution</th>
<th>pH value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic sodium hydroxide solution (NaOH)</td>
<td></td>
</tr>
<tr>
<td>2.0% NaOH solution</td>
<td>13.11</td>
</tr>
<tr>
<td>1.5% NaOH solution</td>
<td>13.05</td>
</tr>
<tr>
<td>1.0% NaOH solution</td>
<td>12.74</td>
</tr>
<tr>
<td>0.5% NaOH solution</td>
<td>12.35</td>
</tr>
<tr>
<td>0.2% NaOH solution</td>
<td>11.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wood ash solutions</th>
<th>pH value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood ash solution</td>
<td></td>
</tr>
<tr>
<td>8% wood ash solution</td>
<td>12.42</td>
</tr>
<tr>
<td>6% wood ash solution</td>
<td>12.29</td>
</tr>
<tr>
<td>4% wood ash solution</td>
<td>12.09</td>
</tr>
<tr>
<td>2% wood ash solution</td>
<td>11.83</td>
</tr>
<tr>
<td>1% wood ash solution</td>
<td>11.42</td>
</tr>
</tbody>
</table>

permeability as compared to the precipitations of the hydroxides or silicate (Cheng, 1986). It is therefore suggested that the use of carbonate buffer solution extracted from wood ash might result in longer alkali breakthrough times and increased tertiary oil recovery.

A series of laboratory experiments was conducted on the natural alkaline solution for its application in chemical flooding. A microscopic study of oil/oil droplets interaction in wood ash extracted solution was carried out to understand the oil/water interface changes with time and its effects on oil/oil droplets coalescence. When the oil droplet was added to the natural alkaline solution, alkali reacted with the organic acids of oil. As a result, surfactant was produced. This surfactant contained hydrophilic molecules and hydrophobic molecules that started to form a layer around the oil droplet called “micelles,” and it caused the smoothing of surfaces, resulting in reduced interfacial friction. Once the micelle is formed, mobility of oil droplets increases and oil droplets move faster under the influence of buoyancy force or viscous force, which results in drainage of thin surfactant water film at the contact between flocculating oil droplets (Figure 5). Consequently, this film reaches the critical thickness at which it ruptures, and oil droplets coalesce to form a larger globule (Figure 6). It is also found that two oil droplets coalesce after 3.5 min in 6% wood ash solution that contain the same alkalinity of 0.5% NaOH and 0.75% Na₂SiO₃ solutions.
IFT measurements between a crude oil and an alkaline solution have generally been accepted as a screening tool to evaluate the EOR potential of the crude oil by alkali (Jennings, 1975; Campbell, 1982; deZabala and Radke, 1982). Recently, Mollet et al. (1996) showed in an experimental study that minimum IFT is not observed in absence of alkali in the aqueous phase. From our experimental studies, it is found that IFT gradually decreases with increasing concentration of natural alkaline solutions (Figure 7) as well as with increasing concentration of NaOH solutions (Figure 8). It is observed that IFT decreases up to a certain limit with pH, which is illustrated in Figure 9. This behavior is typical of dynamic interfacial phenomena, which are known to take place for heterogeneous fluids (Elkamel et al., 2002). The higher concentration of the alkaline solution develops more surface active agents as a result of the reaction between organic acid in the crude oil and alkali in the aqueous phase. Hence, this surface active agent (petroleum soap) can cause the decrease of interfacial tension and increase the mobility of oil in the continuous water phase.
CONCLUSIONS

This study supports the basic idea of the applicability of natural alkaline solution for the EOR scheme. Based on the experimental results presented in this work, the following conclusions can be reached.

- The natural alkaline solution extracted from wood ash is sufficiently alkaline. The alkalinity (pH value) of 6% wood ash solution is very close to 0.5% synthetic sodium hydroxide and 0.75% synthetic sodium metasilicate solution.
Wood ash extracted alkaline solution reduces the interfacial tension with crude oil, which helps to increase oil mobility in an aqueous phase.

Coalescence time of oil droplets seems to be strongly influenced by the early micelles forming stage. It is also dependent on the decrease in interfacial tension. From the study, it is observed that coalescence time of oil/oil droplets decreases with the increasing pH, and two oil droplets are coalesced after 3.5 min in 6% wood ash solution. Wood ash extracted alkaline solution, which contains mainly soda ash (Na$_2$CO$_3$) and potash (K$_2$CO$_3$) could be more advantageous than the alkaline solution of NaOH or Na$_4$SiO$_4$ for alkaline flooding, because the buffered slug would be less reactive with sandstone minerals due to reduction of hydroxyl ion activities. Wood ash extracted alkaline substances are environmentally friendly and naturally abundant, whereas injected synthetic alkaline solutions are cost effective but environmentally harmful.

ACKNOWLEDGMENT

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REFERENCES

An Environment-Friendly Alkaline Solution for EOR


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