PREDICTION, CONTROL AND VALIDATION OF ROCK DISSOLUTION DURING SMART WATER INJECTION AND ITS IMPACT ON WATERFLOOD PERFORMANCE IN HEAVY OIL CARBONATE RESERVOIRS

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ABSTRACT

Smart water injection studies are rewriting the rules and the understanding of water injection as a method for improving oil production. The voluminous research being undertaken in this area has enabled us to better understand the significant impact that the water composition and salinity can make in the outcome of waterflood. A universal consensus has not yet been reached on the main mechanism of oil recovery by smart water injection but it appears that in most previous works the role of injected water/crude oil interactions has been overlooked.

A first approach would be to systematically analyse the fundamental knowledge of such fluid-fluid and rock-fluids interactions. Once this knowledge is defined, we might be able to predict its direct impact in terms of oil production. Then, the presence of such mechanisms could be controlled and validated through more complex multi-variable experiments.

This paper provides new evidence by means of fluid-fluid interactions and coreflood experiments that natural generation of acidic water in the reservoir is responsible for improvement of oil recovery by smart water injection in carbonate rocks through rock dissolution. Laboratory experiments were performed at 92 ºC using a dolomite rock. Four coreflood experiments were conducted by injecting either seawater or low salinity seawater and showed significant additional oil recovery when smart waters were injected in both secondary and tertiary modes. Changes in permeability of the core, derived from rock dissolution, were observed and the magnitude of the changes was bigger when the crude oil was basic in comparison with an acidic one. The rock permeability increased by up to 100% if the injection water was low salinity whereas, if seawater was injected, rock damage was observed. The results indicate that the migration of water-soluble compounds of the crude oil becomes more important for basic oils and causes a drop in the pH of injected water. The results show that it is possible to predict the extent of the rock dissolution based on fluid-fluid contact tests. The findings also show that the amount of oil recovered by smart water depends on the type of crude oil. Less oil production was detected when acidic crude oils were used in the same rock under the same conditions.

INTRODUCTION

Since it has been analytically established that the interactions of crude oil/smart water (especially low salinity waters) can naturally generate acidic water during water injection in carbonate rocks (Gachuz et al, 2016), the goal of this work will be the validation of these observations. The lack of equilibrium in the fluid/rock system may be the underlying cause of changes in wettability and rock dissolution due to such chemical interactions between invading fluids and the initial native fluids, principally with the crude oils. For this reason, one cannot confirm these facts without considering the flow of fluids throughout the cores at reservoir conditions. Moreover, the possibility that these conditions would involve the pressure and its influence cannot be excluded either. Considering that dissolution has been identified as part of the effects that occur during smart water injection, especially in low salinity waters, coreflood experiments should enable us to observe the difference in the enhanced oil recovery if different brines and crude oils are used. This will make it possible to distinguish where and when this vital mechanism occurs.

As indicated by us in 2016, there is probably a pattern that proves that dissolution plays an important role during the additional oil production. Therefore, this technical paper will mainly focus on more elaborate experiments such as coreflood experiments where it will be demonstrated how the simple models previously presented (Gachuz et al., 2016) can be used to predict if dissolution of the rock is taking place in the fluid/rock interaction and then to evaluate its impact on final oil production. Subsequently, coreflood experiments were then carried out under both secondary and tertiary injection modes, in order to experimentally investigate the performance of smart water injection for heavy oils. The effects of the composition of the crude oil on the dissolution of rock were also studied and compared in terms of additional oil recovery. Water composition changes, pH measurements, permeability variation and oil recovery before and after the experiments were all performed during the experiments. That will allow us to examine the fundamentals of fluid flow and analyse whether changes occur, where they occur and how they are influenced by the injected waters. The article ends with the discussion of what implications these results will have for the oil production of carbonate heavy oil reservoirs. The results of this work will supplement previous findings.

EXPERIMENTAL

Two crude oil samples were selected for this research from a group of carbonate formations with similar reservoir conditions. Table 1 shows the basic properties of the selected crude oils. The core was taken from a dolomite core. The dimensions for this used core were as follows: diameter = 5.09 cm, length = 15.20 cm, pore volume = 58.15 cc, brine permeability = 142.21 mD and porosity = 18.80 %. The presence of sulphate was not detected using an Environmental Scanning Electron Microscope (ESEM), however, ionic analysis of the effluents during water saturation confirmed the presence of

sulphate into the core. Brines were made in the laboratory from original compositions. Four brine solutions were prepared for this research (Table 2). Seawater composition from Gulf of Mexico was considered for this study because oil reservoirs are located offshore. Formation brine only contains small amounts of magnesium and sulphate, details may be consulted in Gachuz et al., 2016.

Table 1.- Crude Oil Properties.

Crude Oil	Density* (ºAPI)	Viscosity* (cp)	Asphaltene Content (% wt)	Water Content (ppm)*	Resins Content (% wt)	TAN (mgKOH/g)*	TBN (mgKOH/g)*
A	14.12	53,484.31	13.20	208.40	31.70	1.00	3.50
E	19.27	1,251.80	0.82	2,920.52	16.85	2.40	2.10

*Measured at 20 ºC

Table 2.- Brine Compositions.

Brine/Ion	Na^+	Ca^{2+}	Mg^{2-}	K^+	Cl^-	SO_4^{2-}	HCO_3^-	TDS (mg/l)
FW (mg/l)	9,614	320	218	-	15,117	550	1,135	25,670
SW (mg/l)	11,429	429	1,361	351	20,040	3,500	47	37,198
LSSW10 (mg/l)	1,142	42	136	35	2,004	350	4	3,719
LSSW50 (mg/l)	228	8	27	7	400	70	1	743

*Measured at 20 ºC

The working temperature was at 92 ºC and an overburden pressure of 1,500 psi (reservoir conditions) was kept the same during the whole study. The orientation of the coreflood experiments was horizontal with a back pressure of 500 psi. The formation water was injected into the core at constant rate, which didn't exceed 1 ft³/day. Once the specific water saturation was established using crude oils, the core was aged and flooded with fresh crude oil at different times for 20 days to restore the original wetting conditions. Injection of working brines through the core was performed at 2 cm³/hr. In all the experiments, once the oil production finished, a change in the water injection rate was applied to make sure that there was no more produced oil. The oil volume (expressed as a percentage of the original oil in place) was recorded as a function of pore volume injected. The same core was used for all the reported coreflood tests followed the same experimental procedures.

RESULTS AND DISCUSIONS

For the first coreflood experiments (first and second coreflood experiment) the crude oil "A" was selected and dolomite core was firstly flooded with a diluted version of seawater called LSSW10 (refer to Table 2 for composition brine) as a secondary process. Pressure, pH and effluent composition were constantly monitored, Figure 1. After 22 pore volumes were injected, a 24-hour soak period was applied. No extra oil was recovered after this closure. Because of the high permeability of the core, a high rate was applied at the end of each stage (20 cm³/hr). The LSSW10 injection resulted in the final recovery of 69.30 % OOIP. With respect to pH, after rising slightly and staying almost stable during the injection of 9.5 pore volumes, it fell at 10 pore volumes injected and fluctuated between 7.2 to 7.3 units.

For the effluents of the LSSW10 injection period (Figure 2a and 2b), it may be clearly seen that the calcium and bicarbonate concentrations rose and those of sulphate and magnesium also exhibited small variations in comparison with the original composition of the injected water. The effluent samples were treated with methyl orange and then titrated with hydrochloric acid once it was not possible to detect bicarbonate concentrations using ion chromatography analysis.
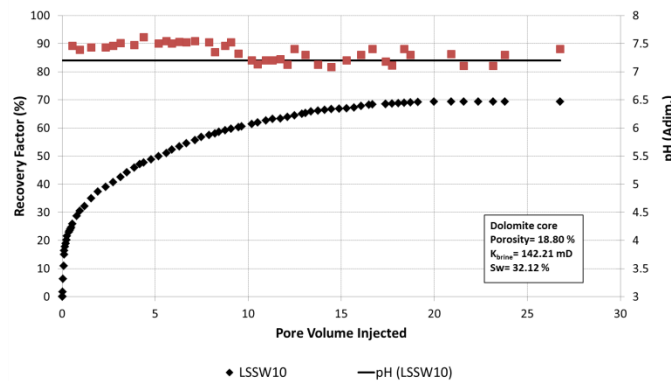
Figure 1.- Cumulative oil recovery with low salinity seawater at 92 ºC.

The concentrations of the rest of the elements remained constant (sodium, potassium and chloride). This production may be linked to the reaction of the injected water, firstly with the crude oil and subsequently with the rock, leading to a possible dissolution effect. Later, this assumption was supported by the measurement of the new permeability, which turned out to be higher, 180.28 md. Permeability changes were studied using Darcy´s Law. A tertiary programme was not applied for this test.

Once the experiment with low salinity seawater was finished, the core was cleaned and reused later. The same process was repeated, except the type of injected brine was changed. This time (second coreflood experiment), the core was brought into contact with seawater. High oil volume was produced at early time. Before 4 pore volumes had been injected, the recovery factor was around 31 %, as shown in Figure 3. From 5 to 10 pore volumes, the recovered oil was around of 2 % more. Later, pH measurements were obtained from the effluents. The pH tended to drop from 7.8 to 7.0, approximately. Alotaibi et al. (2010) obtained similar results using dolomite cores at 90 ºC. In their tests, the recovery factor was around 35.5 % after 2.5 pore volumes. The reactivity of the core towards the divalent ions appeared to be negligible, except for magnesium, Figure 4. This divalent ion and also sulphur showed small variations on their concentrations, staying active at high temperature. The bicarbonate ion was completely inert.
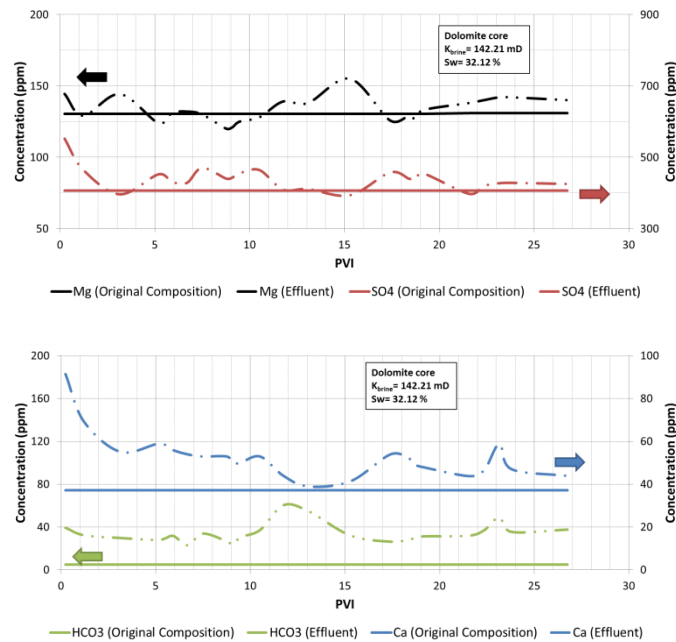
Figure 2.- Changes in ion concentrations of magnesium, sulphate (above), bicarbonate and calcium (below) when low salinity water is flooded through the core at 92 ºC.
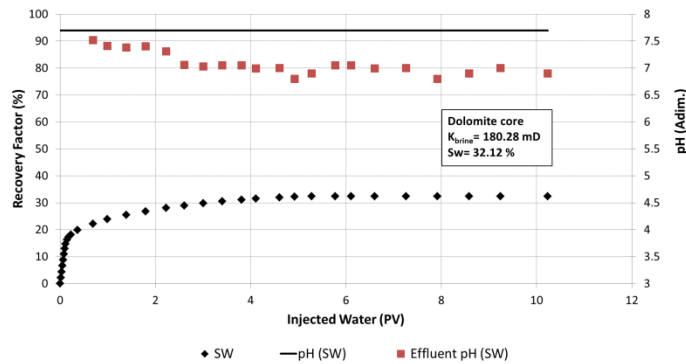

Figure 3.- Oil recovery versus pore volumes of injected seawater at 92 ºC.

Calcium, magnesium and sulphate have been reported as potential determining ions for improving oil recovery in carbonate rocks. For these experiments, the effect of such ions on the wettability change is not in good agreement with the results described by Austad's group (2009 to 2012).

However, there is a contrast between the ion evaluation and the permeability measurements after the experiment. The water permeability decreased dramatically to a stable value of 64.08 md, which was around 65 % below its initial permeability (180.28 md). The decrease in permeability denotes that the permeability was dominated by the damage resulting from the seawater injection. The lack of ion production and the loss of permeability may be linked to this damage caused by seawater injection. Overall, this core was found to suffer permeability loss when seawater is used as a smart fluid.
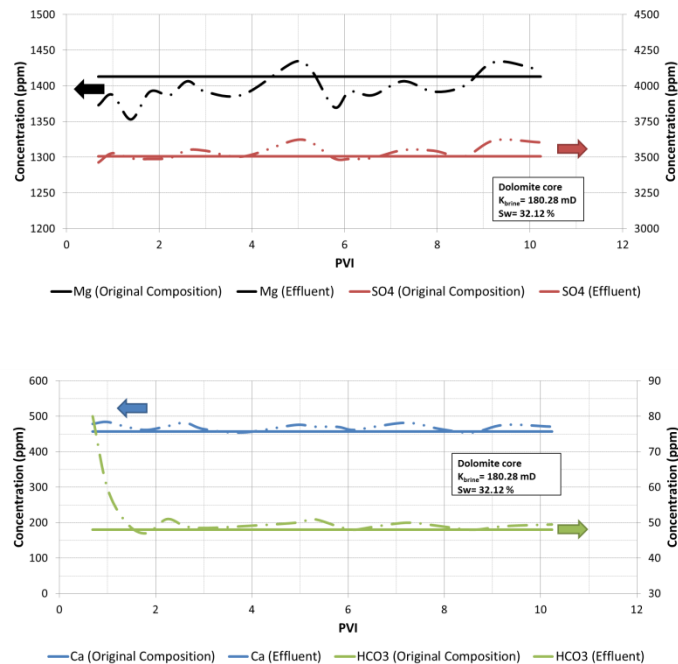
Figure 4.- Changes in ion concentration of magnesium, sulphate (above), calcium and bicarbonate (below) when seawater is flooded as a secondary process.

From the differential pressure curves in Figure 5, it is evident that during each experiment, the pressure first increased then decreased slowly, and later the trend was stabilised. In addition, from this Figure, some small variations of pressure were noticed when both high rates and shut-in periods were applied. Thereafter, other major changes in pressure were not detected or the differential pressure response did not give an indication of any instability and hence unusual behaviour.

For the dolomite core, the seawater was supersaturated (SI>0) at high temperatures. That is, the seawater is fully saturated with diverse ions in solution, so, this state does not allow that material from the rock become dissolved and/or transported. Thus, this condition of saturation set up the potential for particular events such as precipitation, pore blocking (plugging) or loss of permeability.

In the case with inject seawater, it is clear that saturation condition of this fluid will favour the permeability reduction (up to 65 % for the dolomite core), as shown in Table 3. If the saturation index is negative (SI<0) as for the low salinity waters (Gachuz et al., 2016) then no precipitation will take place. Consequently, the low salinity waters may adequately dissolve and transport the released material from the rock, which originated from the action of the acidic water derived from the crude oil/low salinity brine interaction. Crude oil with low TAN was especially prone to create acidic water because of the highest amount of water-soluble compounds that are diffused in the aqueous phase, allowing the hydrogen to be released, creating a more acidic environment (Gachuz et al., 2016).
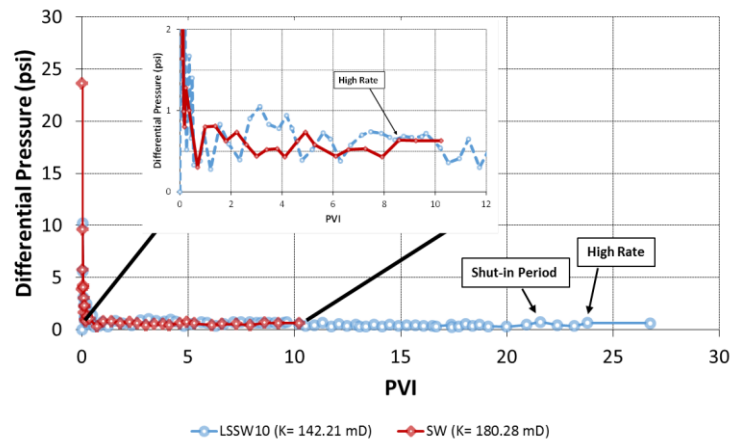
Figure 5.- Differential pressure across core versus pore volumes for the dolomite core with two brines.

Over the long term this process will lead to improving the internal conductivity in the porous media, generating a better permeability, as seen in Table 3 for low salinity water injection (from 142.21 to 180.28 md, respectively). Dissolution of the rock is usually studied in the context of room conditions and hence research for elevated temperatures or pressures is limited in the published literature (Morey, 1962; Plummer et al., 1978; Zhang et al., 2007). For instance, calcite and dolomite minerals have been investigated in terms of the importance of transport control vs pH changes. When the temperature goes up diffusion will control the system. At low temperatures, dissolution is a chemical control mechanism (Sjoberg, 1976 and 1978; Sjoberg et al., 1983-1985; Brantley et al., 2008).

Table 3.- Change of core permeability after coreflood experiments.

Experiment	Initial K_{brine} (mD)	Process	Injected Fluid	RF (%)	Final K_{brine} (mD)
1	142.21	Secondary	LSSW10	69.30	180.28
2	180.28	Secondary	Seawater	32.43	64.08

In order to verify that the oil recovery factor may also be associated with the dissolution effect, other parallel coreflood experiments were conducted using the same core (third coreflood experiment). In this case, the core was saturated with crude oil "E", which is more acidic. The results are plotted in Figure 6. For the first experiment with this crude oil, low salinity seawater was intentionally injected. The aim was to firstly remove the damage which existed. Only 42 % of OOIP was recovered during low salinity water injection as a secondary program. When the brine was changed to another low salinity water, LSSW50, an increase in oil production was noticed. After 10 PV of injection, the recovered oil exceeded 45 %. The effect of the low salinity water was less than that observed in the coreflood experiments for the basic crude oil (crude oil "A"). This demonstrates that low salinity fluids play an important role in the wettability change processes.
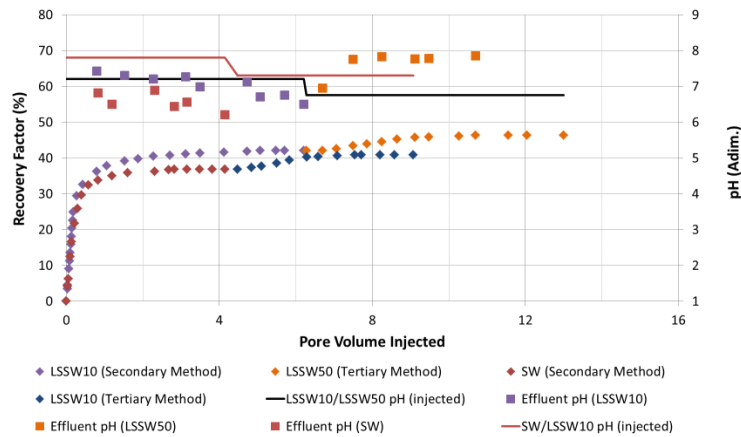
Figure 6.- Oil recovery versus pore volumes of injected seawater at 92 ºC.

In the second case (fourth coreflood experiment), seawater injection was first flooded as a secondary process then low salinity water was injected. The oil recovery for a secondary process using seawater reached a plateau of 36.87 % of OOIP after 4 PVI. The injection fluid was then changed to LSSW10, which resulted in a small increase in oil production with a maximum plateau of 40.62 % after 8 PVI. Previous experiments with the same core and a basic crude oil resulted in higher oil production for low salinity water but slightly lower production for seawater.

Figure 7 illustrates the variations of ion concentrations in terms of pore volumes injected for the low salinity waters system. The concentration of magnesium and sulphate ions did not change for the first period of injection with LSSW10. This is comparable to what was previously observed for the basic crude oil, as shown in Figure 4. The effluents maintained a continuous production of calcium and bicarbonates. When the concentration of the injected fluid was dropped, the production of these ions remained high. As the change in concentration became great enough, the effluents continued producing bicarbonates but the sulphate exhibited a sudden change. This change is perceptible from 7 to 10.70 PVI. The effect of this additional production during the whole experiment can be explained by considering the probable removal of the core damage. Notice also that this low salinity water (LSSW50) has the ability to be less saturated, as it was explained by us in 2016, revealing that the salts in the brine may increase. These results were later confirmed with the permeability measurement, where the final value was 158.57 md, as shown in Table 4. As the low salinity water was injected, the damage was practically removed. The lower the concentration of the brine, the more active the brine will become. Due to contamination with the previous water samples, no analyses were obtained from 10.7 to 13 pore volumes injected. The oil recovery factors, changes in core permeability and ion concentration variations imply that the mechanism of rock dissolution is practically negligible for the experiments using an acidic crude oil (crude oil "E"). Moreover, the wettability change, where it occurred, was relatively lower.

Table 4.- Changes in core permeability after the coreflood experiments for two crude oils.

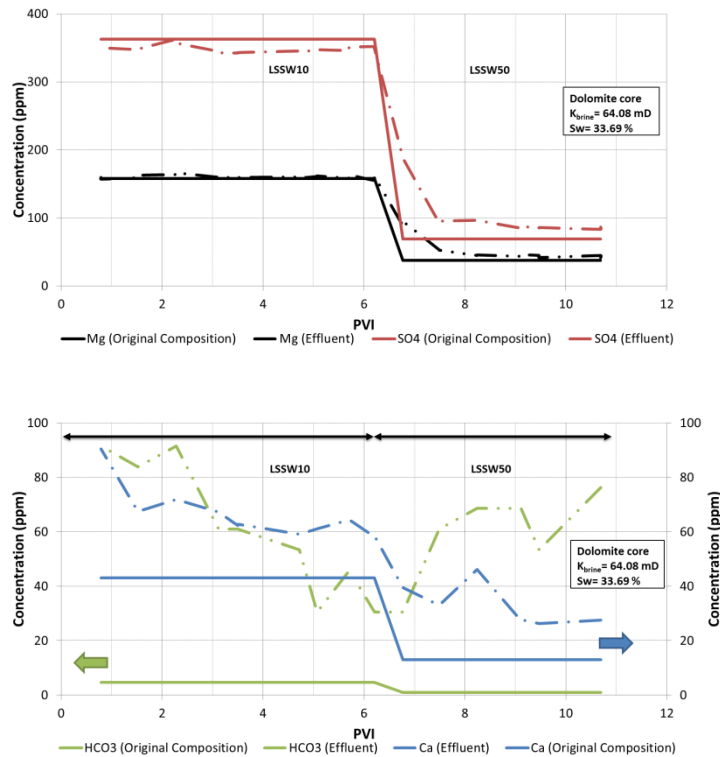| Experiment	Initial k_{brine} (md)	Process	Injected Fluid	RF (%)	Final k_{brine} (md)
Crude Oil "A"					
1	142.21	Secondary	LSSW10	69.30	180.28
2	180.28	Secondary	Seawater	32.43	64.08
Crude Oil "E"					
3	64.08	Secondary/Tertiary	LSSW10/LSSW50	42.05/4.29	158.57
4	158.57	Secondary/Tertiary	Seawater/LSS10	36.87/3.75	141.83

Figure 7.- Changes in ion concentrations of Mg^{2+}, SO_4^{2-} (above), HCO_3^- and Ca^{2+} when low salinity waters were injected through the core using an acidic crude oil (Crude oil "E").

In Figure 8, only very small pressure variations can be noticed during the injection processes. Injection at a high rate caused a rise in pressure to a maximum value of 3 psi. Modification of the rate was not accompanied by an increase in oil recovery. The pressure continued to drop smoothly and stabilised after a while. Additional oil recovery was never gained with high injection rates. In spite of the fact that the permeability changed, no direct experimental evidence is accessible to support the possibility that either dissolution or blockage can be detected by analysing differential pressure across a core, so far. No significant changes can be observed in the pressure behaviour, apart from injection rate adjustments at the end of each sequence.
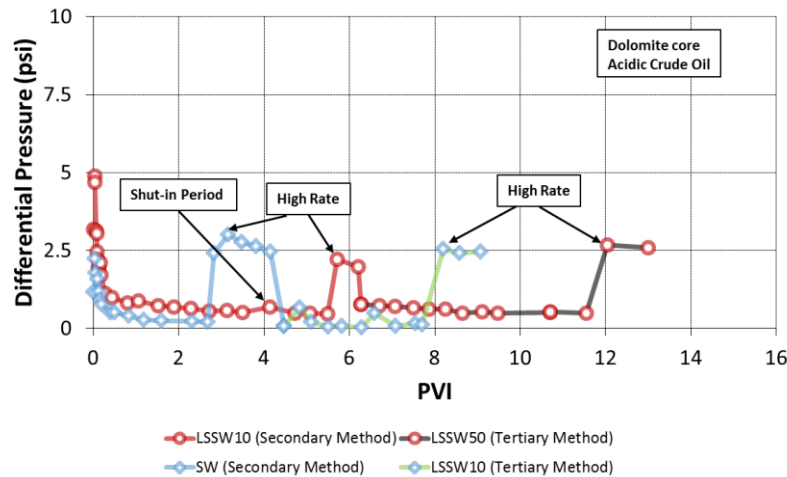
Figure 8.- Differential pressure across core versus pore volumes for the core with four brines.

Morse and Arvidson (2002) compiled dolomite dissolution data as a function of pH from published values. The experiments of Zhang et al. (2007) indicate that the mechanisms of dissolution of dolomite at low temperatures differ from those at high temperatures. Their results indicate that there are linear correlations between concentrations of calcium and magnesium in the aqueous phases. The release rates of calcium and magnesium are proportional (1:1), especially at temperatures below 100 ºC. However, the dissolution product is not proportional (1≠1) at higher temperatures.

Thus, a vast number of studies have provided evidence that the rate of dissolution is highly dependent on diverse variables. Under reservoir conditions where such variables are important, smart waters may then apparently mobilise the released material from the core and produce/transport it to the outside. The observation that smart waters may mobilise this material also suggests that movement and transport are likely to occur during coreflood experiments, in either secondary or tertiary oil recovery methods at high pressure and high temperature, even at reservoir scale, where reservoir conditions could favour better situations for dissolution and transport.

CONCLUSIONS

The effect of the smart waters on rock dissolution has been studied in more detail at dynamic conditions in a dolomitic core. Some conclusions can be drawn as follows:

- The tests of these studies proved that is possible to predict the occurrence of the dissolution phenomenon during smart water injection using simple fluid-fluid contact tests where acidic water generation is easily detected.

- Effluent analysis and permeability evaluations validated the influence caused by low salinity water as acidic water in contact with the rock. The presence of rock

dissolution was principally detected by coreflood experiments through changes in ion concentrations of calcium and bicarbonates and permeability values.

- Crude oil is an important agent playing a vital role in improvement of oil recovery and the rock dissolution effect will be more important at reservoir scale. The findings described here differ from Mahani et al. (2015), where they affirmed that the rock dissolution was only relevant on a laboratory scale and not at reservoir scale. The crude oil, itself, is governing the effects of the smart water injected into the reservoirs.

- Damage to the core occurred when seawater was used for improvement of the oil production. Permeability measurements corroborated these findings.

- Positive effects derivate from the use of seawater were not observed here. In spite the fact that the permeability changes occurred, no direct experimental evidence is accessible to support the possibility that either dissolution or blockage can be detected by analysing differential pressure across the used core, so far.

Therefore, these dissolution studies have help to better understand and verify many of the variables which are taking part during the dissolution in coreflood experiments such as pressure, temperature, rate controlling mechanisms, type of aqueous phase, pH and ionic strength.

ACKNOWLEDGEMENTS

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