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Article

Graphene Oxide as Foam Stabilizing Agent for CO_2 EOR

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Abstract: Graphene oxide (GO), nanographene oxide (nGO) and partially reduced graphene oxide (rGO) have been studied as possible foam stabilizing agents for CO_2 based enhanced oil recovery (EOR). GO was able to stabilize CO_2/synthetic sea water foams. rGO was not able to stabilize foams likely due to the high reduction degree of the material. Particle size had a strong influence on foamability and stability. GO hydrophilicity increased as the particle size decreased and no foams were created when particle size was below 1 μm (nGO). GO brine dispersions showed immediate gel formation, which improved foam stability. Particle growth due to layer stacking was also observed. This mechanism was detrimental for foam formation and stabilization. nGO dispersed in synthetic sea water rapidly formed hydrogels and was not filterable. This work indicates that the particles studied are not suitable for CO_2 EOR purposes.

Keywords: EOR, Graphene Oxide, CO_2 foam, Aquifer Storage, Mobility Control.

1. Introduction

CO_2-based methods for enhanced oil recovery (EOR) in water flooded reservoirs faces various technical challenges. The low density of CO_2 compared to water causes CO_2 migration towards upper zones impairs oil recovery in the lower zones of the reservoir. The low CO_2 viscosity leads to viscous fingering and excessive flow in high permeability layers. The net effect can be early CO_2 breakthrough, reduced sweep efficiency and low oil recovery. Counteracting these effects can be achieved by decreasing the CO_2 mobility, either by adding thickeners into CO_2 or dispersing it into brine (CO_2 foam) [1-4].

Direct thickeners CO_2 require molecules that are CO_2 soluble and have groups that interact giving the increased viscosity. Efforts to develop thickeners have been ongoing through the last decades. Up to now the best results have been obtained with a fluoroacrylate-styrene copolymeric thickener that at typical reservoir conditions is able to increase the CO_2 viscosity by the order of ten using low concentrations (< 1 wt. %) [1]. However, due to costs and environmental concerns these types of additives are unlikely to have practical application.

The apparent viscosity of CO_2 dispersed into foams may be very high, depending on the type of surfactant used. One potential problem is that many foams are sensitive to the presence of oil giving destabilisation through several mechanisms including spreading and entering phenomena [5-7]. During miscible CO_2 flooding oil sensitivity may be an advantage as foam formation is desired where the oil already has been displaced, diverting the CO_2 into oil containing parts of the reservoir. However, also minute amounts of oil remaining after miscible flooding may have detrimental effects on foam propagation [8].

CO_2 foams can also be stabilized by nanoparticles. Nanoparticles adsorb strongly at interfaces which contribute to a higher stability. However, the mixing energy required to adsorb at interfaces

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is larger than traditional surfactant stabilized systems. This is an important disadvantage for oil recovery [9-12]. Typically, oil field flow velocities do not exceed a few feet/day which results in low mixing energy. It may therefore be difficult to utilise nanoparticle stabilized foams under normal process conditions.

The use of binary mixtures of surfactant and nanoparticles may improve foamability at low flooding rates. Singh *et al.* [13] showed that a mixture of anionic surfactant and fly ash could reduce CO_2 mobility more than anionic surfactant alone. Cationic surfactant had the opposite effect, however. Manan *et al*. [14] demonstrated that mixtures of surfactant and different types of nanoparticles improved oil recovery during CO_2 flooding compared to only surfactant, the improvement depended on type of particles used.

Patel *et al*. [15] studied oil-in-brine emulsion stability of silica nanoparticles in presence of sodium dodecyl sulfate. The presence of surfactant allowed to increase suspension stability by diminishing particle flocculation. Even though they observed that nanoparticles were more effective for stabilizing oil emulsions, binary mixtures of particles and surfactant were detrimental for emulsion stability compared to only nanoparticle-stabilized emulsions. These observations are consistent with the competitive adsorption conclusion of Pichot *et al*. [16].

A binary system with surfactant and nanoparticles will be vulnerable to separation of the constituents during transport in porous media and beneficial system properties may thus be lost. Ideally the foam stabilising agent should be uniform to avoid loss of performance. To find foam stabilising agents with a uniform composition having the desired properties (sufficient mobility reduction, desired level of oil sensitivity, low loss, moderate cost, etc.) remains a challenge.

Graphene Oxide (GO) is a relatively new material which is being widely studied due to its characteristics and its relevance to a wide range of fields, such as energy materials, biosensors, catalysis, and biomedicine [17-19]. GO particles have shown to be surface active with a size-depending amphiphilicity and they have been reported to create very stable emulsions with organic solvents [20]. The higher hydrophilicity of smaller particles is attributed to a higher density of -COOH on its edges and epoxy groups on its surface [21]. Having all this under consideration, GO amphiphilicity can be tuned by variations on its size [21] or by partially reducing the particles [22].

Recently, Liu *et al*. [22] have reported for the first time that partially reduced graphene oxide (rGO) can efficiently stabilize CO_2 in water. Foam stability was explained by the large surface area of GO, which diminished contact between CO_2 and water. Moreover, Liu *et al.* [23] demonstrated that GO can be an effective demulsifier for heavy oil-in-water emulsions. This effect was attributed to the strong interactions between the GO nanosheets and the molecules of asphaltenes and resins.

GO is a candidate for application within the oil industry. However, studies for its applications in EOR has up to now not been published. In this work we have studied the possible use of GO/rGO particles as foam stabilizing agents for CO_2 EOR.

In this article dispersions of aqueous solutions and CO_2 is referred as foams whereas dispersions of aqueous solutions and organic solvents are named emulsions.

2. Experimental

2.1. Materials

GO and rGO materials were supplied by Graphenea S.A., San Sebastián, Spain. GO was delivered in a water suspension with a total concentration of 4 mg/ml. The particle size was polydisperse, ranging from 4 to 30 µm. GO suspensions with smaller particle size (nGO) were also provided by Graphenea S.A. The particle sizes of the latter suspension were determined using a Zetasizer Nano ZS (Malvern Instruments Ltd). rGO was obtained in solid powder form. The particle size of rGO ranged from 260 to 295 nm as specified by the provider. The elemental composition of both materials was also obtained from the provider and is described in **Table 1**. The synthetic sea water (SSW) composition used for all experiments is shown in

Table 2.

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Table 1. Elemental composition for GO and rGO (from Graphenea S.A.).

	GO [%]	**rGO [%]**
Carbon	49-56	77-87
Hydrogen	0-1	0-1
Nitrogen	0-1	0-1
Sulphur	2-4	0
Oxygen	41-50	13-22

Table 2. Composition of synthetic sea water.

Salt	**Concentration [g/L]**
NaCl	23.612
$CaCl_2 \cdot 2H_2O$	1.911
$MgCl_2 \cdot 6H_2O$	9.149
KCl	0.746
Na_2SO_4	3.407

The organic solvents used for the initial stability tests were: toluene, obtained from MERK (99.5 %), n-hexane, supplied by VWR (99 %) and n-decane from MERK (99 %).

2.2. *Methods*

2.2.1. Bottle test

The bottle tests were carried out with a volume fraction of 50 % of each phase (6 ml of total volume), SSW and organic solvents. The particle concentrations used were 1 mg/ml and 0.5 mg/ml of GO in the SSW. The mixture was shaken by hand vigorously for 10 seconds and placed in a graduated glass test tube where the volumes of each phase were read.

2.2.2. Phase equilibria studies

An internally stirred windowed high-pressure, high-temperature pVT-cell allowing visual observation along the whole volume of the cell was used for the measurements. The cell was placed inside a temperature-controlled heating cabinet. Equal volumes of dense CO_2 and aqueous solutions were injected into the cell by using high-pressure pumps and the pressure was adjusted to the initial test-pressure. The total test volume was approximately 60 ml. The pressure varied typpically less than 2% during the tests.

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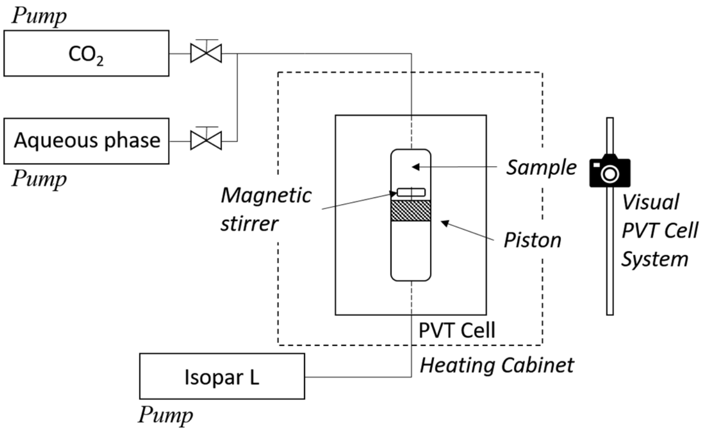

Figure 1. Schematic representation of the pVT Cell used in the experiments.

The foams were created using a magnetic stirrer located inside the cell. The system was stirred for one minute. During stirring, the cell was tilted 180 degrees vertically one time and returned to its original position for favouring phase contact. After the stirring stopped the phase heights (CO_2, foam, SSW) were determined over time using a cathetometer.

3. Results and discussion

3.1. Emulsion stability

Initial tests with organic solvents were carried out just to observe the ability of GO to stabilize organic solvent/water emulsions. **Figure 2** shows both separation profiles, oil phase/emulsion and emulsion/aqueous phase, for each system with a concentration of 1 mg/ml of GO in the aqueous phase.

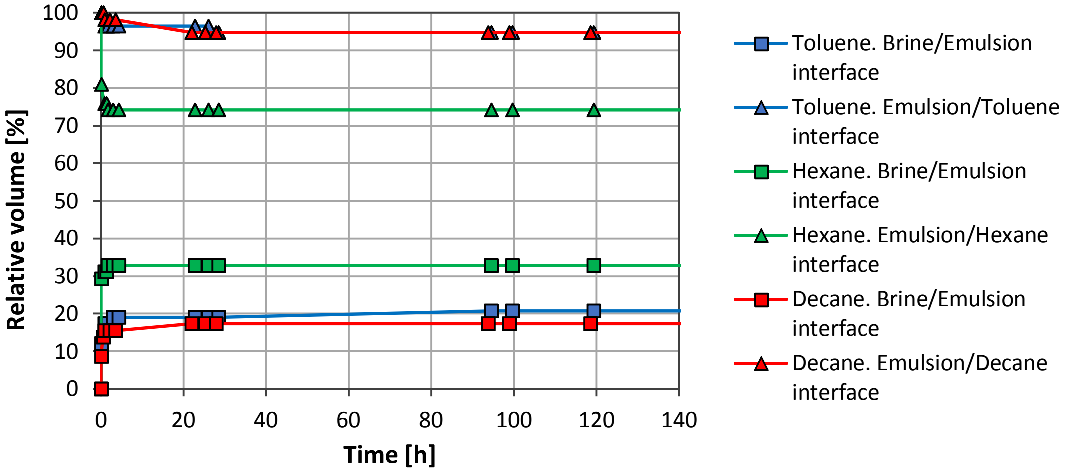

Figure 2. Emulsion stability for SSW/solvent systems. The GO concentration used was 1.0 mg/ml in the aqueous phase.

All systems showed good stability and, after the separation observed during the first minutes, the emulsions remained stable for weeks. Toluene and n-decane had a similar emulsified volume, while hexane showed a lower emulsion volume (~ 41 vol. %).

The samles were immersed in a water bath to study the temperature effect on emulsion stability at 30 °C, 50 °C, and 80 °C. No differences were observed between room temperature, 30 °C, and 50

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°C. However, at 80 °C larger droplets of solvent were observed trapped inside the emulsion phase and there was a slight solvent phase volume increase.

The effect of the particle concentration was also studied using concentrations ranging from 0.1 to 1.0 mg/ml. **Figure 3** shows results for 0.5 mg/ml and 0.3 mg/ml. The stability for 0.7 mg/ml and 0.5 mg/ml was as for 1.0 mg/ml. However, there was a drop in the stability when the concentration was reduced from 0.5 to 0.3 mg/ml. The results obtained with 0.1 mg/ml were the same as the results obtained with 0.3 mg/ml.

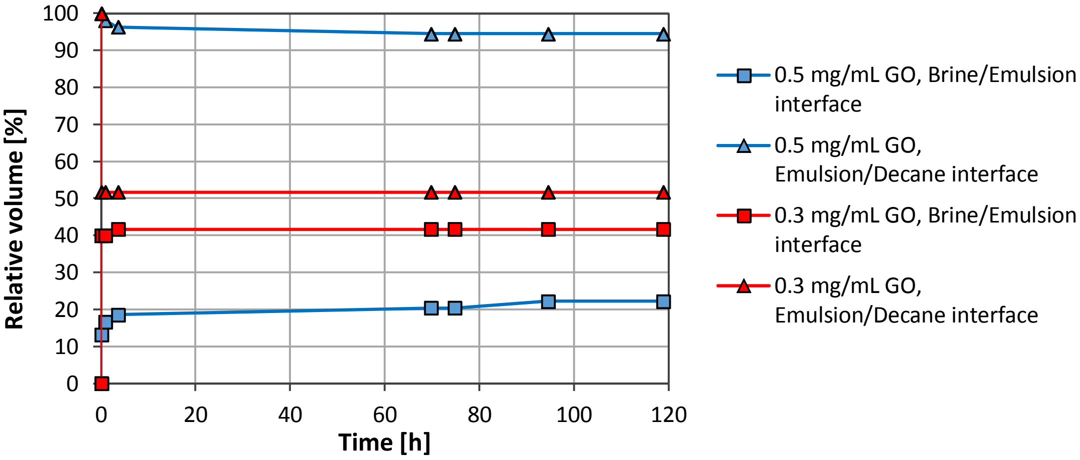

Figure 3. Effect of particle concentration on emulsion stability. N-decane was used as the oil phase.

3.2. *Brine/CO₂ Systems*

3.2.1. Graphene Oxide (GO)

GO-stabilized CO_2 foams were studied using the pVT cell. 30 ml of CO_2 were first charged into the cell. The pressure and temperature were stabilized. Then, 30 ml of GO suspension in SSW (1 mg/ml) were injected into the cell, giving a total volume of 60 ml at the desired conditions. The system was dispersed by stirring for one minute. After the stirring was stopped, the brine and CO_2 heights were measured. Then, 24 h after charging the cell, the same system was re-stirred using the same procedure and the interphase heights were measured again. This process was repeated also 48 h after the cell charge. Hereinafter, the time specified will always refer to the cell charging time.

Figure 4 describes the aqueous phase - foam interface at 0 h, at 24 h, and at 48 h, as a function of time. The pressure and the temperature were 78 bar and 21 °C, respectively. The CO_2-foam interface is not shown since there was not CO_2 phase segregation. The foam initially observed in the cell was totally opaque and occupied the 100 vol. % of the cell. After 3 minutes, the appearance of a clear aqueous phase in the bottom of the cell was observed. This phase increased up to 34 vol. % after 40 minutes, then the aqueous phase volume became constant. In the experiment performed 24 hours later, the water profile flatted out approximately after 40 minutes and was reduced to 22 vol. %. After 48 hours, the amount of free water separated was even lower, only 14 vol. %.

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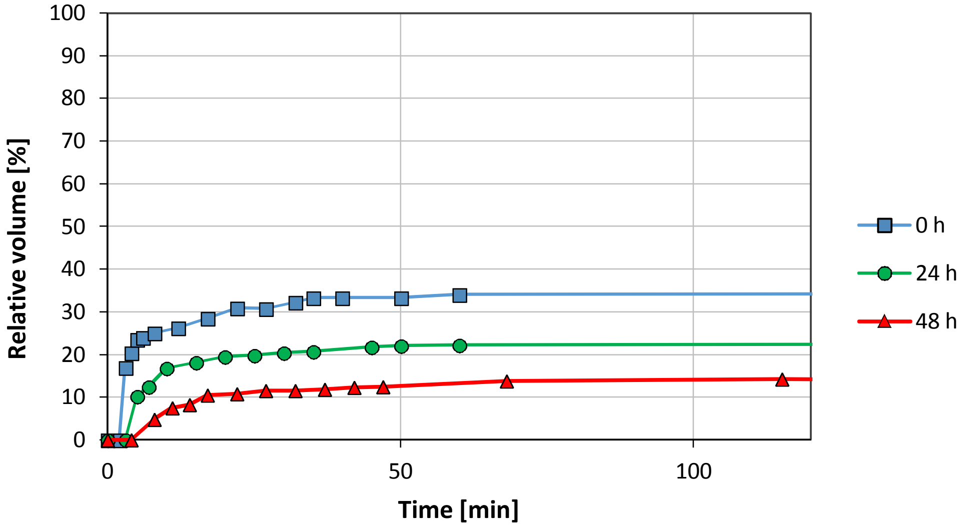

Figure 4. Effect of ageing on foam stability for a concentration of 1 mg/ml of GO in SSW (78 bar, 21°C).

After 72 hours, the sample was again re-stirred and a significant stability reduction was observed. It was not possible to disperse the particles as effectively as observed during the previous days. Just a few minutes after stirring stopped, aqueous and CO_2 phases were separated with a considerable foam phase reduction. Thus, the system stability showed a time-depending effect. Phase volumes were not recorded, however.

The cell was next charged with new fluids at the same conditions as before. After two days ageing (when the previous experiment had shown maximum stability), the temperature was increased from room temperature to 50 °C at constant pressure, 78 bar. Due to the heating, the CO_2 phase expanded exceeding the 50 vol. % as can be seen in **Figure 5**. Shortly after, the pressure was increased to 152 bar at constant temperature.

Increased temperature was detrimental to foam stability as observed from comparing **Error! Reference source not found.** at 48 h and **Figure 5** (78 bar). After 48 h at room temperature the system remained stable with 14 vol. % of water separated and the foam phase occupied 86 vol.%. At 50 °C only 16 vol. % of foam phase remained after 20 minutes.

The pressure increase improved the foam stability. Water did not segregate, and the foam phase stabilised at 60 vol. %.

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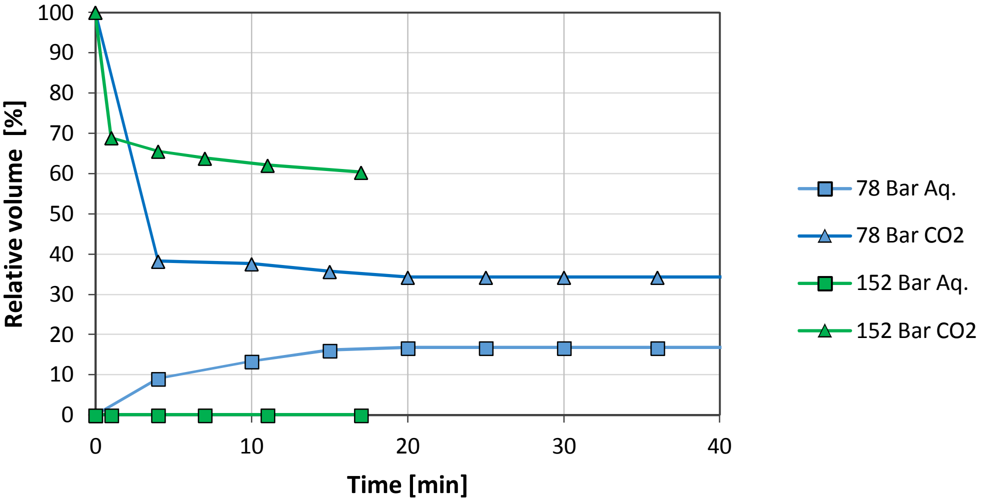

Figure 5. Effect of pressure on foam stability (1 mg/ml GO in SSW, 50 °C). The system had been two days inside the pVT cell prior to the tests.

The time-dependent foam stability was studied further using a lower concentration of particles. The cell was filled with 50 vol. % of each phase at a particle concentration of 0.5 mg/ml at 153 bar. The foam stability was measured after stirring once the sample was injected, after 5 days, after 11 days and 11 days at 226 bar (the system was re-stirred each time).

The results are shown in **Figure 6**. When the new system was charged into the cell the formation of free water appeared after 5 minutes under a large foam phase which immediately started to coalesce. After one hour, the system consisted of 40 vol. % of coarse foam and 40 vol. %of stable foam (**Figure 6**a). The phase observed under the free water phase was foam that adhered to the piston corners and the magnetic stirrer (**Figure 6a**, **Figure 6b**, **Figure 7a**, and **Figure 7b**). After 5 minutes the system remained almost unchanged.

After 5 days, CO_2 phase appeared immediately after the stirring was stopped (ca. 31 vol. %). The total foam volume decreased to 54 vol. %after approximately 30 minutes. 10 vol. % was coarse foam and 15 vol. % was free aqueous phase (**Figure 6b**). After 30 minutes, only small changes in phase volumes were observed.

After 11 days, the appearance of the foam changed. It adopted a self-folding structure appearance which acted as a plug when re-stirring attempts were made. The system was composed of 37 vol. % CO_2, 10 vol. % aqueous phase, and 53 vol. % of foam (**Figure 6c**). Then the system was pressurized to 226 bar and a new attempt to stir was made, but the foam phase continued acting as a plug.

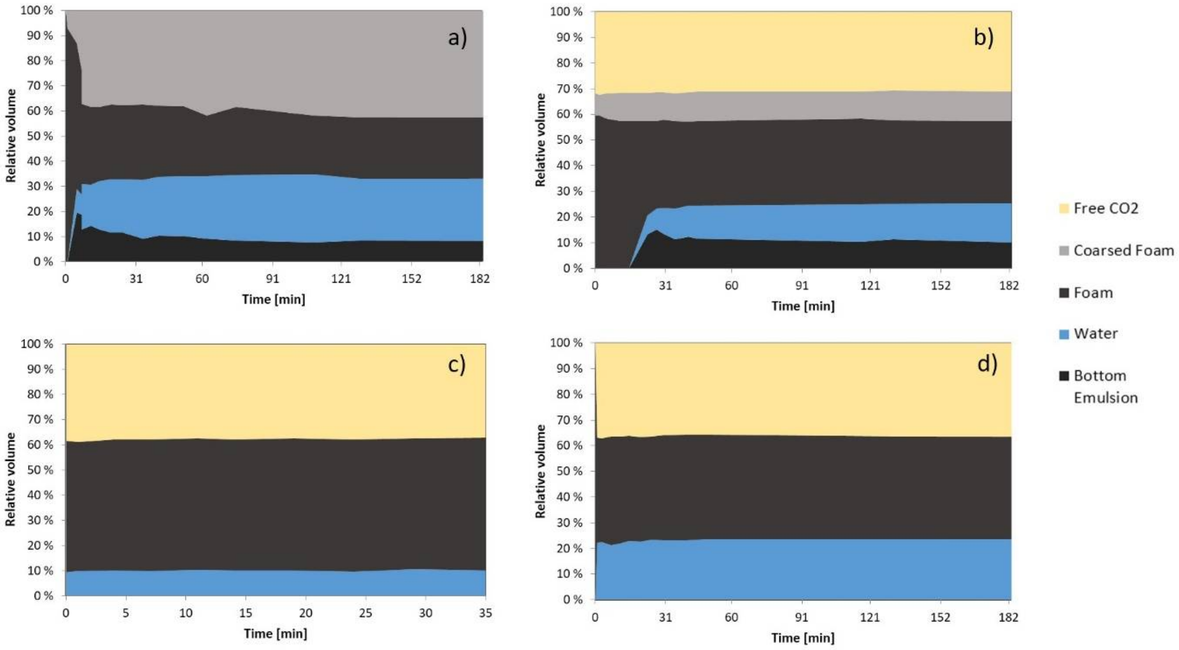

Figure 6. Relative volume of each phase vs. time at 21 °C. The GO concentration was 0.5 mg/ml in SSW. a) Recently made at 153 bar; b) 5 days at 153 bar; c) 11 days at 153 bar; d) 11 days at 226 bar.

3.2.2. Foam morphology

The pVT cell was filled with 1 mg/ml GO in SSW and CO_2 (50 vol. % of each phase) at 226 bar and room temperature and stirred. The system was re-stirred after 1 hour, after 3 hours and after 11 days. Pictures of the cell were taken approximately 5 minutes after each stirring and are shown in **Figure 7**.

There was an evident change in the foam morphology between the freshly made system and after 3 hours. After 3 hours the foam phase occupied the whole volume and large trapped CO_2 bubbles were observed (**Figure 7c**). Then the system was left in static conditions for 11 days.

Figure 7d shows the system after 11 days for the previous experiments carried out with a concentration of 0.5 mg/ml. However, the systems with 0.5 and 1 mg/ml after 11 days had the same appearance. The 11 days aged system showed a noticeable appearance difference with the systems during the first day (**Figure 7a**, **Figure 7b**, and **Figure 7c**). The foam phase exhibited a different morphology, suggesting the formation of film-like structure.

Once the system was re-stirred, the foam phase acted as a rigid plug not allowing mixing of the phases. Thus, the foam phase had solidified supporting the assumption that self-folding structures were formed.

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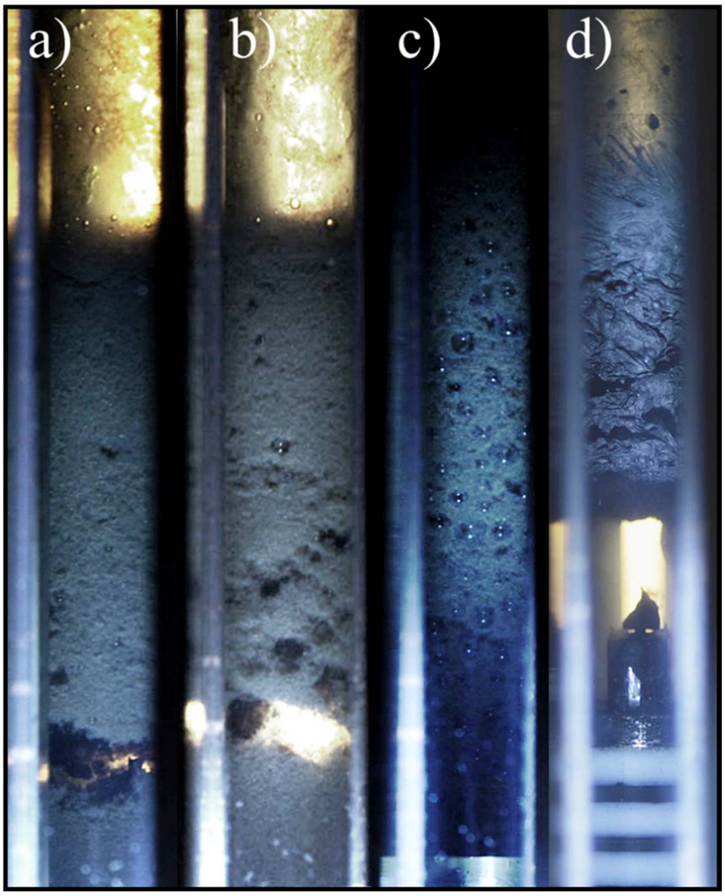

Figure 7. Foam pictures at a different time. a) recently made, b) after 1 h, c) after 3 h, and d) after 11 days. The pressure was 226 bar and the concentration was 1 mg/ml in the synthetic brine except for d), where the concentration was 0.5 mg/ml.

The increase of stability and its consecutive stability reduction might be the effect of two competitive effects: gelation and precipitation. The presence of divalent ions in the brine could promote system gelation, increasing aqueous phase viscosity and thus, improve stability. Bai *et al.* [24] already reported the ability of divalent ions (Ca^{2+} and Mg^{2+}) to promote hydrogel formation with GO in brine. This hydrogel formation was already observed when the GO was dispersing into SSW. The solution became heterogeneous, and the apparition of gel-like aggregates were noticed.

On the other hand, stacking of GO sheets would decrease their interfacial activity and their ability to stabilize dispersed systems. In **Figure 7d**, particle associations in a film-like structure in the foam phase can be intuited. The stacking of parallel layers is energetically more stable than gel structures due to its larger contact area between GO sheets. This can also be strengthened by the presence of the divalent ions like Ca^{2+} and Mg^{2+} [25]. However, this last stacking mechanism seemed to happen at a lower rate than gelation did.

3.2.3. Partially reduced Graphene Oxide (rGO)

A CO_2/SSW system using a concentration of rGO of 1 mg/ml in SSW was studied at 78 bar and 21 °C. However, it was not possible to disperse the CO_2 into the aqueous phase. Moreover, all particles flocculated and gathered at the interfaces, as observed in **Figure 8a**.

An attempt to disperse n-hexane into water using 1 mg/ml rGO failed. (**Figure 8b**). It was neither possible to disperse rGO into n-hexane, toluene nor n-decane.

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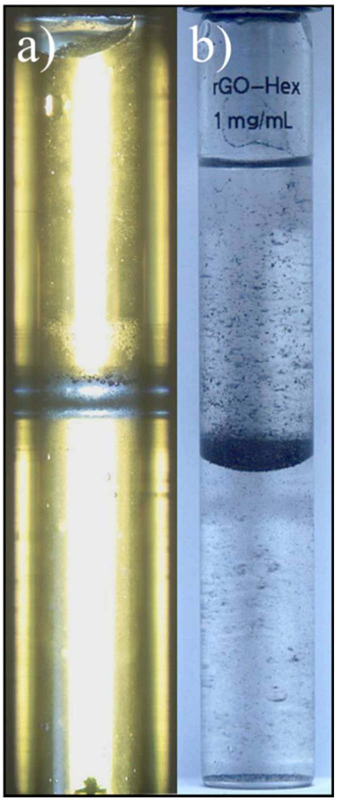

Figure 8. Picture of a) CO_2/SSW (78 bar and room temperature) and b) n-hexane/ SSW.

According to Liu *et al*. [22] reducing the GO increases the CO_2-philicity of the particles which leads to a better foam stability. However, the present observations are not necessarily opposed to Liu *et al*. conclusions. In their research, partially reduced GO was used, but the reduction degree was not specified nor was an elemental analysis of the particles provided. In this study the oxygen content was reduced from 41 – 50 % (GO) to 13 – 22 % (rGO). It is possible that these particles were more reduced, decreasing the sites for interaction between particles and CO_2 (epoxy groups) and thus, increasing both their CO_2-phobicity and the hydrophobicity.

3.2.4. Nanographene Oxide (nGO)

The first experiments using GO particles for stabilisation of CO_2/SSW foam were promising with respect to stabilisation. However, the particles used were large (4 to 30 μm), and the size should be reduced to avoid pore blockage during flow through porous media. Graphenea supplied a reduced particle size nGO suspension in pure water. A diluted sample of the new batch was ultrasonicated and filtrated through a 0.45 μm syringe filter and afterwards, the particle size distribution was measured. **Figure 9** depicts the nGO particle size distribution. The sample showed a peak around 333 nm and a polydispersity ranging from 70 nm to 1.5 μm. The presence of large particles indicate that particle aggregation occurred shortly after the filtration.

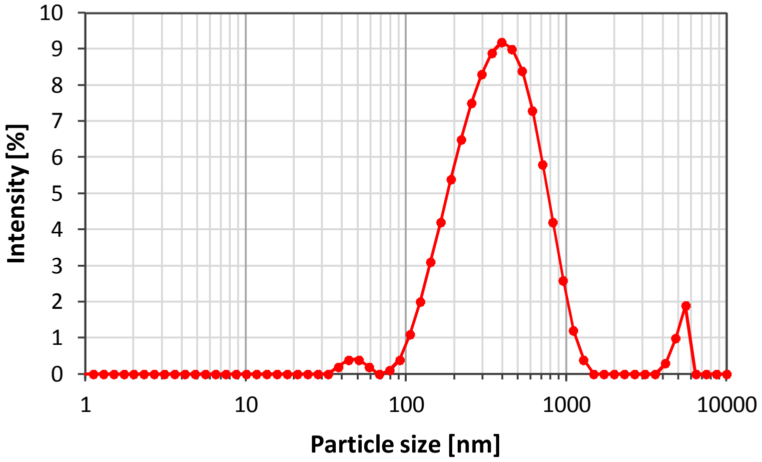

Figure 9. Particle size distribution for nGO particles after ultrasonication and filtration.

This particle size distribution can be adequate for core flooding experiments. However, it has been reported that GO size reduction increases hydrophilicity and diminishes its ability to adsorb at interfaces [21]. Thus, it was important to test the CO_2 in brine foams stability for the new batch with reduced size.

The pVT cell was charged with 1 mg/ml nGO dispersion in SSW and CO_2. The experiments were carried out at 21 °C and at different pressures (100, 150, and 200 bar). The stirring procedure was performed as previously described. For these tests the volumetric ratio between CO_2 and SSW was varied from 1:1 to 3:1, which can be within the range for foam stabilised EOR [26-30]. nGO was not able to stabilize CO_2 foams at any of the studied pressures.

The nGO was found to be too hydrophilic for forming and stabilizing foams, remaining in the aqueous phase and not adsorbing at the CO_2/SSW interface. A size-reduced GO particle would have a higher density of -COOH and epoxy groups, increasing hydrophilicity [21, 22]. However, it may be possible to reduce the particles to an optimal degree. At this hypothetic point, the density of -COOH and epoxy groups for a given particle size may reduce hydrophilicity keeping the particles CO_2-philic enough for interfacial adsorption.

In addition, a filtration test using the initial 1 mg/ml suspension in SSW (heterogeneous suspension as described before) was done using a 1.2 μm cellulose nitrate filter. The filter was blocked immediately. This showed that the particles aggregated in the presence of divalent ions most likely forming hydrogels. Thus, hydrogel formation can stabilise foam, as observed with larger particles, but makes the system useless for injection into porous media.

4. Conclusions

Large GO sheets can be used effectively to disperse CO_2 in brine, but the particles tested were too large (4 to 30 μm) for flow through porous media. Smaller particles were considered. However, reducing particle size had a determinant effect on foamability. nGO with particle size below 1 μm was not able to form foams. This can possibly be adjusted by partially reducing nGO to make the particles less hydrophilic, but the reduction degree must be carefully considered.

CO_2 in SSW foams stabilized by GO showed a time-dependent stability. This was likely the result of the competitive effect of two mechanisms, hydrogel formation and GO layer staking. Both mechanisms apperared to be triggered by the presence of divalent ions. Hydrogel formation was the faster mechanism and played a beneficial role for foam stability which initially increased reaching a maximum after two days. Contrarily, GO layer stacking was a slower process and cancelled out the stabilizing hydrogel formation mechanism giving a rigid dispersion of CO_2 and brine.

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Reduced graphene oxide (rGO) with 13 - 22 % oxygen content was not able to form foams. This contradicts the results obtained by Liu *et al*.[22] and may be due to a the high degree of reduction of the particles used. Thus, the degree of reduction must be taken carefully into account as low contents of oxygen would increase both hydrophobicity and CO_2-phobicity.

Hydrogel formation in presence of divalent ions can make graphene oxide particles not suitable for EOR purposes. A dispersion of nGO in SSW could not flow through 1.2 μm cellulose nitrate filters, most likely due to hydrogel formation. Passing the filtration test was set as a requrement for carrying on with core flooding experiments. Even though GO can stabilize CO_2/SSW foams, the results indicate that they are not suitable for CO_2 EOR.

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