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USING NANOPARTICLES AND INORGANIC SALTS FOR INHIBITION CLAY SWELLING THROUGHOUT EXPERIMENTAL WORK

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ABSTRACT

Clay swelling is considered to be a main cause for the formation damage in oil and gas reservoirs. There for using of non-inhibitive drilling fluids to drill shale formations usually results in wellbore instability problems. Shale cuttings consisting of different montomorillonite content were collected from different core samples. They were evaluated using X-ray diffraction (XRD), X-ray fluorescence (XRF) andcation exchange capacity (CEC) using Methylene Blue (MB), hence classified into Shale A, B and C.Swelling index of the shale measured using compressed disks of shale in contact with OCMA bentonite for 20 hrs using Linear Swell Meter (LSM).Inorganic salts in term of potassium chloride (KCl) and nanoscale oxides in terms of ZnO, TiO_2 and SiO_2 used as inhibitor of shale swelling. The inhibitors are added to OCMA bentonite as well. Swelling of the shale cuttings increased in the order: Shale A<B<C. The inhibition of swelling of these shale cuttings using 1-4% KCl achieved a decrease in swelling that ranged from 17% at 2% (shale A), 22% at 3% (shale B) and 30% at 4% (shale C). Meanwhile, the effect of nanoscale oxides as inhibitor was significant compared with KCl. These nanoscale oxides caused a dramatic decrease in swelling of sales. Nanoscale SiO_2 achieved almost 42% inhibition in swelling of shale at 0.25% in contact with OCMA bentonite. Meanwhile, ZnO and TiO_2 caused swelling decrease at the same concentration (0.25%) ranging between 25% and 37% for ZnO and TiO_2 respectively.

Key words: Clay swelling, Linear Swell Meter, Inhibition, Nano-particles

1. INTRODUCTION

Several oil and gas reservoirs contain shale formations with high sensitivity to the water based mud. These formations are rich in clay minerals and up on drilling with water based mud caused well bore instability problems. When drilling fluid interface (contact) the shale formation, they could interact in several ways. Montmorillonite rich shale is sensitive to water and could swell. Also the clay minerals in shale could disperse into “Ultra” fine colloidal particles and may negatively affect the drilling mud properties. So that the main problems that shale instability may cause in petroleum industry; pipe sticking, bit Balling, tight hole, hole enlargement, cutting disintegration, fracturing, lost of circulation, poor hole cleaning, Sloughing and increased torque (Ismail, 1996).

When drilling is expected to occur in water-sensitive zones, the selection of the fluid becomes even more important. To maintain a stable borehole through such zones, an inhibitor drilling fluid will often be required. The high sensitive water formation may call for the use non-aqueous fluids as oil, alcohol, or foam, but for environmental reasons, the water base fluid with inhibitors preferred to use (O'Brien and Chenevert 1973).

Actually, wide-range of salts has been used to formulate inhibitive drilling fluids such as NaCl, KCl, $CaCl_2$, $MgCl_2$, and $ZnCl_2$. Each salt has its own mechanism in achieving inhibition and shale stability. Potassium chloride (KCl) is widely used in petroleum field as shale inhibitor; it is probably the best-known inhibitor in the oil industry (Oort, 2003). Potassium salts are used most extensively because of their efficiency, low cost, and excellent brine compatibility. Monovalent ions, however, are known to have a temporary effect. In the presence of brines with high NaCl concentrations, the stabilizing effect disappears progressively by the same ion-exchange process that leads to the replacement of K^+ by Na^+ ions (Zaltoun et. al.,1992).

A new form of clay swelling inhibitor that has been reported includes various nanoparticles that have been added to drilling muds or proposed for injection into reservoirs (Baird and Walz, 2006; Jung et al., 2011; Pham and Nguyen, 2014). The main application of nanoparticles would be to control the spurt and fluid loss into the formation and hence control formation damage (Srivatsa, 2010).

According to Amanullah and Al-Tahini (2009) nanoparticles can form a thin, non-erodible and impermeable mud-cake. Due to its high surface to volume ratio the particles in the mud cake matrix can easily be removed by traditional cleaning systems during completion stages. Thus, the nano particles can be used as rheology modifiers, fluid loss additives and shale inhibitors with unparalleled properties for very small concentrations of the particles. Sensoy et al. (2009) studied the effect of adding nanoparticles to water-based drilling muds on Atoka and Gulf of Mexico shale with and without the addition of nanoparticles. The results showed that nanoparticles (particle diameters in the nanometer range) can plug several types of shale, preventing water from flowing into the shale formation. Novel zinc oxide nanoparticles deposited acrylamide composite was synthesized. This composite improved thermal, chemical stability, yield point, lubricity and filtrate loss volume was reduced. Shale swelling was reduced from 16% to 9% after adding synthesized composite in WBDF (Aftab et al., 2016). Sadeghalvaad and Sabbaghi, (2015) reported same results when used the TiO_2/polyacrylamide nanocomposite on water-based drilling fluid. Patel et al., (2016) evaluated the potential of the commercial nanoparticles to mitigate clay swelling. The swelling measurements were performed by a visual swelling test method for clay powder. Nanoparticles more effectively mitigated swelling at concentrations of 0.5 – 1.0 %in the presence of 4 %wt KCl. This study aims to minimizethe shale swelling process throughout additive of potassium chloride (KCl) and nanoparticles oxides in water based mud and using a linear swell meter and Shale compact disks.

2. EXPERIMENTAL

Experimental work targets inhibition shale swelling throughout addition of potassium chloride (KCl) and nanoparticles oxides to the drilling fluid (OCMA, 5%).

2.1. Materials

Shale samples provided by Corex for Petroleum Services were homogenized and grind to 75 μm. OCMA and high gel bentonite provided by Egypt Bentonite & Derivatives Company. Zinc oxide, (ZnO) with 20-30 nm, titanium oxide ($TiO_{2)}$with 30-50 nm and silica (SiO_2) with 50-80 nm in size are prepared throughout electronic and magnetic material division in CMRDI). These nanoparticles and KCl are main additive to bentonite as inhibitor for shale swelling.

2.2 Characterization of shale samples

Three shale samples were prepared based on their montomorellonite content, namely A, B, and C and characterized for mineralogy and chemistry using X-ray diffraction (XRD) and X-ray fluorescence (XRF).

2.2.1. Mineralogical Analysis

A) Whole-rock analysis

Shale cuttings were characterized using X-ray diffraction (XRD) for bulk mineral analysis (Philips powder type PW 1730) with Ni – filtered Fe radiation ($\lambda = 1.79$) at 30 kV and 20 mA. The scans were limited to the range $2\theta = 4° \text{ to } 60°$.

B) Preparation Clay Fraction (<2μm)

Fraction (<2μm) obtained by the sedimentation technique after removing non-clay minerals e.g.- carbonates, organic and salts. Then preparation three slides Oriented, Glycolated and heated were characterized using XRD (Inglethorpe et al; 1993).

2.2.2. Chemical Analysis

Quantitative analysis of shale cuttings was carried out using X-ray fluorescence spectroscopy (XRF) (Philips PW 1410). Tube voltage and current for W target were 40 kV and 60 mA, respectively. Loss on ignition and moisture were obtained by heating sample powder to 1000° C for 2 hrs.

2.3. Chemo-physical Analysis

Cation exchange capacity (C.E.C)

The Cation exchange capacity using methylen blue (MB) is especially designed to determine the montmorellonite content in clay samples. This procedure according to (Inglethorpe et al; 1993).

2.4. Preparation of shale core plug

Shale core samples are homogenized and grind to 75 µm. 0.5 ml fresh water are added to 20 mg of shale cuttings (200 mesh) and mixed by a spatula, then compacted under a constant pressure of 10,000 psi for 1.5 hrs using compactor for linear swell meter.

2.5. Preparation of drilling fluid

- **Drilling fluid without additives**

All the samples of drilling fluid are based on the formulation of 350 ml of fresh water with 5% bentonite only then mixed using a Hamilton Beach mixer for 15-20 min.

- **Drilling fluid with additives**

OCMA bentonite mixed with different percent of nanoparticles (ZnO, TiO_2 and SiO_2) from 0.25% up to 3% and potassium chloride salt (KCl) with 350 ml of fresh water in Hamilton Beach mixer for 15-20 min.

2.6. Shale swelling test

Effect of drilling fluid with and without additives on shale swelling were studied throughout the laboratory work. The change in swelling behavior of different shale samples (core plug) measured using Linear Swell Meter (fann 2100). Shale plugs were adjusted in car holder and placed under the measuring head for 20 hrs.

3. RESULTS AND DISCUSSION

3.1. Characterization of shale samples

3.1.1. Mineralogical analysis

A) Whole-rock analysis

Shale cuttings were characterized using X-ray diffraction (XRD) for bulk samples. The identified non-clay minerals that include: quartz, feldspars, calcite, dolomite, siderite and pyrite. Quartz was reported in all samples in the order of abundance shale (A) > (B) > (C). Quartz was identified by the characteristic reflection peaks at 4.26, 3.34 and 1.82 Å. Feldspar minerals were reported as traces in all samples as Na-feldspar and K-feldspar. Na-feldspar identified by the characteristic reflection peak at 3.19Å and K-feldspar identified by the characteristic reflection peak at 3.25 Å. Calcite was detected in all samples in the order of abundance shale (A) > (B) > (C). It was identified by the characteristic reflection peaks at 3.04, 2.85 and 2.09 Å. Siderite was detected in all samples in the order of abundance shale (B) > (C) > (A). It was identified by the characteristic reflection peak at 2.80, 179 and 3.59 Å. Dolomite was reported only in shale (C); it was identified by its characteristic reflection peak at 2.88, 1.78 and 2.19 Å. The XRD diffractogram of three shale samples (A, B and C) were illustrated in Figures 1-3.

B) Analysis of Clay Fraction (<2µm fraction)

Identification of clay minerals was based upon x-ray diffraction of <2µm fraction before and after treatment with ethylene glycol and heating at 600 ˚C for 2 hrs. XRD of the clay fraction revealed that the smectite is the main constituent followed by kaolinite in addition to traces of illite. Smectite identified by the characteristic reflection peak at 14 Å in oriented <2µm fraction. Upon treatment with ethylene glycol the reflection peak shifted up to 15-16 Å. However, calcinations up to 600˚C for 2 hrs of<2µm fraction caused collapse of smectite structure and shift the characteristic

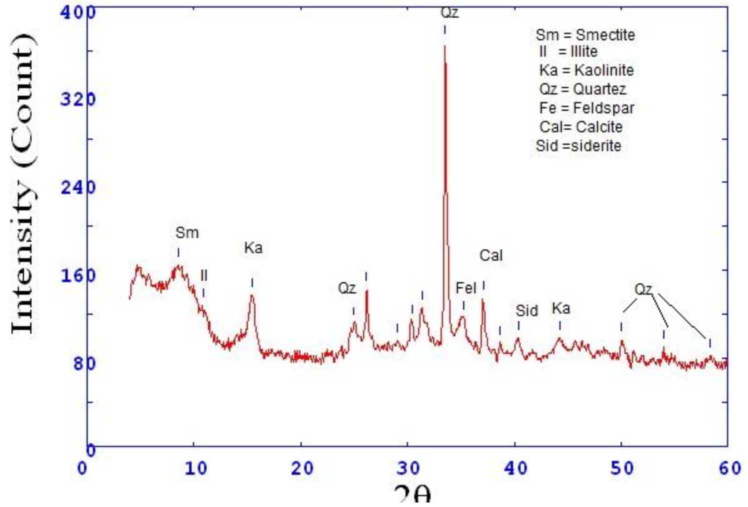

Figure 1: X-ray diffractogram of Shale (A)

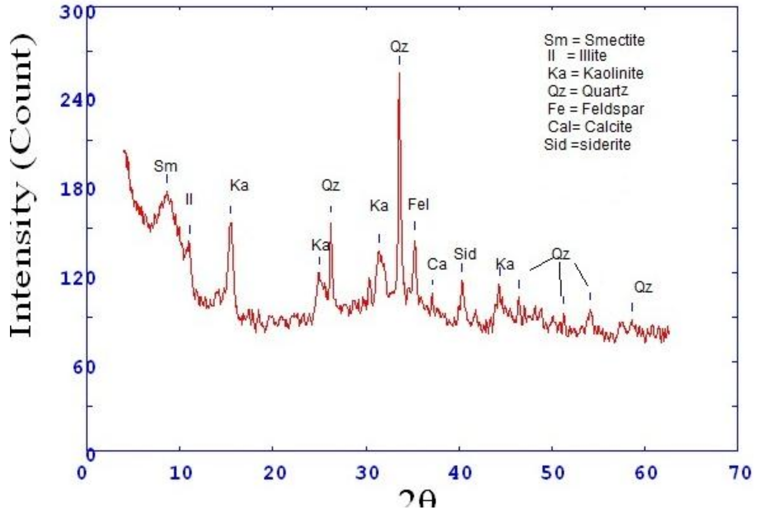

Figure 2: X-ray diffractogram of Shale (B)

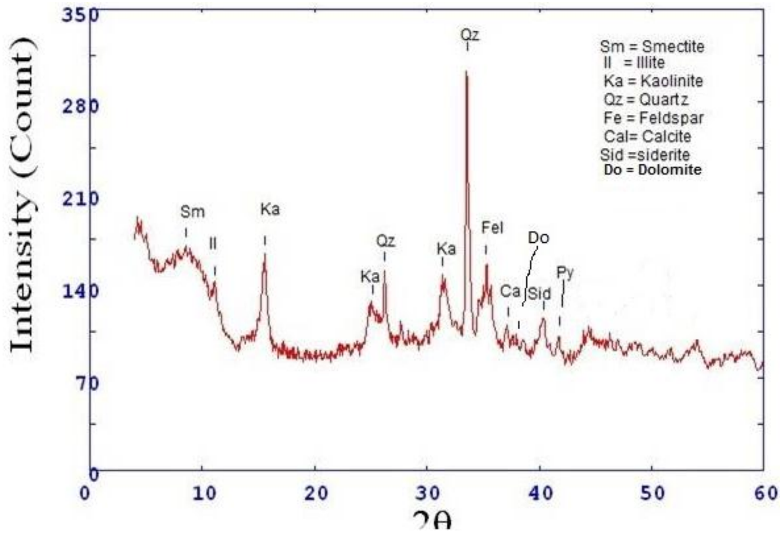

Figure 3: X-ray diffractogram of Shale (C)

reflection peak to illite at 10 Å. Kaolinite identified by the characteristic reflection peaks at 7.20 and 3.57 Å in oriented and glycolated. These characteristic reflection peaks completely disappear upon heated at 600 ˚C for 2 hrs to metakaolinite. Illite is recognized as a minor constituent in all samples. It was identified by its characteristic reflection peaks at 9.79 – 10.02 Å in oriented, glycolated and heated. The XRD diffractogram of the <2µm size fraction (A, B and C) were illustrated in Figures 4-6.

3.1.2. Chemical Analysis

Table 1 shows the chemical composition of the studied samples using X-ray fluorescence (XRF).All the examined samples consist mainly of SiO_2,Al_2O_3 and Fe_2O_3 in a descending order of abundance. A minor to trace amounts of CaO,K_2O,MgO, Na_2O, TiO_2, SO_3, MnO, Cl and P_2O_5were also detected. The percentage of the main oxides SiO_2 and $Al_2O_3$are considered as the main constituent of clay minerals. Total iron (Fe_2O_3) present in two phases in clay minerals as staining iron and structural iron (Hassan and Salem 2001). In addition to traces of iron carbonate siderite ($FeCO_3$) were revealed by XRD. CaO and Na_2O are partly located in the interlayer position (gallery) of smectite (Moore &

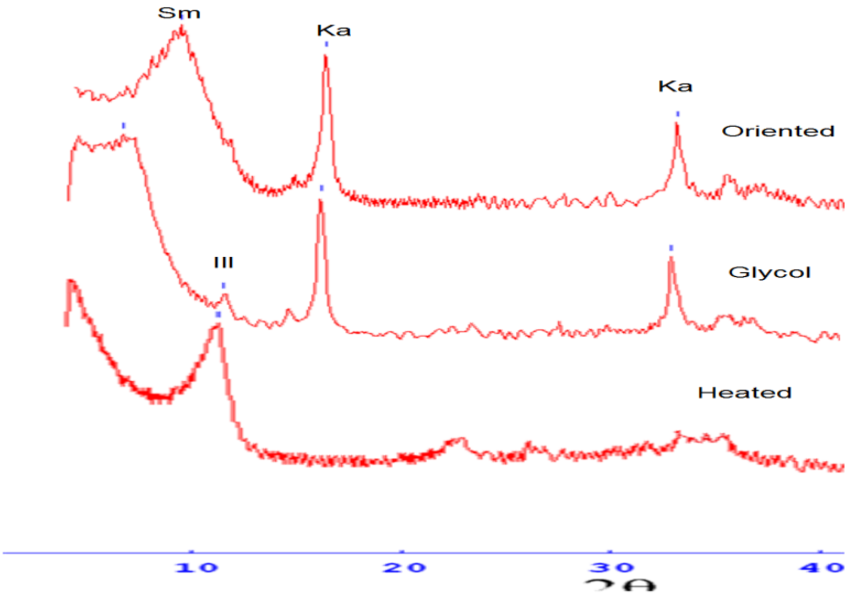

Figure 4: X-ray diffractogram of oriented, glycolated and hated clay mount of Shale (A)

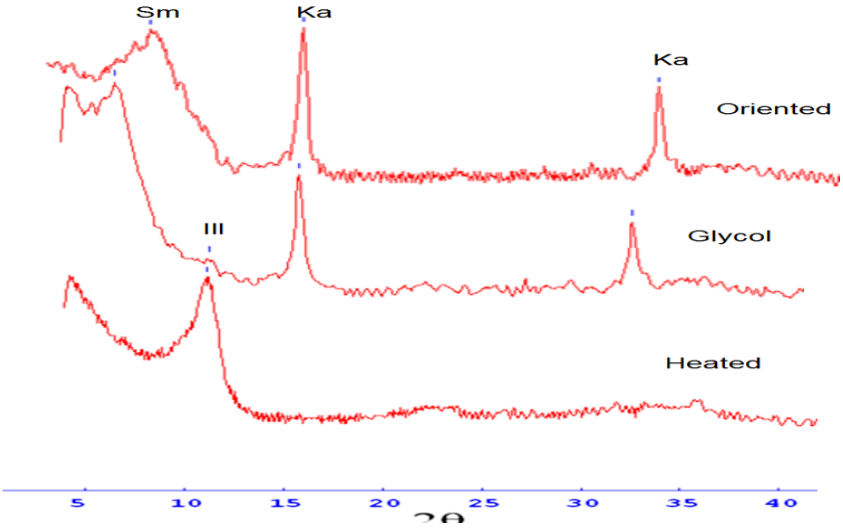

Figure 5: X-ray diffractogram of oriented, glycolated and hated clay mount of Shale (B)

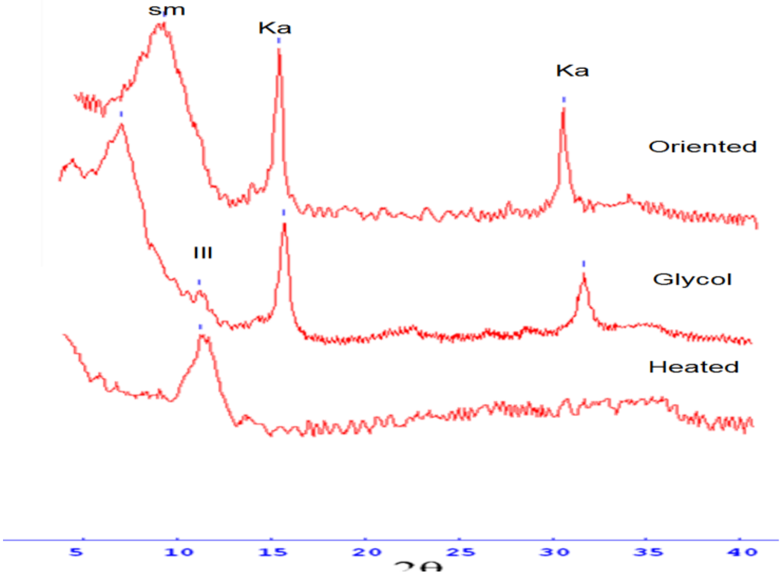

Figure 6: X-ray diffractogram of oriented, glycolated and hated clay mount of Shale (C)

Renyolds 1979). In addition to CaO contents referred to the presence of calcite ($CaCO_3$) revealed by XRD. The small percentage of K_2O was reflected to the presence ofillite and trace of K-feldspar and $Na_2O$was reflected to the presence Na-feldspar were revealed by XRD. The presence of MgO contents suggests that MgO is bonded in smectite and reflected to the presence of dolomite ($CaMg(CO_3)_2$). The loss on ignition indicated to removal of hygroscopic water, loss of the interlayer water in the structure of clay minerals and breakdown of organic matter.

3.2. Physico-Chemical properties

Cation exchange capacity (C.E.C)

The cation exchange capacity in the order of adsorb cations from solution shale (C) > (B) > (A) and this corresponds to the montomorellonite content in samples Table 2.

3.3. Shale Swelling Test

3.3.1. Effect of montomorellonite content in Shale swelling

Linear Swell Meter used to determine the swelling behavior of shale samples A, B and C with different montomorellonite content for 20 hrs. Drilling fluid based on 5% OCMA bentonite was used. From LSM data, we recognized that shale C swelled more than B and A, also shale A swelled less than shale B. Shale C swelled up to 56% of its initial length, while Shales B and A swelled up to 48% and 37% of their initial lengths, respectively. However, shale (A) stops swelling after 2 hrs compared with that of shales B and C which stopped swelling after 3 hrs.

These data revealed the relationship between length of swelling and montomorillonite content, more montomorillonite means more swelling in contact with OCMA bentonite. Swelling of shale cuttings increased in the order Shale A<B<C (Figure 7).

3.3.2. Effect of potassium chloride (KCl) on shale swelling

The effect of KCl at different concentrations as additives to drilling fluids (OCMA, 5%) on swelling of shale A, B and C is shown in Figures8-10. KCl caused a decrease in swelling of shale A from 37% to 34%, 30% and 32% respectively to 1%, 2% and 3% of KCl. It's clear that 2% KCl the best quotient for inhibition swelling of shale A, for about 17% (Figure 8). More concentrations of KCl isrequired for inhibiting swelling of shale B, which has more montomorillonite content. Swelling of shale B reduced from 48% with drilling fluid without KCl to 37%, 34% and

44% respectively to 2%, 3% and 4% of KCl. The best quotient was 3% for inhibition swelling of shale (B) about 22% (Figure9). However, 4% of KCl were enough for inhibiting swelling of shale C that contain the highest content montomorillonite compared with shale A and B. Swelling of shale C reduced from 56% to 50%, 39% and 52% respectively to 2%, 4% and 8% of KCl (Figure 10).

Table 1. Chemical composition of studied samples

Oxides content	Shale (A)	Shale (B)	Shale (C)
SiO_2	53.11	54.40	51.7
Al_2O_3	13.43	11.84	14.11
Fe_2O_3	7.94	8.86	9.09
CaO	3.05	1.94	1.85
Na_2O	0.84	0.85	0.98
K_2O	2.20	1.58	1.47
P_2O_5	0.95	0.78	0.58
MnO	0.07	0.07	0.09
TiO_2	1.02	106	1.22
SO_3	0.59	0.60	0.71
MgO	1.91	1.56	192
Cl	1.07	1.32	1.30
L.O.I	13.80	15.17	14.70

Table 2. Cation exchange capacity of studied samples.

Sample name	(C.E.C) meq/100g
Shale A	40
Shale B	45
Shale C	50

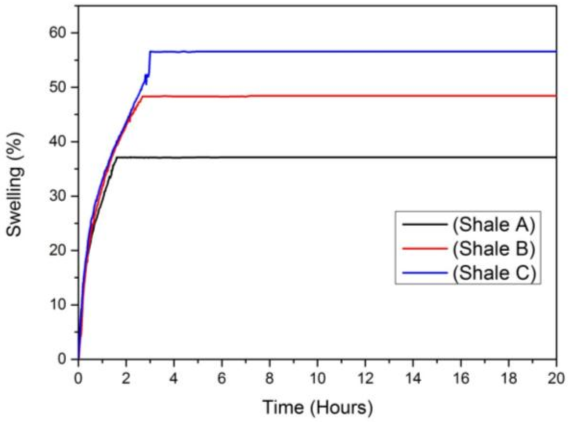

Figure 7: showing contact of OCMA bentonitewith shale (A, B and C).

Oort (2003) explained that potassium chloride effective in the inhibition process of clay swelling due to potassium ion (K^+) cause a cation exchange process where sodium inmontomorillonite converts to potassium in a process called fixation and variation in KCl doses directly related to montomorillonite content.

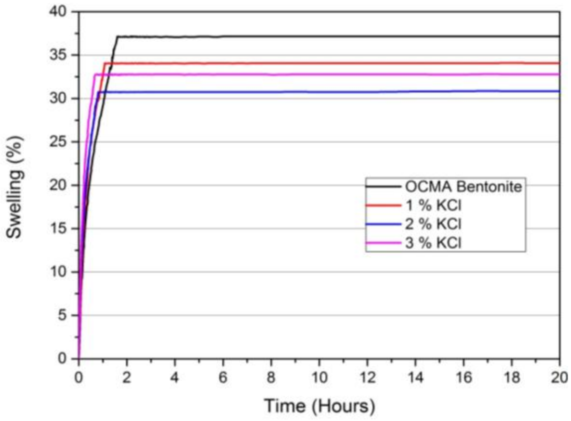

Figure 8: showing the effect of KCl on shale (A).

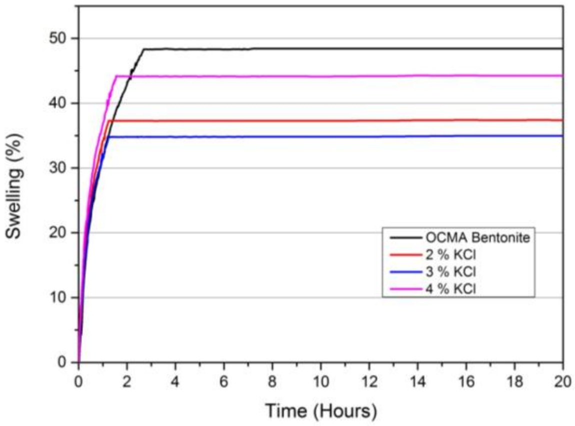

Figure 9: showing the effect of KCl on Shale (B).

3.3.3. Effect of nanoparticles on shale swelling

Different proportions of zinc oxide (ZnO) in nanoscale were added to the drilling fluid (OCMA, 5%) to inhibit swelling of shale A. Figure 11 shows the inhibition swelling of shale at about 37% to 27 %, 31%, 35%, 38% and 34 % respectively to 0.25%, 0.5%, 1%, 2% and 3% of zinc oxide. Also, shale A stopped swell after 1 hr in case of .025% ZnO in nanoscale compared to othter proportions were continued to 3 hrs.

In case of utilization of titanium oxide (TiO_2) as inhibitor of shale B swell, it is clear from Figure 12 that the swelling of shale B was reduced from 48% down to 30%, 30%, 44%, 39% and 44% with respect TiO_2proportions0.25%, 0.5%, 1%, 2% and 3%. Shale B stopped swell after 1 hr in case of .025% TiO_2 in nanoscale compared to other proportions.

A silica nanoparticle (SiO_2) was added to the drilling fluid to inhibit swelling of shale (C) as shown in Figure 13. Swelling of shale (C) inhibited from 56% down to 34%, 33%, 33.5%, 40% and 46%, corresponding to 0.25%, 0.5%, 1%, 2% and 3% of silica nanoparticles. Proportion 0.5% of SiO_2 achieved the highest reduction of shale C swelling and the percent of inhibition at this proportion was 42%.

The utilization of 3 nanoparticles ZnO, TiO_2 and SiO_2 as swelling inhibitor of shale C in Figure 14. The curves revealed that 0.25% of nanoparticles caused a decrease of shale C from 56% to 41% with ZnO, 37% with TiO_2 and 33% with SiO_2. It is clear that, SiO_2more effective as inhibitor compared with TiO_2 and ZnO.

From the previous experiments, nanoparticles were effective in the reduction of clay swelling and it can be used as a permanent solution for the shale swelling problem because nanoparticles have potential to plug nano-pore throat size of shale and preventing water from flowing into the shale formation, these results agreed with (Sensoy et al. 2009; Aftab et al, 2016; Patel et al, 2016). Patel et al, (2016) used shale powder in their research, but we used compact shale to simulate the field.

By comparing the results of the three nanoscale oxides, it was found that the SiO_2 was more effective to inhibit the swelling percentage than TiO_2 and ZnO. This agrees with Patel et al, (2016).

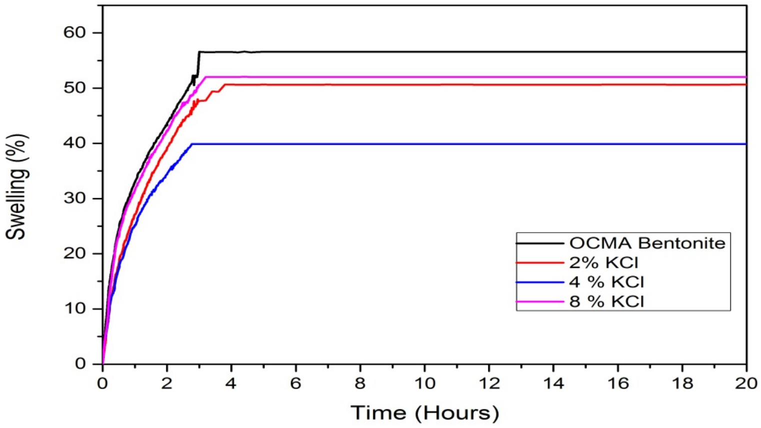

Figure 10: showing the effect of KCl on Shale (C).

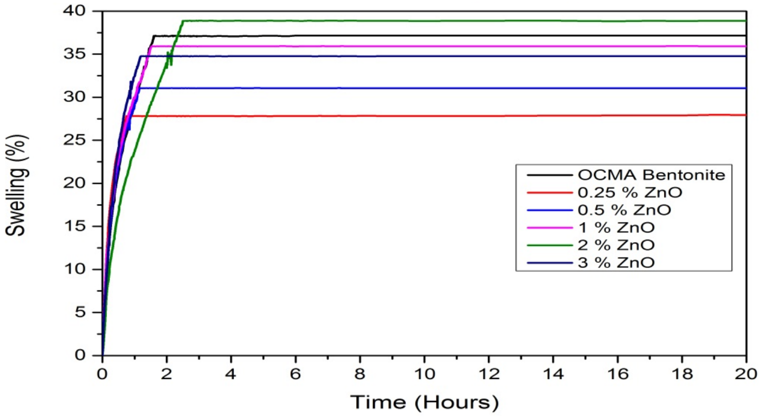

Figure 11: showing Effect of additive ZnO to drilling fluid on shale (A).

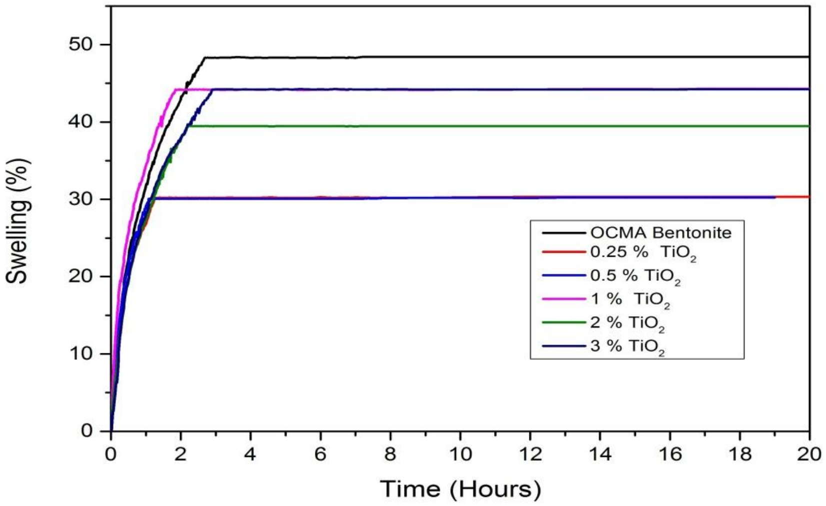

Figure 12: showing Effect of additive TiO_2 to drilling fluid on shale (B).

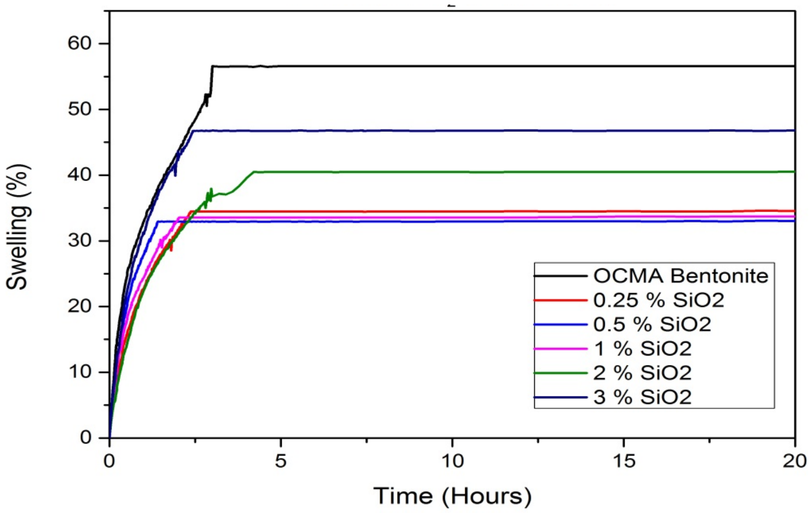

Figure 13: showing Effect of additive SiO_2 to drilling fluid on shale (C).

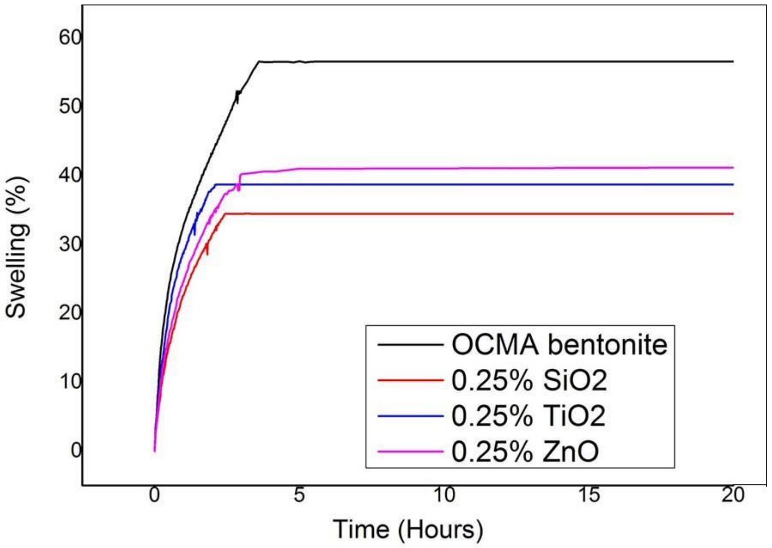

Figure 14:showing Effect of additive same dose of nanoscale oxides to drilling fluid on shale (C).

5. CONCLUSION

From all the above discussions we concluded that:

1- Swelling of shale is directly related to montmorillonite content, where more montmorillonte means more swelling in contact with OCMA bentonite. Swelling of shale cuttings increased in the order A<B<C.

2- Adding KCl to OCMA bentonite achieved decreasing in swelling that ranged from 17% at 2% (shale A), 22% at 3% (shale B) and 30% at 4% (shale C).

3- Nanoscale oxides are effective in the reduction of clay swelling and it can be used as a permanent solution for the clay swelling problem compared to KCl.

4- The mechanism of KCl and nanoscale oxides at inhibitor is different. Nanoparticles have potential to plug nano-pore throat size of shale and preventing water from flowing into the shale formation.

5- By comparing the results of the three nanoscale oxides, it was found that the SiO_2 was more effective in minimizing the swelling percentage than ZnO and TiO_2.

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