

# APPLICATION OF ENVIRONMENTALLY FRIENDLY SCALE INHIBITORS IN CARBONATE COREFLOODING EXPERIMENTS

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*This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Abu Dhabi, UAE, 29 October-2 November 2008*

## ABSTRACT

Due to the new governmental regulations, the oil industry is currently facing severe restrictions concerning the discharge of oilfield chemicals into the environment. The purpose of this study was to test the possibility of replacing a phosphonate scale inhibitor (diethylenetriamine penta (methylphosphonic acid)) DETPMP by more environmentally friendly “green” scale inhibitors. The green scale inhibitors tested in this study are the Carboxy Methyl Inulin (CMI) and the polyaspartate (PASP). The corefloods have been performed on a Jurassic Portlandian carbonate, which has two cement types, micrite and calcite; and  $\Phi \sim 19.80\%$ ,  $k = 600 - 700\text{mD}$ . This study showed that the results of coreflood performed with polyaspartate (PASP) scale inhibitor are much better than those performed with CMI scale inhibitor. The retention of PASP although lower than DETPMP, is higher than CMI scale inhibitor. The PASP levels drop much more rapidly than the DETPMP levels but the squeeze lifetime is much longer than the CMI corefloods. The coreflooding results obtained from the PASP scale inhibitor are very promising however; the hyamine method used for analyzing the green scale inhibitors (CMI and PASP) has to be replaced by a more accurate and less time consuming method of measurement.

**Keywords:** green scale inhibitor, phosphonate, polyaspartate, Carboxy Methyl Inulin, coreflood, Portlandian carbonate

## 1. INTRODUCTION

A common problem in the oil and gas production is scale deposition causing permeability reduction near the wellbore. Oilfield scale is an assemblage of deposits that can develop in the formation pores near the wellbore as a result of the precipitation of solids from brines present in the reservoir and production flow system. It can also block flow by clogging perforations or forming a thick lining in the production tubing (Fig.1). The build-up of scale inside well bores causes millions of dollars in damage every year. The precipitation of these solids occurs as the result of changes in the ionic composition, pH, pressure and temperature of the brine. Common scales are calcium carbonate ( $\text{CaCO}_3$ ) and barium sulphate ( $\text{BaSO}_4$ ). When the formation of sulphate or carbonate scale is a problem in producer wells, the most common remedy is to treat the formation with a scale inhibitor in a “squeeze” treatment (Vetter, 1973). In squeeze treatments, the intention is to retain the maximum amount of inhibitor in the formation itself either by (i) Adsorption of the inhibitor on the rock substrate

by a physico chemical process or (ii) Precipitation (or phase separation) of the inhibitor in a controlled manner, away from the near wellbore area. This is generally achieved by adjusting the solution chemistry ( $[Ca^{2+}]$ , pH, temperature etc). Reactions that govern the inhibitor adsorption and release are very complicated. Several factors, such as pH,  $[Ca^{2+}]$ ,  $[Mg^{2+}]$ , temperature, rock mineralogy etc, affect the adsorption level and the shape of the adsorption isotherm (Baraka-Lokmane and Sorbie, 2006).

## 2. GREEN SCALE INHIBITORS

The oil industry is currently facing severe restrictions concerning the discharge of oilfield chemicals into the environment. More and more severe environmental constraints have prompted users to assume a rational management of industrial waters and brines and to take more restrictive steps concerning its disposal. At the present time, one of the common approaches for controlling calcium carbonate or barium sulfate scale formation is to use an organic phosphorous scale inhibitor conjointly with other additives to avoid corrosion or bacterial fouling. Bacterial fouling can be described as well screen clogging and failure due to the growth of iron and manganese bacteria including oxide and hydroxide deposition and incrustation caused by the activities of the iron and manganese bacteria. High levels of phosphonates are becoming increasingly restricted in terms of release to the environment. The structural formula of phosphonate (DETPMP) is given in Fig.2. The same is true for some metallic additives such as for example zinc or chromium (Kohler et al., 2004). A number of regulations were implemented for the protection of the environment. The most known among them are for the North Sea (UK, Norway, Denmark, The Netherlands) and the US Gulf Coast oil and gas fields. Miksic et al. (2005) have published lists of the chemicals environmentally acceptable in these regions, limiting the number of chemicals allowed for use in accordance with their level of biodegradability, bioaccumulation and toxicity. The conventional phosphorous inhibitors have first been replaced by less toxic organic phosphoro compounds such as carboxy hydroxyl methyl phosphonic acid and dibutyl phosphoro dithoic acid. Then new classes of compounds not based on phosphorous chemistry, and being less toxic have been introduced into the marketplace. These are polymers such as polyacrylates and derivatives and various maleic and sulfonic acid homo- and copo-lymers. Some new chemistries were also proposed including natural compounds and carboxylated plant polysaccharides such as carboxylated inulins (Putilova et al., 1960). Among them the “greenest” scale inhibitors are the biodegradable Aspartate and Inulin derivatives.

### 2.1 Polyaspartate (PASP)

Polyaspartates are prepared from L-aspartic acid through 3 different syntheses that are based on intermolecular dehydration: thermal polycondensations without or with an acid catalyst and bulk polycondensations with catalyst (Collins, 1999). The structural formula of PASP is given in Fig.3. Laboratory studies using the jar tests and the tube blocking tests demonstrated that Polyaspartate can inhibit both carbonate and sulphate based scales (Inches et al., 2007). Laboratory tests showed that polyaspartate has a dual functionality acting as both a scale and corrosion inhibitor under oil field conditions (Collins, 1999; Inches et al.,

2007). Polyaspartate can be readily biodegradable and has achieved the stringent standards required for its use in the North Sea.

## 2.2 Carboxy Methyl Inulin (CMI)

The carboxy methyl inulins (CMI) are derivatives from inulin which is a natural  $\beta$  (2-1) poly-fructoside with a glucose unit at the reducing end, extracted from chicory roots. Carboxylate groups are introduced into the polysaccharide by carboxy methylation with sodium monochloro acetate as reagent in alkaline medium (Verraest et al., 1996). Inulin has an excellent calcium tolerance thus allowing its application in various oilfield conditions. It is an inherently biodegradable SI (scale inhibitor) with an excellent ecotoxicity profile for fresh and seawater species. CMI is particularly effective in sequestration of hard water cations, and thus serves as an anti-scalant which could find uses in food processing (Johannsen, 2003). The structural formula of Carboxy Methyl Inulin is given in Fig.4.

## 2.3 Previous Corefloods with Green Scale Inhibitors

The only coreflood reported so far using Carboxy Methyl Inulin was carried out by the Institut Français du Pétrole, France. Comparative dynamic adsorption/desorption tests with both CMI and a polyacrylate (10g/L, pH 6, 60°C) were performed on consolidated Lavoux limestone from South West of France. The main characteristics of the cores used were; Porosity  $\Phi = 21.5\%$ , Permeability  $k_{brine} = 5.3\text{mD}$  (Bazin et al., 2004). The studies showed that the length of time required for the CMI to fall below 1 ppm active (squeeze lifetime) was found about 2.5 times longer with Forties formation water than with SW (synthetic seawater) postflush. This is related to the difference in  $\text{Ca}^{2+}$  concentration of the brines used for the desorption (400ppm in SW, 3100ppm in the formation water). The higher levels of  $\text{Ca}^{2+}$  in the formation water potentially improves the CMI retention profile. No study on the interaction between a reservoir rock material and the green scale inhibitor polyaspartate has been published in the literature to date.

# 3. EXPERIMENTAL CONDITIONS

## 3.1 Brine and Scale Inhibitors Solutions

The composition of the brine solution (synthetic seawater, SW) used for the dilution of the scale inhibitor stock solutions and for the coreflood tests is presented in Table 1. The phosphonate scale inhibitor (SI) used for the coreflood P1 was prepared from a 25% active DETPMP phosphonate solution. A partly neutralized DETPMP seawater solution containing 5,000ppm active SI at pH 4 was used. The analysis by inductively coupled plasma (ICP) of the phosphorus content of the DETPMP solution allowed determining the SI concentration in the core effluents. The Carboxy Methyl Inulin (CMI) scale inhibitor solutions used for the corefloods P2 and P3 were prepared from a 17.5% active CMI solution. The injected solutions contained 23,000ppm and 135,000ppm active CMI respectively at pH 7.82 (P2) and pH 6 (P3). The inhibitor used for the core flood P4 was polyaspartate (PASP). The PASP solution was prepared from a 39% active PASP solution. The injected scale inhibitor solution contained 5,000ppm active PASP at pH 4. The CMI and PASP contents were determined by the Hyamine 1622 titrimetric method. This method of measurement is extremely time consuming, only 10 samples can be analysis per day, while at least 60

samples from the 600 samples collected per experiment, need to be analyzed. The desired dilutions were prepared using a Microprocessor-controlled dilutor (Gilson Dilutor 401). For the calibration, matrix matched standards were used to suppress the interferences of the brine solution. The different SI solutions were dosed with a lithium tracer, in a ratio of 1:100. The 50ppm lithium tracer solution and the inhibitor solutions (DETPMP, CMI and PASP) were filtered through a 0.45 $\mu$ m membrane filter prior to use. The effluent samples from the different corefloods were also analyzed for the cation concentrations, [Ca<sup>2+</sup>], [Mg<sup>2+</sup>], [Fe<sup>2+/3+</sup>], and [Li<sup>+</sup>], by inductively coupled plasma (ICP).

### 3.2 Carbonate Rock Material

This rock material originates from the Portland Basebed stone and is an open textured oolitic limestone from the Jurassic Portlandian Formation. The results of the bulk rock XRD and XRF analyses show that the rock material is composed mainly of magnesium calcite (98 to 99.9%). The rock material contains 0.53% of MgO. Quartz comprises between 2 to ~ 0.1% of the rock. Analysis of the fines showed that no clay minerals are present. The rock material is a pure porous marine oolitic limestone composed of fine-grained remains of microorganisms with calcite shells, ooids with micrite (microcrystalline calcite) and sparite calcite cement (Fig.5). The rock material presents three major types of porosity: a high intergranular porosity, a moldic, secondary porosity, created by dissolution of the carbonate shell fragments later in the diagenetic history of the limestone and a high microporosity which occurs between the micritic matrix of the sample (Fig.5). The petrophysical measurements of the rock material show that the limestone has a porosity (helium porosimeter),  $\Phi = 19.80\%$ , grain density,  $\rho = 2.61\text{g/cm}^3$  and respective brine permeabilities:  $k(P1) = 606\text{mD}$ ;  $k(P2) = 618\text{mD}$ ;  $k(P3) = 699\text{mD}$  and  $k(P4) = 625\text{mD}$ .

### 3.3 Dynamic Corefloods Experiments

Coreflood experiments in the laboratory are a vital tool in understanding the mechanisms controlling scale inhibitor/rock interaction since: they allow complete temperature and pressure control, the complete mineralogical petrophysical characteristics of the rock can be determined, and it is possible to perform post-scale inhibitor treatment petrography to quantify the magnitude of retained scale inhibitor and its mineralogical structure and location. The main steps in the corefloods broadly follow the field inhibitor treatment stages and are as follows: (i) Seawater saturation, permeability measurement and core characterization; (ii) Injection of the main scale inhibitor slug (containing 50ppm lithium tracer) followed by a shut-in of 24 hours; (iii) Seawater postflush or back production until the inhibitor concentration drops below 0.5ppm (MIC level). The MIC is the minimum inhibitor concentration for some defined level of inhibition efficiency; (iv) Permeability measurement to check if the treatment has caused any degradation in reservoir properties and a detailed petrography analysis is finally carried out. The coreflooding procedures adopted are designed to study the inhibitor retention and return characteristics in single phase flow. The corefloods P1, P2, P3 and P4 were conducted in Hassler-type core holders with a confining pressure of approximately 1,200 psi and a line pressure of approximately 200psi (Fig.6). Pressure drops ( $\Delta P$ ) between inlet and outlet of the cores (2.5" length and 1"

diameter) were monitored throughout all of the experiments. Variable flow rate vs.  $\Delta P$  measurements were performed to determine the pre- and post-flood permeabilities.

## 4. RESULTS AND DISCUSSION

In this study we present the results of three corefloods (P2, P3 and P4) performed at 40°C using two green inhibitors (CMI and PASP). The results of these corefloods have been compared with another coreflood (P1) performed with DETPMP (a phosphonate SI) at room temperature. The purpose of these corefloods is to compare SI/carbonate interactions of the phosphonate (DETPMP) and green inhibitors (CMI and PASP) in order to see if in the future, the phosphonate can be replaced by more environmentally friendly scale inhibitors. The main features of these floods are as follows:

- (i) Coreflood P1: This coreflood was performed with a 5,000ppm active seawater solution of the phosphonate (DETPMP) at pH adjusted to 4 and at room temperature.
- (ii) Coreflood P2: This coreflood was performed with a 23,000ppm active seawater solution of Carboxy Methyl Inulin (CMI) at pH 7.82 and at a temperature of 40°C.
- (iii) Coreflood P3: This coreflood was performed with a 135,000ppm active seawater solution of Carboxy Methyl Inulin (CMI) at pH 6 and at a temperature of 40°C.
- (iv) Coreflood P4: This coreflood was performed with a 5,000ppm active seawater solution of polyaspartate (PASP) at pH 4 and at a temperature of 40°C.

### 4.1 Permeability Measurements

Table 2 shows the measured values of permeability for the pre- and post-treatment stages. In corefloods P1, P2, P3 and P4, the initial permeabilities before the SI treatment were 606mD, 618mD, 699mD and 625mD respectively. After the SI treatment an increase of 17% ( $k = 709\text{mD}$ ), 12% ( $k = 691\text{mD}$ ), 24% ( $k = 866\text{mD}$ ) and 10% ( $k = 688\text{mD}$ ) were observed respectively for the floods P1, P2, P3 and P4. Table 3 shows that following the corefloods performed with the Carboxy Methyl Inulin SI a higher increase in permeability is observed both as the concentration of the SI increases and the pH of the SI decreases.

### 4.2 Scale Inhibitor Adsorption

Fig.7 shows the SI and lithium tracer normalized effluent concentration profiles ( $(C/C_0)$  vs. Pore volumes (PV)) recorded during the main treatments and the initial post-flush stages for the unidirectional corefloods P1, P2, P3 and P4. For flood P1, a large SI adsorption can be observed from the retardation between scale inhibitor effluent and the lithium tracer effluent. Flood P2 shows a much lower Carboxy Methyl Inulin adsorption as the retardation between the green scale inhibitor and the lithium tracer effluent is not evident. Flood P3 shows a slightly higher Carboxy Methyl Inulin adsorption than for flood P2. Retardation between both SI and the lithium tracer effluents can also be observed (Fig.7). The core flood P4 performed with polyaspartate (PASP) scale inhibitor presents much better results than the core floods performed with 23,000 ppm (P2) and 135,000 ppm (P3) CMI scale inhibitor (Figs 7 and 8). The retention of the PASP (P4) although lower than the DETPMP scale inhibitor (P1), is higher than the CMI scale inhibitor (Figs 7 and 8).

### 4.3 Scale Inhibitor Desorption by Brine Post-flush

Fig.9 presents the late (~800 PV) post-flush SI return profiles for all four corefloods. Floods P2 and P3 performed with Carboxy Methyl Inulin drop more rapidly than flood P1 performed with DETPMP. For the flood P1, DETPMP concentration drops to ~ 1ppm after ~ 530PV and to ~ 0.5ppm after ~ 700PV. As previously shown by other investigators in carbonate cores (Bazin et al., 2004; Baraka-Lokmane and Sorbie, 2006) longer squeeze lifetimes are usually observed for a DETPMP phosphonate compared to other phosphonates. This may be explained by the fact that in the presence of calcium, and especially at pH 4, DETPMP is retained by a precipitation mechanism. CMI being less sensitive to the presence of divalent ions, retention by precipitation is not expected to occur as readily. In post-flood P2, CMI concentration drops to ~ 1ppm after ~100PV and in post-flood P3, [CMI SI] drops to ~ 1ppm after ~127PV (Fig.9). Thus Flood P2 performed with 23,000ppm Carboxy Methyl Inulin SI at pH 7.82 drops more rapidly than flood P3 performed with 135,000ppm Carboxy Methyl Inulin SI at pH 6. Thus results of the corefloods P2 and P3 are comparable with those performed on the Lavoux limestone (Bazin et al., 2004; Kohler et al., 2004). Table 4 shows that the amount of SI retained in the rock is respectively 2.72% for flood P2 and 4.80% for flood P3, compared to 21.33% of for flood P1. Flood P3 performed with a higher concentration of CMI at pH 6 shows a higher percentage of SI retained in the rock (4.80%) than flood P2 (2.72%) with a lower injection concentration of CMI at pH 7.82. Both low solution pH and high inhibitor concentration seem to favor CMI retention in the core. These results, although in contradiction with the observed squeeze lifetimes in favor of the DETPMP vs. the CMI green scale inhibitor, may be explained by the differences in the retention mechanisms of both inhibitors: pure reversible adsorption for the CMI inhibitor, retention by precipitation for the DETPMP inhibitor, as observed by others (Bazin et al. 2004). The adsorption and the desorption mechanisms of the CMI SI, which is a polyelectrolyte scale inhibitor, are controlled by the electrostatic forces, which depend on the following factors: (i) chemical structure of the inhibitor, (ii) the composition of the mineral surface and (iii) the aqueous phase. The adsorption of the CMI SI on the mineral surfaces of the carbonate rocks (calcite) is complicated because calcite minerals are soluble, in addition the dissolution of calcium carbonate (calcite), negative and positive species are present in the aqueous solution.

Fig.9 shows that although the polyaspartate drops much more rapidly than the DETPMP levels, the squeeze lifetime is much longer than the squeeze lifetime of the CMI corefloods (P2 and P3); the polyaspartate levels reach 1ppm after 550 pore volumes (PV). However after 550 PV, the accuracy of the measured SI levels is questionable because the concentration of the SI is too low to be measured with the Hyamine method. Fig.9 shows that the results are comparable with those obtained with the DETPMP SI. Indeed, after 350 PV of the postflush stages, the levels of polyaspartate are about the same as the levels of DETPMP. The calculated percentage of SI return was 83.32% for flood P4, which was performed with 5,000ppm PASP SI at pH 4, compared to 78.67% for flood P1, which was performed with 5,000ppm DETPMP SI at pH 4. The amount of SI retained in the rock is equal to 2.47mg/g compared to 2.71mg/g for flood P1. The results of this study have shown that the core flood performed with the PASP SI (P4) present equivalent amount of the SI retained in the rock compared to the flood performed with the DETPMP SI (P1) (Table 4).

#### 4.4 Cation Analysis – Calcium and Magnesium Effluents

Several factors, such as pH,  $[Ca^{2+}]$ ,  $[Mg^{2+}]$ , rock mineralogy etc, affect the adsorption level and the shape of the adsorption isotherm. Baraka-Lokmane and Sorbie (2006) showed that the higher the concentration of SI (DETPMP) and the lower the pH, the more  $Ca^{2+}$  dissolution is observed. The concentration levels of both  $Ca^{2+}$  and  $Mg^{2+}$  correlate with the concentration of the SI, with a larger effect being seen at higher concentrations. This is explained by the binding of both  $Mg^{2+}$  and  $Ca^{2+}$  to DETPMP. Fig.10 shows the  $Ca^{2+}$  and the  $Mg^{2+}$  concentrations profiles during SI adsorption and over the initial post-flush period for floods P1 and P4. For the flood P1, the calcium level in this flood remains above that of the injected inhibitor slug during the main treatment and the injected postflush brine. Since the  $[Ca^{2+}]$  concentration in the SI stock solution is about 400ppm, then this gives a total dissolution level of 642.07mg (Table 3). Two contrary effects influence the effluent  $[Ca^{2+}]$  concentration; some  $Ca^{2+}$  remains bound to the DETPMP and, due to the dissolution of the carbonate rock, additional free calcium ions are produced. This last effect is predominant. Fig.10 shows that for flood P1, the  $[Mg^{2+}]$  concentration drops to a level of 1360ppm during the injection of the DETPMP and a spike is observed just following the shut in (at 22 PV). In the postflush stages of flood P1, the  $[Mg^{2+}]$  concentration increases to a value of about 1600ppm. Thus during the injection of the SI, we observe a loss of  $Mg^{2+}$  (from 1400 to 1360ppm), the  $Mg^{2+}$  being adsorbed together with the SI. After the shut-in during the SW postflush we observe a spike in the  $[Mg^{2+}]$  concentration released together with the SI. Fig.10 shows that for Flood P4 performed with PASP SI at pH 4 and post flushed with seawater at pH 6, the calcium dissolution occurs mainly during the main treatment stage (where  $[Ca^{2+}] > 860$ ppm), the dissolution continues also in the postflush stage through to the end of the flood; where the calcium level ( $[Ca^{2+}] = 450$ ppm) remains above that of the postflush brine ( $[Ca^{2+}] = 416$ ppm). Although the results for the  $Mg^{2+}$  effluents in Fig.10 appear quite interesting, on closer analysis they indicate that  $Mg^{2+}$  does not interact significantly with the carbonate rock or the Polyaspartate SI. Table 3 shows that there is a gain of 1006mg of  $Mg^{2+}$ . This is explained by the dissolution of the Mg-rich calcite, which contains  $Mg^{2+}$  in its composition ( $(Ca, Mg) CO_3$ ). Fig.11 suggests that floods P2 and P3 show as for flood P1 (Fig.10), a dropping of the  $Mg^{2+}$  levels during the injection of the SI; However as it can be seen in Fig.11, the stock levels of the  $[Mg^{2+}]$  of the CMI solutions are low (1300ppm for P2 and 630ppm for P3) during the injection of the CMI SI. This is explained by the low activity (17.30%) of the CMI SI, therefore the levels of  $Mg^{2+}$  contained in the SW are low. The same effect of lower dilution levels by seawater explains also the low effluent  $[Ca^{2+}]$  concentration measured during the CMI injection (higher levels for P3 than for P2), the  $[Ca^{2+}]$  concentration increasing then during the postflush to SW levels (i.e. about 420ppm).

#### 5. CONCLUSION

The adsorption/desorption mechanisms being very dependant on experimental conditions (pH of the injected SI solution and brine post-flush, concentration of the SI, temperature, rock mineralogy,..), other experiments are required for both the CMI and PASP before drawing general conclusions on lifetime performance of these inhibitors. Results show that far higher SI lifetimes inside the porous medium are observed with the DETPMP compared

to the CMI; however; these first results could be improved by reducing the pH of the injected CMI solution and by changing the chemistry the salinity, and hardness of either main flush or postflush brine.

The squeeze lifetime of the PASP is much longer than the squeeze lifetimes of the CMI. The results of the PASP are comparable with those obtained with the DETPMP. However after 550 PV, the accuracy of the measured inhibitor levels is questionable because the concentration of the scale inhibitor is too low to be measured with the Hyamine method. The coreflooding results obtained from the polyaspartate are very promising however; the hyamine method used for analyzing the PASP inhibitor has to be replaced by a more accurate and less time consuming method of measurement.

## **ACKNOWLEDGEMENTS**

The sponsors of the Heriot-Watt University, Flow Assurance and Scale Team (FAST) JIP are thanked for their support, input and permission to publish this work: Baker Petrolite, BG Group, BP, Champion Technologies, Chemtura, Chevron, Clariant, ConocoPhillips, Halliburton, Hydro Oil and Energy, M I Production Chemicals, Nalco, Petrobras, REP, Rhodia, Shell, Solutia, Statoil and Total.

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**Table 1** The composition of brine solution used for the tests

Component	Concentration (g/l)	Ion	Concentration (ppm)
NaCl	24.08	Sodium (Na <sup>+</sup> )	10,890
CaCl <sub>2</sub> .2H <sub>2</sub> O	2.34	Calcium (Ca <sup>2+</sup> )	428
MgCl <sub>2</sub> .6 H <sub>2</sub> O	11.44	Magnesium (Mg <sup>2+</sup> )	1,368
KCl	0.877	Potassium (K <sup>+</sup> )	460
NaSO <sub>4</sub>	4.38	Sulphate (SO <sub>4</sub> <sup>2-</sup> )	2,960
		Chloride (Cl <sup>-</sup> )	19,773

**Table 2** Brine permeability values before and after the scale inhibitor treatment

Coreflood	Permeability (k), mD Pre-treatment	Permeability (k), mD Post-treatment	Increase in permeability, %
P1	606	724	19
P2	618	691	12
P3	699	866	24
P4	625	688	10

**Table 3** Scale inhibitor adsorption, calcium carbonate (dissolution) and magnesium (gain and loss) during the main treatment and postflush stages

Coreflood	Inhibitor adsorption (mg/g)	CaCO <sub>3</sub> Dissolution (mg)		Mg Gain (mg)		Mg Loss (mg)	
		MT*	PF*	MT	PF	MT	PF
P1 (SI pH = 4) SW pH = 6)	2.71	135.74 (1.94)	506.33 (7.20)		836.24	7.21	
P2 (SI pH = 7.82 SW pH = 6)	0.64	23.56 (0.35)	428.50 (6.39)		808.61	65.02	
P3 (SI pH = 6 SW pH = 6)	0.89	136.09 (2.04)	452.43 (6.78)	19.99	803.98		
P4 (SI pH = 4 SW pH = 6)	2.47	163.45 (2.40)	79.48 (1.17)		1006.62	8.10	

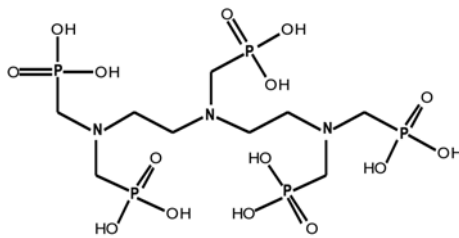
The values in brackets are in mg/g; \* MT = main treatment; PF = post-flush; SI = scale inhibitor; SW = seawater

**Table 4** Values of scale inhibitor adsorption calculated using mass balance

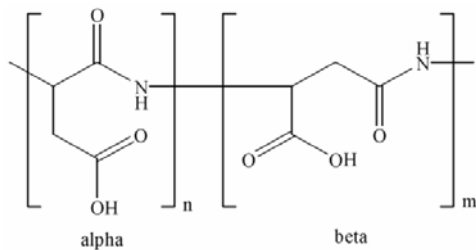
Coreflood	Total SI injected (mg)	Total SI retained (mg)	% SI return	% SI retained	SI adsorption (mg/g)
P1	822.19	175.34	78.67	21.33	2.71
P2	4671.30	42.97	97.28	2.72	0.64
P3	27000.00	74.54	95.20	4.80	0.89
P4	1109.20	184.99	83.32	16.68	2.47



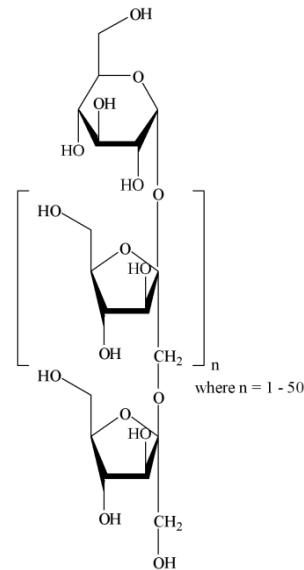
**Fig.1:** Scale deposition in a pipe



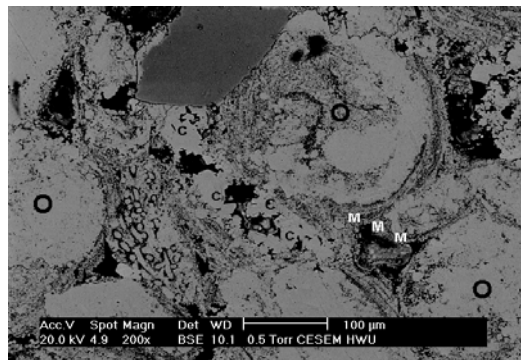
**Fig.2:** Structure of phosphonate (DETPMP)



**Fig.3:** Structure of polyaspartate (PASP)



**Fig.4:** Structure of Carboxy Methyl Inulin (CMI)



**Fig.5:** SEM photo showing cement containing scale inhibitor micrite and sparite crystals, around the ooid grains (M: micrite, C: calcite, O: ooid)

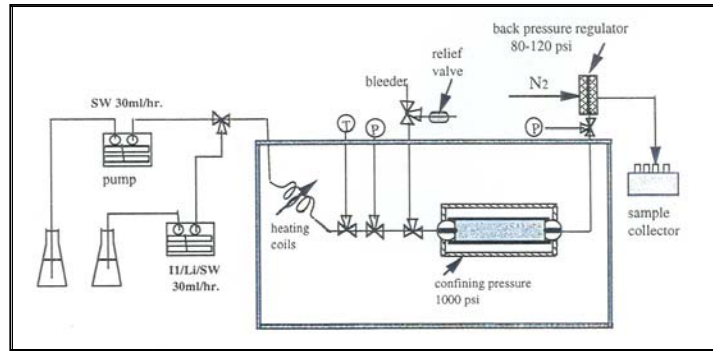


Fig.6: Flow diagram of experimental set up for corefloods experiments

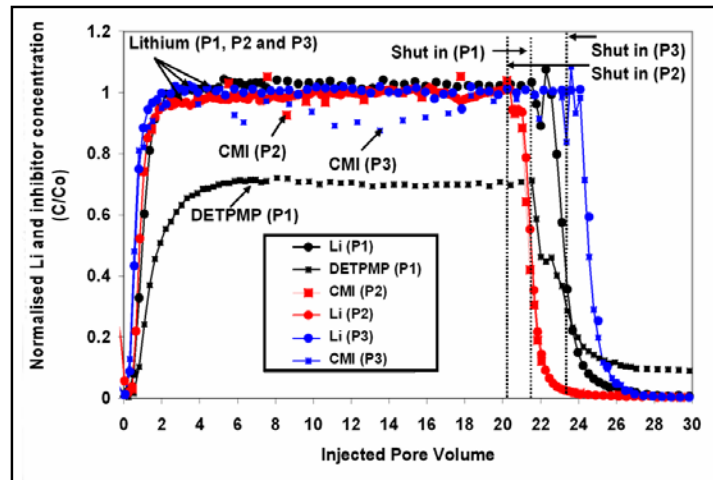


Fig.7: Normalised (C/Co) scale inhibitor (DETPMP and CMI) and lithium concentration profiles initial adsorption and early postflush stages

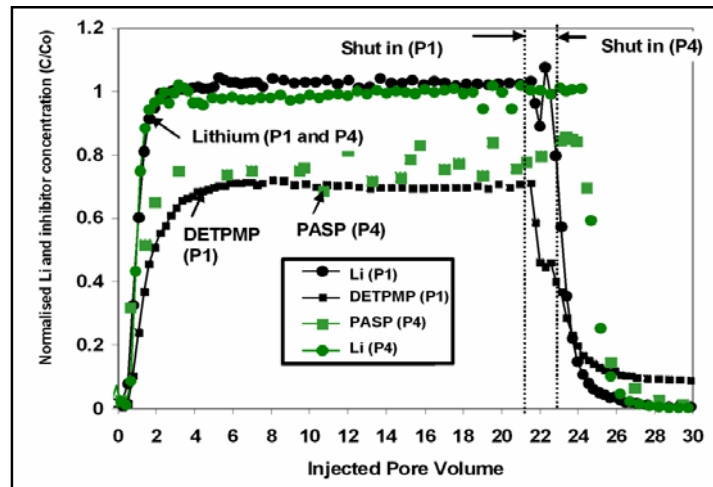


Fig.8: Normalised (C/Co) scale inhibitor (DETPMP and PASP) and lithium concentration profiles initial adsorption and early postflush stages

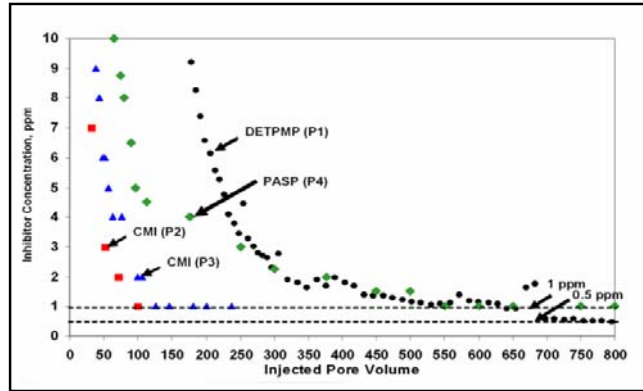


Fig.9: Inhibitor return profiles, late post-flush (0 -> 800 pore volumes)

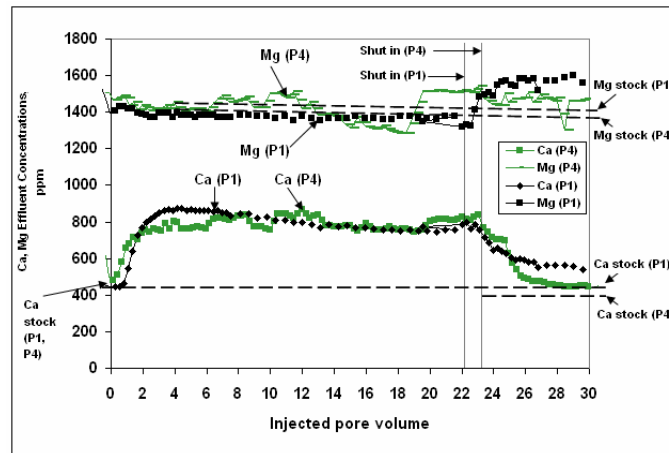


Fig.10: Recorded calcium and magnesium concentration profiles, compared with the stocks obtained during adsorption and post-flush stages, floods P1 and P4

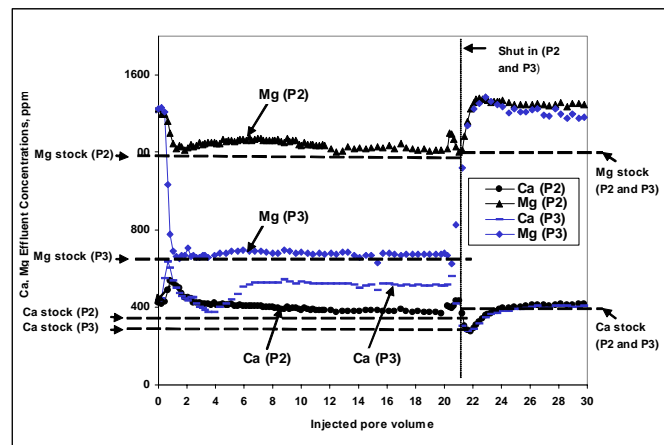


Fig.11: Recorded calcium and magnesium concentration profiles, compared with the stocks obtained during adsorption and post-flush stages, floods P2 and P3