Experimental Investigation of the interaction between a phosphate ester scale inhibitor and carbonate rocks for application in squeeze treatments

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Abstract

Studying the interaction between scale inhibitors (SIs) and chemically-reactive carbonate minerals is crucial for determining SI retention in "squeeze" treatments. This study investigated the retention of the environmentally-friendly SI, polyhydric alcohol phosphate ester (PAPE), on calcite and dolomite substrates. Elemental analysis of the supernatant solution, pH measurement and Environmental Scanning Electron Microscopy (ESEM) with Energy Dispersive X-ray analysis (EDX) were all used to investigate SI retention and to identify the morphology/composition of the resultant SI-Ca precipitates. Results revealed that PAPE was retained by calcite via pure adsorption at an initial test pH (pH_0) of 4 and then precipitation at pH_0 6. In contrast, the PAPE/dolomite system was found to be effectively pH independent, with precipitation dominating at both pH_0 values. Any temperature effect was negligible for dolomite/PAPE retention, while with calcite, retention was smaller at lower temperature, attributed to the temperature dependence of the substrate solubility. Overall, the final pH of the system, and resulting degree of SI-dissociation, contributed more to PAPE retention than did the final calcium concentration. EDX analysis confirmed scale-inhibitor phosphorus in the deposited solids, indicating coupled adsorption/precipitation. This phosphorus increased with the amount of precipitation and with the temperature, confirming the corresponding static adsorption test results.

Introduction

Despite several decades of research and development projects, flow assurance issue is still under debate[1,2]. Deposition of mineral scales is a common production problem encountered in the oil industry which may lead to the loss of well integrity and productivity if not properly managed[3–5]. The main reasons for scale formation are usually either the mixing of incompatible waters in production flow systems, for example formation brine and sea water injected for maintaining downhole pressure, or changing the reservoir conditions such as temperature, pressure, brine pH etc.[6]. Scale inhibitor (SI) squeeze treatments are recognised to be one of the most economically and technically favourable options for scale management in both conventional and subsea oilfields[7–9]. Squeeze treatments commonly comprise of injecting a scale inhibitor, usually by "bullhead" injection, into the near wellbore

area followed by an over-flush brine, which displaces the SI deeper into the formation. After a shut-in period to allow the chemical to adequately "retain" in the formation rock, the well is put back on production[10–14]. The efficiency and lifetime of the squeeze treatment depends on the interaction of the SI with the rock minerals in the porous medium[15–22]. Scale inhibitors are retained within porous media by the two main mechanisms of adsorption (Γ) and precipitation (Π) as shown schematically in Figure 1.
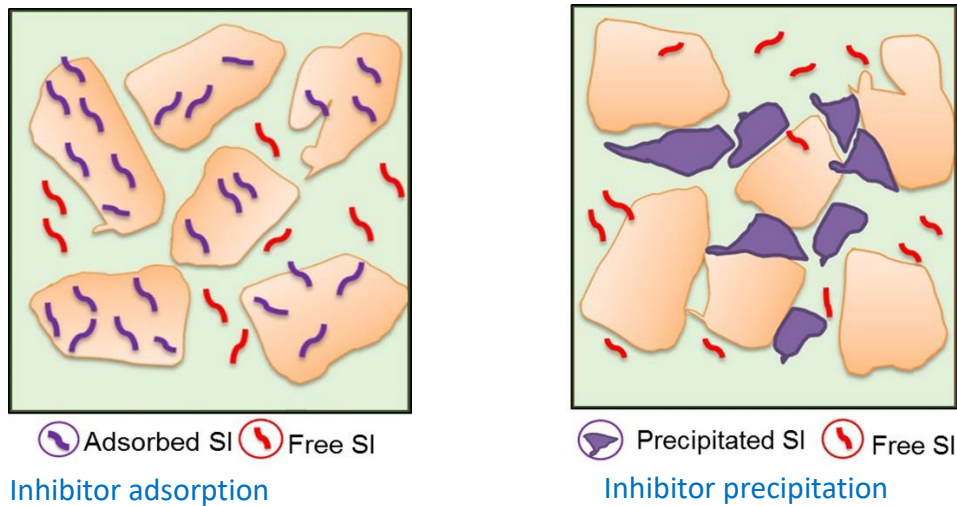

Figure 1. Two main mechanisms of scale inhibitor retention in porous media

Coupled adsorption/precipitation (Γ/Π) or "Apparent adsorption", Γ_{app} (in mg SI/g substrate), is determined in an experiment as shown in Figure 2, and it is calculated using the formula in equation 1:
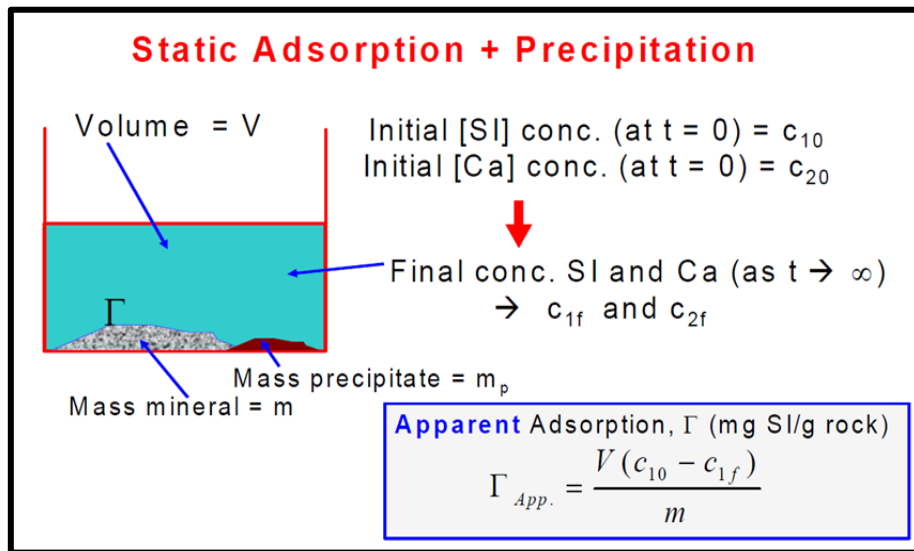

Figure 2. Scheme of how "Apparent adsorption, Γ_{app}, can occur [17]

$$\Gamma_{app} = \frac{V\left(C_o - C_f\right)}{m} \tag{1}$$

where C_o and C_f are the initial and final SI concentrations, respectively, V is the volume of SI solution and m is the mass of mineral substrate. Note that the term "apparent adsorption" is used to refer to the mixture of both adsorption (Γ) and precipitation (Π), which may be occurring simultaneously[17]. For pure adsorption, the degree of SI retention is independent of (m/V) the mass to volume ratio of substrate to liquid, and a plot of adsorption (Γ) vs. final SI concentration (C_f) would lead to a smooth single adsorption isotherm, $\Gamma(C)$. However, if deviation from this isotherm are observed as a function of (m/V) then this is evidence of the fact that both adsorption and precipitation are occurring together and this is described mathematically in Kahrwad et al[17]. Simultaneous adsorption and precipitation is denoted as a (Γ/Π) process.

Various "schools of thought" on the retention issue have emerged. These include;

(i)   the Heriot-Watt University (HWU) view, where adsorption is described by a generalised adsorption isotherm, Γ (C), and precipitation is described by a solubility function, Π (C), and a dissolution rate constant[11,23];

(ii)   the Halliburton view, which describes retention through an adsorption mechanism based on the specific mineralogy of the (sandstone) rock[23,24]; and

(iii) the Rice University view, which describes SI retention by a precipitation/dissolution mechanism based on the precipitation and solubility of the various Ca-SI salts that are formed[18,25–27].

It is noted in the literature that there is no clear-cut line between the two basic types of squeeze retention, adsorption and precipitation[28–30]. Both mechanisms can occur concurrently depending upon the chemical nature of the inhibitor and on formation parameters such as mineralogy, divalent-cation concentration, pH and temperature[31].

The first detailed mechanistic study on SI retention was conducted by Vetter[32]. It was found that the "adsorption isotherms" of sand at different pH values at low temperature were almost identical and there was a very small increase at higher pH. Sorbie et $al.$ [31] investigated the impact of pH, temperature and calcium on the retention of phosphonate scale inhibitors onto consolidated and crushed sandstone. They showed scale inhibitor adsorption onto the crushed rock material increased at higher temperatures. Moreover, inhibitor adsorption onto crushed rock was lower at pH 4 than at pH 2 or 6; when calcium ions are present. Finally, the adsorption of a phosphonate inhibitor (DETPMP) decreased predictably as pH increased (at 25°C) in the absence of Ca^{2+} ions.

Tantaykom et $al.$ [3] considered a kinetic study of phosphonate scale inhibitor amino-trimethylene phosphonic acid (ATMP) precipitation in squeeze treatments. They concluded that pH plays an important role in controlling the precipitation of Ca-ATMP and has both positive and negative effects for field applications. At higher pH, more Ca-ATMP was precipitated; however, the precipitation was relatively fast and more likely in the vicinity of the wellbore, thereby reducing the effectiveness of the treatment. They also suggested that nucleation kinetics play an important role in the spread of the

inhibitor in the treatment zone during precipitation squeeze treatments as the injected fluid flows out into the formation.

Tomson *et al.* [33] carried out work on inhibitor/rock interactions and the parameters governing inhibitor retention in carbonate-rich formations during scale inhibitor squeeze treatments. They showed that there are two mechanisms which control the SI retention in carbonate formations; (a) SI-Ca^{2+} coating resulting in the reduction of calcite dissolution and surface poisoning; and (b) the formation of a SI-Ca^{2+} complex because of either low or high calcium ion concentrations. Ibrahim *et al.* [34] investigated static inhibitor compatibility and coupled adsorption/precipitation experiments using a range of phosphonate scale inhibitors and several mineral substrates. They concluded that for all phosphonate SI/mineral systems, pure adsorption would correctly describe the SI/mineral retention mechanism at low [SI] concentrations, whilst coupled adsorption/precipitation occurs at high concentrations and a coupled adsorption/precipitation (Γ/Π) model would then be required. Jarrahian *et al.* [35] conducted static adsorption experiments for two types of polymeric scale inhibitor on calcite and dolomite beds. They concluded that for a poly-phosphino carboxylic acid (PPCA), a low pH yielded higher apparent adsorption and that PPCA was retained more on calcite than on dolomite, whilst for a P-functionalized co-polymer (PFC), the inhibitor was retained more on dolomite than on calcite.

The previous experimental studies detailed above have included phosphonate and phosphorus-tagged polymeric scale inhibitors due to their high performance, adsorption efficiency and ease of detection[36,37]. However, the use of conventional scale inhibitors has been limited recently in certain areas such as the North Sea and the Norwegian Sea, where strict environmental regulations have been applied[38,39]. Therefore, many production companies are replacing the conventional scale inhibitors with more environmentally friendly ones, such as polyhydric alcohol phosphate ester (PAPE)[40,41]. In fact, phosphorus within phosphate ester scale inhibitors improves the adsorption capacity, squeeze lifetime and the detectability of the inhibitors, while their environmental friendliness allows them to be applied in sensitive environments[42].

Some of the fundamental chemistry of phosphate esters is quite well established, however their field application and retention in chemically reactive carbonate rocks has not been examined extensively. The aim of this study was to generate data to describe the adsorption/precipitation behaviour of PAPE, as a common representative of phosphate ester inhibitors. PAPE was studied in the context of precipitation squeeze treatments, in order to identify the dominant mechanisms (Γ, Π or coupled Γ/Π) governing its retention on calcite and dolomite substrates as a function of pH and temperature. This was achieved by carrying out a range of static apparent adsorption experiments, which yield apparent adsorption (Γ_{app}) values alongside the final SI concentration, *i.e.* Γ_{app}, vs. C_f, as a function of (m/V), where m is the mass of substrate (calcite or dolomite) and V is the solution volume, to easily identify

concentration regions where pure adsorption (Γ) and coupled adsorption/precipitation (Γ/Π) occur[17]. All of the SI-calcium precipitates generated were studied by ESEM/EDX [17,34,35].

Materials and methods

The data presented was drawn from a series of static adsorption/precipitation tests carried out at 60 and 80°C[17,34]. The basic steps in the experiments were:

1) North Sea Seawater (NSSW) brine was prepared by the dissolution of the relevant salts in distilled water (DW) and the subsequent filtration of this brine through a 0.45 µm filter paper.

2) A 10,000 ppm SI stock solution was prepared in the test brine and was further diluted to appropriate scale inhibitor concentrations for the adsorption test in the same test brine.

3) The pH of all stock solutions (blanks & SI/SW samples) was adjusted to the required initial test pH value *i.e.* pH_0 4 & 6.

4) Samples of calcite and/or dolomite mineral substrate were weighed into bottles (m = 5 and 10 g);

5) 40 mL of the appropriate SI solution was added to each bottle (V = 0.04 L);

6) Bottles were capped and shaken for five seconds before being placed in an oven at 60 or 80°C and atmospheric pressure;

7) The bottle caps were checked for tightness after 1 h to avoid evaporation;

8) After 24 h in the oven, the sample bottles were removed and the test solutions were immediately filtered through a 0.22 µm membrane filters;

9) The supernatant solution was then left to cool to room temperature for approximately 24 h;

10) The post-test pH was measured and then samples were diluted and analysed by ICP-OES for [SI], $[Ca^{2+}]$ and $[Mg^{2+}]$;

11) ESEM/EDX analysis was performed on the collected solid phases (precipitate as well as mineral) to analyse the surface of calcite/dolomite grains and any bulk precipitate formed.

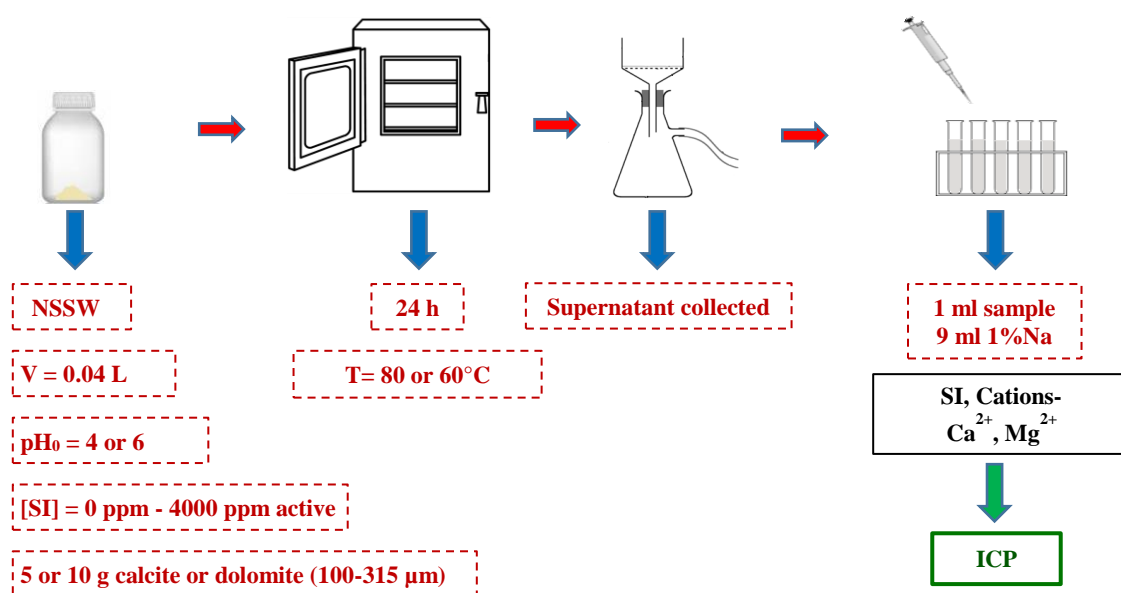The schematic of the static adsorption and compatibility experiment is illustrated is Figure 3.

Figure 3. Scheme of Static Adsorption and Compatibility Experiment

Adsorbents

The substrates used were Moroccan calcite and Skye dolomite which were sourced from the UK Geology Company (UKGE). These rocks were crushed and sieved down to the desirable size fraction $(100 – 315\,\mu m)$, before being washed with distilled water to remove any fines. Prior to use, the materials were allowed to air dry. We have checked the effect of particle size (i.e. specific surface area) of the crushed carbonate and results are not dependent on this, indicating that the effect is controlled by extent of chemical reaction rather than surface effects (although the kinetics is a little faster for the smaller particle size)". ESEM/EDX analysis revealed the morphology and elemental compositions of the pure substrates, as shown in Figure 4 and Table 1.
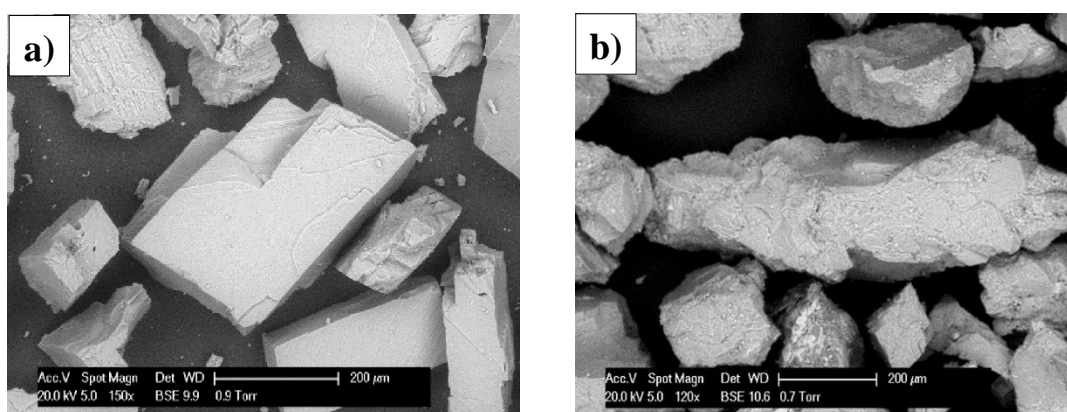

Figure 4. ESEM images of (a) pure calcite and (b) dolomite grain morphology (size range 100-315 µm)

Table 1. EDX analysis of pure calcite and dolomite samples

Element	Pure calcite (weight %)	Pure calcite (atomic %)	Pure dolomite (weight %)	Pure dolomite (atomic %)
C	14	21	26	36
O	57	66	52	53
Ca	29	13	9	6
Mg	--	--	13	5

For pure calcite and dolomite, the elements detected by EDX analysis were calcium, oxygen, carbon and magnesium (dolomite only) confirming the composition of the substrates. From the above, the compositions of calcite and dolomite were taken as $CaCO_3$ and (approximately) $CaMg(CO_3)_2$, respectively[35].

Brine

The brine used throughout was synthetic North Sea Seawater (NSSW). The brine was prepared by dissolving the appropriate quantity of salts in distilled water (Table 2) and was then filtered through a 0.45 µm filter.

Table 2. Composition of synthetic North Sea seawater

Ion	Concentration (ppm)	Salt used	Mass of salt (g/L)
Na^+	10,890	NaCl	24.08
Ca^{2+}	428	$CaCl_2.6H_2O$	2.34
Mg^{2+}	1368	$MgCl_2.6H_2O$	11.44
K^+	460	KCl	0.88
SO_4^{2-}	2960	Na_2SO_4	4.38
Li^+	50	LiCl	0.3055
Cl^-	19,766	-	-

Adsorbate – Scale Inhibitor (SI) PAPE

The scale inhibitor adsorbate used in this work was polyhydric alcohol phosphate ester (PAPE), a phosphate ester water treatment chemical that has been proposed as a scale inhibitor. PAPE contains more than one polyethylene glycol group, hence the scale inhibition for calcium carbonate scale is improved and it also has reasonably good inhibition efficiency for barium and strontium sulphate scales[6,41]. Structural details of PAPE are presented in Table 3.

Table 3. Specifications of PAPE

Generic Name	Type	Chemical Structure
PAPE	Polyhydric alcohol phosphate ester	$$R-O-\overset{\displaystyle O}{\overset{\displaystyle \|}{\underset{\displaystyle \underset{\textstyle OH}{\|}}{P}}}-OH$$

Inductively-Coupled Plasma- Optical Emission Spectrometry (ICP- OES)

ICP-OES (Ultima 2 ICP Optical Emission Spectrometer with upgraded solid-state generator and software V5) was used to analyse the supernatant solution before and after filtration, specifically to quantify the concentrations of SI (via P) and cations; Ca^{2+}, Mg^{2+}, Fe^{2+} and Li^+[43].

Environmental Scanning Electron Microscopy - Energy Dispersive X-ray (ESEM/EDX) analysis

ESEM-EDX analysis was employed to view the crushed calcite/dolomite surfaces before and after the static adsorption tests. This was carried out to investigate the morphology of the precipitated complex in the presence of calcite or dolomite substrates. In particular, it was used to establish if the precipitate was formed as a grain coating around the calcite or dolomite particles or whether it formed independently in the bulk solution. Therefore, after filtration, all the filter papers containing calcite/dolomite substrate and (in some cases) the precipitated complex for each of the SI concentrations tested, were dried and sent for ESEM-EDX analysis[34,35]. For this study, a Philips XL30 ESEM, with an Oxford Instruments cryo-stage, and an energy dispersive X-ray detector was used for the analysis.

Results and discussion

Impact of pH on apparent adsorption of PAPE on Moroccan calcite and Skye dolomite

From the stock solution of [SI] = 10,000 ppm active PAPE, lower SI concentrations of 50, 100, 500, 800, 1000, 2000 and 4000 ppm were prepared by dilution and used for the apparent adsorption and compatibility (no mineral substrate) experiments. The pH values of the various PAPE solutions were adjusted to initial pH values (pH_0) of 4 or 6 for the various experiments. Due to the lower thermal stability of PAPE, the maximum temperature for the experiments was limited to 80°C [4,42,44].
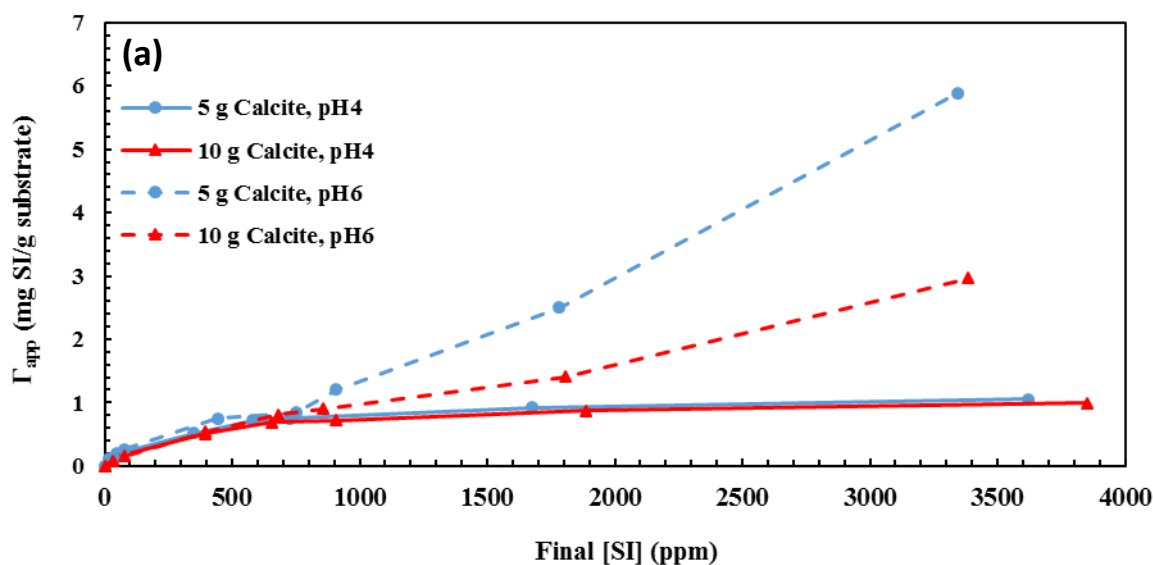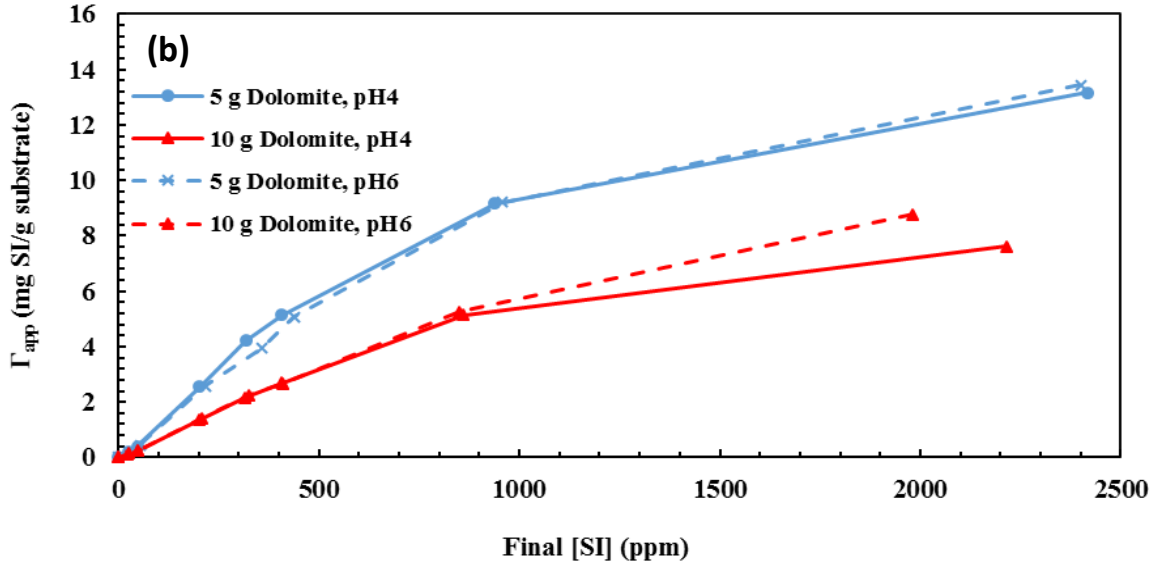
Figure 5. Apparent adsorption (Γ_{app}, vs. C_f) for PAPE with 5 and 10 g of (a) calcite and (b) dolomite at pH_0 4 & 6; T = 80°C

Figure 5(a) shows that, for calcite at pH_0 4 (solids lines), pure adsorption was observed for all concentrations of PAPE. For the same substrate at pH_0 6 (dashed lines, Figure 5(a)), pure adsorption was observed up to ~800 ppm with deviation at higher PAPE concentrations indicating the occurrence of coupled adsorption/precipitation (Γ/Π)[17,34]. This behaviour can be explained by the pH-dependence of scale inhibitor dissociation in relation to the final pH of the solutions. It has been shown previously that at lower pH values, phosphonate inhibitors are less dissociated, which would lead to lower propensity for precipitation and therefore lower apparent adsorption[35,45].

For the PAPE/dolomite system shown in Figure 5(b), both pure adsorption and coupled adsorption/precipitation predominates for both initial pH values. Only pure adsorption was seen for [SI] up to ~100 ppm, but above a PAPE concentration of 100ppm, the curves deviate indicating a change in retention regime to coupled adsorption/precipitation. Unlike the calcite system, the apparent adsorption of the PAPE/dolomite system was effectively pH independent[6].

When compared with the retention mechanisms of other scale inhibitors, it is believed that the weak polyacidic nature of PAPE could lead to a greater degree of dissociation at higher pH. This may be attributed to the different chemistry of the PAPE/carbonate systems compared to the retention of other conventional inhibitors (phosphonate and polymeric scale inhibitors) where the retention increases as pH increases for phosphonate SIs and as pH decreases for polymeric inhibitors[31,34,35]. Here, PAPE was retained more on dolomite than on calcite, which is consistent with previous phosphonate inhibitor/carbonate system observations. This can be related to the higher final pH values in the PAPE/dolomite system compared to those for the PAPE/calcite system (see the corresponding figures showing final pH below). Since the inhibitors such as PAPE can be considered as weak polyacids, schematically represented as H_nA, these can be partly dissociated (i.e. $H_nA \leftrightarrows H^+ + H_{n-1}A^-$). Therefore,

at very low (acidic) pH, the H_nA equilibrium is to the left and the molecule is more associated as H_nA, and at higher pH it is more dissociated into H^+ and $H_{n-1}A^-$. The SI (H_nA) is much more likely to complex with Ca^{2+} to form a SI/Ca complex in its dissociated form (i.e. at higher pH values) and less likely to form complexes at lower pH values[42,46].

In the PAPE/dolomite system, the final pH is higher than for PAPE/calcite, due to the higher solubility of dolomite in the matrix brine (NSSW), so the PAPE inhibitor would therefore be somewhat more dissociated (more $H_{n-m}A^{m-}$ in solution) than in calcite. Thus, PAPE is much more likely to interact with divalent cations and form SI-M^{2+} in dolomite than in calcite[6,47]. Hence, it was observed that the degree of apparent adsorption of PAPE on dolomite was more than on calcite, even though the calcium content of calcite was relatively higher than that of dolomite. It can therefore be concluded that pH, in particular pH_f, controls PAPE retention in carbonate systems as opposed to the calcium concentration. These results have implications on the application pH that should be used when PAPE is deployed in carbonate reservoirs.

Impact of temperature on apparent adsorption of PAPE on Moroccan calcite and Skye dolomite

As PAPE was seen to be retained more on the carbonate substrates at pH_0 6, the experiments were repeated at an initial pH of 6 and a temperature of 60°C to investigate the effect of temperature on apparent adsorption.
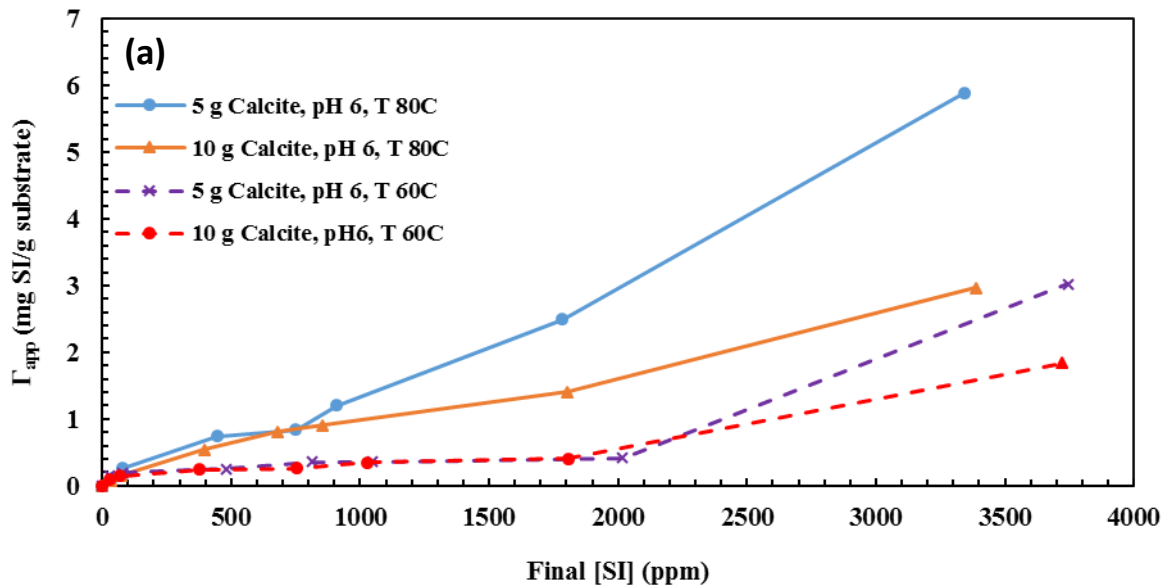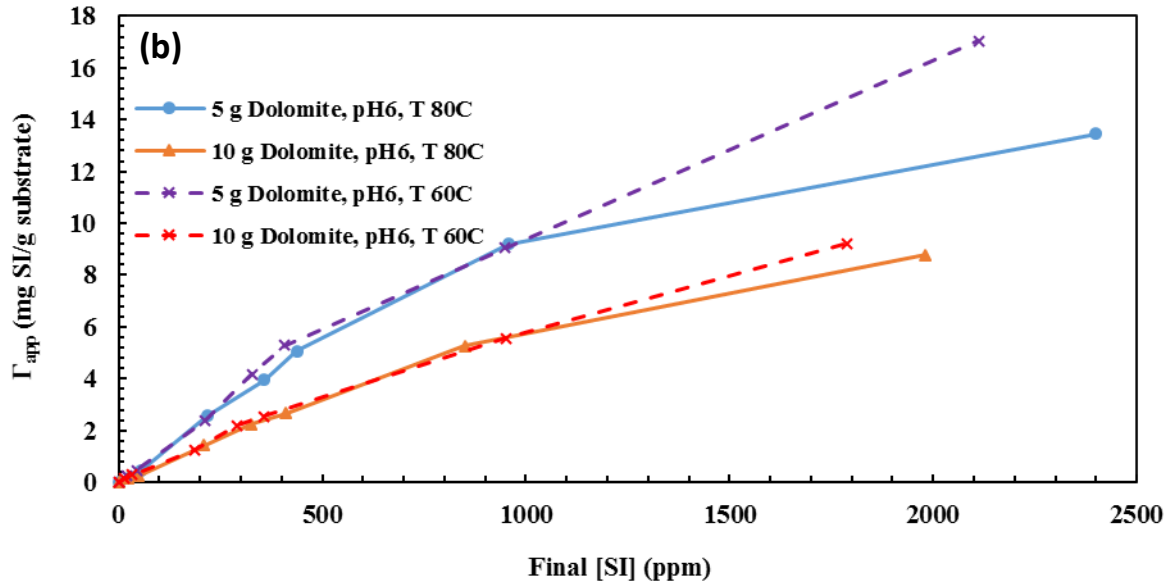
Figure 6. Apparent adsorption (Γ_{app} vs. C_f) for PAPE with 5 and 10 g of (a) calcite and (b) dolomite at T = 60 & 80°C; pH_0 6

As shown in Figure 6(a), the resultant Γ_{app} with calcite was lower at 60°C than at 80°C. Calcite is less soluble at higher temperature, however the interactions between the scale inhibitor and Ca^{2+}, including the strength of SI-M^{2+} binding, increases significantly with temperature and thus the solubility of the SI-M^{2+} complex decreases, resulting in more precipitation/retention[44,47].The dominant retention mechanism of PAPE with calcite at 60°C changes from coupled adsorption/precipitation to pure adsorption, although both mechanisms exist above 2000 ppm PAPE. In fact, temperature affected apparent adsorption of PAPE on calcite quite significantly.

It was therefore concluded that PAPE works more effectively at higher temperature in calcite formations, at least in terms of retention, although there may be chemical stability issues at elevated temperature.

The Γ_{app} of PAPE on dolomite was not as temperature dependent (Figure 6(b)) as it was for calcite, with apparent adsorption increasing as lower temperature only at the highest PAPE concentration[44,47]. These results show that PAPE has good retention characteristics at both temperatures and is therefore a good SI candidate for these reservoir and operational conditions. In addition, it should be mentioned that the temperature effect on the association/dissociation of PAPE is very slight. The temperature mainly affects the solubility of the SI complex with Ca^{2+} and it is thermodynamically driven since all reactions reach equilibrium relatively quickly.

To sum up, what is observed in Figure 6(a) for calcite is that at lower temperature there is a large zone of pure adsorption (up to ~2000ppm [PAPE]). However, at higher temperature, the extent of this pure adsorption region is greatly reduced (up to ~800ppm [PAPE]) i.e. there is more precipitation (as expected). This therefore appears as a "big" effect. For Dolomite case (Figure 6(b)) there is already

extensive precipitation at the lower $T = 60^o\,C$ and so increasing the temperature appears not to have much effect. The system is not "unaffected" since there is already extensive precipitation (because of the pH (See Figures 7 & 8)). Moreover, both calcite and dolomite solubility in NSSW change very slightly with changing temperature; the change is negligible between the 2 temperatures used in this work $T = 60^oC$ and 80^oC. In these experiments this change is imperceptible for 2 reasons (i) an excess of carbonate is always present and (ii) the main changes of Ca uptake and dissolution in solution are associated with the pH and carbonate dissolution and also the chelation with the scale inhibitors. These latter 2 effects completely dominate any solubility effects with temperature. In fact, as temperature increases, the solubility of $CaMg\,(CO_3)_2$ increases slightly, contrary to $CaCO_3$.

When the scale inhibitor is injected into carbonate formations, the SI (weak polyacid) solution contacts the carbonate mineral substrate and causes rock dissolution leading to an increase of initial pH to ~7 and 8 for calcite and dolomite substrates, respectively. The increased solution pH causes the inhibitor to become more dissociated, and these negatively charged species (dissociated scale inhibitor) are then able to be adsorbed onto the positively-charged rock surface through electrostatic interactions[31,48]. In addition, if the scale inhibitor concentration is sufficiently high, Ca^{2+} binds with the dissociated scale inhibitor (SI-Ca^{2+} complexation)[45,46]. Thus, the entire system is coupled and the 3 parts of the equilibrium system are:

(i)   The dissociation of SI as a weak polyacid (H_nA) to form dissociated species, such as $H_{n-m}A^{m-}$ right up to A^{n-} at very high pH values;

(ii)   These dissociated SI species, which are very strong chelating agents, then bind with Ca^{2+} (and/or Mg^{2+}) ions to form SI/Ca complexes which are known to be sparingly soluble;

(iii)   The above reactions are coupled to the carbonate system since the lower pH solution conditions and the chelating power of the dissociated SI cause the carbonate equilibrium to change.

To explain these observations, further ancillary results will be presented below on carbonate dissolution and on the final pH values of the system. Figures 7(a) and 7(b) show the final solution pH as a function of final SI concentration for the corresponding apparent adsorption experiments presented in Figures 5(a) and 5(b).
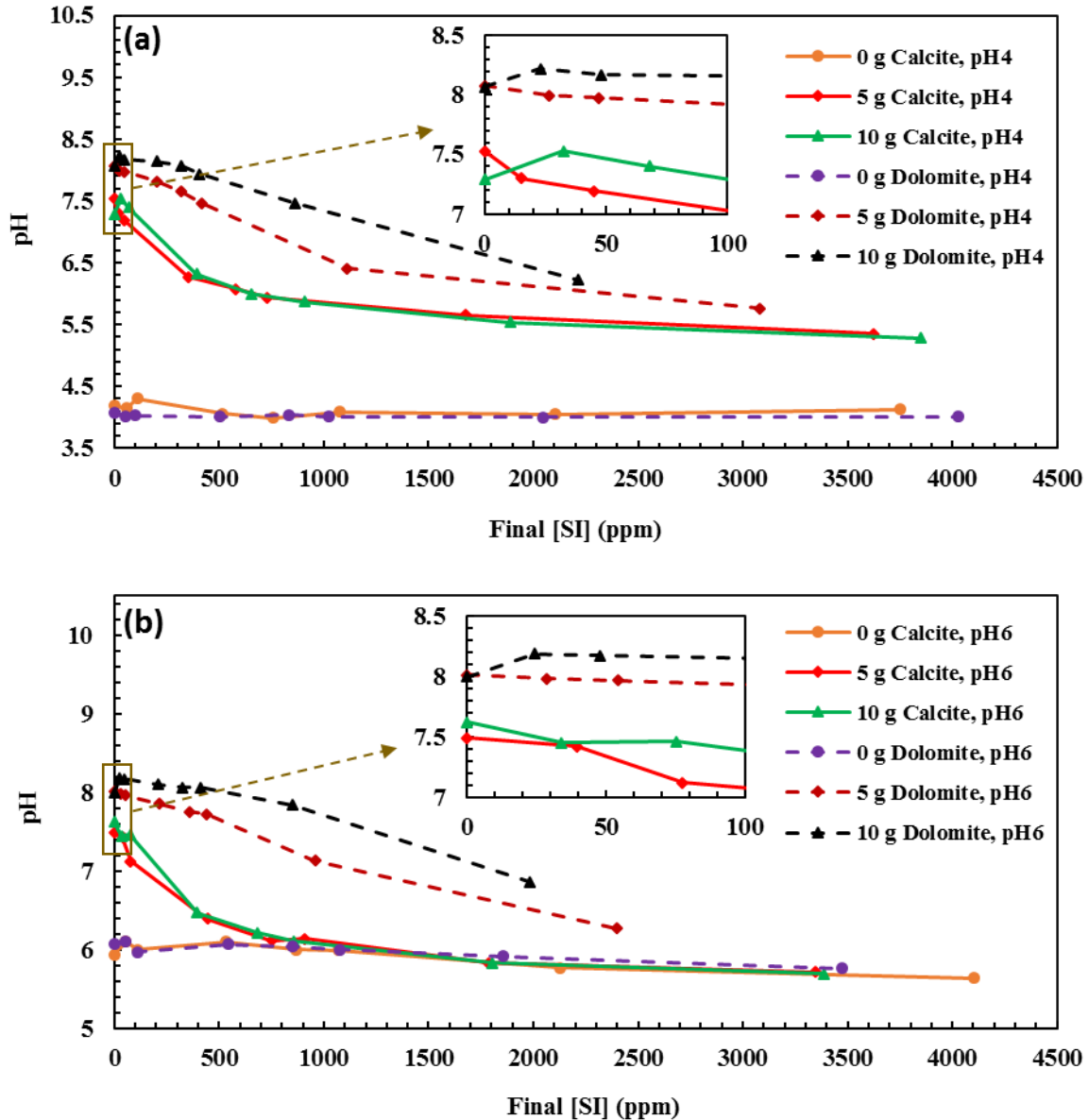
Figure 7. Final pH as a function of [PAPE] with 0, 5 or 10 g of calcite or dolomite at T = 80°C, (a) pH_0 4 and (b) pH_0 6

For pH_0 4 at 80°C compatibility tests (no substrate) there was no noticeable change in final pH (see Figure 7(a)), showing that PAPE was compatible with NSSW at these conditions. The final pH increased when the tests were repeated in the presence of 5 or 10 g of either carbonate substrate due to the dissolution of calcite or dolomite with the associated liberation of Ca^{2+} (& Mg^{2+} for dolomite) and carbonate (CO_3^{2-})[18,35]. This trend was observed until the retention regime changed from pure adsorption to coupled adsorption/precipitation, at which point the divalent cations generated *in situ* were consumed by the formation of a SI-M^{2+} complex[33,48]. The final pH for dolomite was higher than the calcite system, resulting in a greater degree of PAPE dissociation and a higher tendency for apparent adsorption (as shown in Figures 5(a) and 5(b)).

When the tests were repeated at pH_0 6 (Figure 7(b)), a slight decrease in final pH (to ~pH 5.6) was noted at high [PAPE] in the absence of any carbonate substrate, suggesting a slight incompatibility of the SI with NSSW at these conditions. This incompatibility is not desirable, as the inhibitor should precipitate far away from the wellbore, therefore it would be prudent to inject PAPE/NSSW at a lower pH to avoid this issue.

The final solution pH as a function of final scale inhibitor concentration is shown in Figures 8(a) and 8(b) for the carbonate systems at T = 60°C and 80°C, for a single pH_0 of 6.
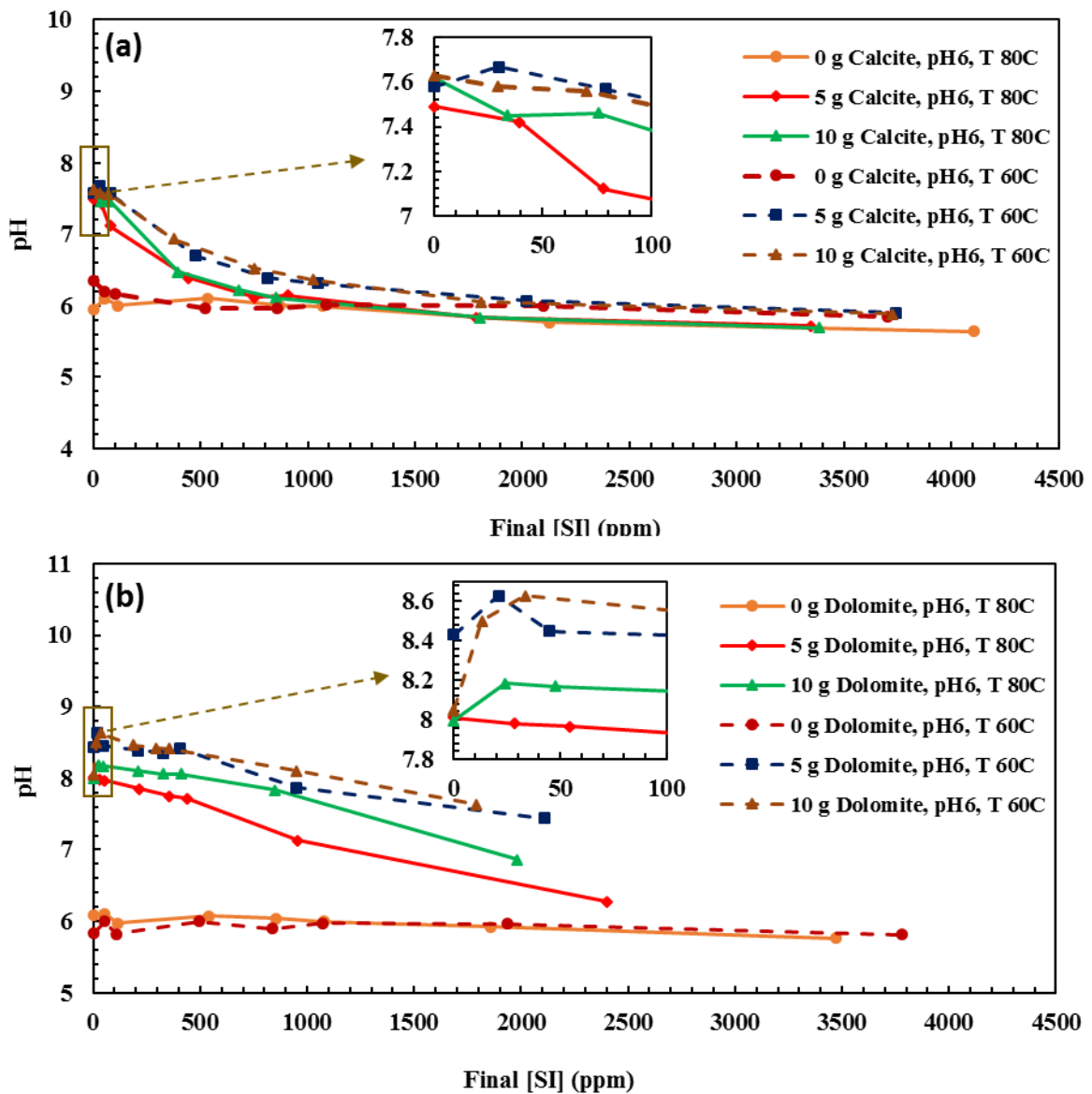

Figure 8. Final pH as a function of [PAPE] with 0, 5 and 10 g of (a) calcite or (b) dolomite at T = 60 & 80°C, pH_0 6

Figure 8(a) shows that PAPE was not compatible with NSSW at 60°C which was similar to the PAPE/NSSW behaviour at 80°C (Figure 7(b)). Thus, the final pH at the highest concentration ([PAPE] = 4000 ppm), decreased due to the reaction between PAPE and the calcium in NSSW. In the presence

of calcite, the final pH of the scale inhibitor solution increased due to rock dissolution and then decreased due to a change in the retention mechanism from pure adsorption to coupled adsorption/precipitation along with the associated phosphorus and calcium removal from solution due to complexation and precipitation. Moreover, the final pH at 60°C decreased so sharply that it was lower than the pH required for PAPE dissociation[45,46]. In other words, the scale inhibitor was in its more associated form and the apparent adsorption of PAPE on the calcite mineral at the lower temperature was reduced and the dominant mechanism of retention was pure adsorption[6]. However, at 4000 ppm, PAPE was sufficiently dissociated that the retention mechanism switched to precipitation. Thus, the retention mechanism of PAPE on calcite was dependent on temperature; lower temperature results in less dissociated PAPE and accordingly less precipitation. In the PAPE/dolomite system (Figure 8(b)), the final pH values for 60°C and 80°C were quite similar from 0 – 2000 ppm, however, the pH at 4000 ppm, T = 60°C was a little higher than that at T = 80°C, which indicates greater PAPE dissociation and supports the conclusion that the apparent adsorption of PAPE on dolomite is greater at 60°C than at 80°C for [PAPE] = 4000 ppm (Figure 5(b)).

To further establish the pure adsorption and coupled adsorption/precipitation behaviour, changes of $[Ca^{2+}]$ and $[Mg^{2+}]$ concentration were measured before and after the experiments[34,35]. Results are shown in Figures 9(a) and 9(b), where a decrease in divalent ions from input concentration can be attributed to the precipitation of a M^{2+}-PAPE complex and any increase was due to carbonate substrate dissolution. That said, it is possible for $[Ca^{2+}]$ to reach levels above the input concentration and for precipitation to occur as the $[Ca^{2+}]$ increases due to dissolution and $[Ca^{2+}]$ decreases because of complexation. These figures show the calcium and magnesium concentrations normalised to their initial solution values of $[Ca^{2+}] = 428$ ppm and $[Mg^{2+}] = 1368$ ppm.
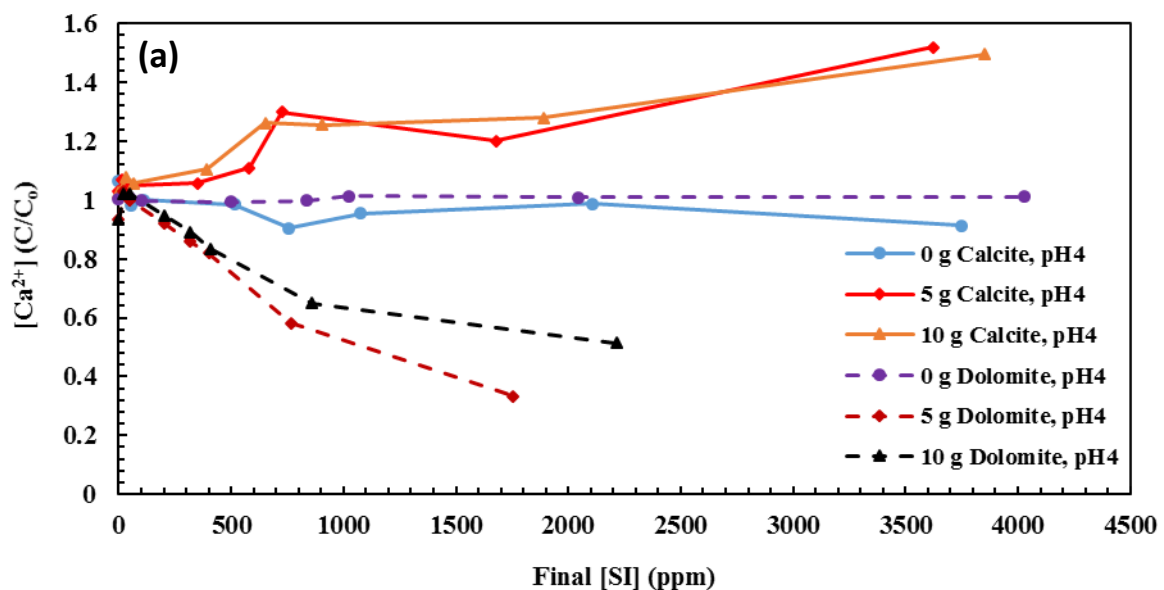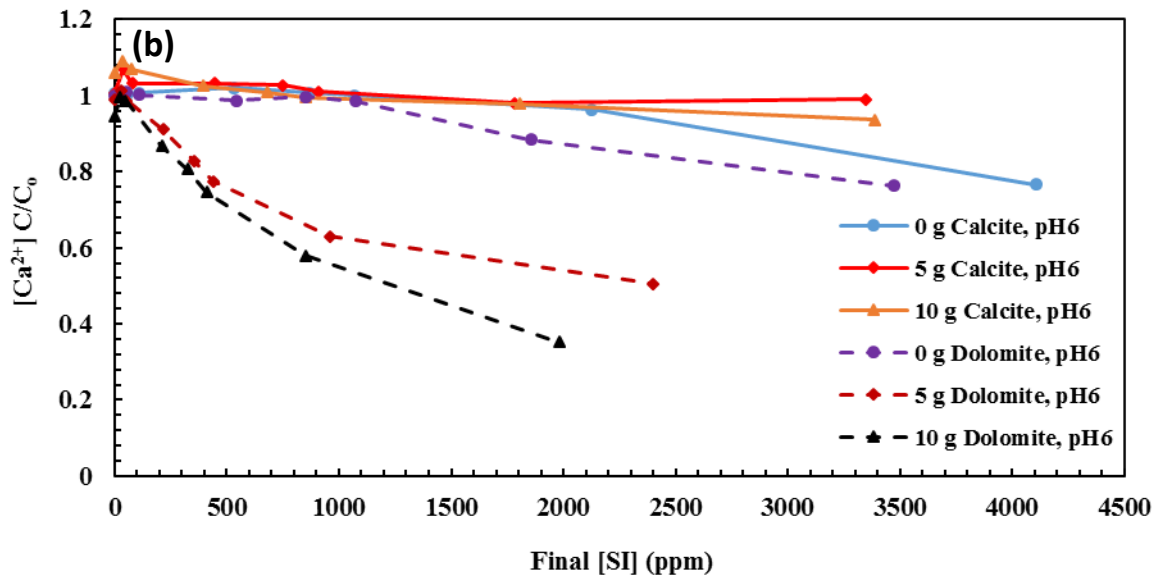
Figure 9. Comparison of C/C_0 Ca^{2+} for PAPE with 0, 5 or 10 g of calcite or dolomite at T = 80°C, (a) pH_0 4 and (b) pH_0 6

As shown in Figure 9(a), at pH_0 4 there was no noticeable change in normalised $[Ca^{2+}]$ in the absence of calcite or dolomite substrates (compatibility tests), therefore PAPE was seen to be compatible with NSSW at this pH_0. Furthermore, in the presence of calcite, the calcium concentration increased as a function of PAPE concentration up to ~1.6 times the initial value[47]. For dolomite, calcium decreased as [PAPE] increased, down to approximately a third of input concentration for 4000 ppm SI.

When the tests were repeated at pH_0 6 (Figure 9(b)), calcium consumption was noted in the compatibility tests due to chemical reaction between SI and calcium from the solution, which confirms PAPE was incompatible with NSSW at pH_0 6. In addition, the normalised calcium concentration was lower for pH_0 6 than pH_0 4 for both substrates, due to the low-pH-driven dissolution (~ 0.4 and ~ 1 in dolomite and calcite, respectively)[16,18].
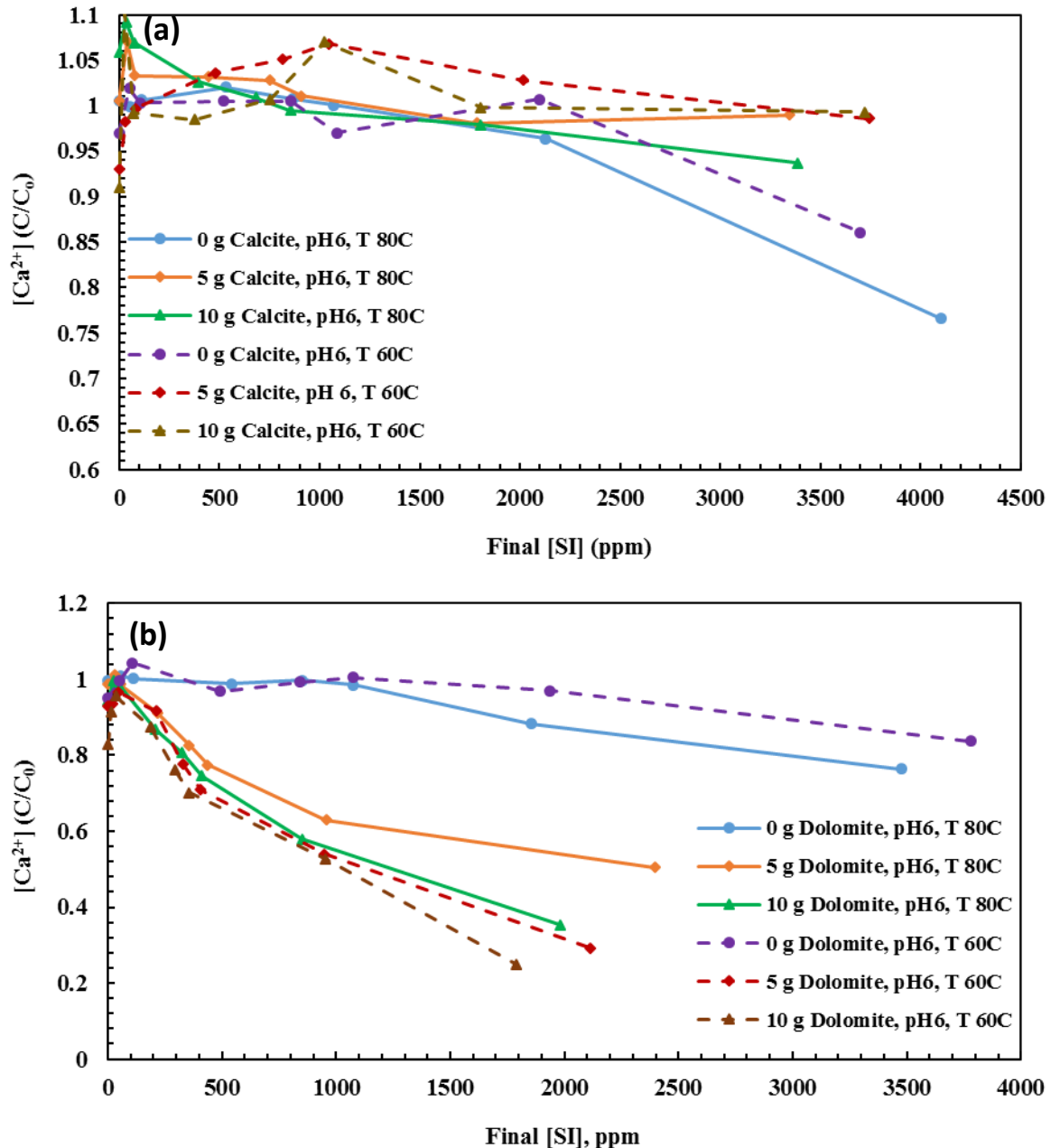
Figure 10. Comparison of C/C_0 Ca^{2+} for PAPE with 0, 5 and 10 g of (a) calcite or (b) dolomite at T = 60 & 80°C, pH_0 6

The calcium concentration decreased in the absence of a carbonate substrate (Figures 10(a) and 10(b)), indicating that PAPE was incompatible with NSSW in these conditions. For 2000 and 4000 ppm PAPE, a SI-M^{2+} complex was formed at 80°C, while 4000 ppm PAPE was required for precipitation at 60°C, suggesting that PAPE incompatibility increased at higher temperature. Because the solubility of PAPE-Ca^{2+} was lower at higher temperature, this results in more precipitation being formed at higher temperature.

In the PAPE/calcite system, the normalised calcium concentration in PAPE/calcite system at 60°C levelled off ~ 1, which means that all calcium generated *in situ* was consumed and there was no excess calcium in solution, while in the same system at 80°C, normalised [Ca^{2+}] decreased even below the

baseline, which means that some calcium was consumed from the NSSW. Indeed, the calcium involved in complexation for PAPE/calcite system at 60°C was less than that at 80°C, meaning that less reaction occurred at lower temperature leading to less apparent adsorption[6,48].

Figure 10(b) shows that the calcium decrease for dolomite was more significant than for calcite, and this is thought to be due to the lower solubility of dolomite at these conditions[35]. Furthermore, the normalised calcium concentration in the dolomite system was similar at both temperatures, except for the highest [PAPE] = 4000 ppm, ~ 0.6 and 0.5 at 60 & 80°C, respectively, meaning that calcium consumption was about the same.

The level of Mg^{2+} should also be taken into account when examining the retention of PAPE and research has shown that magnesium has a poisoning effect for phosphonate scale inhibition performance[48]. The normalised magnesium concentration is presented to in Figures 11 (a) and 11(b); note that Mg is present in the initial NSSW brine ([Mg^{2+}] = 1368 ppm) and it may be available from the dolomite substrate ($CaMg(CO_3)_2$) but it is only present at trace levels in calcite.
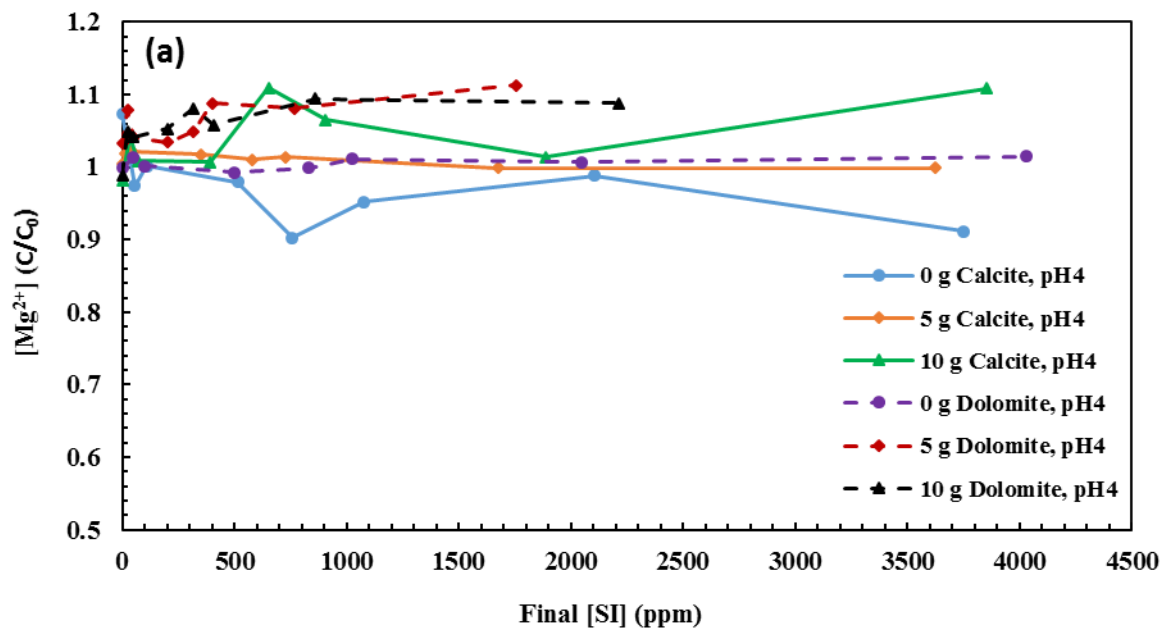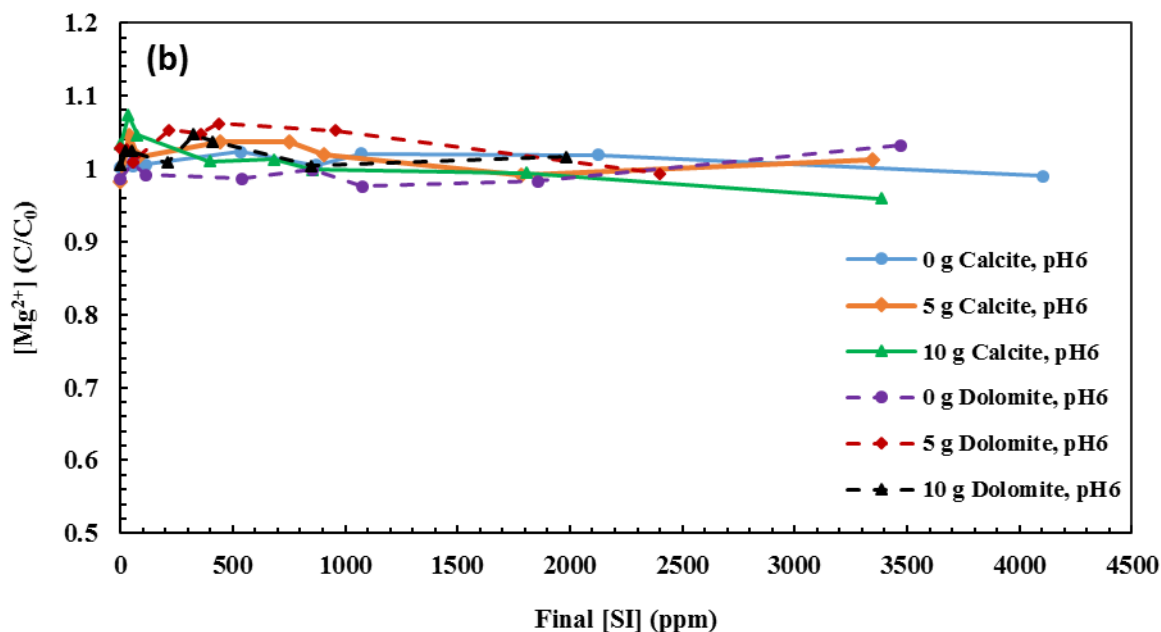
Figure 11. Comparison of C/C_0 Mg^{2+} for PAPE with 0, 5 and 10 g of calcite and dolomite at T = 80°C, (a) pH_0 4 and (b) pH_0 6

As shown in Figures 11(a) and 11(b), there was no significant change in Mg^{2+} concentration in the compatibility tests, *i.e.* no reaction/precipitation. When dolomite was present in the SI solutions, a continuous increase in the normalised magnesium concentration was observed ($[Mg^{2+}] \sim$ x1.1), which was higher at pH_0 4 for Ca^{2+} (due to complexation of SI-Ca^{2+}). However, at pH_0 6, *in* situ magnesium generation (for dolomite) was less than that at pH_0 4 and the overall result was that the final magnesium levels in solution approximately levels off at a normalised value of $[Mg^{2+}] \sim 1$. The change in magnesium concentration was insignificant in comparison to the calcium concentration, indicating that magnesium is effectively not involved in any chemical reactions with PAPE to form a complex, while the calcium concentration changes more significantly, clearly demonstrating that it has greater tendency to complex with PAPE than the magnesium does (Figures 11(a) and 11(b))[35,48].

The initial and final Mg^{2+} concentrations were also measured for the 60°C (not presented here) and were seen to be identical to those at 80°C, indicating that the role of Mg^{2+} was also secondary in these systems.

**ESEM/EDX analysis of PAPE-carbonate precipitates at various temperatures and pH values**

After filtration, all of the solids collected from the static apparent adsorption tests were examined using ESEM/EDX to investigate the morphology of the precipitated complex in the presence of calcite and dolomite substrates and to analyse the surface elemental composition of all the solids present[34,35].
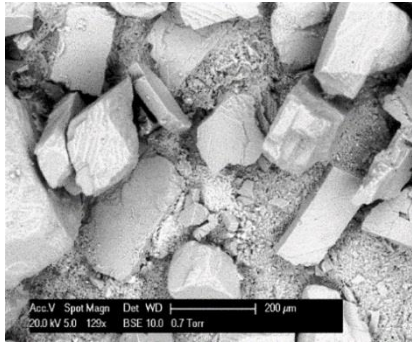
a) Calcite grain, 1000 ppm PAPE
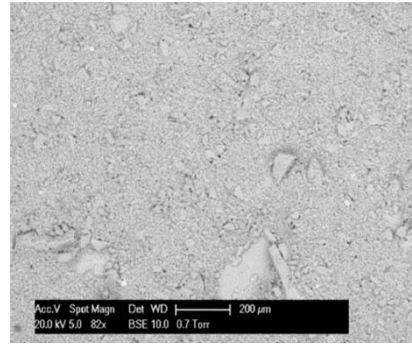
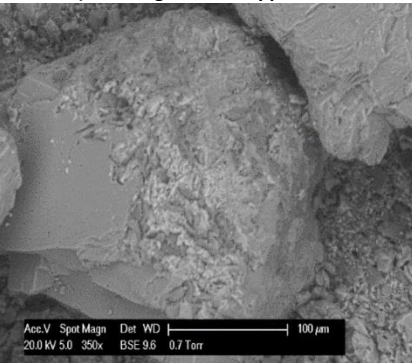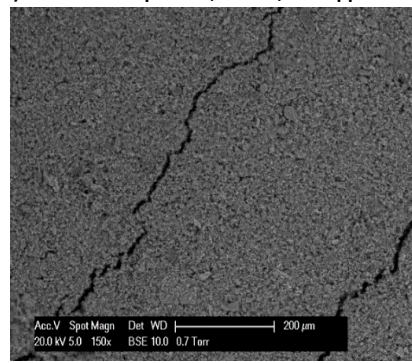**b) Fine solids deposited, calcite, 1000 ppm PAPE**
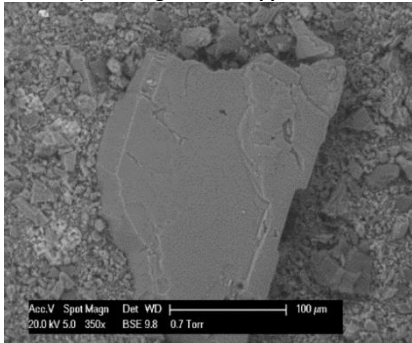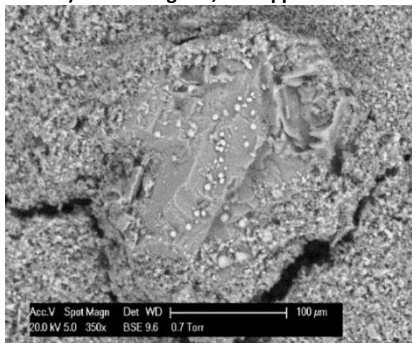
c) Calcite grain, 4000 ppm PAPE
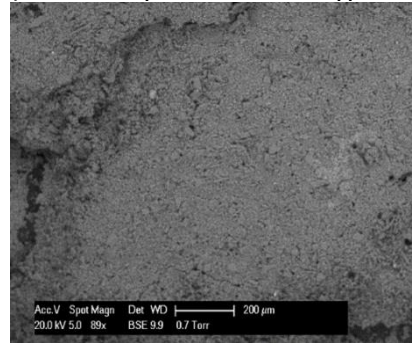
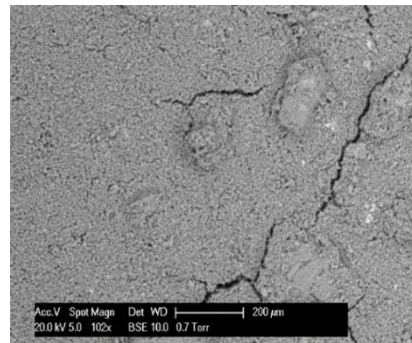**d) Fine solids deposited, calcite, 4000 ppm PAPE**

e) Dolomite grain, 1000 ppm PAPE

f) Precipitate, dolomite, 1000 ppm PAPE

g) Dolomite grain, 4000 ppm PAPE

h) Precipitate, dolomite, 4000 ppm PAPE

Figure 12. ESEM images of solids recovered from tests at 1000 and 4000 ppm PAPE at pH 4, T = 80°C

Table 4. EDX analysis of the solids from 1000 and 4000 ppm PAPE for 100-315 µm calcite at pH_0 4, T = 80°C

Element	Calcite grain 1000 ppm		Fine Solids Deposited 1000 ppm		Calcite grain 4000 ppm		Fine Solids Deposited 4000ppm	
	% Weight	% Atomic	% Weight	% Atomic	% Weight	% Atomic	% Weight	% Atomic
C	18	29	12	20	14	20	13	20
O	41	48	52	63	56	62	53	64
Na	7	6	-	-	1	0.5	-	-
Mg	-	-	1	0.4	11	9	0.23	0.48
P	-	-	1.46	0.3	-	-	1.26	0.68
Cl	8	4	0.54	0.3	1	0.5	0.45	0.24
Ca	26	13	33	16	17	8	32	15

Table 5. EDX analysis of the solids from 1000 and 4000 ppm PAPE for 100-315 µm dolomite at pH_0 4, T = 80°C

Element	Dolomite grain 1000 ppm		Bulk Precipitate 1000 ppm		Dolomite grain 4000 ppm		Bulk Precipitate 4000 ppm	
	% Weight	% Atomic	% Weight	% Atomic	% Weight	% Atomic	% Weight	% Atomic
C	13	19	15	23	13	20	12	19
O	58	65	54	61	54	62	54	62
Na	-	-	-	-	2	1	1	1
Mg	11	7	-	-	8	5	8	5
P	-	-	1	1	5	3	6	4
Cl	1	1	1	1	1	1	2	1
Ca	17	8	29	14	17	8	17	8

The results in Figure 12 and Table 4, show that phosphorous (indicative of the PAPE scale inhibitor) was clearly detected at low levels (1.26% and 1.46% at both 1000 ppm and 4000 ppm, respectively) on the calcite substrate. The amount of phosphorus did not change significantly as [SI] increased, which suggests that the retention regime at pH_0 4 was pure adsorption. In other words, the Ca/P ratio becomes constant as [PAPE] increases which confirms the corresponding apparent adsorption of PAPE on calcite at pH_0 4.

For the equivalent dolomite samples (Figure 12 and Table 5), phosphorous was clearly detected at high levels (~5 % at 4000 ppm PAPE), significantly higher than was detected for calcite grains. In addition, phosphorus was detected around the dolomite grains (Figures 12(e) & 12(g)), which indicated the SI-Ca precipitate adhering to the dolomite surface. Moreover, the phosphorus detected by EDX in the bulk precipitate for dolomite increased in line with PAPE concentration, contrary to the calcite system, which adds further evidence that PAPE retention differs between these systems. PAPE is retained on dolomite through coupled adsorption/precipitation while pure adsorption is the predominant mechanism with calcite[35].
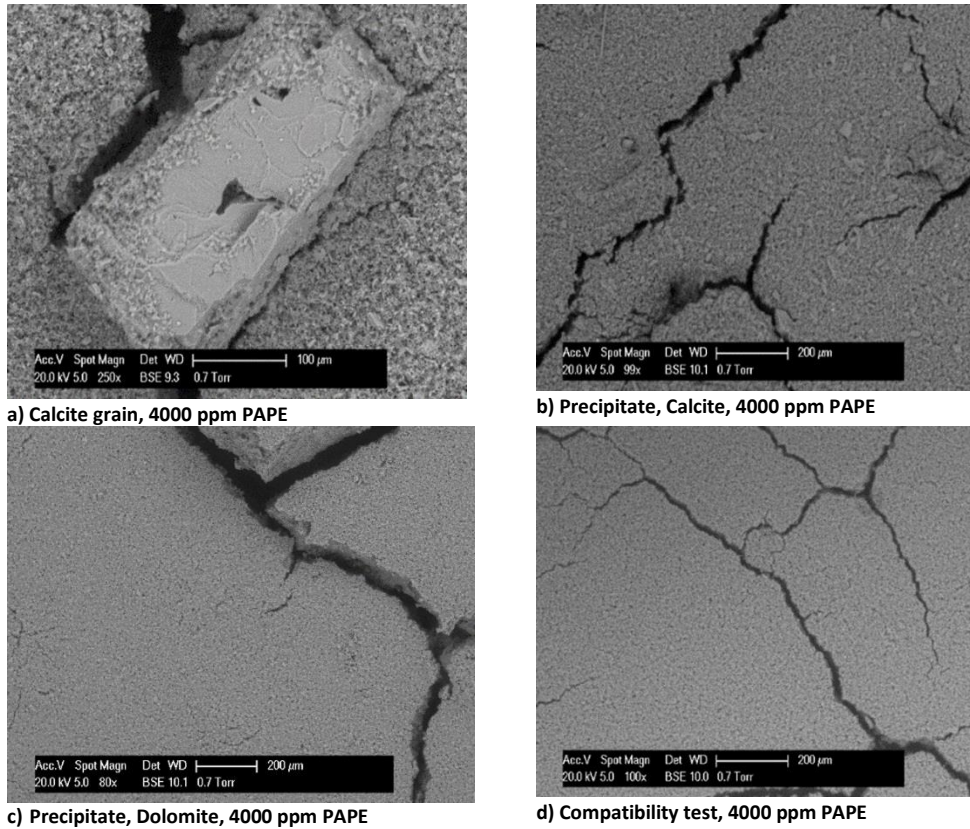
a) Calcite grain, 4000 ppm PAPE

b) Precipitate, Calcite, 4000 ppm PAPE

c) Precipitate, Dolomite, 4000 ppm PAPE

d) Compatibility test, 4000 ppm PAPE

Figure 13. ESEM images of solids recovered from tests calcite and dolomite grains at 4000 ppm PAPE at pH_0 6, T = 80°C

Table 6. EDX analysis of the solids from 4000 ppm PAPE for 100-315 μm calcite and dolomite at pH_0 6, T = 80°C

Element	Calcite grain 4000 ppm		Bulk Precipitate 4000 ppm (PAPE/Calcite)		Bulk Precipitate 4000 ppm (PAPE/Dolomite)		Compatibility test 4000ppm	
	% Weight	% Atomic	% Weight	% Atomic	% Weight	% Atomic	% Weight	% Atomic
C	13	21	11	18	-	-	12	19
O	51	60	52	61	55	71	52	60
Na	1	1	1	1	2	2	2	1
Mg	3	2	3	3	6	5	4	4
P	7	4	9	5	18	12	15	9
Cl	2	4	2	1	5	3	4	2
Ca	23	11	21	11	14	7	11	5

As shown in Figure 13 and Table 6, a high level of phosphorus (15 wt%) was detected in the compatibility test for 4000 ppm PAPE, while the quantity of phosphorous detected at 4000 ppm with calcite and dolomite in the bulk precipitate were 9 and 18 wt%, respectively. There was also a significant amount of phosphorus (7 wt%) detected on the calcite grains themselves at 4000 ppm PAPE, which suggests SI-Ca precipitate adhering to the calcite surface or (less likely) part of an adsorbed SI layer[35]. Moreover, as the pH of the PAPE solutions increased, the amount of phosphorus detected in bulk precipitate clearly increased. Finally, the extent of phosphorus detected for dolomite was higher than for calcite, which confirms the corresponding apparent adsorption results**.**
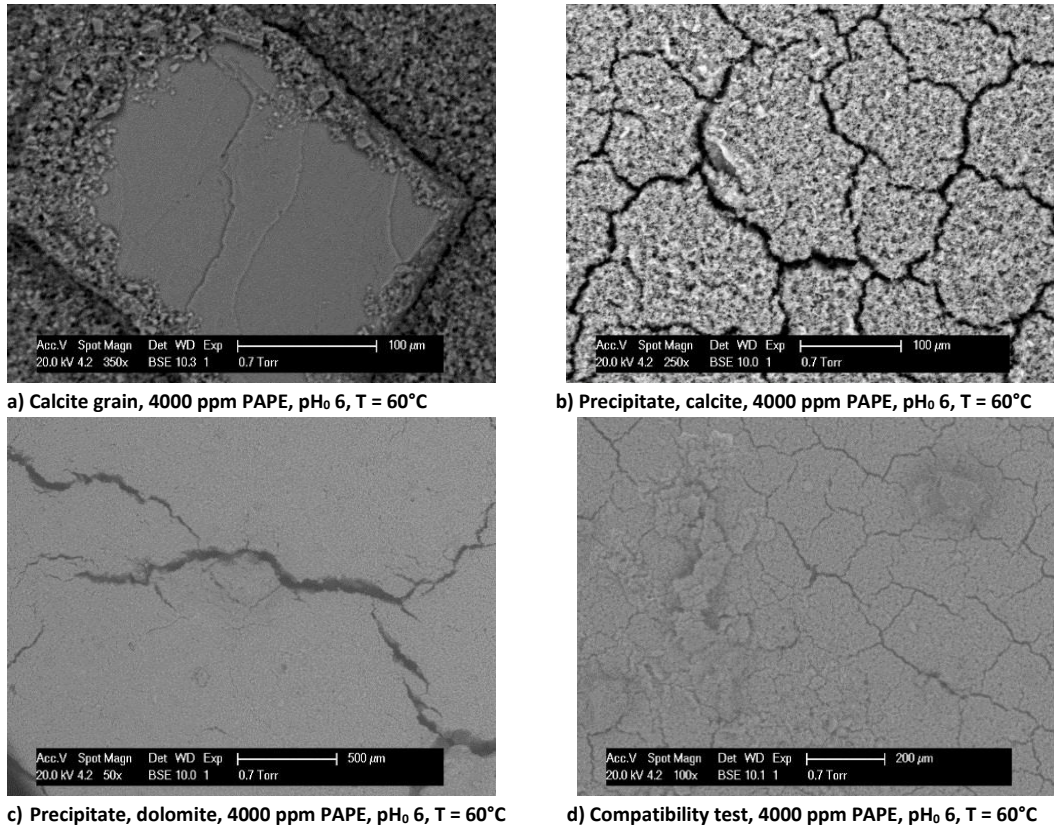
a) Calcite grain, 4000 ppm PAPE, pH₀ 6, T = 60°C

b) Precipitate, calcite, 4000 ppm PAPE, pH₀ 6, T = 60°C

c) Precipitate, dolomite, 4000 ppm PAPE, pH₀ 6, T = 60°C

d) Compatibility test, 4000 ppm PAPE, pH₀ 6, T = 60°C

Figure 14. ESEM images of solids recovered from tests calcite and dolomite grains at 4000 ppm PAPE at pH_0 6, T = 60°C

Table 7. EDX signals on the solids from 4000 ppm PAPE for 100 – 315 µm calcite and dolomite at pH_0 6, T = 60°C

Element	Calcite grain 4000 ppm		Bulk Precipitate 4000 ppm (PAPE/Calcite)		Bulk Precipitate 4000 ppm (PAPE/Dolomite)		Compatibility test 4000ppm	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C	14	23	12	19	11	17	-	-
O	54	63	50	61	52	62	41	58
Na	1	0.7	1	1	1	1	3	3
Mg	1	1	2	1	8	6	8	8
P	2	1	5	3	8	5	20	15
Cl	1	0.3	1	1	2	1	8	5
Ca	27	12	29	14	18	7	20	11

As shown in Figure 14 and Table 7, there was significant phosphorus detected in the samples (bulk precipitation for both PAPE/carbonates and compatibility test (no minerals present)) and the amount of phosphorus in the calcite system was lower than for the dolomite system and these results are consistent with the corresponding apparent adsorption results. In addition, PAPE was seen to be incompatible with NSSW as bulk precipitation was observed in the absence of minerals (Figure 14(d)). The quantity of phosphorus in the compatibility experiment at 60°C was ~ 20% wt and 15% wt at 80°C. For calcite, the amount of phosphorus detected, either around the calcite grain or in bulk precipitation, was lower at lower temperature (2 and 5 wt%, and 7 and 9 wt% for the calcite grain and bulk precipitate at 60 and 80°C, respectively). In the PAPE/dolomite system, the phosphorus content was greater at 80°C for the

highest concentration of PAPE (4000 ppm), which indicates that PAPE retention was greater at 80°C than at 60°C (18 and 8 wt% at 80°C and 60°C, respectively).

Conclusions

The bulk "apparent adsorption" behaviour (Γ_{app} vs. C_f,) of PAPE scale inhibitor (SI) on calcite and dolomite mineral substrates has been studied over a range of conditions. These carbonate systems (both calcite and dolomite) are much more chemically reactive than previously studied sandstone minerals[17,31,34]. A systematic application of ICP-OES (to determine [P] from the SI, [Ca^{2+}] and [Mg^{2+}]), pH analysis and ESEM/EDX of the SI/Ca precipitates formed has allowed for the rationalisation of the results in reference to the intrinsic functionality of the scale inhibitor and the reactivity of the carbonate mineral substrates.

The specific conclusions from this work are as follows:

1. Both pure adsorption (Γ) and coupled adsorption precipitation (Γ/Π) regimes were clearly observed for PAPE with a dolomite substrate at pH_0 4 and 6, while for the PAPE and calcite case at initial adjusted pH 4, only pure adsorption was observed at 80°C. However, precipitation is more dominant for PAPE/carbonate retention than adsorption. At 60°C and pH 6, the situation is different in that pure adsorption is the dominant retention regime for calcite/PAPE, while in the PAPE/dolomite system, precipitation is the dominant mechanism.

2. In general, the degree of apparent adsorption increased at higher pH for PAPE/calcite system (contrary to polymeric scale inhibitors). In the PAPE/calcite system at pH_0 4, the retention regime was only pure adsorption, while for PAPE/dolomite and PAPE/calcite systems at pH_0 6, precipitation was the more dominant mechanism.

3. The amount of apparent adsorption in the PAPE/dolomite system was seen to be effectively pH independent, which is quite different to the PAPE/calcite system in which the apparent adsorption was greater at higher pH.

4. For all concentrations of PAPE, the amount of apparent adsorption of with calcite was lower at 60°C than at 80°C. In contrast, apparent adsorption did not change due to temperature for the PAPE/dolomite system, except at [PAPE] = 4000 ppm, where precipitation was lower at 80°C.

5. The carbonate mineralogy plays an important role in determining the detailed retention mechanism of PAPE in carbonate systems. Greater retention was observed for PAPE with dolomite than on calcite, despite the former being less chemically reactive. Therefore, during the design of squeeze treatments in carbonate formations, the rock composition should be taken into consideration.

6. Calcium has much higher affinity for chemical interaction with PAPE than magnesium. Thus, it is mainly the calcium-PAPE complex that is involved in the retention process.

7. In the PAPE/calcite system, apparent adsorption increased at higher temperature, which may be a kinetic effect leading to the rapid formation of a SI-Ca^{2+} complex. However, in the PAPE/dolomite system, apparent adsorption did not change noticeably as a function of temperature, possibly highlighting the dominance of pH in this system. For PAPE/calcite, both temperature and pH affected retention.

8. Results from the ESEM/EDX generally confirm and are very consistent with the static adsorption results. EDX detectable phosphorus levels (indicating the presence of the PAPE inhibitor) were observed in the precipitated deposits formed by combined Γ/Π. The amount of phosphorus detected, though not strictly quantitative, was seen to increase as Γ_{app} (precipitation) increased. In addition, phosphorus (PAPE) was detected on the surface of the calcite or dolomite grains directly, with the amount detected higher at 80°C than at 60°C (only at 4000 ppm for dolomite), in line with the corresponding apparent adsorption results.

Implications of these Findings for Industry

Approximately 50% of the world's oil production is from carbonate formations. Carbonate rocks are more chemically reactive substrates than sandstones, and chemical scale inhibitors (SIs) not only adsorb on these rock but they also react with them chemically. This interaction contributes to the retention mechanism of the SI in a squeeze treatment since the SI can precipitate, generally as a sparingly soluble calcium complex. Understanding the retention mechanism of different scale inhibitors in carbonate reservoirs allows us to build models to describe these processes; PAPE is the subject of this paper, but the same approach applies to all SI types. Such models can then be used by well technologists and oilfield chemists to design and optimise SI squeeze treatments. The input data to carry out these calculations can be derived from experiments of the type described in this paper and also by supporting core floods. As a result of this work, longer squeeze lifetimes and improved efficiency of SI deployment in carbonate reservoirs can be achieved.

Acknowledgments

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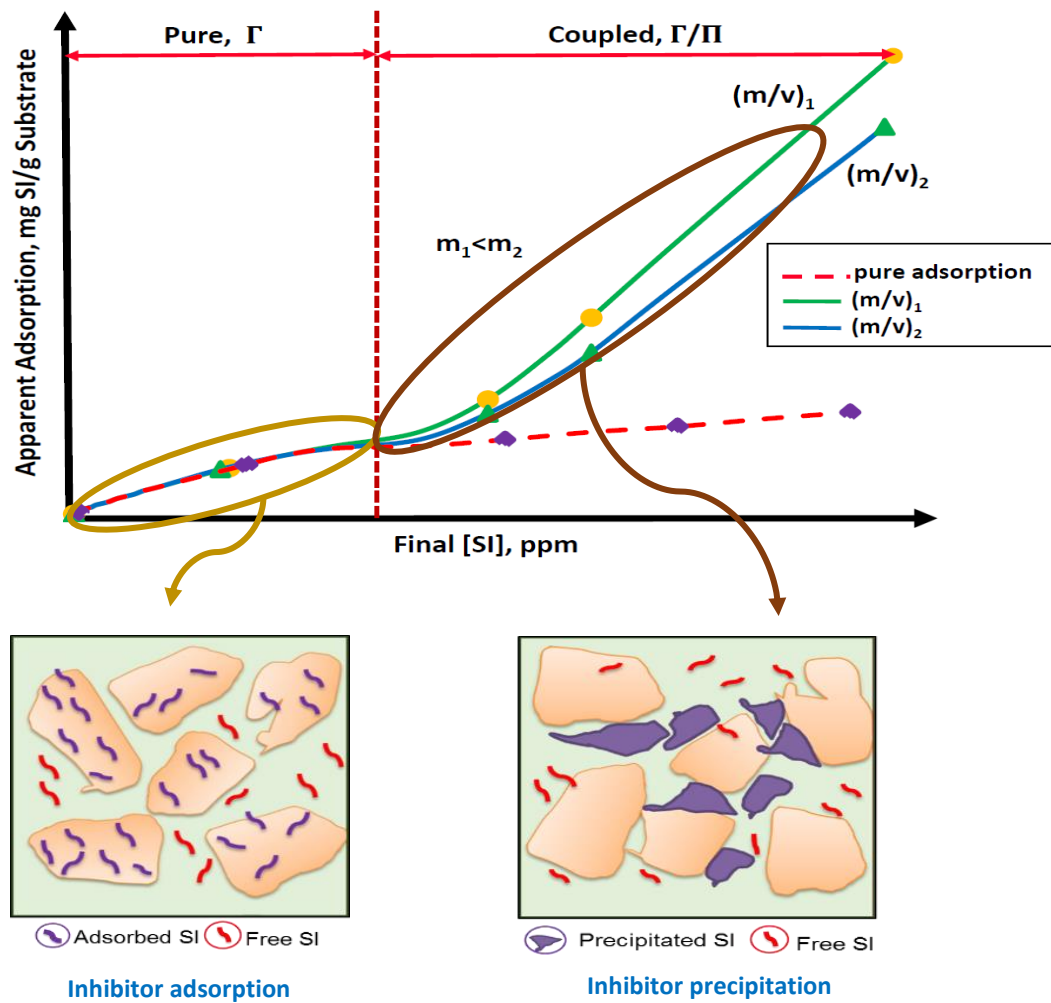
Schematic showing how both coupled adsorption and precipitation can occur

Synopsis:

The current work is focused on the bulk "apparent adsorption" behaviour of a new environmental friendly phosphate ester SI (PAPE) onto carbonate mineral substrates for initial solution pH values at two different temperatures. A systematic study has been carried out on the SI/Ca precipitates formed, by applying both ESEM/EDX to identify the morphology and the approximate composition of the precipitates.