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Degradation Study on Materials for Dissolvable Frac Plugs

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1. Abstract

Dissolvable frac plugs (DFPs) can eliminate milling out, enable longer lateral wellbores, and reduce operational risks. Although DFPs have been successfully used in many cases, uncertainty about their degradation has also been known. For example, some DFPs have not degraded under certain conditions even though many of the conditions were similar to those under which successful degradation occurred. We report the degradation behaviors of dissolvable materials used in DFPs to understand the reasons for the uncertainty and to share our knowledge about how to deploy DFPs under various conditions to maximize the benefits of DFPs.

The two major dissolvable materials for DFPs, polyglycolic acid (PGA) and a dissolvable Mg alloy, were chosen for the degradation study. The effects of various factors, such as temperature, salinity, and chemicals added to the fracturing and pump-down fluid, were investigated to understand the degradation behaviors comprehensively. The temperature range was 50 - 150 °C (120 - 300 °F), which covers the bottom hole temperature range in most unconventional areas. The salinity dependence study considered species such as sulfate and bicarbonate in addition to chloride because these are also commonly found in actual water sources. Other chemicals studied were biocides, friction reducers, and scale inhibitors, which are often added to fracturing and pump-down fluids.

The study results were as follows. (1) PGA had a simpler temperature dependence than the Mg alloy. The degradation rate of PGA was proportional to temperature, whereas the Mg alloy had a degradation rate peak and showed a sharp rate decrease at high temperature in fresh water. (2) The degradation rate of PGA was stable and was not affected by salinity level, ionic species, degradation byproduct, and chemicals. (3) Mg alloy degradation had high salinity dependence, as expected. Each ionic species (chloride, sulfate, bicarbonate) had a different effect on the degradation and a thorough analysis of water is needed to predict Mg alloy degradation accurately. (4) The Mg alloy degradation rate was affected by chemicals. Certain chemicals, such as biocides and friction reducers, may decrease the rate in fresh water.

The difference in degradation behaviors for major dissolvable materials was discussed. The results presented in this paper will assist completion engineers in using DFPs in their well completions by sharing the following conclusions. (1) Degradation of PGA DFPs is simpler because it is not affected by salinity or chemicals. The usability of PGA frac plugs is higher and they can be used in both fresh water and high-salinity water fracturing. (2) Degradation of Mg alloy DFPs is complex when they are used in fresh water with chemicals, and in fresh water in high-temperature wells. To avoid uncertainty, the addition of salt or acid is recommended.

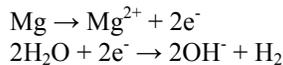
2. Introduction

Multi-stage hydraulic fracturing by plug-and-perforation is an effective method to increase production in unconventional reservoirs (Xu et al. 2015). The operation requires an isolation tool, such as frac plugs, for zone isolation. After the fracturing treatment has been completed, conventional frac plugs must be removed with a coiled-tubing unit to maximize production. The milling-out process is not only costly, but can also be risky, especially with increasing stage count and extended-reach applications.

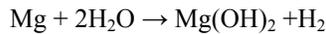
Dissolvable frac plugs (DFPs) can eliminate milling out, enable longer lateral wellbores, and reduce operational risks. DFPS are made of dissolvable materials, which can degrade, dissolve, or disintegrate in fluids used in fracturing operations. Two types of DFPS, polyglycolic acid (PGA) DFPS and Mg alloy DFPS, are widely used. Both types of DFPS can degrade, dissolve, or disintegrate in fluids used in fracturing operations, although the degradation mechanism of the primary materials constituting the DFPS is different.

PGA DFPS mainly consist of parts made of the degradable plastic, PGA. The simple molecular structure of PGA enables the molecular chains to pack densely in both the crystalline and amorphous phase, leading to its high mechanical strength, which is comparable to engineering plastics (Okura et al. 2015). Moreover, PGA shows high degradability in the presence of water because of the large numbers of hydrolysable ester groups per unit volume. These properties make this polymer an ideal material for many applications in oil and gas recovery that require both mechanical strength and degradability (Tran et al. 2017). The degradation mechanism of PGA is hydrolysis; therefore, the temperature and presence of water are the essential factors governing the degradation of PGA in principal. PGA is first degraded into the water-soluble monomer, glycolic acid, which is further degraded into water and carbon dioxide by microorganisms.

Mg alloy DFPS are degraded via local galvanic corrosion (Fripp et al. 2016), consisting of the anodic and cathodic reactions, when the alloys are exposed to wellbore fluids. The reactions are



The total reaction is



This reaction requires the transfer of electric charge; thus, the fluid must be conductive. Therefore, the wellbore fluids must contain a sufficient amount of conducting substances, such as salt or acid, to allow the degradation of Mg alloys. In the reaction, Mg alloys form magnesium hydroxide, $\text{Mg}(\text{OH})_2$, which is barely soluble in water; the water solubility is only 0.0064 g/L at 25 °C and 0.04 g/L at 100 °C.

The usage of DFPS can be divided into the following two major applications (Walton et al. 2017).

Toe application: This application reduces the risks and cost of milling out in the toe section for long lateral wellbores. The lateral length of horizontal wells is increasing yearly to improve the recovery efficiency of shale oil and gas. In such long lateral wellbores, milling out with a coiled-tubing unit often faces problems. Milling out frac plugs in the toe section in long lateral wellbores is slow compared with in the heel section, resulting in high costs. Moreover, there is a risk of stacking of the coiled-tubing unit. Using DFPS in the toe section has the major advantage in avoiding these problems.

Full-bore application: Using DFPS in full-bore applications may completely eliminate the milling out process, reducing the completion cost and risk of problems with milling out. Although this is a large advantage, DFPS for this application require fast degradation. DFPS in the heel section must degrade faster than those in the toe section because the soaking time of DFPS in wellbore fluid in heel section is shorter than that in the toe section.

In recent years, successful case histories for DFPS have been reported; however, it has also been known inconsistent degradation of DFPS in other cases. For example, DFPS degraded well in a wellbore, but DFPS did not degrade sufficiently in other wellbores, even though the environmental conditions were similar. This may be because the

various well conditions, such as temperature, salinity, fluid chemicals, and degradation byproducts, affect the degradation behaviors of the materials used for DFPS.

In this paper, we studied the degradation behaviors of two major materials for DFPS, namely, PGA and Mg alloys, for various temperatures, salinities, ionic species, and fluid chemicals. We discuss the possible reasons for the inconsistency of the degradation of DFPS and advise how to maximize the performance of DFPS under various conditions to use them for both toe and full-bore applications.

3. Methods

The PGA material used in this study is high molecular weight PGA for Kureha Degradable Plug (KDP), medium temperature grade, which is typically used for bottom hole temperatures (BHTs) of 90 - 160 °C (200 - 325 °F). There are also other PGA grades for lower BHTs (typically 50 - 120 °C [125 - 250 °F]). Although the results of the PGA grades for lower BHTs are not presented in this paper, they were similar because the degradation of both PGA grades proceeds via hydrolysis. The difference between each grade is only the absolute degradation rate; the PGA grades for lower BHTs have faster degradation rates than the medium temperature grade.

A Mg alloy was produced and used for this study as the Mg material. The degradation rate of the Mg alloy was adjusted to 1,000 - 1,500 mg/cm²/day in 2% KCl solution, which is a typical degradation rate for Mg alloys used for DFPS. Although there are alloys with slower and faster degradation grades available, they should show the same degradation behavior under various conditions. This is because the degradation mechanism is galvanic corrosion for all Mg alloys.

The PGA molded specimen was produced by solid-state extrusion and the Mg alloy specimen was produced via extrusion. The PGA coupons and Mg alloy cubes were prepared by cutting the molded specimens. A glass beaker containing an aqueous solution was placed in a water bath and heated to the specified temperature, and then a coupon or a cube was placed in the beaker. The decrease in the thickness of the PGA coupon and the Mg cube with time via the surface degradation mechanism was recorded. Hereafter, we call the decrease rate in the thickness of a coupon or cube per unit time the degradation rate.

Comprehensive degradation testing was varying temperature, salinity, and fluid chemicals. The temperature range in this study was 50 - 150 °C (120 - 300 °F), which covers the BHTs typically seen in the areas for unconventional reservoirs in North America. Ionic species, such as sodium, calcium, potassium, sulfate, bicarbonate, and chloride, were used to make model solutions that imitate the actual water sources commonly found in base fluids to stimulate operational conditions (Figure 1). The salinity level was in the range 0.05 - 10%, corresponding to the fluids from fresh water to brine. In this paper, we used 0.05% KCl conditions as typical fresh water conditions. The fluid chemicals tested were biocides, clay control agents, friction reducers, and surfactants, which are commonly added to fracturing fluid and pump-down fluid.

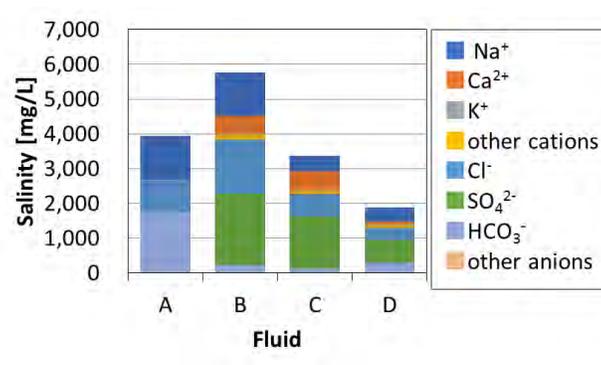


Figure 1: Cation and anion composition of actual fresh-water-based-fluids from four water sources.

4. Results

4.1. Temperature dependence

Figure 2 shows the temperature dependence of the degradation rate of PGA and the Mg alloy in fresh water conditions (0.05% KCl solution). The degradation rate of PGA increased exponentially with temperature. The degradation of PGA occurs via hydrolysis, and the reaction rate of hydrolysis simply increases with temperature. The degradation rate of PGA can be expressed by an Arrhenius equation (Okura et al. 2015), which is commonly used to express the relationship between reaction rate and temperature. This makes the degradation of PGA easily predictable.

The degradation rate of the Mg alloy was more complicated than PGA degradation in fresh water conditions. The degradation rate of the Mg alloy increased with temperature at low temperatures (<90 °C [<200 °F]) and reached the highest degradation rate at around 90 °C (200 °F). At high temperatures (>90 °C [>200 °F]), the degradation rate decreased with increasing temperature. The degradation of the Mg alloy proceeds via local galvanic corrosion, and the conductivity of water increases as the temperature increases; therefore, this temperature dependence indicates that other factors affect the degradation rate of the Mg alloy. This degradation behavior can be explained by the degraded Mg alloy forming $Mg(OH)_2$ passivation film, which covers the surface of the Mg alloy cube and inhibits the degradation (Fripp et al. 2016). The formation of $Mg(OH)_2$ at high temperatures is faster than at low temperatures. Because of the competition between degradation and the surface becoming covered with $Mg(OH)_2$, the temperature dependence of the Mg alloy's degradation rate is complicated.

The complicated temperature dependence of the Mg alloy's degradation rate may be a reason for the inconsistent degradation behavior of Mg alloy DFPs. In the bottom of the drill hole, the temperature around the DFP cools from the static BHT, and it continues to cool until the end of fracturing. After fracturing, the temperature recovers to the static BHT. The degradation rate of PGA DFPs increases with increasing temperature, whereas the degradation rate of the Mg alloy DFPs increases with temperature to around the temperature at which the Mg alloy shows its maximum degradation rate, and then the degradation rate decreases with further temperature increases. The decrease in the degradation rate is large, for example, 10 times slower (Figure 2(b)).

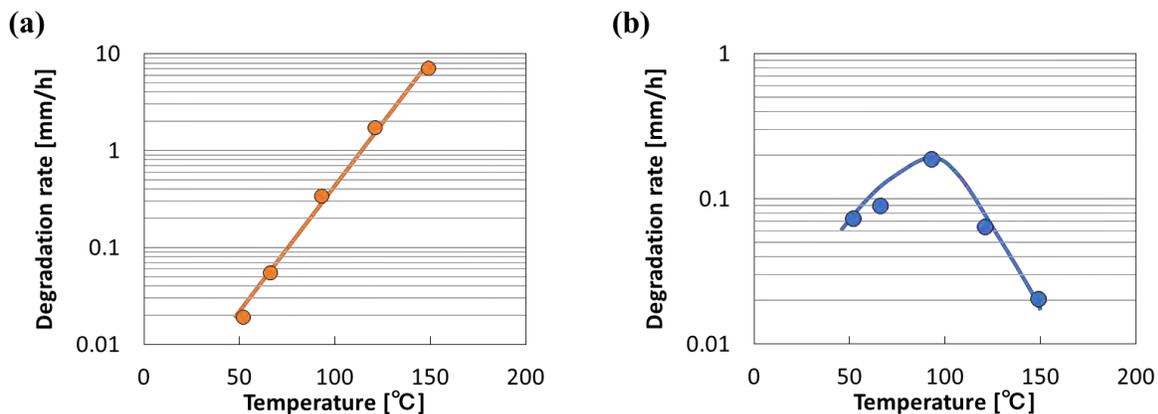


Figure 2: Temperature dependence of the degradation rate of (a) PGA and (b) Mg alloy in 0.05% KCl solution.

4.2. Effect of salinity level

The degradation rates of PGA and the Mg alloy were measured in KCl solutions at various concentrations at 93 °C (200 °F), to understand their salinity level dependence. The degradation rate of PGA remained constant at KCl concentrations of 0 - 10% (Figure 3), indicating that the degradation of PGA is not affected by salinity. The mechanism of PGA degradation is hydrolysis, and the salinity does not affect PGA hydrolysis greatly.

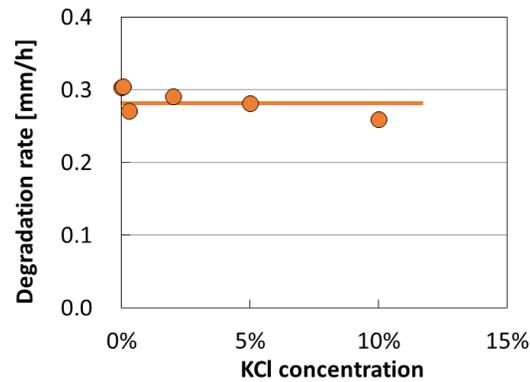


Figure 3: Degradation rate of PGA in KCl solutions of various concentrations at 93 °C (200 °F).

The degradation rate of the Mg alloy increased with increasing KCl concentration (Figure 4). The enlarged view of the degradation rate of the Mg alloy at low KCl concentrations shows that the degradation rate abruptly increases from almost 0 to 0.5 mm/h (0 to 0.02 inch/h) in solutions at concentrations of 0 - 0.4%, which are typical salinity levels for fresh water. The rate continues to increase to 1.0 mm/h (0 to 0.04 inch/h) with increasing salinity.

In actual bottom hole conditions, PGA DFPs can be stably used under a wide range of salinity conditions from fresh water, water containing added KCl (typically 2 - 8%), and water mixed with recycled water because the degradation rate is not affected by salinity. The consistency of the degradation of PGA DFPs may bring simple and easy operation, without having to worry about adjusting the salinity level of fracturing fluid and pump down fluid, neither during the accidental change in salinity level of the fluid due to pump failure and/or shortage of produced water.

The difficulty in predicting the degradation rate of Mg alloys may require careful stimulation operations with Mg alloy DFPs. If fresh water is used as the base fluid for the fracturing and pump-down fluids, the salinity of the fluids must be checked, ideally for every job, because the degradation rate in the salinity range of fresh water depends strongly on the salinity level of the water source. Moreover, if the salinity level of the fluids is high, it is essential to check the salinity level to prevent problems, such as decreasing the degradation rate by the accidental addition of low-salinity water to the fluids due to pump failure or a shortage of produced water.

Modifying Mg alloys can increase the degradation rate; however, the degradation rate at higher salinity levels increases in addition to that in fresh water. Namely, the degradation stability in fresh water range can be improved, although the reliability of the plug performance during running and pressurizing may decrease (i.e., increase in pre-set and/or decrease in holding pressure), especially at higher salinities. Therefore, extra care is required to prevent the degradation of Mg alloy DFPs before the fracturing process is completed if Mg alloy DFPs with higher degradation rates are used.

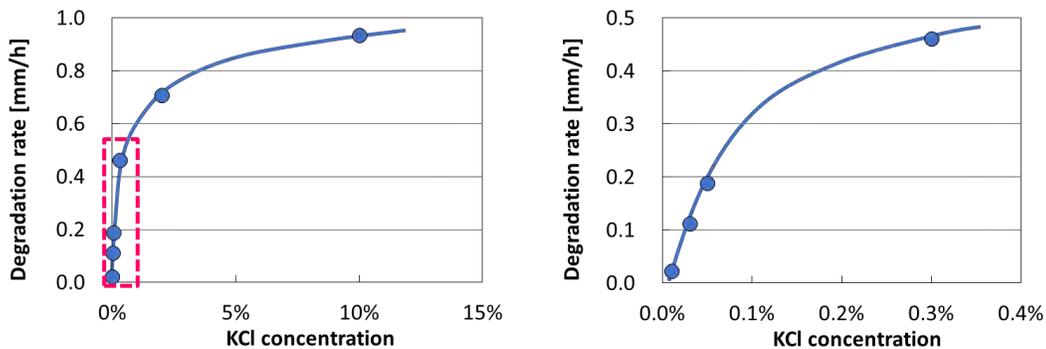


Figure 4: Degradation rate of Mg alloys in KCl solutions at 93 °C (200 °F).

The right plot shows the enlargement of the concentration range 0.05 - 0.3%.

4.3 Stability of degradation rate

The decrease in the thickness of PGA and the Mg alloy with time in 0.05% KCl solution at 93 °C (200 °F) was measured (Figure 5). The thickness of PGA decreased linearly with immersion time. During PGA degradation, the molecular weight of PGA decreases initially, and then it is converted to PGA oligomers (low-molecular weight PGA) before degrading into the monomer, glycolic acid. The mechanical strength of the PGA oligomer is low; hence, it is easily removed from the PGA surface and does not prevent water contact. Consequently, the degradation rate of PGA is stable.

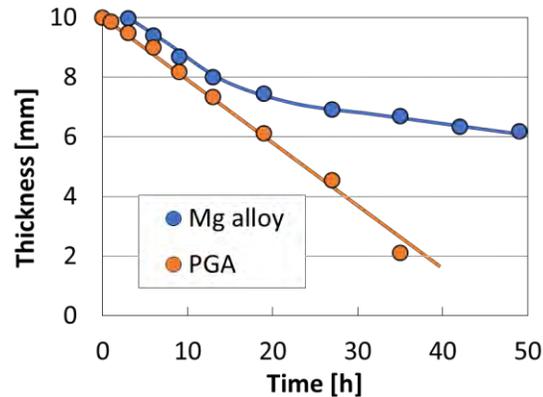


Figure 5: Decrease in thickness of PGA and Mg alloy with time in 0.05% KCl solution at 93 °C (200 °F).

The thickness of the Mg alloy decreased linearly with immersion time, and the decrease became gradual at around 20 h. The degradation of Mg alloy occurs via local galvanic corrosion. The Mg alloy reacts with water in the wellbore fluids, producing $Mg(OH)_2$. The byproduct can precipitate on the metal surface because of its low solubility in water, and it forms a passivation film on the surface (Figure 6), decreasing the degradation rate. The formation of the passivation film is important in low-salinity solutions, such as in fresh water-based wellbore fluids.

In wellbores, PGA DFPs should undergo stable degradation over time. However, in the case of Mg alloy DFPs, the byproduct remains around the downhole tools, and thus the complete degradation of Mg alloy downhole tools may take longer than expected, especially in stimulation operations with fresh water.

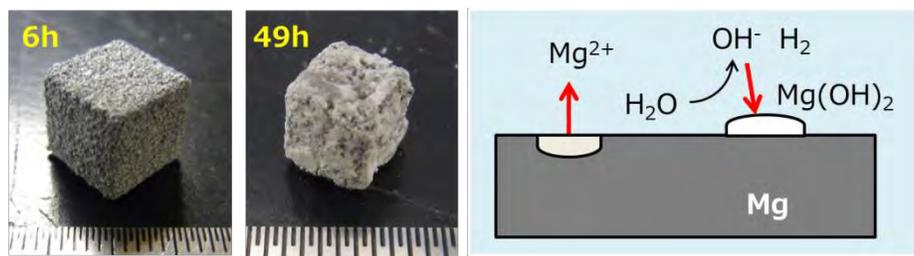


Figure 6: Photographs of Mg alloy cubes after 6 and 49 h immersion (left and middle) and the formation mechanism of the magnesium hydroxide passivation film (right).

4.4 Effect of ionic species

Figure 7 shows the decrease in thickness of PGA and the Mg alloy in solutions containing various salts at 66 °C (150 °F). The salinity of all the solutions was 2% for comparison. The thickness of PGA decreased monotonically with immersion time and was independent of salt species. In addition, the degradation rate of PGA was not affected by the concentration of ionic species or KCl concentration.

The salt species strongly affected the degradation rate of the Mg alloy. The decrease in thickness was fast in the KCl and NaCl solutions; however, in the CaCl₂ solutions, the time period for degradation to start was longer. In Na₂SO₄ solution, a passivation film was formed on the surface of the Mg alloy by the precipitation of the byproduct, leading to an initial increase in thickness followed by a decrease after a long time period. NaHCO₃ did not contribute to the degradation of the Mg alloy, at least under these conditions.

The performance of PGA DFPs is stable in actual wellbores, regardless of the salts dissolved in the fluids. However, due to the strong dependence of the Mg alloy degradation rate on the ionic species in fluids, Mg alloy DFPs may undergo inconsistent degradation in actual wellbores. Actual water sources contain various kinds of salts, and the total salinity and the ratio of each salt differ between water sources (Figure 1).

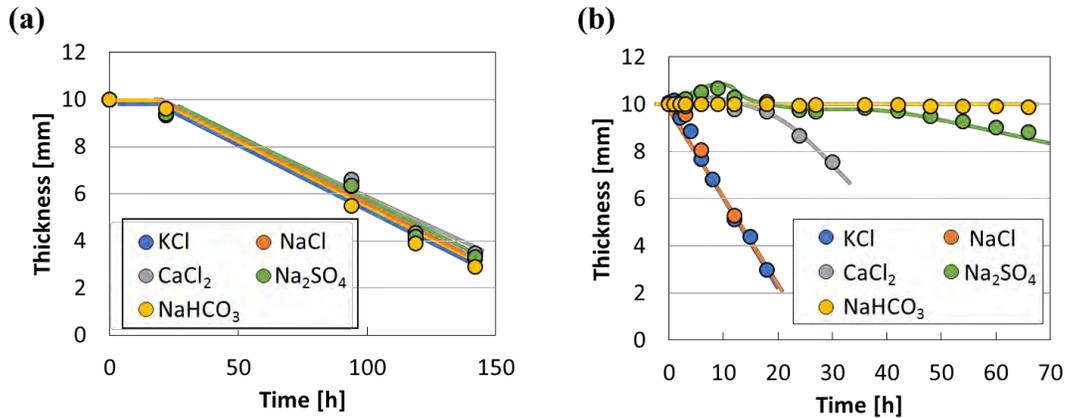


Figure 7: Decrease in thickness of (a) PGA and (b) the Mg alloy in various salt solutions at 66 °C (150 °F).

4.5. Effect of fluid chemicals

The effect of fluid chemicals on the degradation rate of PGA and the Mg alloy was also measured in fresh water conditions (0.05% KCl solution) at 93 °C (200 °F). The degradation rate of PGA was measured in a 0.05% KCl solution containing the fluid chemicals shown in Table 1. The degradation rate of PGA was similar to the rate in the solution without chemicals (Figure 8(a)). The degradation rates of PGA in solutions containing individual fluid chemicals were also measured, and the degradation rates were independent of the chemicals (data not shown).

Table 1: Concentrations of fluid chemicals.

Chemicals	Concentration [%]
Biocide	0.025
Clay control agent	0.075
Friction reducer	0.1
Surfactant	0.075

The degradation rate of the Mg alloy in the solution containing the fluid chemicals was measured, and the degradation rate was much slower than that in the solution without chemicals. Therefore, the degradation rates of the Mg alloy were also measured in solutions containing individual fluid chemicals (Figure 8(b)). The biocide greatly decreased the degradation rate of the Mg alloy. (We conducted degradation testing with various biocides, and found that each biocide has different effects. The biocide shown in Figure 8 greatly decreased the degradation rate of the Mg alloy; however, other biocides did not affect the degradation rate or accelerated it.) The friction reducer also decreased the degradation rate of the Mg alloy, but the effects of the surfactant and clay control agent were negligible.

Our results indicate that PGA DFPs can be used in actual wellbores without serious concerns about fluid chemicals. In contrast, the degradation rate of the Mg alloy was strongly affected by fluid chemicals; therefore, the effect of each chemical commonly used in oilfields must be understood. Furthermore, chemicals that decrease the degradation rate of the Mg alloy must be avoided to use Mg alloy DFPs safely.

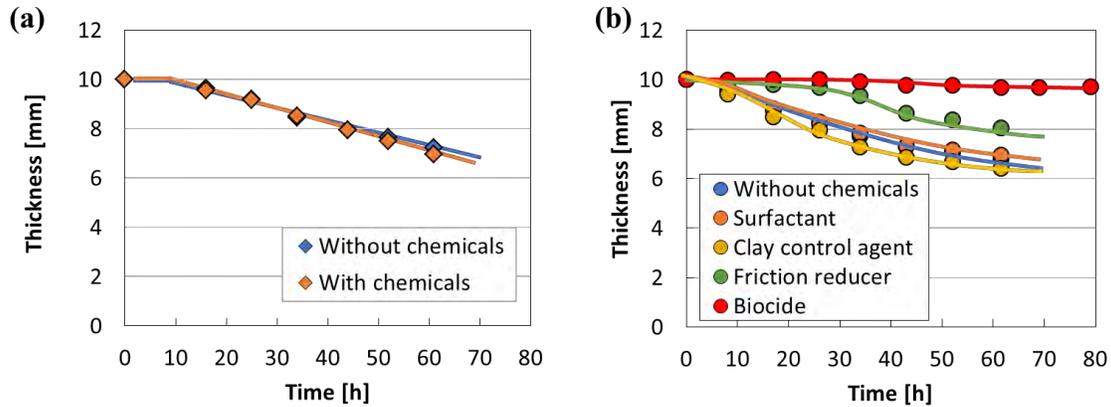


Figure 8: Decrease in thickness of (a) PGA and (b) Mg alloy in 0.05% KCl solution with fluid chemicals.

5. Discussion

As described above, the degradation of PGA is much simpler than that of the Mg alloy (Table 2). The only factor that affects the degradation rate of PGA DFPs is temperature, and the degradation rate can be accurately estimated. Therefore, the most important decision in using PGA DFPs is choosing one with an appropriate degradation rate (i.e., PGA grade) for the BHT of the target well.

The degradation rate of the Mg alloy depends on many factors other than temperature, including salinity, byproducts, ionic species, and fluid chemicals. The effects of combinations of these factors are complicated, and it is difficult to predict the degradation behavior in wellbores, especially in fracturing operations with fresh-water-based fluids. Therefore, the addition of salt or acid to fluids should be highly recommended to avoid uncertainty about degradation.

Table 2: Summary of PGA and Mg alloy degradation.

	PGA	Mg alloys
Temperature	Simply proportional	Have a peak
Salinity level	Independent	Dependent
Byproduct	Independent	Dependent
Ion species	Independent	Dependent
Fluid additives	Independent	Dependent

Using PGA DFPs for full-bore applications has an advantage over Mg alloy DFPs. PGA DFPs mainly consist of PGA which degrades predictably. In contrast, the majority of Mg alloy DFPs may remain if the degradation of the Mg alloy is not sufficient because of the salinity, byproducts, ionic species, or fluid chemicals. The slow degradation may make flow back difficult, or may restrict the rate of flow back. In this case, a coiled-tubing unit may be required to drill out the Mg alloy DFPs.

6. Conclusions

The degradation behaviors of major dissolvable materials were discussed. The findings presented in this paper will assist completion engineers in using DFPs in well completions. The conclusions are as follows.

(1) Degradation of PGA DFPs is simpler than that of Mg alloy DFPs because PGA degradation is not affected by salinity, byproducts, or fluid chemicals. PGA DFPs are easier to use and are recommended for both fresh water and high-salinity water fracturing, and for toe and full-bore applications.

(2) Degradation of Mg alloy DFPs is complex, especially when they are used in fresh water, in fluids containing chemical additives, and in high-temperature wells. To avoid uncertainty, the addition of salt or acid is recommended.

7. References

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