Journal of Petroleum Exploration and Production Technology (2019) 9:2343–2351
https://doi.org/10.1007/s13202-019-0634-9

ORIGINAL PAPER - PRODUCTION ENGINEERING

Determination of critical alkalinity (pH) in Fahliyan carbonate reservoir using a new methodology

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Received: 30 December 2018 / Accepted: 19 February 2019 / Published online: 25 February 2019

Abstract

Formation damage is a great concern in reservoir management and can potentially occur due to exposure of formation to alkaline fluids. Exceeding pH over a critical pH may result in an in situ release of fine particles and therefore can cause pore plugging. In this study, a series of core-flooding experiments was carried out to determine the critical pH of alkaline fluids flooding through core samples of Fahliyan carbonate formation. Alkaline fluids with different pH were injected into the core samples and the alkaline sensitivity of the carbonate formation was measured in both qualitative and quantitative forms. The applied approach provides an accurate determination of the degree of formation damage at a base pH (pH = 7) following successive changes in the fluid alkalinity. In addition, the pH values corresponding to different degrees of formation damage, determined qualitatively in other works, are calculated precisely in this paper. The flooded cores showed different response when exposed to fluids with different alkalinity while the degree of induced formation damage varied from 'negligible' to 'severe' which were, in some cases, noticeable and often irreversible. A polynomial relationship between the fluid alkalinity and the corresponding degree of formation damage was proposed for core no.3, which is compared with the conventional methods (Renpu method) underestimating the degree of formation damage (D_k) compared to the modified approach introduced in this paper.

Keywords Sensitivity measurement · Critical pH · Core flooding · Formation damage · Renpu method

Introduction

Most of sandstone and some carbonate reservoirs contain clay minerals with different degrees of sensitivity. The clay minerals which are originally contained on pore walls are fine grained with equivalent diameters less than 20 µm and are extremely exposed to different reservoir fluids (Leone and Scott 1988; Civan 2007; Renpu 2011). The normal production (natural depletion) or injectivity of reservoir can be affected as a result of formation damage during drilling, production and EOR stages and in most cases are irreversible (Civan 2007; Moghadasi et al. 2002). The formation damage can take place in various forms such as physical, chemical and biological with different degree of damages (Miranda and Underdown 1993; Civan 2007; Renpu 2011).

Permeability reduction which is generally caused as a result of reactions between invading fluid and formation rock can lead to precipitations which may result in pore plugging or in another form may cause detachment of insoluble particles migrating through the porous media (Civan 2007). The temperature, invading fluid composition, injection flow rate, pH and also the mineralogical properties of the rock are the most important parameters that can affect the rock nature and the reaction between rock/fluid systems (Mungan 1965; Patino et al. 2003).

The pH of formation water is usually between 4 and 9, while drilling and completion fluids as well as filtration water of cement slurries exhibits a pH in the range of 8–12 (Renpu 2011). After entering the alkaline fluid into the reservoir rock,

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the texture of the clay and siliceous minerals in the reservoir rock is affected due to cement and clay minerals' dissolution and also detachment of particles that can cause pore plugging (depending on the particle size). Alkaline sensitivity analysis can be performed to determine the critical pH above which the detachment occurs, and therefore completion and drilling fluids can be designed at pH values below the critical pH of the reservoir rock to minimize formation damage. (Wojtanowicz et al. 1987; Renpu 2011).

In addition to drilling fluid filtration invasion, alkaline fluids such as NaOH and KOH, sea water, saturated and half-saturated saline waters can be exposed to reservoir rock during the reservoir recovery processes. The permeability reduction occurs as a result of introducing alkaline fluids, e.g., NaOH or $NaSiO_4$ (Bagci and Kok 2001; Liu et al. 2010), or may be initiated from injecting a combination of salt water, calcium chloride and potassium chloride (Mungan 1965). Precipitation of scales during alkaline flooding also occurred at a certain critical pH (Bertaux and Lemanczyk 1987; Eleri et al. 1992). To determine the degree of formation damage and its related causes, the permeability of the core sample is measured at different pH values and each step is compared to its previous value (Surkalo 1990).

To determine the critical pH and its associated formation damage mechanism, a series of core-flooding experiments were carried out on Fahliyan carbonate reservoir core samples. Alkaline fluids with different pH values (7, 8.5, 10 and 12) were injected into core samples at a constant injection rate of 0.5 cc/min. The permeability of the core samples was calculated using linear Darcy law and the pH of the alkaline fluids is increased in steps. A baseline permeability is adopted at a pH of 7, where the initial permeability is measured. Then the permeability is obtained at a higher alkalinity, after which the core is flooded with the base pH and the permeability recovery is obtained. The permeability of the base pH after each step is then compared to characterize the extent of the formation damage.

The degree of formation damage (D_k) is measured at baseline permeability stage. The results were used to determine critical alkaline values and the extent of damage. Also, the core samples exhibit different behaviors when exposed to different alkaline fluids, and the degree of formation damage varies from undamaged to strongly damaged, which is in some cases irreversible. It should be kept in mind that the sensitivity of the reservoir rock to alkaline fluids and its associated critical pH must be determined before designing any working fluids (drilling and completion fluids and also cement slurry). Therefore, the pH of the injection fluids must be kept less than its threshold value to prevent formation damage. Furthermore, the mineralogy of the reservoir rocks and the type of clay minerals, particularly Kaolinite which is known as the common migrating type, are dominant factors affecting the permeability and may cause pore plugging in Fahlyian formation.

Previous works

To evaluate the sensitivity of reservoir rock to injecting fluid pH, the permeability of samples is measured during injection of different alkaline fluids. In this way, it is possible to measure and determine the critical pH, above which formation damage occurs. Renpu (2011) presented D_k parameter to characterize the extent of formation damage as a result of introducing fluids with different salinity, injection rate, pH (alkalinity), and also confining stress, which is defined as below:

$$D_k = \frac{K_{i-1} - K_i}{K_{i-1}} \times 100 \quad (1)$$

For the case of pH sensitivity, K_{i_1} is the permeability of injecting fluid with pH_{i-1} (pH value of stage $i-1$), K_i is the permeability of injecting fluid with pH_i (pH value of stage (1) and D_k is the degree of formation damage. In Eq. (1), pH_{i-1} is called the critical pH of the injected fluid if the following condition is established (Eq. 2). The different scales of damage and their corresponding boundaries can be found in Table 1.

$$D_k = \frac{K_{i-1} - K_i}{K_{i-1}} \times 100 \geq 5\% \quad (2)$$

Renpu (2011) carried out a series of alkali-sensitivity test to determine the critical pH at which permeability decreases and formation damage occurs (induced) based on a Chinese standard (SY/T5358-2002). He injected salt water with different pH values ranging from formation water pH to 13 and salt water pH increased in stages with an injection rate lower than its critical value for Talimu East oil field. Figure 1 shows the result of the experiment. It can be seen that as the pH of the injected water increased the permeability decreased as a result of formation damage. In other words, the pH value of the injecting water started from point one (pH = 8.5) which is the formation water pH and increased in stages (pH = 8.5, 9.41 and 10.24). The core permeability decreased in pH = 9.41 and kept constant up to the pH = 10.24. There is no specific change in the value of permeability when the pH of the injecting water is restored from 10.24 to 8.5 (Initial pH value, formation water pH, point two). Overall, the ratio of final-to-initial

Table 1 Evaluation criteria for degree of alkalinity sensitivity damage

Formation damage degree (%)	$D_k \leq 5$	$5 < D_k \leq 30$	$30 < D_k \leq 50$	$50 < D_k \leq 70$	$D_k > 70$
Scale of damage	None	Weak	Medium to weak	Medium to strong	Strong

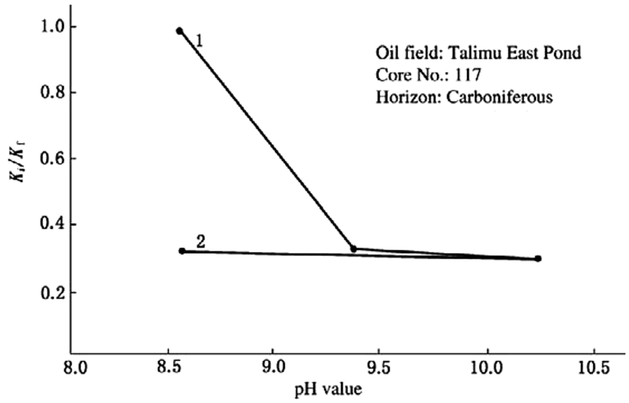


Fig. 1 Sensitivity evaluation of Talimu East oil field core sample to the alkalinity (Renpu 2011)

permeability decreased from 1 to about 0.35 as a result of formation damage and is irreversible.

We used the degree of formation damage (D_k) to determine the amount of damage caused by alkalinity. In previous works, the degree of formation damage was determined at each increasing or decreasing stages of fluid alkalinity as stated. However in this work, D_k has been measured only at pH = 7 (base pH) and considered as the baseline permeability. The most important advantage of this procedure is that any increase or reduction in permeability values could be interpreted as formation damage but after injecting the base fluid (pH = 7), the permeability may revert to its initial value which means no permeability reduction and hence no formation damage. Therefore, the Eq. (1) can be rewritten as below:

$$D_k = \frac{K(\mathrm{pH} = 7)_{i-1} - K(\mathrm{pH} = 7)_i}{K(\mathrm{pH} = 7)_{i-1}} \times 100 \tag{3}$$

Materials and methods

Core samples

The core samples were taken from Fahliyan carbonate formation of Yadavaran oil field located in south-west of Iran which is mostly an oil-bearing formation. The core samples were cleaned using a mixture of toluene and methanol, and the petrophysical properties such as porosity and air permeability were measured. Then they were saturated by a 4% KCl (synthetic brine at pH of seven) under sufficient vacuum pressure. It is noteworthy to mention that the core samples were selected in a way to cover the most parts of the lower Fahliyan formation to have a better insight into the sensitivity analysis. Table 2 shows the petrophysical properties of the core samples selected for flooding experiments. Furthermore, the composition of the selected samples was determined using XRD method (Table 3).

Injection fluids

The injecting fluids used in this study were 4 wt% KCl (synthetic brine) with different pH values (7, 8.5, 10, and 12). The viscosity of injection fluids was measured using a rolling ball viscometer (0.1977 cp). The pH of different alkaline fluids was adjusted to the elevated values using 4 wt% NaOH solution.

Experimental setup

The core-flooding system used for this study is composed of a core holder, four fluid chambers which two of them are acid resistant (Hastelloy C276), a differential pressure transducer to measure the pressure drop across the core sample, a Gilson pump for fluid injection and a pneumatic pump to exert overburden pressure over the viton rubber sleeve covering the core sample, back pressure regulator, fluid fraction collector and the data acquisition system to display and record the data (Fig. 2).

Experimental procedure

For each flooding experiment, the sample was placed in the core holder and kept under the reservoir pressure and

Table 3 Composition of core samples determined by XRD method

Plug no.	Calcite ($CaCO_3$)	Dolomite ($CaMg(CO_3)_2$)	Quartz (SiO_2)	Kaolinite
1	96%	1%	< 1%	2%
2	78%	18%	2%	2%
3	82%	17%	–	1%

Table 2 Petrophysical properties of the core samples

Core no.	Depth (m)	Porosity (ϕ)	Air permeability (md)	Pore volume (cc)	Plug dimensions	
					D (cm)	L (cm)
1	4259.53	6.77	11.103	3.86	3.81	5
2	4278.5	20.31	6.729	11.58	3.81	5.1
3	4283.79	30.45	16.237	17.36	3.80	5.12

temperature over a 24 h period simulating the reservoir condition. The oven temperature was set at 140 °C (284 °F) and a back pressure of 1000 psi was applied. The brine aqueous solution at pH of seven was initially injected into core samples to restore the saturation status and also to measure the absolute permeability.

The core-flooding experiments were carried out at flow rates corresponding to laminar flow where Darcy law can be applied, which is below a critical flow rate at which colloidal particles detached moving along the porous media. To determine the critical flow rate, the same testing procedure introduced by Hassani et al. (2014) on Fahliyan carbonate reservoir was employed. In this method, a minimum flow rate in which no formation damage occurs is selected and the baseline permeability is calculated (step 1). Then the flow rate was increased in an incremental manner (step-wise manner, step 2) and returned to the base flow rate (after each incremental step, step 3). The baseline permeability which is recalculated in the third step will be compared to the value obtained in the first step and the degree of formation damage is determined. If the value obtained for D_k be greater than five, then the flow rate at step 2 can be considered as the critical flow rate which causes weak degree of formation damage. Otherwise, the flow rate is increased to track a degree of formation damage as provided in Table 2.

The pH of alkaline fluids was increased to the elevated values (8.5, 10, and 12) and after each incremental stage, the base pH fluid (pH = 7) injected into the core samples and the degree of formation damage calculated based on the permeability values obtained in the base fluid injection stages (Fig. 3). The fluid injection was continued and then the critical pH values and its corresponding degrees of formation damage were determined.

The injection rate in each stage is 0.5 cc/min. The amount of permeability in each stage was calculated using linear Darcy law. Then the amount of D_k in the base fluid injection stage (pH = 7) is calculated using Eq. (3) to determine the scale of formation damage.

The differential pressure and the amount of the effluent fluids were recorded periodically. Initially, the plug is flooded for a certain time until the flow is steady state, after which the data points are considered for permeability measurement.

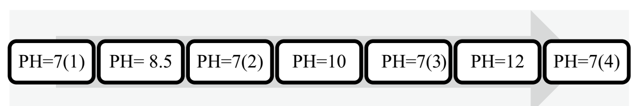


Fig. 3 The flooding schedule of fluids with different alkalinity (pH) in Fahliyan core samples

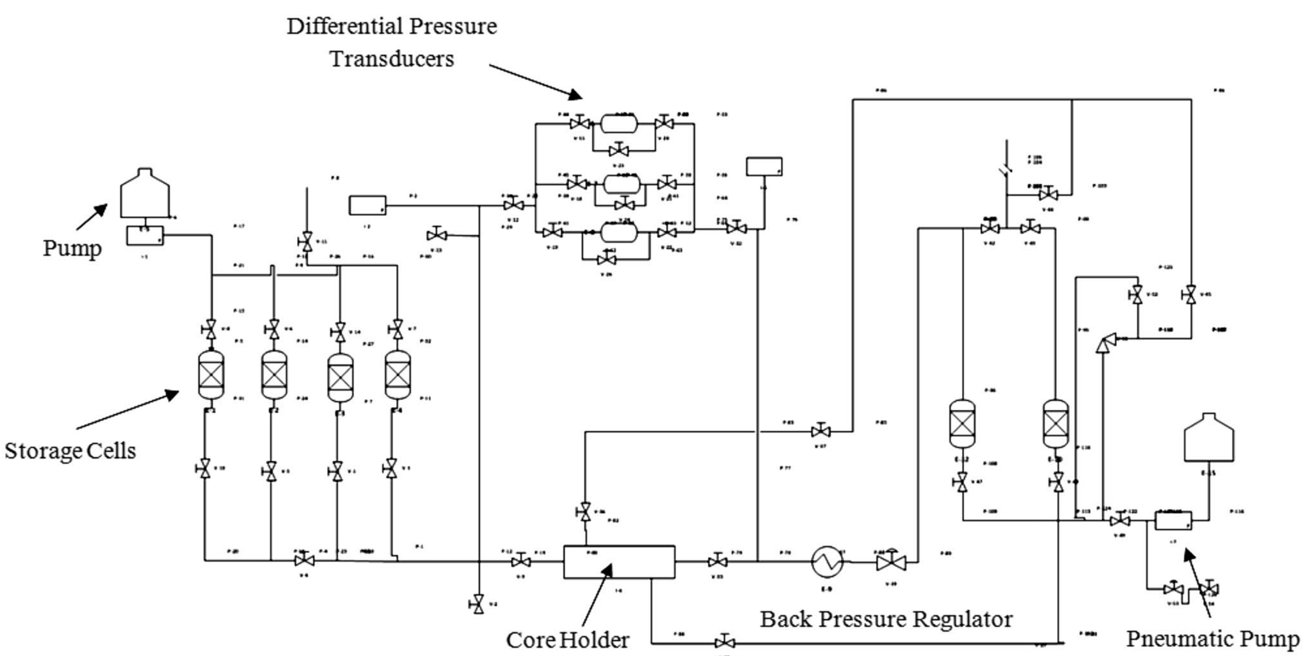


Fig. 2 Schematic of experimental setup used for flooding experiments (Hassani et al. 2014)

Results and discussion

Core-flooding experiments

Core no.1

The flooding started by the injection of 4 wt% KCl aqueous solution at the injection rate of 0.5 cc/min which was kept constant for all flooding stages. The data points were considered for permeability calculation after four pore volumes' flooding of formation water (steady-state condition). The permeability alteration versus pore volumes to breakthrough for core no.1 has been shown in Fig. 4. It can be seen that at the third flooding stage [pH = 7(2)], the average end-point permeability decreased up to 20% compared to the first stage and there is no considerable permeability change up to the end of last flooding stage (seventh stage). The permeability decrease observed in the third stage is as a result of injection of alkaline fluid with pH = 8.5 which is the critical pH for this sample. The amount of permeability decrease has been remained constant and irreversible (Fig. 4).

The value of formation damage degree calculated only at base pH fluid injection stages has been brought in Table 4.

It can be seen that the degree of formation damage after flooding of the alkaline fluid at pH = 8.5 is weak ($5 < D_k \leq 30$). If we consider Renpu's method without returning the flooding stage to the base pH step, the value of D_k between stage 1 and 2 becomes 4.462 which shows no formation damage ($D_k < 5$). We can see that Renpu's method in this case underestimates the scale of damage and there is a considerable discrepancy between values obtained.

Table 4 Determination of the degree of formation damage (D_k) for core no. 1

Stage	pH of alkaline fluid	Parameter	Value	Type of damage
1 and 3	7	$D_{k\,(1,3)}$	22.462	Weak
3 and 5	7	$D_{k\,(3,5)}$	2.778	None
5 and 7	7	$D_{k\,(5,7)}$	3.673	None

Results of XRD and SEM analysis confirm that there is about 2% Kaolinite, which is known as a migrating clay mineral (Fig. 5). During core-flooding process, the minerals presented in the porous media can react with the injecting alkaline fluids and can detach and transported by the fluid. If the diameter of detached fines is greater than the pore-throat size then it can plug pores resulting in formation damage (pore plugging). Otherwise the fines will move out of the porous media within the fluid (Khilar and Fogler 1998). Increasing the alkalinity of injection fluids in other stages has not changed the scale of damage (Stage 4–7).

Core no.2

The flooding scenario for this core sample is identical to that of core no.1 and the pH of the alkaline fluid increased in stages as depicted in Fig. 6. It can be seen that the sample undergoes a strong degree of formation damage when exposed to alkaline fluid at pH = 8 and the amount of permeability increased more than five times (Table 5). Using Renpu's approach, the degree of formation damage evaluated is

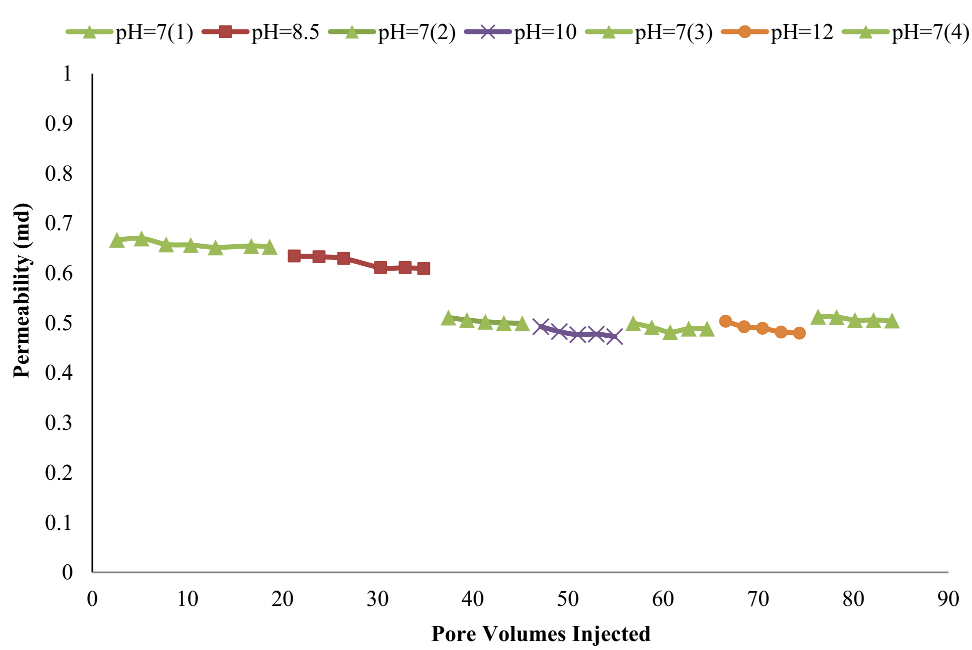


Fig. 4 The permeability alteration during injection of different alkaline fluids in core no.1

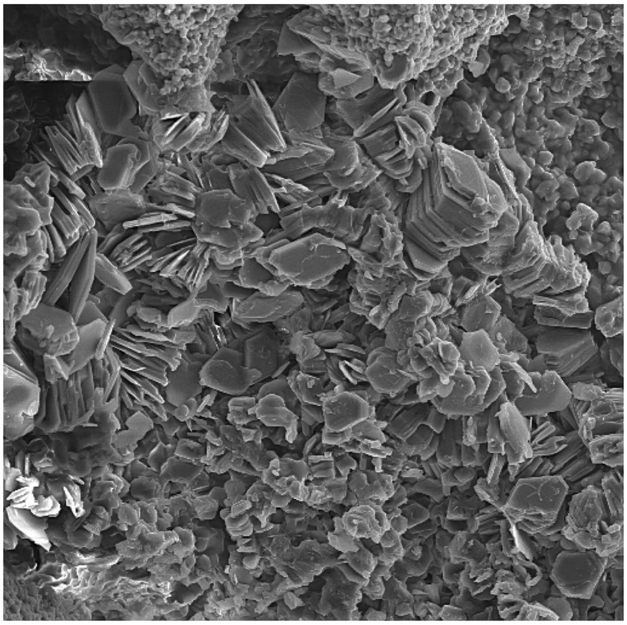


Fig. 5 SEM image of kaolinite flakes attached to pore walls of core no.1

about half of the value which was calculated by presented method ($D_k = 226$).

An interesting point of the flooding process is that after injecting a fluid of pH = 10, the amount of permeability increased again (about two times of the initial value) which can be due to re-attachment of small particles in low-velocity regions of the porous media (Russell et al. 2017, Fig. 7). The particles like kaolinite which are known as migrating minerals (as presented in the rock, Fig. 9) can be detached by fluid and transported from zone of high velocity (lower pore-throat size) to the zone with low velocity (larger pore-throat size) where the flow rate is constant. In this way, the pressure drop between the inlet and outlet decreases resulting in higher permeability values without straining.

Such physical phenomenon has resulted in medium–weak degree of formation damage compared to second injection stage. Hence, the critical pH for this sample can be expressed in two ways, pH = 8.5 for permeability improvement and pH = 10 for permeability decline but overall the average endpoint permeability at final stage [pH = 7(4)] has been increased about three times compared to the initial stage [pH = 7(1)]. Figure 8 shows the result of CT scan analysis for core no. 2 after flooding. Figure 9 shows SEM images of core no.2 before flooding which mainly demonstrates the location of kaolinite flakes attached to pore walls.

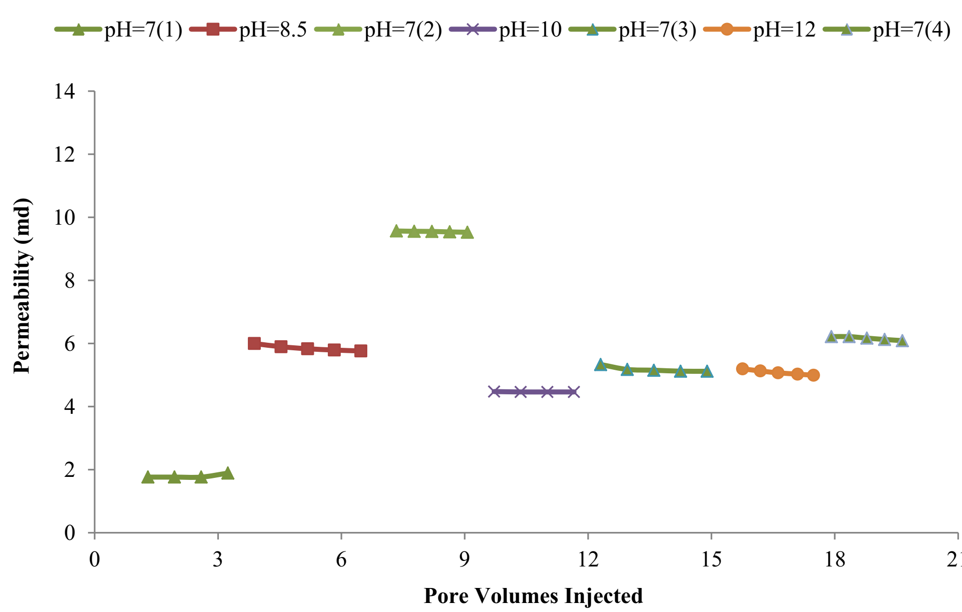
Core no.3

The injection schedule for this sample was kept the same as others but the number of stages was increased to 15 stages to completely picture the sample behavior when it comes into contact with a fluid with wide pH limits (pH = 7–14).

Table 5 Determination of the degree of formation damage (D_k) for core no. 2

Stage	ph of alkaline fluid	Parameter	Value	Type of damage
1 and 3	7	$D_{k\,(1,3)}$	431.386	Strong
3 and 5	7	$D_{k\,(3,5)}$	45.733	Medium–weak
5 and 7	7	$D_{k\,(5,7)}$	18.970	Weak

Fig. 6 The permeability alteration during injection of different alkaline fluids in core no.2



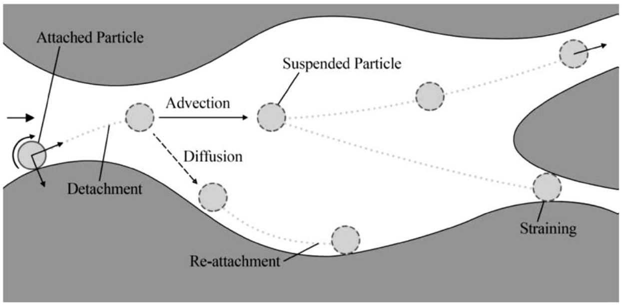


Fig. 7 Schematic of the particle transport in porous media and its related physical mechanisms—particle mobilization, migration, diffusion, and straining (courtesy Russel et al. 2017)

The sample response can be divided into two trends, first decreasing trend up to pH = 12 and then increasing trend up to the end of flooding. The first trend is same as core no. 1 and the second trend is identical to core no.2 (Fig. 10). The corresponding degree of formation damage has been summarized in Table 6.

There is no sign of strong formation damage as observed in core no. 2 even at high pH values. Again the same physical mechanisms can be used for this case where the permeability decline is due to fine detachment and straining in thin pore throats and the rest increasing trend is due to re-attachment of small particles (kaolinite particles as migrating clays, Fig. 11) in low-velocity regions of the porous media.

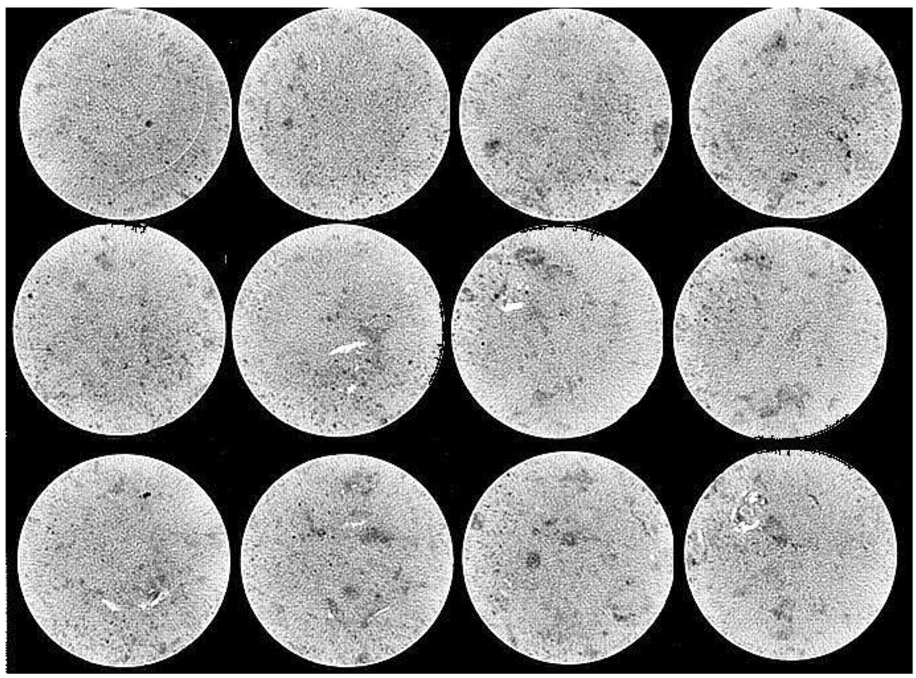


Fig. 8 CT images of core no.2

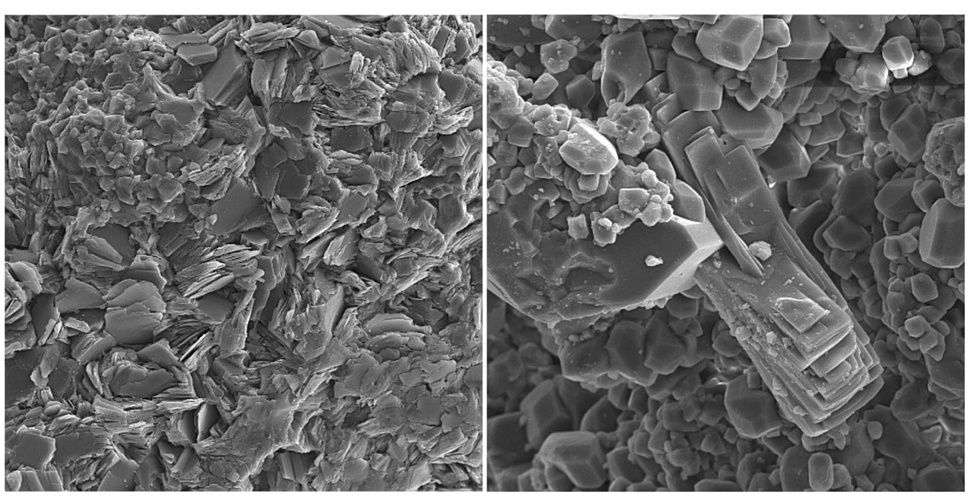


Fig. 9 SEM images of kaolinite flakes attached to pore walls of core no.2

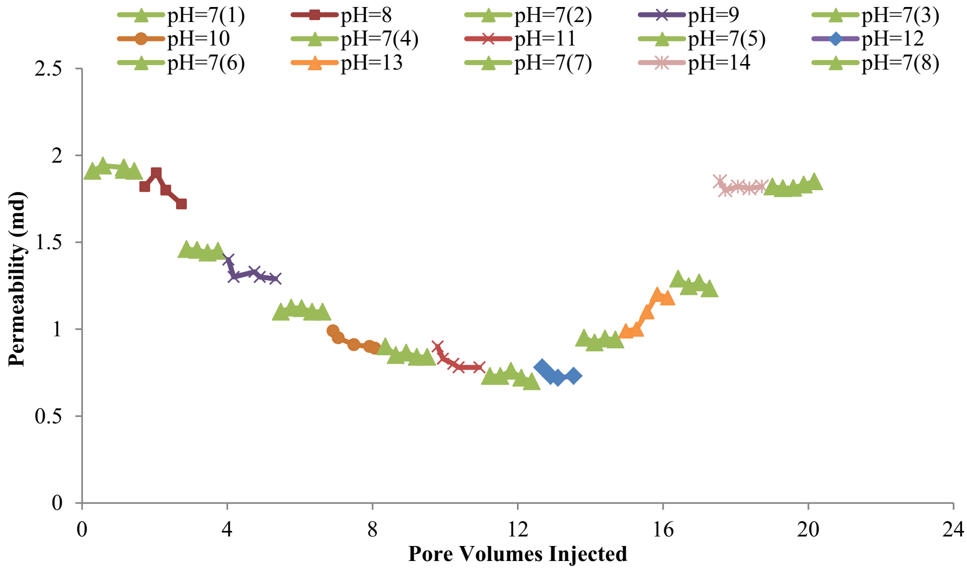


Fig. 10 The permeability alteration during injection of different alkaline fluids in core no.3

Table 6 Determination of the degree of formation damage (D_k) for core no. 3

Stage	pH of alkaline fluid	Parameter	Value	Type of damage
1 and 3	7	$D_{k\,(1,3)}$	24.51848	Weak
3 and 5	7	$D_{k\,(3,5)}$	24	Weak
5 and 7	7	$D_{k\,(5,7)}$	22.32305	Weak
7 and 9	7	$D_{k\,(7,9)}$	15.65421	Weak
9 and 11	7	$D_{k\,(9,11)}$	29.77839	Weak
11 and 13	7	$D_{k\,(11,13)}$	33.72465	Medium–weak
13 and 15	7	$D_{k\,(13,15)}$	48.52354	Medium–weak

Relationship between D_k and pH

In this section the relationship between the fluid alkalinity (pH) and the resulting degree of formation damage is evaluated. Considering the falling and then rising behavior for core no.3, if a polynomial function is be fitted to the data, the highest relationship factor will be obtained (Fig. 12).

It can be seen there is a polynomial relationship between the D_k and the amount of alkalinity (pH) with high relationship coefficient for core no. 3 ($R^2 = 0.9032$). Also, Fahliyan formation will not undergo medium–strong and strong degree of formation damage as we go deeper (lower Fahliyan) and the strong degree of damage is more likely for intermediate depths only (more data must be available for confirmation).

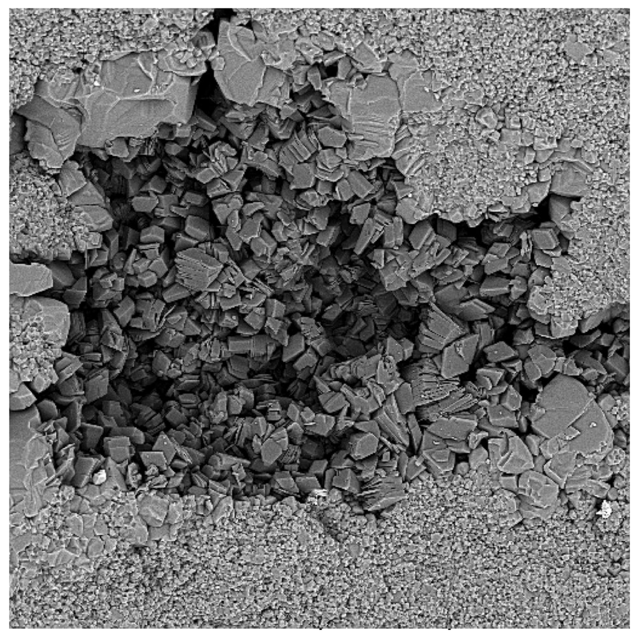


Fig. 11 SEM image of kaolinite flakes attached to pore walls for core no.3

Conclusions

In this work a series of core-flooding experiments were carried out to determine the critical alkalinity (pH) and the extent of damage using a new methodology (modified Renpu's method). The injection tests were conducted on Fahliyan core samples in a step-wise manner and the amount of permeability alteration was determined by comparing the permeability variation using a brine at pH of seven before and after flooding the sample at elevated pH. The degree

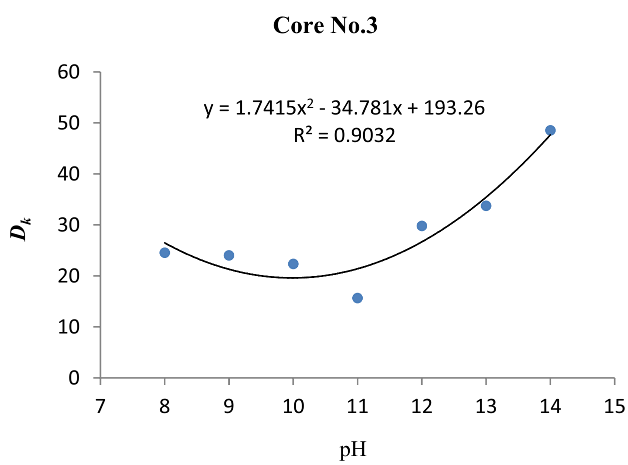


Fig. 12 Relationship between fluid alkalinity and D_k for core no.3

of formation damage as addressed by Renpu (2011) was only calculated at the base pH stage (alkalinity).

Experimental results show that the core samples exhibit different behavior when exposed to alkaline fluid with different pH and the degree of formation damage is varied from 'negligible' to 'strong' which were in some cases noticeable and irreversible. Pore plugging as observed for core no.1 and reattachments of particles to surface walls (core no.2 and 3) are the main dominant mechanisms observed during core flooding occurred as a result of formation damage. The difference between inlet and outlet pressure was bigger for core no.1 compared to other samples which will result in small changes in permeability.

It is noteworthy mentioning that the conventionally used methods (Renpu method) always underestimate the degree of formation damage (D_k) compared to the modified approach introduced in this paper. Based on the experimental data of core no.3, a quadratic relationship exists between the fluid alkalinity and the corresponding degree of formation damage that enables us to estimate the different damage boundaries where D_k was measured at more pH data points.

Acknowledgements The authors wish to acknowledge Research Institute of Petroleum Industry for permission to publish these results.

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