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Carbon Sequestration through CO_2 Foam-Enhanced Oil Recovery: A Green Chemistry Perspective

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ABSTRACT

Enhanced oil recovery (EOR) via carbon dioxide (CO_2) flooding has received a considerable amount of attention as an economically feasible method for carbon sequestration, with many recent studies focusing on developing enhanced CO_2 foaming additives. However, the potential long-term environmental effects of these additives in the event of leakage are poorly understood and, given the amount of additives injected in a typical CO_2 EOR operation, could be far-reaching. This paper presents a summary of recent developments in surfactant and surfactant/nanoparticle-based CO_2 foaming systems, with an emphasis on the possible environmental impacts of CO_2 foam leakage. Most of the surfactants studied are unlikely to degrade under reservoir conditions, and their release can cause major negative impacts on wildlife. With recent advances in the use of additives (e.g., nonionic surfactants, nanoparticles, and other chemicals) the use of harsh anionic surfactants may no longer be warranted. This paper discusses recent advances in producing foaming systems, and highlights possible strategies to develop environmentally friendly CO_2 EOR methods.

1. Introduction

Carbon dioxide (CO_2) flooding is one of the most widely used enhanced oil recovery (EOR) methods. In the United States, CO_2 EOR has recovered over 1.5 billion barrels of oil, and estimates of the amount of oil that is recoverable by CO_2 EOR range from 47 billion to 137 billion barrels [1–3]. Even though CO_2 flooding is an attractive EOR method by itself, it can be enhanced using additives that improve the ability of the CO_2 to displace trapped oil. Under the conditions of a typical oil reservoir, the viscosity of CO_2 can be 10–50 times lower than that of the oil, which makes CO_2 likely to channel through the oil and preferentially flow through more permeable rock sections [4]. This problem can be alleviated by adding surfactants to generate *in situ* CO_2 foams [2–10]. These foams have higher viscosity than each of their components, and their viscosity increases with increasing pore diameter, making them less likely to preferentially flow through more permeable rock sections. The result is a more uniform front of foam that pushes oil rather than fingering through the reservoir's most open geological formations.

Ideally, using CO_2 foams for EOR would be a nontoxic method of carbon sequestration that would reduce industrial contributions to global warming. This process meets the criteria established by the US Environmental Protection Agency (EPA) for a process to be considered "green chemistry" [11]. The use of CO_2 foams would decrease our impact on global climate change by trapping carbon in the depleting reservoir, thus reducing greenhouse gas emissions. Incorporating CO_2 EOR into carbon capture and sequestration systems results in lower environmental impact and higher thermodynamic efficiency compared with schemes that do not use it [12]. Furthermore, experiments have shown that CO_2 foams are most effective at low pressures [13], thus reducing compression costs and improving the thermodynamic efficiency of the process.

Given the appeal of CO_2 EOR as an economically feasible method of carbon sequestration, there have been numerous recent studies on the physics and economics of the process [14,15] as well as research on novel foaming agents such as CO_2-soluble surfactants, polymer-coated nanoparticles, and surfactant/nanoparticle blends [15,16]. Although much progress has been made in improving the stability and performance of CO_2 foams for EOR, the rapid development of foaming agents raises the question of their environmental safety. Most studies on the potential environmental impacts of carbon sequestration via CO_2 EOR focus on CO_2 leakage;

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far fewer studies consider the potential impact of the leakage of foaming agents. Considering the large amounts of surfactant injected into the ground in commercial CO_2 EOR operations—typically hundreds to thousands of tons of surfactant [17]—this impact could be substantial. In this paper, we explain why the environmental impact of foaming agents warrants concern and highlight the recent advances in developing stable CO_2 foams for EOR, with an emphasis on their potential environmental effects. We will show how new technology has enabled future research to revisit the necessity of using harsh anionic surfactants.

The rest of this work is organized as follows: Sections 2 and 3 outline the most recent developments in surfactant and surfactant/nanoparticle-based CO_2 foam systems. Section 4 discusses recent studies on the potential environmental impacts of CO_2 leakage, and Section 5 considers the potential impact of leakage of the foaming agents. Finally, we offer some closing remarks, including suggestions for future research.

2. Advances in surfactant CO_2 foam systems

There are several CO_2 flooding processes that rely on surfactants to produce foams [2,4–10]. Surfactant/polymer (SP) flooding involves *in situ* foam creation as the surfactant interacts with the brine and oil present in the reservoir, while the added polymer improves the mobility of the displacing phase. Foam flooding involves injecting a foamed gas into the reservoir to displace the oil and to improve the mobility of the oil as the gas dissolves in it. Water alternating gas (WAG) flooding involves the alternate injection of CO_2 with slugs of soapy brine containing ionic surfactants, leading to *in situ* foam generation. The majority of studies and field tests for surfactant-enhanced CO_2 EOR have used the WAG process.

Several improvements to the WAG process have been proposed, including the foam-assisted WAG (FAWAG) process, which integrates foam flooding and WAG flooding [10], and the chemically augmented WAG process, which combines WAG with the injection of alkali/surfactant/polymer (ASP) mixtures [18]. Research on these improved methods has found success in utilizing amine-functionalized CO_2-switchable chemicals such as *N*-erucamidopropyl-*N,N*-dimethylamine [18,19] and *N,N,N′,N′*-tetra methyl-1,3-propanediamine [20]. Upon contact with CO_2, these chemicals react with the dissolved carbonic acid, leading to the formation of foams and gel-like structures with enhanced sweeping efficiency. *N*-erucamidopropyl-*N,N*-dimethylamine has been shown to provide good mobility control and foam performance under harsh conditions [18].

More recently, there has been increased interest in the development of CO_2-philic surfactants, whether by means of functional groups or by modifying the tail group topology. Using CO_2-soluble surfactants has several advantages [2,4,21]. First, it ensures that the surfactant is available for foam generation right where the CO_2 flows. Second, it eliminates the need to inject water (brine is usually present in the reservoir from prior water flooding). Third, it makes the surfactant less likely to be lost due to adsorption on rock surfaces or trapping in "thief zones," thus reducing the amount of surfactant required.

In a recent study, Sagir et al. [21] examined the performance of a synthetic CO_2-philic surfactant, nonylphenol ethoxylate sulfonate (NPES), using betaine as a foam booster. The study found that NPES lowers the surface tension of the CO_2/brine interface from 30 to 5.2 mN·m^{-1} and reduces the mobility of the CO_2 by a factor of three, making it a very promising surfactant for CO_2 EOR. However, the study did not consider the potential environmental impact of the surfactant. Another recent study by Talebian et al. [22] tested blends of three newly developed surfactants,

FomaxII, FomaxVII, and UTP-Foam, which also contain CO_2-philic groups, as foaming agents in surfactant alternating gas (SAG) flooding. The study found that surfactants containing bulky, branched tail groups resulted in more stable foams, and that CO_2-philic surfactants with higher activity at the gas/water interface resulted in improved stability in the presence of oil. The results of these studies support prior findings that surfactants with bulkier, branched tail groups result in improved stability of the CO_2/brine interface [8]. More recent molecular simulation studies have also found that branching increases the effectiveness of the surfactant, although there is a complex relationship between the tail group architecture and the surfactant performance.

Alkalis are often used as additives in WAG flooding. Recent work by Farzaneh and Sohrabi [23] studied the stability of CO_2 foams in the presence of crude oil using eight different surfactants and three different alkaline additives (sodium hydroxide, sodium carbonate, and sodium borate). The study included one nonionic alcohol ethoxylate surfactant (Neodol 25-7™) and seven anionic surfactants: four from the sodium olefin sulfonate family (Petrostep C1™, C2™, and S2™, and Bio-terge AS-40™), two ammonium alkyl ether sulfate surfactants (Rhodapex CD-128™ and Alpha Foamer®), and a proprietary surfactant (XP-0010™). All the anionic surfactants resulted in more stable foams than the nonionic surfactant, with XP-0010™ resulting in the most stable and oil-resistant foam. Of the alkalis, sodium hydroxide was found to decrease foam stability. Sodium carbonate and borate resulted in more stable foams, with the borate outperforming the carbonate. In all cases, the study observed that there is an optimal concentration of alkali and surfactant that produces the most stable foams.

Polymer additives are another method of improving foaming properties. A recent study found that combining foam flooding and SP flooding significantly increases the oil recovery in CO_2 EOR, particularly at higher reservoir pressures [24]. The study used a mixture of sodium alpha olefin sulfate (AOS), the foaming agent N70K-T, and the thickener AVS (consisting of a novel ter-polymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and an additional (variable) monomer [25]). Other recent studies have tested mixtures of sodium dodecyl benzene sulfonate (SDBS) with partially hydrolyzed polyacrylamide (HPAM) [26], and of sodium dodecyl sulfate (SDS) with a hydrophobic modified water-soluble polymer, alkyl acrylate cross polymer (HMPAA) [27]. The latter system led to ultra-stable foams due to the formation of an HMPAA hydrophobic network on the CO_2/water interface.

Several recent studies have also considered foams prepared with the nonionic surfactant Triton X-100™ (TX-100), an octylphenol ethoxylate with 9–10 ethylene oxide units [25,28–30], as well as nonylphenol polyethoxylates (NPs) [31]. One flooding study sought to improve sweep efficiency by blending surfactant concentrations at reservoir conditions [28]. The study tested three surfactants: pure AOS, a blend of equal parts of AOS and lauramidopropyl amine oxide (LMDO), and a blend of equal parts of AOS and TX-100. The study found significant enhancements in oil recovery in all cases, with the AOS/TX-100 blend resulting in the highest recovery.

A study by AttarHamed and Zoveidavianpoor [29] in 2014 also tested mixtures of AOS and TX-100 at different concentrations, and found that a 4:1 mixture produced better foamability and stability than other mixtures or the surfactants alone. A more recent study by Xu et al. [25] tested several mixtures of surfactants, including TX-100, alkyl polyglycoside (APG), SDS, and AOS with the additives N70K-T, triethanolamine (TEA), AVS, and HPAM. The study found that the AOS/AVS/N70K-T mixture showed superior performance in terms of foamability, foam stability, relative modification ability, and amount of oil recovered.

From the studies discussed so far, it is clear that anionic surfactants are generally superior to nonionic options and more stable in

brine for CO_2 EOR, although adding the nonionic surfactant TX-100 to an anionic formulation can result in improved foam properties. The results also suggest that modifying the chemistry and architecture of the surfactant tail can be an effective way to improve foaming performance. However, these studies mostly focus on the properties of the resulting foams and not on the potential toxicity or environmental impact of the formulations (see Section 5). The use of biosurfactants would be a greener alternative [32]. In addition to discovering that the foaming performance and thermal stability of nonylphenol polyethoxylate surfactants increased with the number of ethylene oxide units, recent work by Wang et al. [31] found that APG-1214, a biodegradable polyglycoside nonionic surfactant, is a very effective CO_2 foaming agent. In their study, the addition of APG-1214 produced a foam that outperformed all the individual NP and anionic surfactant systems alone. The authors attributed this result to the presence of negative charges on the APG micelles, due to excess adsorption of OH^- at the interface. This results in a higher effective hydrophilicity of the surfactant, leading to higher foaming capability. Another recent study found that polyoxyethylene sorbitan monooleate (Tween 80), an inexpensive nontoxic emulsifying agent commonly used in food and cosmetics, can be used in combination with small amounts of SDS (10:1 weight ratio of Tween 80 to SDS) to produce stable CO_2 foams suitable for injection in hydrate reservoirs [33]. These studies suggest that synthetic and caustic additives could be replaced by greener alternatives in CO_2 EOR operations in order to reduce the impact of such operations on the environment.

3. Advances in surfactant/nanoparticle CO_2 foam systems

Most of the recent research in the field of CO_2 EOR has focused on the use of nanoparticles as foaming additives. Emulsions, including solid nanoparticles, often exhibit higher long-term stability, and can be designed to be biocompatible and environmentally friendly [34,35]. In this section, we discuss studies from the last five years on the use of surfactant/nanoparticle foams for CO_2 EOR, with their environmental impact in mind. A recent general review of the uses of nanoparticles in various EOR applications has been published by Sun et al. [36].

A recent study by Yekeen et al. [37] showed that the synergy of SDS with either alumina (Al_2O_3) or silica (SiO_2) nanoparticles resulted in smaller bubbles, a longer half-life, and greater viscosity. The authors attributed these properties to the accumulation of nanoparticles in the foam lamellae and plateau borders, which led to increased film thickness and elasticity. The positioning of the nanoparticles prevents liquid drainage, film thinning, and bubble coalescence. This analysis was supported by similar recent studies on foams that were stabilized by polyelectrolyte complex nanoparticles with the nonylphenol ethoxylate surfactant Surfonic N120™ [38], and by studies that combined SiO_2 nanoparticles with bis(2-ethylhexyl) sulfosuccinate (AOT) [39], SDS [40], AOS [41,42], cetyl trimethylammonium bromide (CTAB) [43], and ethyl hexadecyl dimethylammonium bromide [44]. A separate study confirmed the improvement in the properties of foams formulated with AOS and mixtures of AOS with guar gum and viscoelastic surfactants (VESs) when nanoparticles are added [45].

Silica nanoparticles are the most commonly studied nanoparticles in the recent literature. Silica is an abundant natural material; for this reason, it is generally assumed that silica nanoparticles are an environmentally friendly additive, even though it is unclear whether this is true (see Section 5). Furthermore, silica nanoparticles often outperform other additives. A few recent studies have compared silica with other materials. Emrani and Nasr-El-Din [46] recently compared the foaming properties of AOS/guar gum solutions containing SiO_2 and iron(III) oxide (Fe_2O_3) nanoparticles,

and found that silica nanoparticles resulted in higher stability. They attributed the poorer performance of Fe_2O_3 nanoparticles to their tendency to aggregate due to their high surface energy. Another study by Manan et al. [47] compared the performance of SiO_2, Al_2O_3, copper(II) oxide (CuO), and titanium dioxide (TiO_2) nanoparticles as additives to AOS. Their study found that alumina nanoparticles resulted in more stable foams that recovered the highest amount of oil after water flooding, with silica nanoparticles being a close second.

One disadvantage of silica nanoparticles is that they have a negatively charged surface, which precludes the tuning of their hydrophobicity [48–50]. In order to control hydrophobicity, a chosen surfactant should have a charge that is opposite to that of the nanoparticle. The negative charge of the silica nanoparticles means that cationic surfactants should be used for this purpose; however, these surfactants are easily trapped in the negatively charged rock surfaces [49]. For this reason, other materials such as boehmite (AlOOH) have been studied. Yang et al. [49] tested SDS foams stabilized with AlOOH nanoparticles, and found that the resulting foam exhibited much better stability at high temperature and in the presence of oil than SDS foams. In a separate study, Yang et al. [51] used foams stabilized by AlOOH nanoparticles combined with sodium cumenesulfonate (SC), and found that the foams were highly stable over a wide electrolyte concentration range, and resulted in improved oil displacement.

Recent studies have also tested other nanoparticle materials for CO_2 EOR. Guo and Aryana [52] studied foams stabilized by different mixtures of SDS, AOS, and lauramidopropyl betaine (LAPB) in combination with nanoclays and silica nanoparticles. Their study found that the combination of a mixture of AOS and LAPB with silica nanoparticles resulted in better foamability and higher stability. However, an AOS/LAPB mixture with nanoclay particles produced a better oil-recovery performance. As another alternative material, Lee et al. [53] explored the use of nanoparticles made by grinding coal fly ash, a waste product of coal power plants. Their study found that due to their negative charge, the fly ash particles could not stabilize CO_2 foams by themselves. However, adding dimethyl trimethylammonium bromide (DTAB), a cationic surfactant, to low-carbon fly ash resulted in stable foams. Nevertheless, a cationic surfactant would typically be adsorbed by the reservoir rocks, making this process inefficient. On the other hand, the study also found that highly carbonaceous fly ash particles combined with turpentine oil did produce stable foams, suggesting that these particles might produce a foam *in situ* due to interactions with the oil in the reservoir.

Several recent studies have tested nanoparticle/surfactant systems with other additives, particularly alkalis, alcohols, and polymers. Adding polymers to nanoparticle/surfactant foams at optimal concentration enhances the foam stability due to steric repulsion between bubbles. However, too much polymer can break the foam due to settling. Alcohols and alkalis also exhibit optimal concentrations for foaming performance [54]. A recent study by Wang et al. [55] used mixtures of the "green" nonionic surfactant APG in combination with SiO_2 nanoparticles and the gemini surfactant $C_{12}C_3C_{12}Br$ to form a stable foam. Although anionic surfactants are known to outperform nonionic surfactants in brine [56], their results suggest a possible line of research in developing "green" foaming blends.

4. Environmental impacts of CO_2 foam leakage

Liu et al. [57] have compiled a thorough analysis of the environmental impacts and risks of CO_2 EOR due to short-term leakage, large-scale leakage, and long-term diffusion or seepage of stored CO_2. Examples of these phenomena are illustrated in Fig. 1 [57].
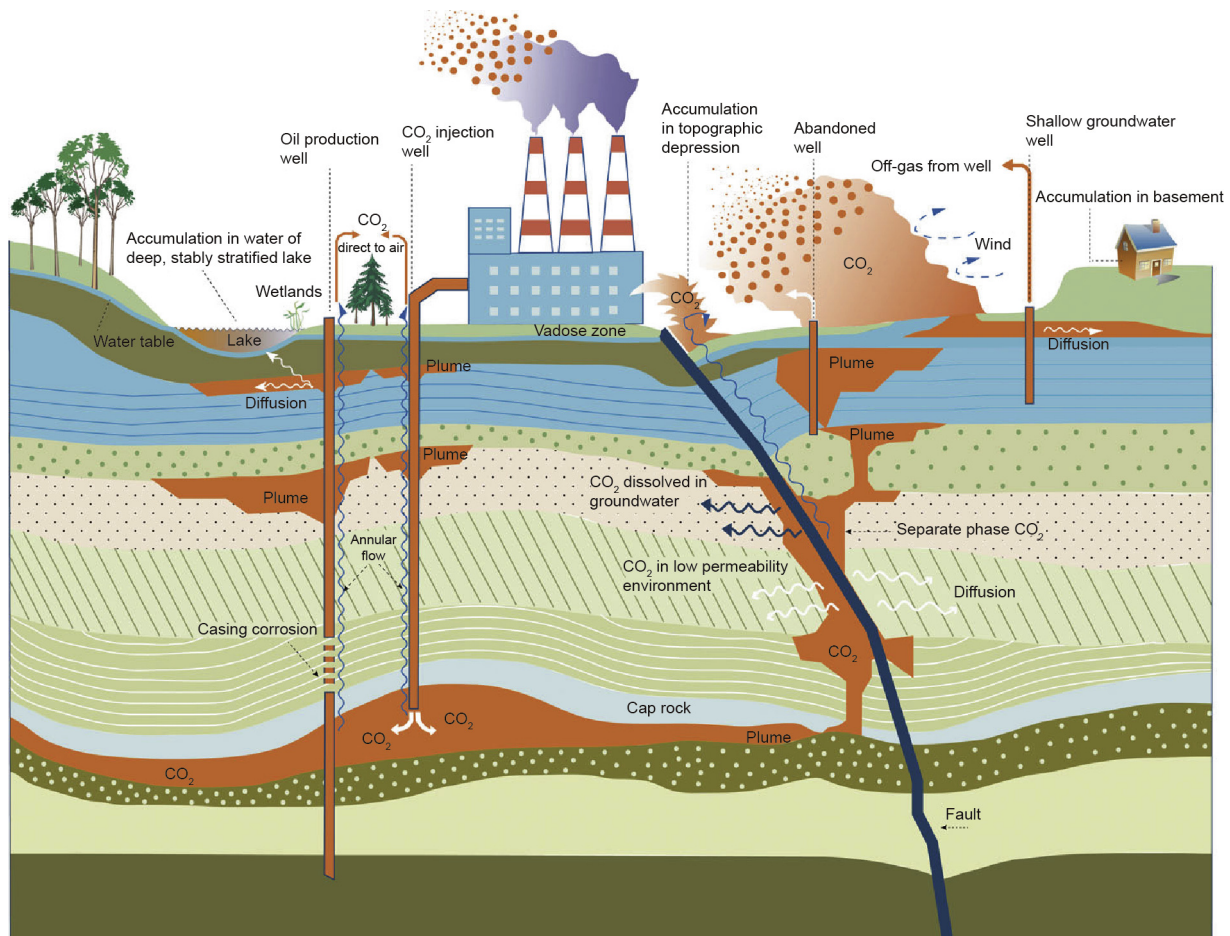
Fig. 1. Mechanisms and impacts of CO_2 leakage from geological sequestration sites [57]. (Copyright 2016 Springer, reproduced with permission)

These processes have direct and indirect impacts on human health and the environment, at both local and global levels. At the local level, the increased CO_2 levels in the vicinity of the leaking reservoir cause changes in the groundwater and soil chemistry, leading to impaired plant health and diminished crop yields [58]. These high CO_2 concentrations can also have a direct impact on human health, with levels above 5%–10% potentially resulting in loss of consciousness and death. At the global level, the release of CO_2 results in increased greenhouse gas levels, thereby diminishing or eliminating the benefits of geological storage [57].

Given the different possible failure scenarios for CO_2 storage and the lack of an empirical knowledge base for evaluating the related risks, it is very difficult to carry out a quantitative risk analysis with high confidence [59]. Developing models for fluids within oil reservoirs is also challenging, as the fluids are complex and their properties within a rock formation may be very different from those of a bulk fluid [60–62]. Several recent case studies have considered potential risks due to gas leakage in individual CO_2 reservoirs, as well as monitoring and remediation strategies. The Zama Lake site in Alberta, Canada, has been the subject of a few such studies [63–65]. This site contains tens of thousands of metric tons of a mixture of carbon dioxide and hydrogen sulfide that has been used for EOR. These sites are typically sealed after the injection process has completed in order to keep the toxic gas deep underground. However, the cement and steel used to seal the wellbore will degrade over time, and this toxic mixture will inevitably leak into the environment, as it is predicted that the mixture will remain unreactive and thus free-flowing [63]. Another area that has recently been studied extensively is the Jingbian Gas Field in Shaanxi Province, China, which houses a major CO_2 EOR demonstration project that has been running since 2012 [66]. The Ordos Basin, where the Jingbian Gas Field is located, is the second-largest sedimentary basin in China, and has a very large potential capacity for CO_2 storage [67,68]. However, even though the Jingbian Gas Field is located in the most geologically stable area of the Ordos Basin, a number of potential risks have been identified: The region has a history of earthquakes and also contains collapsed mine shafts and abandoned boreholes, which could result in CO_2 leakage [67,69]. Therefore, a comprehensive geological and environmental monitoring strategy is essential for the success of the project.

Besides the environmental risk due to CO_2 leakage, there is a potential risk due to the additives used to stabilize the CO_2 foams. Given the recent advances in both surfactant-based and surfactant/nanoparticle-based foaming additives, there is a need for a comprehensive study of the potential environmental impact of these additives. These impacts are discussed in the next section.

5. Environmental impacts of surfactant and nanoparticle leakage

In contrast to the large number of studies on the potential risks of CO_2 leakage, few studies have been performed on the potential risks of foaming agent leakage in the context of CO_2 EOR. When the risks of chemical exposure involve adverse environmental or human health effects (whether acute or chronic), the US EPA classifies that chemical as toxic [70]. In this section, we outline some of

the risks associated with the components used in the previously described studies, in the hope that it will be helpful to guide future studies of CO_2 EOR as a "green" process.

The research reviewed in the present paper examines an assortment of anionic surfactants, as well as a much narrower set of nonionic surfactants (since cationic surfactants are unattractive due to their propensity to adsorb in rock formations, we do not consider them in this discussion). The anionic and nonionic surfactants used in the most recent studies (Sections 2 and 3) are summarized in Table 1. All of the anionic and most of the nonionic surfactants listed have potential toxic effects on the environment, depending on the amount released. For example, alkylphenol ethoxylates, which include some of the anionic and most of the nonionic surfactants discussed in this work, are well known for being endocrine disruptors and for having major deleterious impacts on aquatic organisms [71–73]. Releasing large quantities of these surfactants near bodies of water is very likely to catastrophically impact the aquatic wildlife in those environments.

Anionic surfactants deserve the most attention here, as they are the most effective for CO_2 foams for EOR and are also a cause for great concern in terms of ecological impact. Among the anionic surfactants described in Sections 2 and 3, SDS and AOS are by far the most common. In high concentrations, even common household surfactants such as SDS can have major, widespread environmental impacts [74]. The hazardous effects of SDS on the environment have motivated studies on how to rapidly degrade SDS for wastewater treatment [75,76]. Of the remaining surfactants considered, many are olefin sulfonates, which provoke that the same environmental concerns as AOS. Olefin sulfonates show greater toxicity to aquatic life than alkyl sulfates such as SDS [77]; however, unlike SDS, olefin sulfonates have not been shown to have toxic effects on microorganisms [78]. Similarly, alkyl benzene sulfonates negatively affect aquatic life [79,80]. On the other hand, sulfosuccinates, such as AOT, have been found to be toxic to aquatic microorganisms and harmless to crustaceans [81].

When addressing the degradation of surfactants, however, it is important to indicate whether aerobic or anaerobic conditions are involved. Most reports refer to aerobic conditions; however, in the case of EOR, we are concerned with anaerobic degradation, which is not as well understood. Surfactant biodegradation is dependent on multiple factors [82]: Microorganisms either cause a structural change that eliminates their function as surfactants, or are completely broken down. Because degradation is carried out by microorganisms, the presence of organisms capable of metabolizing a surfactant, as well as appropriate pH, temperature, nutrients, and water content, is necessary. Studies under anaerobic conditions have shown that alkyl and olefin sulfonates will not degrade, while sulfosuccinates are digested [78] and alkyl ester sulfonates and alkyl benzene sulfonates are slowly digested [82]. The difference in biodegradation is thought to be due to the presence of functional groups (i.e., ester, ether, and aromatic groups) that allow anaerobic microorganisms to cleave the sulfonate from the tail group. Although there is some information on the degradation of surfactants under *ideal* anaerobic conditions [83], our understanding of how various environmental conditions relate to the degradation rate is still limited. Most oil reservoirs are unlikely to exhibit ideal degradation conditions; thus, the storage of these compounds in a reservoir with a risk of leakage or seepage can be seen as a significant environmental risk.

Nanoparticle additives also pose environmental risks. Silica nanoparticles have traditionally been regarded as environmentally friendly due to the common natural occurrence of silica. However, the toxicity of silica nanoparticles is poorly understood. Recent studies have found that silica nanoparticles exhibit significant cytotoxicity depending on the particle size and level of exposure [84,85], and *in vivo* experiments have shown that silica nanoparticles can lead to liver [86] and kidney injury [87], among other harmful effects [85]. More studies are needed to understand the potential environmental effects of injecting large quantities of silica nanoparticles underground.

Other nanoparticle systems are equally uncertain regarding their environmental impact. As discussed in Section 4, AlOOH nanoparticles have also shown enhanced performance as foaming additives. However, AlOOH nanoparticles are known to be toxic, depending on the size of their agglomerates [88]. As in the case of silica nanoparticles, a study on the potential impact of releasing large quantities of AlOOH nanoparticles into the environment is necessary in order to outline an effective monitoring and mitigation strategy.

6. Closing remarks

In recent years, there has been an increasing focus on novel technologies for CO_2 EOR, given its special status as an economically feasible process for carbon sequestration. Recent studies have resulted in highly effective foaming additives to enhance stability, resilience, and oil recovery. These additives include nonionic surfactants, nanoparticles, and other additives such as polymers, alcohols, and alkalis. The continued preferential use of anionic

Table 1
Summary of environmental impacts of surfactants used in recent CO_2 foam studies.

Classification	Surfactant	Environmental threat	References
Anionic	Bis(2-ethylhexyl) sulfosuccinate (AOT)	Toxic to microorganisms	[24,39]
	Ammonium alkyl ether sulfate	Toxic to aquatic life	[23]
	Alpha olefin sulfonate (AOS)	Toxic to aquatic life	[22,23,25,28,29,42,45–47,52]
	Sodium olefin sulfonate	Toxic to aquatic life	[23,50]
	FomaxII	Unknown	[22]
	FomaxVII	Unknown	[22]
	Nonylphenol ethoxylate sulfonate (NPES)	Toxic to aquatic life	[21,31]
	Sodium dodecyl benzene sulfonate (SDBS)	Toxic to aquatic life	[26,31]
	Sodium dodecyl sulfate (SDS)	Toxic to aquatic life and microorganisms	[20,25,31,33,37,40,51,52,54]
	Sodium dodecyl sulfonate	Toxic to aquatic life	[31]
	UTP-foam	Unknown	[22]
	XP-0010™	Unknown	[23]
Nonionic	Alkyl polyglycosides (APG)	Nontoxic	[25,31,55]
	N70K-T	Unknown	[24,25]
	Neodol 25-7™	Toxic to aquatic life	[23]
	Surfonic N120™	Toxic to aquatic life	[38]
	Triton X-100™	Toxic to aquatic life	[25,28–30]
	Tween 80	Nontoxic	[33,54]

surfactants that are known to be toxic may no longer be necessary, given recent advances in using additives, although studies regarding their toxicity are needed.

Studies from recent years have resulted in a large knowledge base on the use of different types of additives to improve foams for CO_2 EOR. Given this knowledge, and considering the potential environmental risk of a major leak from a sealed CO_2 reservoir, we believe that it is imperative to focus on characterizing and developing less toxic, biodegradable anionic surfactants and foaming additives, considering the particular challenges of biodegradation under reservoir conditions.

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Compliance with ethics guidelines

Jennifer A. Clark and Erik E. Santiso declare that they have no conflict of interest or financial conflicts to disclose.

References

[1] Moritis G. CO_2 miscible, steam dominate enhanced oil recovery processes. Oil Gas J Tulsa 2010;108(14):36–40.
[2] Enick RM, Olsen DK. Mobility and conformance control for carbon dioxide enhanced oil recovery (CO_2-EOR) via thickeners, foams, and gels—a detailed literature review of 40 years of research. Report. Pittsburgh: National Energy Technology Laboratory, US Department of Energy; 2012.
[3] Duda JR, Kuuskraa V, Godec M, Van Leeuwen T. Modeling exercises assess US CO_2-EOR potential. Oil Gas J Tulsa 2010;108(13):52–5.
[4] Bernard GC, Holm LW, Harvey CP. Use of surfactant to reduce CO_2 mobility in oil displacement. SPE J 1980;20(4):281–92.
[5] Eastoe J, Hatzopoulos MH, Tabor R. Microemulsions. In: Tadros T, editor. Encyclopedia of colloid and interface science. Berlin: Springer-Verlag; 2013. p. 688–728.
[6] Li RF, Yan W, Liu S, Hirasaki GJ, Miller CA. Foam mobility control for surfactant enhanced oil recovery. SPE J 2010;15(4):928–48.
[7] Hirasaki GJ, Miller CA, Puerto M. Recent advances in surfactant EOR. SPE J 2011;16(4):889–907.
[8] Xing D, Wei B, McLendon W, Enick RM, McNulty S, Trickett K, et al. CO_2-soluble, nonionic, water-soluble surfactants that stabilize CO_2-in-brine foams. SPE J 2012;17(4):1172–85.
[9] Cummings S, Enick R, Rogers S, Heenan R, Eastoe J. Amphiphiles for supercritical CO_2. Biochimie 2012;94(1):94–100.
[10] Sagir M, Tan IM, Mushtaq M, Talebian SH. FAWAG using CO_2-philic surfactants for CO_2 mobility control for enhanced oil recovery applications. In: Proceedings of the SPE Saudi Arabia Section Technical Symposium and Exhibition; 2014 Apr 21–24; Al-Khobar, Saudi Arabia. Richardson: Society of Petroleum Engineers; 2014.
[11] Basics of green chemistry [Internet]. Washington, DC: Green Chemistry Program, US Environmental Protection Agency; [cited 2017 Nov 4]. Available from: https://www.epa.gov/greenchemistry/basics-green-chemistry.
[12] Iribarren D, Petrakopoulou F, Dufour J. Environmental and thermodynamic evaluation of CO_2 capture, transport and storage with and without enhanced resource recovery. Energy 2013;50:477–85.
[13] Aarra MG, Skauge A, Solbakken J, Ormehaug PA. Properties of N_2- and CO_2-foams as a function of pressure. J Petrol Sci Eng 2014;116:72–80.
[14] Perera M, Gamage R, Rathnaweera T, Ranathunga A, Koay A, Choi X. A review of CO_2-enhanced oil recovery with a simulated sensitivity analysis. Energies 2016;9(12):481.
[15] Talebian SH, Masoudi R, Tan IM, Zitha PLJ. Foam assisted CO_2-EOR: a review of concept, challenges, and future prospects. J Petrol Sci Eng 2014;120:202–15.
[16] Shamsijazeyi H, Miller CA, Wong MS, Tour JM, Verduzco R. Polymer-coated nanoparticles for enhanced oil recovery. J Appl Polym Sci 2014;131(15):4401–4.
[17] Barnes JR, Regalado DP, Doll MJ, King TE, Pretzer LE, Semple TC. Essentials of upscaling surfactants for EOR field projects. In: Proceedings of the Twentieth SPE Improved Oil Recovery Conference; 2016 Apr 11–13; Tulsa, OK, USA. Red Hook: Curran Associates, Inc.; 2016. p. 681–98.
[18] Li D, Ren B, Zhang L, Ezekiel J, Ren S, Feng Y. CO_2-sensitive foams for mobility control and channeling blocking in enhanced WAG process. Chem Eng Res Des 2015;102:234–43.
[19] Zhang YM, Chu ZL, Dreiss CA, Wang YJ, Fei CH, Feng YJ. Smart wormlike micelles switched by CO_2 and air. Soft Matter 2013;9(27):6217–21.
[20] Zhang YM, Feng YJ, Wang YJ, Li XL. CO_2-switchable viscoelastic fluids based on a pseudogemini surfactant. Langmuir 2013;29(13):4187–92.
[21] Sagir M, Tan IM, Mushtaq M, Pervaiz M, Tahir MS, Shahzad K. CO_2 mobility control using CO_2-philic surfactant for enhanced oil recovery. J Pet Explor Prod Technol 2016;6(3):401–7.
[22] Talebian SH, Tan IM, Sagir M, Muhammad M. Static and dynamic foam/oil interactions: potential of CO_2-philic surfactants as mobility control agents. J Petrol Sci Eng 2015;135:118–26.
[23] Farzaneh SA, Sohrabi M. Experimental investigation of CO_2-foam stability improvement by alkaline in the presence of crude oil. Chem Eng Res Des 2015;94:375–89.
[24] Xu X, Saeedi A, Liu K. An experimental study of combined foam/surfactant polymer (SP) flooding for carbon dioxide-enhanced oil recovery (CO_2-EOR). J Petrol Sci Eng 2017;149:603–11.
[25] Xu X, Saeedi A, Liu K. Experimental study on a novel foaming formula for CO_2 foam flooding. J Energy Resour Technol 2017;139(2):022902.
[26] Lv M, Wang S. Studies on CO_2 foam stability and the influence of polymer on CO_2 foam properties. Int J Oil Gas Coal Technol 2015;10:343–58.
[27] Lv W, Li Y, Li Y, Zhang S, Deng QH, Yang Y, et al. Ultra-stable aqueous foam stabilized by water-soluble alkyl acrylate crosspolymer. Colloids Surf Physicochem Eng Asp 2014;457:189–95.
[28] Memon MK, Elraies KA, Al-Mossawy MI. Impact of new foam surfactant blend with water alternating gas injection on residual oil recovery. J Pet Explor Prod Technol 2017;7(3):843–51.
[29] AttarHamed F, Zoveidavianpoor M. The foaming behavior and synergistic effect in aqueous CO_2 foam by in situ physisorption of alpha olefin sulfonate and triton X-100 surfactants and their mixture. Petrol Sci Technol 2014;32(19):2376–86.
[30] Wang C, Li HA. Stability and mobility of foam generated by gas-solvent/surfactant mixtures under reservoir conditions. J Nat Gas Sci Eng 2016;34:366–75.
[31] Wang Y, Zhang Y, Liu Y, Zhang L, Ren S, Lu J, et al. The stability study of CO_2 foams at high pressure and high temperature. J Petrol Sci Eng 2017;154:234–43.
[32] Dey S, Malik S, Ghosh A, Saha R, Saha B. A review on natural surfactants. RSC Adv 2015;5(81):65757–67.
[33] Yuan Q, Wang XH, Dandekar A, Sun CY, Li QP, Ma ZW, et al. Replacement of methane from hydrates in porous sediments with CO_2-in-water emulsions. Ind Eng Chem Res 2014;53(31):12476–84.
[34] Tang J, Quinlan PJ, Tam KC. Stimuli-responsive Pickering emulsions: recent advances and potential applications. Soft Matter 2015;11(18):3512–29.
[35] Liu N. Nanoparticle-stabilized CO_2 foam for CO_2 EOR application. Final report. Pittsburgh: National Energy Technology Laboratory, US Department of Energy; 2015 Apr.
[36] Sun X, Zhang Y, Chen G, Gai Z. Application of nanoparticles in enhanced oil recovery: a critical review of recent progress. Energies 2017;10(3):345.
[37] Yekeen N, Idris AK, Manan MA, Samin AM, Risal AR, Kun TX. Bulk and bubble-scale experimental studies of influence of nanoparticles on foam stability. Chin J Chem Eng 2017;25(3):347–57.
[38] Kalyanaraman N, Arnold C, Gupta A, Tsau JS, Ghahfarokhi RB. Stability improvement of CO_2 foam for enhanced oil-recovery applications using polyelectrolytes and polyelectrolyte complex nanoparticles. J Appl Polym Sci 2017;134(6):44491.
[39] Zhang C, Li Z, Sun Q, Wang P, Wang S, Liu W. CO_2 foam properties and the stabilizing mechanism of sodium bis(2-ethylhexyl) sulfosuccinate and hydrophobic nanoparticle mixtures. Soft Matter 2016;12(3):946–56.
[40] Li S, Li Z, Wang P. Experimental study of the stabilization of CO_2 foam by sodium dodecyl sulfate and hydrophobic nanoparticles. Ind Eng Chem Res 2016;55(5):1243–53.
[41] Rognmo AU, Horjen H, Fernø M. Nanotechnology for improved CO_2 utilization in CCS: laboratory study of CO_2-foam flow and silica nanoparticle retention in porous media. Int J Greenhouse Gas Control 2017;64:113–8.
[42] AttarHamed F, Zoveidavianpoor M, Jalilavi M. The incorporation of silica nanoparticle and alpha olefin sulphonate in aqueous CO_2 foam: investigation of foaming behavior and synergistic effect. Petrol Sci Technol 2014;32(21):2549–58.
[43] Li S, Qiao C, Li Z, Wanambwa S. Properties of carbon dioxide foam stabilized by hydrophilic nanoparticles and hexadecyltrimethylammonium bromide. Energy Fuels 2017;31(2):1478–88.
[44] Farhadi H, Riahi S, Ayatollahi S, Ahmadi H. Experimental study of nanoparticle-surfactant-stabilized CO_2 foam: stability and mobility control. Chem Eng Res Des 2016;111:449–60.
[45] Emrani AS, Nasr-El-Din HA. Stabilizing CO_2 foam by use of nanoparticles. SPE J 2017;22(2):494–504.
[46] Emrani AS, Nasr-El-Din HA. An experimental study of nanoparticle-polymer-stabilized CO_2 foam. Colloids Surf Physicochem Eng Asp 2017;524:17–27.
[47] Manan MA, Farad S, Piroozian A, Esmail MJA. Effects of nanoparticle types on carbon dioxide foam flooding in enhanced oil recovery. Petrol Sci Technol 2015;33(12):1286–94.
[48] Dong X, Xu J, Cao C, Sun D, Jiang X. Aqueous foam stabilized by hydrophobically modified silica particles and liquid paraffin droplets. Colloids Surf Physicochem Eng Asp 2010;353(2–3):181–8.
[49] Yang W, Wang T, Fan Z, Miao Q, Deng Z, Zhu Y. Foams stabilized by in situ-modified nanoparticles and anionic surfactants for enhanced oil recovery. Energy Fuels 2017;31(5):4721–30.

[50] Singh R, Mohanty KK. Synergy between nanoparticles and surfactants in stabilizing foams for oil recovery. Energy Fuels 2015;29(2):467–79.

[51] Yang W, Wang T, Fan Z. Highly stable foam stabilized by alumina nanoparticles for EOR: effects of sodium cumenesulfonate and electrolyte concentrations. Energy Fuels 2017;31(9):9016–25.

[52] Guo F, Aryana S. An experimental investigation of nanoparticle-stabilized CO_2 foam used in enhanced oil recovery. Fuel 2016;186:430–42.

[53] Lee D, Cho H, Lee J, Huh C, Mohanty K. Fly ash nanoparticles as a CO_2 foam stabilizer. Powder Technol 2015;283:77–84.

[54] Kumar S, Mandal A. Investigation on stabilization of CO_2 foam by ionic and nonionic surfactants in presence of different additives for application in enhanced oil recovery. Appl Surf Sci 2017;420:9–20.

[55] Wang J, Xue G, Tian B, Li S, Chen K, Wang D, et al. Interaction between surfactants and SiO_2 nanoparticles in multiphase foam and its plugging ability. Energy Fuels 2017;31(1):408–17.

[56] Al-Anssari S, Arif M, Wang S, Barifcani A, Iglauer S. Stabilising nanofluids in saline environments. J Colloid Interface Sci 2017;508:222–9.

[57] Liu LC, Li Q, Zhang JT, Cao D. Toward a framework of environmental risk management for CO_2 geological storage in China: gaps and suggestions for future regulations. Mitig Adapt Strategies Global Change 2016;21(2):191–207.

[58] Xue L, Ma J, Wang S, Li Q, Ma J, Yu H, et al. Effects of CO_2 leakage from CCS on the physiological characteristics of C4 crops. Energy Procedia 2014;63:3209–14.

[59] Koornneef J, Ramírez A, Turkenburg W, Faaij A. The environmental impact and risk assessment of CO_2 capture, transport and storage—an evaluation of the knowledge base using the DPSIR framework. Energy Procedia 2011;4:2293–300.

[60] Hamoodi AN, Abed AF, Firoozabadi A. Compositional modelling of two-phase hydrocarbon reservoirs. J Can Pet Technol 2001;40(4):49–60.

[61] Hoteit H, Santiso E, Firoozabadi A. An efficient and robust algorithm for the calculation of gas-liquid critical point of multicomponent petroleum fluids. Fluid Phase Equilib 2006;241(1–2):186–95.

[62] Santiso E, Firoozabadi A. Curvature dependency of surface tension in multicomponent systems. AIChE J 2006;52(1):311–22.

[63] LeNeveu DM. Potential for environmental impact due to acid gas leakage from wellbores at EOR injection sites near Zama Lake, Alberta. Greenhouse Gases Sci Technol 2012;2(2):99–114.

[64] Smith SA, Sorensen J, Steadman E, Harju JA. Acid gas injection and monitoring at the Zama Oil Field in Alberta, Canada: a case study in demonstration-scale carbon dioxide sequestration. Energy Procedia 2009;1(1):1981–8.

[65] Smith SA, Sorensen JA, Steadman EN, Harju JA, Ryan D. Zama acid gas EOR, CO_2 sequestration, and monitoring project. Energy Procedia 2011;4:3957–64.

[66] Cai B, Li Q, Liu G, Liu L, Jin T, Shi H. Environmental concern-based site screening of carbon dioxide geological storage in China. Sci Rep 2017;7(1):7598.

[67] Ma J, Wang X, Gao R, Zhang X, Wei Y, Wang Z, et al. Monitoring the safety of CO_2 sequestration in Jingbian Field, China. Energy Procedia 2013;37:3469–78.

[68] Tang Y, Yang R, Bian X. A review of sequestration projects and application in China. Sci World J 2014;2014(6):381854.

[69] Hawkes CD, McLellan PJ, Zimmer U, Bachu S. Geomechanical factors affecting geological storage of CO_2 in depleted oil and gas reservoirs. J Can Pet Technol 2005;44(10):52–61.

[70] Toxics Release Inventory (TRI) Program: TRI-listed chemicals [Internet]. Washington, DC: TRI Program, US Environmental Protection Agency; [cited 2017 Nov 4]. Available from: https://www.epa.gov/toxics-release-inventory-tri-program/tri-listed-chemicals.

[71] Asimakopoulos AG, Thomaidis NS, Koupparis MA. Recent trends in biomonitoring of bisphenol A, 4-t-octylphenol, and 4-nonylphenol. Toxicol Lett 2012;210(2):141–54.

[72] Soares A, Guieysse B, Jefferson B, Cartmell E, Lester JN. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environ Int 2008;34(7):1033–49.

[73] Lu Z, Gan J. Isomer-specific biodegradation of nonylphenol in river sediments and structure-biodegradability relationship. Environ Sci Technol 2014;48(2):1008–14.

[74] Rebello S, Asok AK, Mundayoor S, Jisha MS. Surfactants: toxicity, remediation and green surfactants. Environ Chem Lett 2014;12(2):275–87.

[75] Ambily PS, Rebello S, Jayachandran K, Jisha MS. A novel three-stage bioreactor for the effective detoxification of sodium dodecyl sulphate from wastewater. Water Sci Technol 2017;76(8):2167–76.

[76] Paulo AMS, Plugge CM, García-Encina PA, Stams AJM. Anaerobic degradation of sodium dodecyl sulfate (SDS) by denitrifying bacteria. Int Biodeterior Biodegrad 2013;84(5):14–20.

[77] Könnecker G, Regelmann J, Belanger S, Gamon K, Sedlak R. Environmental properties and aquatic hazard assessment of anionic surfactants: physico-chemical, environmental fate and ecotoxicity properties. Ecotoxicol Environ Saf 2011;74(6):1445–60.

[78] García MT, Campos E, Marsal A, Ribosa I. Biodegradability and toxicity of sulphonate-based surfactants in aerobic and anaerobic aquatic environments. Water Res 2009;43(2):295–302.

[79] Bressan M, Marin MG, Brunetti R. Effect of linear alkylbenzene sulphonate (LAS) on skeletal development of sea urchin embryos (*Paracentrotus lividus* Lmk). Water Res 1991;25(5):613–6.

[80] Mungray AK, Kumar P. Fate of linear alkylbenzene sulfonates in the environment: a review. Int Biodeterior Biodegrad 2009;63(8):981–7.

[81] Rosal R, Rodea-Palomares I, Boltes K, Fernández-Piñas F, Leganés F, Petre A. Ecotoxicological assessment of surfactants in the aquatic environment: combined toxicity of docusate sodium with chlorinated pollutants. Chemosphere 2010;81(2):288–93.

[82] Merrettig-Bruns U, Jelen E. Anaerobic biodegradation of detergent surfactants. Material (Basel) 2009;2(1):181–206.

[83] Olkowska E, Polkowska Ż, Namieśnik J. Analytics of surfactants in the environment: problems and challenges. Chem Rev 2011;111(9):5667–700.

[84] Kim IY, Joachim E, Choi H, Kim K. Toxicity of silica nanoparticles depends on size, dose, and cell type. Nanomedicine (Lond) 2015;11(6):1407–16.

[85] Murugadoss S, Lison D, Godderis L, Van Den Brule S, Mast J, Brassinne F, et al. Toxicology of silica nanoparticles: an update. Arch Toxicol 2017;91(9):2967–3010.

[86] Chen Q, Xue Y, Sun J. Kupffer cell-mediated hepatic injury induced by silica nanoparticles *in vitro* and *in vivo*. Int J Nanomed 2013;8:1129–40.

[87] Chen X, Wang Z, Zhou J, Fu X, Liang J, Qiu Y, et al. Renal interstitial fibrosis induced by high-dose mesoporous silica nanoparticles via the NF-κB signaling pathway. Int J Nanomed 2014;10:1–22.

[88] Forest V, Pailleux M, Pourchez J, Boudard D, Tomatis M, Fubini B, et al. Toxicity of boehmite nanoparticles: impact of the ultrafine fraction and of the agglomerates size on cytotoxicity and pro-inflammatory response. Inhal Toxicol 2014;26(9):545–53.