The role of chemical potential and molecular diffusion on the geomechanical stability of shale

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Abstract

Experimental data showed that water content has a profound influence on the compressive strength of shale. Testing has shown significant decrease in the uniaxial compressive strength as the water content increases. The magnitude of strength reductions for shales studied are significantly higher than those reported in the literature.

The impact of ionic diffusion on the compressive strength of shale has been investigated under three saturation conditions: wet shale, dry shale and chemically balanced wet shale. A chemically balanced shale has a water activity (chemical potential) which equals that of the test solution. Results show that, except for KCl, ionic diffusion has reduced the compressive strength of all shales studied. It has also been confirmed that diffusion osmosis has a detrimental effect on the mechanical stability of shale by reducing its compressive strength. Furthermore, it was found that when the water activity of shale is slightly higher than that of the test solution, chemical osmosis plays a major role in strengthening the shale by extracting water out of the shale. However, when the water activity of the shale is much higher than that of the test solution, diffusion osmosis weakens the shale. In other words, the detrimental impact of diffusion osmosis overtakes the beneficial effect of chemical osmosis. Moreover, this work shows that compressive strength measurements for completely dried shale could be misleading due to the development of capillary forces that significantly modifies the compressive strength of shale.

Finally, the impact of ionic diffusion on the compressive strength of shale was carried out in the absence of both chemical osmosis and capillary forces. Results show that the invasion of sodium and calcium ions into shale reduced its compressive strength considerably while the invasion of potassium ions enhanced its compressive Strength.

Keywords: shale collapse, ionic diffusion, compressive strength.
Introduction & Background

Shale is considered to be the most bothersome and challenging porous medium to handle. Nearly, 90% of the formations drilled worldwide are classified as shale formations and about 75% of drilling operations’ problems is related to shale (Dzialowski et al, 1993). Wellbore instability, hole enlargement, stuck pipe, high torque and drag, and side tracking are some of the most challenging drilling problems related to shale. Shale is a low permeability porous rock that has distinct laminated layers and moderate to high clay content. Manohar (1999) states that shale rocks are characterized by its clay content and low permeability arising from poor pore connectivity through narrow pore throats (typical pore diameters range from 3 nm to 100 nm). These features make them susceptible to phenomena such as hydration, swelling, shrinking, strength reduction and ultimately failure.

Shale failure phenomenon is very complicated and not yet fully understood. In addition to mechanical, thermal and electrical mechanisms, many researchers argue that shale failure is attributed to chemical phenomena. Namely, many authors think that shale failure is caused by the transfer of water and ions into shale. The transfer of water and ions into shale could impact the mechanical and physicochemical properties of shale (Bol et al, 1992; Chenevert, 1970; Zhang et al, 2004; AL-Bazali, 2005; Fam & Dusseault, 1998; Horsud et al, 1998 Low & Anderson, 1958 and Santarelli et al, 1992). The alteration of mechanical and physicochemical properties of shale could cause wellbore instability problems while drilling. Wellbore instability, especially in deviated wells, is the most costly and troublesome problem in shale drilling. According to van Oort et al (1996), wellbore instability problems cost the drilling industry over $1 billion annually.

Recently, wellbore instability problems have been linked to the unfavorable chemical interaction between shale and water based drilling fluids. The direct contact between the aqueous phase in the drilling fluid and the shale pore fluid permits the transfer of water into shale when the chemical potential of the drilling fluid is greater than that of the shale, causing shale swelling and failure. Thus, many have embraced the concept of stopping the flow of water into shale or osmotically extracting water out of shale during drilling in order to avoid shale swelling and failure.

In the absence of a hydraulic pressure gradient, the transfer of drilling fluid filtrate into shale is mainly ruled by the chemical potential difference between the shale pore fluid and the drilling fluid (Ewy and Stankovich, 2000 and Low, 1987). Scientifically speaking, osmosis is accepted as a way to extract water out of shale when the water activity of the shale is higher than that of the drilling fluid. Therefore, many have recommended using low water activity (high salinity) drilling fluids when drilling shale in order to osmotically extract water out of it. This requires adding salts to the drilling fluid in order to lower its water activity and achieve the desired osmotic potential between the shale and the drilling fluid.

While the addition of salt lowers the water activity of the drilling fluid and generates a favorable osmotic potential, it could create an unfavorable ionic concentration imbalance that provokes the transfer of ions by Fickean diffusion in the direction of decreasing ionic concentration (Santos & Perez, 2001; Chenevert, 1989 and AL-Bazali et al, 2011). Ionic diffusion into shale may change the ionic
concentration and composition of the shale pore fluid which could affect the shale mechanical properties and lead to shale swelling, cohesion degradation, cementing bonds weakening and overall rock strength reduction (Talal M. AL-Bazali, 2011; Fam and Dusseault, 1998; Fritz & Marine, 1983; Bird, 1984; Hale & Mody, 1992 and Keijzer et al, 1999). In order to better exploit osmosis as a means for stabilizing shale, many studies have focused on understanding how water and ions transfer impacts shale stability.

While many researchers have focused on studying the impact of water and ions transfer on shale stability (AL-Bazali et al, 2008; Chenevert, 1989; Hale & Mody, 1992; Ballard et al, 1992; Lomba et al, 2000; Ghassemi et al, 2001; Mody et al, 2002; Simpson et al, 1995; Yu et al, 2001; Zhang et al, 2008; Schlemmer et al, 2003; Tan et al, 1996 and van Oort, 2003), their work have mainly focused on understanding and quantifying the overall and final impact of water and ions transfer on shale stability. In other words, these studies investigated the end result (equilibrium status) of water and ions transfer into shale as it interacted with water based drilling fluids. While this work definitely helped in understanding the final impact of water and ions transfer on shale stability, it did not discuss the time dependent effect of water and ions transfer into or out of shale. Consequently, these studies have failed to explain how water and ions move into or out of shale as a function of time.

I believe a better understanding of water and ions movement into or out of shale as a function of time could greatly explain how such phenomenon affects wellbore stability in shales especially when taking into account that wellbore instability in shale is time related. Moreover, monitoring water and ions movement into shale as a function of time could help in optimizing salt concentration in drilling fluids.

This paper discuses the time dependent impact of water and ions flux into shale as it interacts with aqueous solutions. Moreover, the time dependent water and ions flow profile is generated as shale interacts with different aqueous solutions. Furthermore, the impact of salt type and concentration on water and ions movement as shale interacts with aqueous solutions is closely investigated. Finally, the impact of the time dependent water and ions on the compressive strength of shale is addressed.

**Experimental Methodology**

**Time Dependent Water and Ions Uptake into Shale**

The impact of water and ions flow on shale's stability as a function of time was investigated using a new procedure developed by the author. This new procedure accounts for the time factor, which is frequently ignored, to analyze the time dependent water and ions flux as shale interacts with aqueous solutions. This was made possible through employing immersion and gravimetric techniques to monitor water and ions flow as a function of time. Since the objective of this work was to investigate the time dependent water and ions flow into shale, the author used one type of shale only as variation of shale type is irrelevant to the outcome of this work. The mineralogical composition of the shale used in this study is shown in Table 1.
This shale was donated by an oil company that operates in the Middle East. When it arrived, it was coated and wrapped in a thick polyethylene bag and housed inside a sealed barrel. Care was taken during handling the shale specimen to lessen shale exposure and interaction with the atmosphere during cutting, handling and transporting. Air interaction with shale could change its properties, especially the native water activity (Chenevert and Amanullah, 1997). The shale was carefully unwrapped to avoid creating fissures and micro fractures. Using a special coring machine, a 2.5” diameter by 5” length cores were cored. These cores were then stored in cans full of oil to minimize air interaction.

The following describes the experimental procedure used to quantify the time-dependent water and ions flux into shale during interaction with aqueous solutions.

- Obtain a well preserved shale core.
- Cut several cubical samples of size (1x1x1 inch) from the shale core using an electrical saw which uses mineral oil as the cooling fluid. Using small samples speeds up the interaction between the shale and the test fluid.
- Randomly select several shale samples and determine their initial water content. The initial water content ($W_C$) is measured as follows:
  - Clean the shale sample and weigh it ($W_1$)
  - Dry the shale sample in a 200F oven for 24 hours and weigh it again ($W_2$). It is experimentally proven that heating the shale for 24 hours is adequate to drive out all the free water in the shale especially for small samples like the ones used in this experiment (AL-Bazali 2005 and Zhang et al 2004).
  - The original water amount in the shale $W_w$ is calculated as follows:
    $$W_w = W_1 - W_2$$
  - Calculate the water content ($W_{Ci}$) for each shale sample:
    $$W_{Ci} = W_w/W_1$$
  - Calculate the average shale water content as follows:
    $$W_{Cavg} = \sum (W_{Ci})/n$$
    This value will be used as the average original water content for all shale samples.

- After determining the average water content of the shale, put the remaining cubical samples in a desiccator of 0.98 water activity for a week. It is experimentally proven that when shale samples are put in a desiccator of a certain water activity, it takes a week for the shale sample to reach the desiccator's water activity and maintain it without further change (AL-Bazali, 2005 and Zhang et al, 2004).
- Prepare salt solutions of varying concentrations (8%, 12% and 20% by weight). Three salts were used in this study; NaCl, KCl & CaCl₂. The water activities of the salt solutions corresponding to the above mentioned concentrations are shown in Table 2.
- At this stage, I will conduct the time dependent immersion and gravimetric test to quantify water and ions uptake as a function of time when shale interacts with different salt solutions of different concentrations. The test procedure is as follows:
- Obtain 15 cubical shale samples (size 1x1x1 inch) out of the 0.98 desiccator. The water activity of the shale samples should equal 0.98 which is the water activity of the desiccator.
- Weigh all shale samples in air (W₁).
- Fill 15 plastic bags with the prepared 8% by weight NaCl solution.
- Place a shale sample inside each plastic bag that is filled with the 8% by weight NaCl solution and squeeze the air out of it then seal it. Number the plastic bags from 1 to 15.
- After 15 minutes, take out the shale sample in bag number 1 and calculate the amount of water and ions uptake. Remember that all shale samples were conditioned to have a 0.98 water activity while the 8% by weight NaCl solution has a water activity of 0.95. Therefore, once expect water to be driven out of shale due to osmosis while ions will flow into the shale due to ionic concentration imbalance. The amount of water and ions uptake is calculated as follows:
  - Weigh the shale sample after taking it out of the plastic bag (W₂).
  - The weight of both water and ions added/lost during the interaction of the shale sample with the test fluid is estimated as follows:
    \[ W_3 = W_2 - W_1 \]  
  - Dry the shale sample in a 200F oven for 24 hours and weigh it (W₄). In this process, all water (original and added) will be removed. The amount of water removed during the drying process is estimated as follows:
    \[ W_5 = W_2 - W_4 \]  
  - The amount of water added/lost during interaction with the test fluid is:
    \[ W_w = W_5 - W_{Cavg}W_1 \]  
  - The amount of ions added/lost as shale interacted with the test fluid is:
    \[ W_i = W_3 - W_w \]  
  - The amounts of water (Wₚ) and ions (Wᵢ) represent the water and ions uptake when the shale sample interacted with an 8% by weight NaCl solution after 15 minutes.
- Repeat the test and calculate the amount of water and ions uptake as the other shale samples interacts with the 8% by weight NaCl solutions for 1/2, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60 and 70 hours.
- Plot the time dependent water and ions uptake as shale interacts with an 8% by weight NaCl solution. The time scale goes from zero to 70 hours.
- Repeat the above procedure, for the same periods of time, to obtain the time dependent water and ions uptake when shale interacts with 12% and 20% by weight NaCl solutions.
- Repeat the above procedure, for the same periods of time, to obtain the time dependent water and ions uptake when shale interacts with 8%, 12% and 20% by weight KCl and CaCl₂ solutions.

The above discussed procedure shows the effect of time and ionic concentration on water and ions uptake as shale interacts with salt solutions.

### Impact of Salt Type and Concentration of the Compressive Strength of Shale
In order to investigate the impact of salt type and concentration on the compressive strength of shale, shale samples were placed inside a standard biaxial test chamber where its compressive strength is measured. A 4500 psi confining pressure was applied to the shale sample for 3 h before subjecting the shale to an axial load. This was done to insure pore pressure dissipation within the shale prior to applying the axial load. Next, a 2.5x10^{-5} s^{-1} axial strain rate was used until shale failure occurred. It worthy to point out that this test yields qualitative measurements since pore pressure build up cannot be completely stopped under this strain rate.

First, the compressive strength of a native unaltered shale sample was measured to be used as a reference point. Then, several shale samples were immersed into 8%, 12% and 20% NaCl, KCl and CaCl₂ solutions for 70 hours. After 70 hours, the compressive strength of all immersed shale samples was measured and compared with that of the native shale sample to investigate the impact of salt type and concentration on the compressive strength of shale.

While the aforementioned test sheds light on the final impact of salt type and concentration on shale's compressive strength, it did not explain the impact of time dependent water and ions uptake on the shale's compressive strength. To address this phenomenon, the compressive strength of shale was measured after immersion in 12% NaCl, KCl and CaCl₂ solutions for 1/4, 1/2, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60 and 70 hours. Shale cores were not available to repeat the test with 8% and 20% NaCl, KCl and CaCl₂ solutions.

Results & Discussion
Time Dependent Water Uptake into Shale

Using the above described immersion and gravimetric techniques, the time dependent water uptake into shale when immersed in NaCl, KCl and CaCl₂ solutions has been quantified. Figures 1, 2 and 3 show the time dependent water uptake into shale when immersed in NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations respectively. These figures show that the time dependent water uptake exhibited the same general trend for all salt solutions. More precisely, water uptake went through three distinct stages as follows:

1. Water movement out of shale
2. Water movement into shale
3. Water movement steadiness

The following discusses the three stages of the time dependent water uptake phenomenon as shale interacted with NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.

Water movement out of shale

To better understand this phenomenon, I plotted the water uptake behavior during the first 4 hours to investigate the early time water transport activities. Figures 4, 5 and 6 show the early time water uptake into shale when immersed in NaCl, KCl and CaCl₂ solutions.
solutions of 8%, 12% and 20% concentrations respectively. Figure 4 shows that when shale interacted with 8% NaCl solution, water moved out of shale in the first 2 hours. After 2 hours water started moving into shale. Similarly, water movement out of shale continued for 40 minutes and 25 minutes when shale interacted NaCl solutions of 12% and 20% concentrations respectively. After such times, water movement into shale dominated.

The early time water loss can be attributed to chemical osmosis phenomenon. Osmosis is the flow of water from a dilute solution (high chemical potential) to a more concentrated solution (low chemical potential) across a semi-permeable membrane. It is argued that shale could act as a leaky semi-permeable membrane that freely allows water flow and partially restricts ions flow. I believe that water was osmotically extracted out of shale in response to the imposed chemical potential difference between shale and NaCl solutions. The same analysis can be drawn from figures 5 and 6 for shale interaction with KCl and CaCl₂ solutions.

The driving force for chemical osmosis is the chemical potential imbalance between two solutions of different concentrations. If a perfect semi-permeable membrane (i.e. a membrane that totally excludes the flow of ions) separates two solutions of different concentrations, the driving osmotic force equals to the pressures required to stop water flow to the more concentrated solution. The pressure required to stop the flow of water to the concentrated solution is given by a well-known thermodynamic relation.

\[ \frac{RT}{V_w} \ln \frac{a_{w1}}{a_{w2}} \]  

Where; \( \pi \) is the osmotic pressure, \( R \) is the gas constant, \( T \) is the absolute temperature, \( V_w \) is the partial molar volume of water and \( a_w \) is the water activity. When conducting the immersion tests, the chemical potential of the shale was initially higher than the chemical potential of the salt solutions. Therefore, water should flow out of shale by osmotic means.

It is agreed upon that extracting water out of shale could increase its mechanical strength and reduce its pore pressure and thus avoid wellbore collapse while drilling. Van Oort (2003) argues that stimulating water flow out of the shale and into the wellbore could strengthen the shale. This can be achieved by creating a chemical potential difference where the chemical potential of the drilling fluid is less than that of the shale. If such situation exists, water will flow in the direction of lower chemical potential provided that the shale acts as a semi-permeable membrane. **Water movement into shale**

This stage is dominated by diffusion osmosis. Diffusion osmosis is defined as the transport of ions and their associated water (water cloud) in response to ionic concentration imbalance. As shown in figure 4, water movement into shale started after 2 hours, 40 minutes and 25 minutes when shale interacted NaCl solutions of 8%, 12% and 20% concentrations respectively. This is mainly attributed to the flow of associated water of ions into shale. I believe that associated water started to move into shale earlier than that since ionic transport should take place owing to the imposed concentration imbalance. However, water transport out of shale due to osmosis was faster and dominated this process initially.

Many argue that chemical osmosis and diffusion osmosis take place at the same time in the presence of ionic concentration imbalance (Chenevert, 1989; Hale & Mody, ...
1992; Ballard et al, 1992; Lomba et al, 2000; Mody et al, 2002; Simpson et al, 1995; Yu et al, 2001; Zhang et al, 2008; Schlemmer et al, 2003; Tan et al, 1996; Talal AL-Bazali, 2011 and van Oort, 2003). However, the flux of free water due to osmosis is higher than that of associated water due to diffusion osmosis. Associated water moves along with its respective ion which slows down its flux rate. As time goes by, it becomes a quantity issue rather than a flux issue as more ions move into shale. Thus, the quantity of associated water overtakes the quantity of osmotic water and this should explain the water movement into shale after some time. This is supported by the fact that water movement into shale when it interacted with 20% NaCl solution took less time than when shale interacted with 12% NaCl solution. Also, water movement into shale when it interacted with 12% NaCl solution took less time than when shale interacted with 8% NaCl solution. Therefore, the quantity of associated water movement into shale is controlled by the ionic concentration imbalance. The same observations can be seen when shale interacted with KCl and CaCl2 solutions as shown in figures 5 and 6.

From the above discussion, one can argue that water uptake into shale is time dependent. Chemical osmosis seems to dominate water movement in early times while diffusion osmosis takes over later. The amount of water movement due to diffusion osmosis is highly related to the ionic concentration imbalance. This presents a good challenge to the argument of using highly concentrated solutions to osmotically extract water out of shale in order to prevent wellbore failure. I believe that such practice does more damage since diffusion osmosis will increase the flux and quantity of ionic associated water owing to the imposed ionic concentration gradient. Talal M. AL-Bazali (2011) showed that when using highly concentrated solutions, the osmotic transfer of water out of shale was not effective enough to stabilize shale when compared to the destabilizing impact of ionic diffusion and their associated water into shale.

Water movement steadiness

In this stage, water movement seems to hold steady for all salt solutions regardless of their ionic concentration, as shown in figures 1, 2 and 3. Namely, water uptake into shale did not change significantly after 8 hours when shale interacted with NaCl, KCl and CaCl2 solutions of different concentrations. This could be due to the fact that the imposed ionic concentration imbalance between shale and salt solutions has been destroyed. Namely, the movement of ions into shale has equalized the chemical potential and ionic concentration between shale and salt solutions. The absence of a chemical potential gradient and ionic concentration imbalance has stopped the movement of ions and water into shale.

Time Dependent Ions Uptake into Shale

The diffusion of ions and their associated water is controlled by a concentration gradient that can be expressed by Fick's law:

\[ J = - D_{si} \left( \frac{C_{i,shale} - C_{i,solution}}{x} \right) \]

\[(9)\]
where $J$ is mass flux of $i$th ion; $D_{si}$ is the diffusion coefficient of $i$th ion; $C_{i,\text{shale}}$ is the concentration of $i$th ion in pore fluid; $C_{i,\text{solution}}$ is the concentration of $i$th ion in solution and $\Delta x$ length of shale. Figures 7, 8 and 9 show the time dependent ions uptake into shale when immersed in NaCl, KCl and CaCl$_2$ solutions of 8%, 12% and 20% concentrations respectively.

Figures 7, 8 and 9 show three interesting facts pertaining to the behavior of ionic diffusion into shale in the presence of an ionic concentration difference.

1. The diffusion of ions into shale increased exponentially up to 8 hours for all salt solutions tested. After 8 hours, the diffusion of ions held steady in all cases. I believe ions moved into shale in response to the imposed ionic concentration gradient as per equation 9. The driving ionic diffusion force promoted the flux of ions for 8 hours. This explains why wellbore failure occurs during the first hours when using concentrated salt solutions. After 8 hours, the ionic concentration imbalance between shale and salt solutions had equalized which ceased the movement of ions into shale.

2. The ionic concentration difference between shale and salt solution did not affect the time at which ionic transport into shale stabilized. This is true for all salt solutions tested as seen in figures 7, 8 and 9. However, at any given time prior to ionic flux stability, the diffusion rate of ions seems to depend on the imposed concentration gradient. For example, after 2 hours, the flux of ions is higher when shale interacted with 20% NaCl solution than when shale interacted with 8% and 12% NaCl solutions. This could be related to the driving ionic diffusion force which controls ionic diffusion. This force is proportional to the ionic concentration difference.

3. The amount of ions uptake at equilibrium depends on the concentration and type of salt solution as shown in figure 10. It can be seen from figure 10 that the amount of transported ions into shale increased as the concentration of the test solution increases. This is expected since the flux of ions is directly proportional to the concentration difference between shale and salt solution as shown in equation 9. Also, figure 10 shows that the amount of calcium ions was greater than sodium and potassium ions when shale interacted with NaCl, KCl and CaCl$_2$ solutions of the same concentrations. This could be attributed to the size of calcium ions which is bigger than potassium and sodium ions. The same argument can be made to explain the higher amount of sodium ions when compared to potassium ions as shale interacted with NaCl and KCl solutions of similar concentrations.

I believe ionic diffusion into shale has a detrimental impact on shale stability. Ionic diffusion into shale may change the ionic concentration and composition of the shale pore fluid which could affect the shale mechanical properties and lead to shale swelling, cohesion degradation, cementing bonds weakening and overall rock strength reduction (Talal M. AL-Bazali, 2011; Fam and Dusseault, 1998; Fritz & Marine, 1983; Bird, 1984; Hale & Mody, 1992 and Keijzer et al, 1999). The following investigates the impact of ions and water uptake on the compressive strength of shale.

**Impact of Ions and Water Uptake on the Compressive Strength of Shale**
First, the shale's native compressive strength was measured to be used as a reference point. Then, the shale's compressive strength was measured after immersion for 70 hours into NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations. Figure 11 compares the native compressive strength of shale with the altered ones after immersion for 70 hours into NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.

**Compressive Strength of Shale after Immersion into NaCl, KCl and CaCl₂ Solutions**

Figure 11 shows that the compressive strength of shale decreased after immersion in NaCl and CaCl₂ solutions for all concentrations. Moreover, it can clearly be seen that the compressive strength of shale decreased as the concentration of the salt solution increased. I believe that the strength reduction is mainly attributed to the flow of ions (sodium and calcium) and their associated water into shale. This confirms the belief that the diffusion of sodium and calcium ions into shale has a detrimental impact on shale strength and stability. The flow of these ions into shale alters the mechanical properties of the shale, causes cohesion degradation and cementation bonds weakening, all of which could lead to strength reduction and failure.

Potassium ion seems to have a strengthening effect on shale as shown in figure 11. Namely, the compressive strength of shale had enhanced when exposed to KCl solutions of different concentrations. This may be attributed to the diffusion of potassium ions into the shale. It is believed that potassium ions transfer into the shale could decrease the distance between the clay platelets leading to slight shale shrinkage and thus promoting strength enhancement and stability. Gazaniol et al (1995) argues that potassium ions are less hydratable than other classic ions and they dehydrate and illitize smectites, thus producing shale hardening. Field observations have shown the superiority of potassium chloride solutions in combating shale instability during drilling.

**Compressive Strength Alteration as a Function of Time**

While figure 11 shows the final impact of salt type and concentration on shale's compressive strength, it did not explain the impact of time dependent water and ions uptake on the shale's compressive strength. To address this phenomenon, the compressive strength of shale was measured after immersion in 12% NaCl, KCl and CaCl₂ solutions for 1/4, 1/2, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60 and 70 hours as shown in figure 12. Shale cores were not available to repeat the test with 8% and 20% NaCl, KCl and CaCl₂ solutions.

Figure 12 shows that in the first 8 hours, the shale's compressive strength decreased exponentially when it interacted with NaCl and CaCl₂ solutions and increased exponentially when it interacted with KCl solution. After 8 hours, the measured compressive strength of shale did not change significantly. I believe that the shale's compressive strength alteration is highly related to the flux of water and ions. As discussed earlier, ions and water movement into shale continued for 8 hours. After 8 hours, the movement of water and ions has ceased as shown in figures 1, 2, 3, 7, 8 and 9.
Osmotic Water versus Associated Water

Osmotic water is the flow of water in response to a chemical potential gradient. Water will osmotically move from a higher chemical potential region to a lower chemical potential region across a semi-permeable membrane. It is difficult to directly measure the chemical potential of a system. However, the chemical potential of the water phase in a system can be closely estimated through its water activity. The pressure required to stop the osmotic flow of water to the lower chemical potential region, called osmotic pressure, is given by equation 8. It is believed that manipulating the chemical potential (water activity) of the drilling fluid could solve wellbore instability in shale by extracting water out of shale. This can be achieved by making the chemical potential (water activity) of the drilling mud less than that of the shale.

Associated water is a water cloud that is attached to ions and serves as a hydration shell which neutralizes the charges on ions. When ions flow in response to an ionic concentration difference, its associated water travels along with it. Besides the adverse impact of ions, except for potassium ions, on shale stability, associated water could increase shale’s pore pressure and decrease its strength, all of which could cause shale instability. The flow of ions and their associated water is governed by equation 9.

The process describing the flow of osmotic water is called "chemical osmosis" while the process describing the flow of associated water is called "diffusion osmosis". Many argue that these processes take place at the same time when shale interacts with drilling fluids; however, they were unable to quantitatively separate their impact on shale stability (Talal AL-Bazali, 2011; Ewy and Stankovich, 2000; Fam and Dusseault, 1998; Ghassemi et al., 2001; Hale and Mody, 1992; Horsud et al., 1998; Schlemmer et al., 2003; Tan et al., 1996; van Oort, 2001 and Jianguo Zhang et al., 2008).

To separately quantify the impact of chemical osmosis and diffusion osmosis on shale, the following experimental procedure was employed.

- NaCl, KCl and CaCl$_2$ solutions of 8%, 12% and 20% concentrations were prepared and placed in different desiccators.
- Nine shale samples were initially weighted and placed in the desiccators above the solutions. The desiccators were evacuated using a vacuum pump.
- The concentration of each salt solution is constantly monitored and maintained at the desired concentration. This is done by changing the salt solution in the desiccators every day. It is very important to maintain the concentration of the salt solution at the desired value.
- The shale sample’s weight is monitored every day until no further change is reached.
- The final sample’s weight is recorded.
- The difference between the shale’s initial weight and final weight is recorded as the water uptake due to chemical osmosis (osmotic water).
- The osmotic water is subtracted from the bulk water which was obtained as a result of shale immersion in NaCl, KCl and CaCl$_2$ solutions of 8%, 12% and 20% concentrations. The bulk water is shown in figure 10.
- The difference between osmotic water and bulk water is labeled as associated water.
Figure 13 compares osmotic water and associated water uptake into shale as it interacts with NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations. It can clearly be seen from figure 13 that osmotic water moved out of shale in response to the imposed chemical potential difference while associated water moved into shale due to diffusion osmosis owing to the ionic concentration imbalance.

This brings up a very interesting question; does adding salt to drilling fluids promote shale stability? Obviously, it does not since the beneficial effect of osmotically extracting water out of shale is counteracted by the detrimental impact of associated water flow into shale. The detrimental impact of associated water increases when incorporating concentrated salts, except for KCl, in drilling fluids as more ions invade the shale in response to the imposed concentration imbalance. This holds true when using water based muds to drill shale since shale acts as a leaky semi-permeable membrane where it does not completely restrict the flow of ions. Using concentrated salts in the formulation of oil based muds could prove to be beneficial since the oil film acts as a perfect semi-permeable membrane that completely restricts the flow of ions. Therefore, chemical osmosis could be employed to osmotically extract water out of shale when oil based muds are used.

Conclusions

In this work, the impact of the time dependent water and ion uptake on shale stability has been investigated. The outcome of this study describes, for the first time, the transport of water and ions into and out of shale as a function of time. The following key points were deduced from this study.

- When shale interacts with salt solutions, water uptake into shale goes through three distinct stages; water movement out of shale (due to chemical osmosis), water movement into shale (due to diffusion osmosis) and water movement steadiness (equilibrium stage).
- Chemical osmosis seems to dominate water movement in early times while diffusion osmosis takes over later.
- The amount of water movement due to chemical osmosis depends on the chemical potential gradient while the amount of water movement due to diffusion osmosis is highly related to the ionic concentration imbalance.
- The amount of ions uptake into shale at equilibrium depends on the type and concentration of salt solution.
- Potassium ion seems to have a strengthening effect on shale while sodium and calcium ions have a weakening effect on shale.
- The shale's compressive strength alteration is greatly influenced by the type and concentration of the salt solution.
- The shale's compressive strength alteration is time dependent and correlates very well with the time dependent flux of water and ions.
- Chemical osmosis and diffusion osmosis take place simultaneously when shale interacts with water based muds. The overall impact on shale stability is governed by the net water flow from chemical osmosis and diffusion osmosis.
- Using concentrated salt solutions in water based muds to osmotically extract water out of shale could be detrimental as more associated water move into shale by diffusion osmosis.
- Using concentrated salt solutions in oil based muds to osmotically extract water out of shale could be beneficial since the oil film acts as a perfect semi-permeable membrane which completely restricts the flow of ions and their associated water.

References


Table 1: The mineralogical composition of shale.

<table>
<thead>
<tr>
<th>X-Ray Diffraction</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>13.5</td>
</tr>
<tr>
<td>Feldspar</td>
<td>2.1</td>
</tr>
<tr>
<td>Calcite</td>
<td>0</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.9</td>
</tr>
<tr>
<td>Siderite</td>
<td>0</td>
</tr>
<tr>
<td>Total Clay</td>
<td>75.9</td>
</tr>
<tr>
<td>Chlorite</td>
<td>N/A</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>38.9</td>
</tr>
<tr>
<td>Illite</td>
<td>N/A</td>
</tr>
<tr>
<td>Smectite</td>
<td>N/A</td>
</tr>
<tr>
<td>Mixed Layer</td>
<td>N/A</td>
</tr>
<tr>
<td>Water Activity</td>
<td>0.98</td>
</tr>
<tr>
<td>Water Content</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 2: Water activities of salt solutions.

<table>
<thead>
<tr>
<th>Salt Concentration %</th>
<th>NaCl water activity</th>
<th>KCl water activity</th>
<th>CaCl₂ water activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.95</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>12</td>
<td>0.92</td>
<td>0.94</td>
<td>0.93</td>
</tr>
<tr>
<td>20</td>
<td>0.83</td>
<td>0.89</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Figure 1: Time dependent water uptake into shale when immersed in NaCl solutions of 8%, 12% and 20% concentrations.
Figure 2: Time dependent water uptake into shale when immersed in KCl solutions of 8%, 12% and 20% concentrations.

Figure 3: Time dependent water uptake into shale when immersed in CaCl$_2$ solutions of 8%, 12% and 20% concentrations.
Figure 4: Early time water uptake into shale when immersed in NaCl solutions of 8%, 12% and 20% concentrations.

Figure 5: Early time water uptake into shale when immersed in KCl solutions of 8%, 12% and 20% concentrations.
Figure 6: Early time water uptake into shale when immersed in CaCl₂ solutions of 8%, 12% and 20% concentrations.

Figure 7: Time dependent ions uptake into shale when immersed in NaCl solutions of 8%, 12% and 20% concentrations.
Figure 8: Time dependent ions uptake into shale when immersed in KCl solutions of 8%, 12% and 20% concentrations.

Figure 9: Time dependent ions uptake into shale when immersed in CaCl₂ solutions of 8%, 12% and 20% concentrations.
Figure 10: Equilibrium water and ions uptake when shale interacted with NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.

Figure 11: Native compressive strength of shale compared with the altered ones after immersion for 70 hours into NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.
Figure 12: Compressive strength of shale after immersion in 12% NaCl, KCl and CaCl₂ solutions for 1/4, 1/2, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60 and 70 hours.

Figure 13: Osmotic water and associated water uptake into shale as it interacts with NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.