RELATION BETWEEN CATIONIC EXCHANGE CAPACITY, CLAY SWELLING AND CHEMICAL FORMATION DAMAGE OF PETROLEUM RESERVOIR

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Abstract

Chemical formation damage as a result of clay swelling in Asmari reservoir, SW Iran, was investigated. In the first part of the work, a relation between pH of water based mud (WBM) filtrate and cationic exchange capacity (CEC) of clays was investigated. Clay samples were prepared from sample rocks. XRD method was applied for air dried, ethylene glycol solvated and heat treated clay samples. CEC values at standard and non standard pH values of filtrate were measured. There was a non linear relationship between pH of WBM filtrate and CEC. As pH of WBM filtrate increases, CEC decreases. In the second part of this work, permeability reduction due to the injection of WBM filtrate into core samples of shaly dolomite was measured. Filtrate with different pH values was injected into the core samples and percentage of permeability reduction due to clay swelling was measured. As pH of injected filtrate increases, severity of chemical formation damage reduces. The results could be used to investigate a qualitative relation between pH of filtrate, CEC of clay minerals, clay swelling and chemical formation damage potential of shaly dolomite.

Key Words: Chemical formation damage; clay swelling; CEC and pH.

1. Introduction

Formation damage caused during drilling operation can be broken into four general categories, mechanical, chemical, biological and thermal formation damage [3]. Each of the categories can further be subdivided to some minor categories. Chemical formation damage can be as a result of three main mechanisms; rock and fluid integration, fluid and fluid interaction and wetability alterations. In the case of rock and fluid interaction, there are two main phenomenons. First one is chemical and/or polymer adsorption on the rock surface and the second one is clay swelling. Clay swelling occurs when water based filtrate from drilling or completion fluids enter the near wellbore formation. Swelling potential of clay minerals depends on the charge distribution and the cationic exchange capacity (CEC).

CEC is a measure of the cations, which balance the negative charge sites of the clay [5]. These cations are held by the negatively charged clay and organic matter particles in the rock or soil through electrostatic forces. Knowledge of CEC and cation distribution of the exchanger surfaces can be used as a powerful tool for the characterization of clay minerals and also their swelling potential which controls the extent of related formation damage.

2. Experimental

2.1. Sample preparation

The logging data from different wells in Asmari reservoir in three different Iranian fields were used to select shaly rock intervals for coring operation. Twenty four sample rocks were selected from the cited reservoir as shown in Tables 1, 2, and 3. The thin section of each sample was prepared and analyzed using a microscope to study the lithology of samples and type of shale. The samples were dolomite with dispersed shale. Then, the sample rocks were used to prepare the core plugs and also the powder samples. The core plugs, with a diameter of 3.7 cm and length of 5.2 cm, were prepared. The samples were cleaned by Dean Stark and

Soxhlet extractor according to [1]. Toluene as a solvent was used. Cleaned samples were placed in a furnace at a temperature of 400°C for 48 hrs. A helium porosimeter and an air permeameter were used for porosity and absolute permeability measurements, respectively. Tables 1, 2, and 3 also show the measured porosity and absolute permeability of each sample.

Table 1- Petrophysical properties of samples, field A

Sample no.	Formation	Lithology	Porosity (%)	Permeability (md)
1	Asmari	dolomite	13.43	50
2	Asmari	dolomite	14.57	48
3	Asmari	dolomite	14.98	52
4	Asmari	dolomite	13.09	51
5	Asmari	dolomite	13.56	48
6	Asmari	dolomite	14.86	49
7	Asmari	dolomite	14.11	53
8	Asmari	dolomite	13.90	47

Table 2-Petrophysical properties of samples, field B

Sample no.	Formation	Lithology	Porosity (%)	Permeability (md)
9	Asmari	dolomite	24.50	80
10	Asmari	dolomite	26.40	82
11	Asmari	dolomite	25.46	75
12	Asmari	dolomite	23.40	76
13	Asmari	dolomite	24.50	83
14	Asmari	dolomite	24.89	76
15	Asmari	dolomite	23.54	81
16	Asmari	dolomite	23.11	79

Table 3-Petrophysical properties of samples, field C

Sample no.	Formation	Lithology	Porosity (%)	Permeability (md)
17	Asmari	dolomite	9.85	35
18	Asmari	dolomite	9.82	35
19	Asmari	dolomite	9.76	33
20	Asmari	dolomite	10.04	31
21	Asmari	dolomite	9.43	30
22	Asmari	dolomite	10.24	37
23	Asmari	dolomite	10.65	32
24	Asmari	dolomite	9.56	34

Rock samples were also used to prepare powder samples to obtain clay fractions. In order to separate clay fractions from the other fractions, grain-size analysis were performed using a mesh (no. 200, ASTM, E: 11) followed by settling tube for the coarse-grained (>50 μm) fraction and SediGraph 5100 for the silt and clay (<50 μm) fractions [4]. The division at 50 μm instead of 63 μm was established in order to have enough sediment samples for the settling tube, since a correct measurement requires a minimum 0.2 g of clay material. After separation, grey colored clay fractions were obtained.

Next step was to prepare the clay fractions for X-Ray diffraction (XRD). XRD is the most common technique used to study the characteristics of crystalline structure and to determine the mineralogy of finer grained sediments, especially the clays. XRD was used to recognize clay minerals types qualitatively and to obtain percentage of abundance for each mineral present in the clay samples. XRD device available in department of physics at Shahid Chamran University of Ahwaz was used to do the XRD experiment. Pretreatments prior to the XRD experiment were done which were acetic acid washing to remove the carbonates, hydrogen peroxide washing to remove the organic matter, ethylene glycol solvation and heating the clay sample to 550°C.

2.2 XRD Experimental Procedure

Twenty four clay samples were investigated with diffractometer type PW1840, (a 0.2 mm receiving slit, copper Kα radiation). The samples were applied on a glass sample holder, and then passed over several times with a glass slide in an attempt to achieve the texture. The dry samples were analyzed on a Si (001) sample holder. Diffractogram was recorded from 2Θ = 2.020° to 49.980° for air dried, ethylene glycol solvated and heat treated clay samples in steps of 0.04° with 0.8 second counting time for each step. The scanning process was continuous for both cases. Additional data pertinent to XRD process for air dried, ethylene glycol solvated and heat treated clay samples are given in Table 4.

Table 4- XRD process data for air dried, ethylene glycol solvated and heat treated clay samples

	Air dried clay	EG solvated clay	Heat treated clay
Maximum intensity	1059.610	3158.440	967.210
Minimum peak tip width	0.00	0.00	0.00
Maximum peak tip width	1.00	1.00	1.00
Peak base width	2.00	2.00	2.00
Minimum significance	0.95	0.95	0.95
Number of peaks	14	15	13

2.3. XRD Results

The diffractograms for air dried, ethylene glycol solvated and heat treated clay samples were mostly similar and are shown in Figs 1, 2 and 3, respectively. Using [6] method, clay mineral types were determined. The percentage of presence of each clay mineral in clay sample is listed in Table 5.
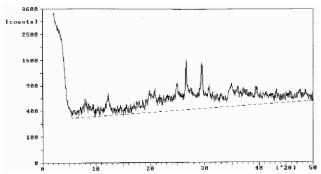

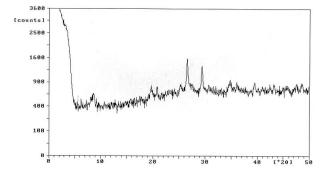Fig.1- X-Ray diffractogram of a air dried clay sample

Fig.2- X-Ray diffractogram of a ethylene glycol solvated clay sample

Fig.3- X-Ray diffractogram of a heat treated clay sample

Table 5 Clay mineral types and their percentage of abundance

Mineral type	Abundance (wt %)
Kaolinite	34.0
Illite	18.9
Montmorillonite	13.2
Illite-Montmorillonite	18.9
Sepiolite	15.0

2.4. Laboratory Determination of CEC

For determination of CEC, WBM filtrate with different pH values was prepared. Concentration of each cation (sodium, potassium and etc) in the filtrate solution was obtained using spectrophotometry. Knowing that XRD results for all twenty four samples were the same,
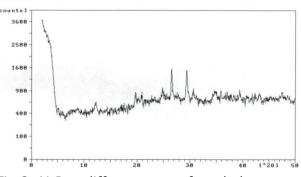
therefore, we just work on one clay sample for CEC determination process. To do the experiment clay sample was mixed with filtrate solution. Ultrasonic treatment was used to enhance the dispersion of clay particles in the solution. After centrifugation, the concentration of each cation in supernatant was determined using spectrophotometry. Finally the CEC respect to each cation was calculated from the difference between the concentration of present cation and the initial concentration of cation and the mass of clay used (see Eq. 1). Total CEC was then obtained by summation of all individual CEC's (see Eq. 2). Fig.4 shows CEC values at different pH values. As it is shown in Fig.4 there is a non linear relationship between pH of filtrate and CEC. A fourth order polynomial fitted the data.

$$CEC = \left(\frac{C_i - C_f}{m} \right) I_c \qquad (1)$$

Where CEC is cationic exchange capacity in meq/100gr, C_i is initial concentration of cation in the solution in milli moles, C_f is final concentration of cation in the solution in milli moles, m is mass of dry clay, and I_c is cation index (one for sodium, two for potassium and etc).

$$CEC = \sum_{i=1}^{n} CEC_i \qquad (2)$$

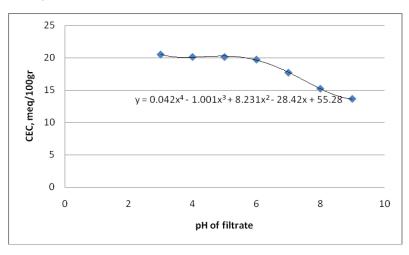Where CEC_i is CEC respect to each cation in the filtrate solution.

Fig.4 CEC values at different pH values

2.5. Initial and treated permeability measurement

Filtrate with different pH values were injected to core samples. For each sample treated permeability was measured. Tables 6, 7, and 8 show pH of each filtrate and measured permeability.

Table 6- initial and treated permeability for core samples of Asmari reservoir, filed A

Sample no	pH of injected filtrate	CEC (meq/100gr)	Initial permeability (md)	Treated permeability (md)	Permeability reduction (%)
1	3	20.474	50	20	60
2	4	20.100	48	25	48
3	5	20.095	52	28	46
4	6	19.695	51	29	43
5	7	17.674	48	33	31
6	8	15.195	49	40	18
7	9	13.621	53	45	15
8	10	12.537	47	44	6

Table 7- Initial and treated permeability for core samples of Asmari reservoir, field B

Sample number	pH of injected filtrate	CEC (meq/100g)	Permeability initial, md	Permeability treated, md	Permeability reduction, %
9	3	20.474	80	50	38
10	4	20.100	82	54	34
11	5	20.095	75	56	25
12	6	19.695	76	59	22
13	7	17.674	83	65	22
14	8	15.195	76	70	8
15	9	13.621	81	73	10
16	10	12.537	79	75	5

Table 8- Initial and treated permeability for core samples of Asmari reservoir, field C

Sample number	pH of injected filtrate	CEC (meq/100gr)	Permeability initial, md	Permeability treated, md	Permeability reduction, %
17	3	20.474	35	15	57
18	4	20.100	35	20	42
19	5	20.095	33	21	36
20	6	19.695	31	24	23
21	7	17.674	30	24	25
22	8	15.195	37	29	22
23	9	13.621	32	24	25
24	10	12.537	34	29	15

3. Conclusions

Twenty four sample rocks from Asmari reservoir in three different Iranian fields were selected. Core plugs and clay samples were prepared from sample rocks. For the case of clay samples, XRD technique, in conjunction with determination of CEC, were used to recognize the clay types. Also a relationship between pH of filtrate and CEC was observed. CEC was dependent of pH of filtrate solution and varies non-linearly with that. As pH of filtrate increases, CEC decreases which means lower swelling potential. Also as pH of filtrate decreases, CEC increases which is translated into higher swelling potential. Consequently, lower and higher swelling potentials represents trivial and sever chemical formation damage.

For the case of core samples percentage of permeability reduction due to injection of filtrate with different pH values were measured. The whole experiments show that there is a relation between pH of filtrate, CEC and permeability reduction which can be used to know the potential of chemical formation damage of a known reservoir under different mud conditions.

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