

where J is mass flux of i th ion; D_{si} the diffusion coefficient of the i th ion; $C_{i,shale}$ is the concentration of i th ion in pore fluid; $C_{i,solution}$ is the concentration of i th ion in solution and Δx 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 CaCl₂ 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 CaCl₂ 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 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.

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Table 1: The mineralogical composition of shale.

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

Table 2: Water activities of salt solutions.

Salt Concentration %	NaCl water activity	KCl water activity	CaCl ₂ water activity
8	0.95	0.97	0.97
12	0.92	0.94	0.93
20	0.83	0.89	0.83

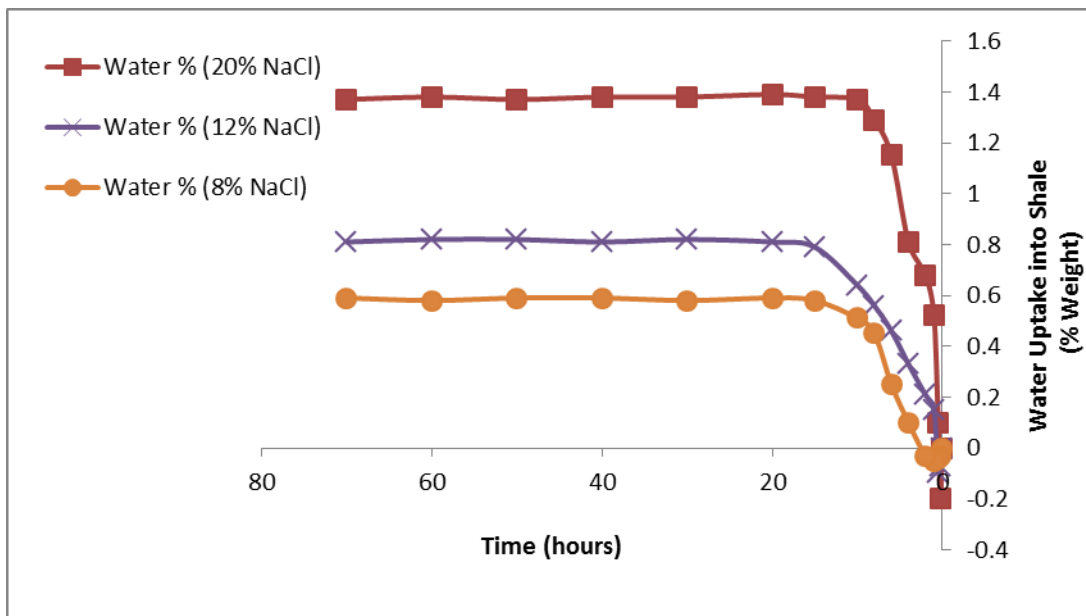


Figure 1: Time dependent water uptake into shale when immersed in NaCl solutions of 8%, 12% and 20% concentrations.

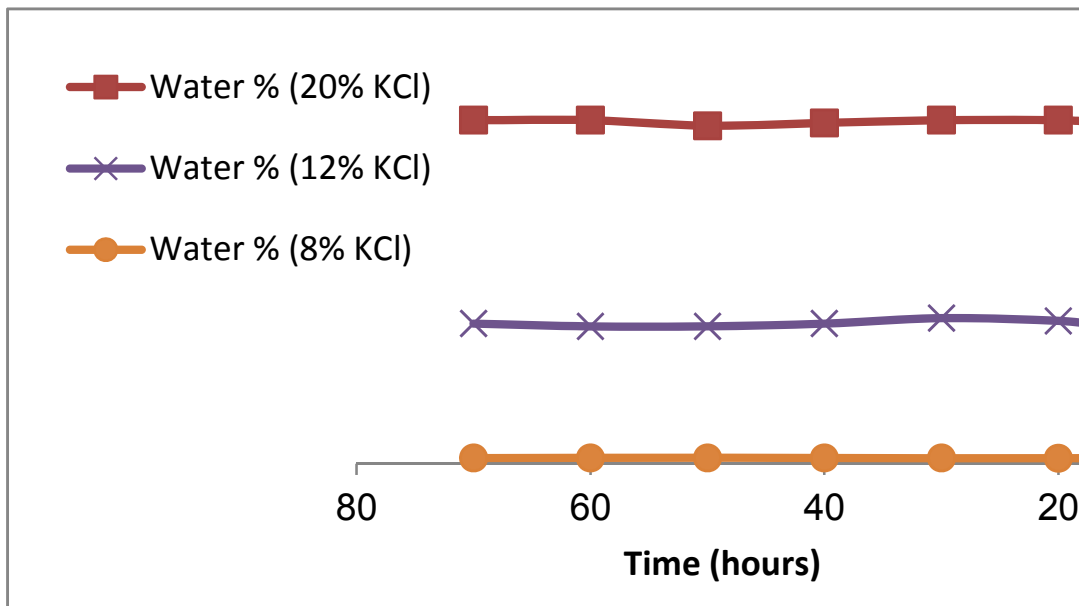


Figure 2: Time dependent water uptake into shale when immersed in KCl solutions of 8%, 12% and 20% concentrations.

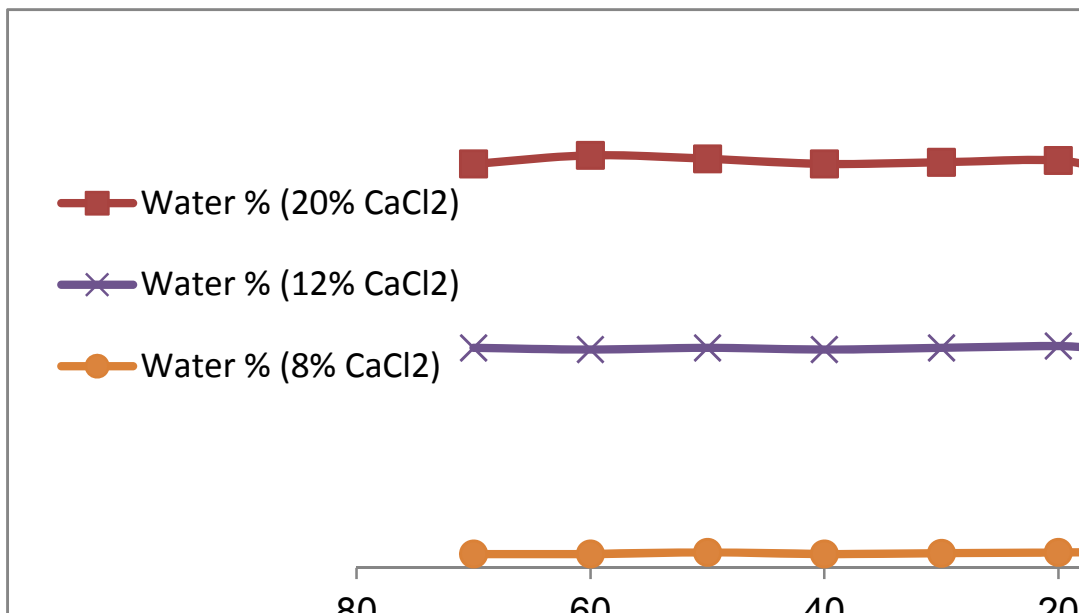


Figure 3: Time dependent water uptake into shale when immersed in CaCl₂ solutions of 8%, 12% and 20% concentrations.

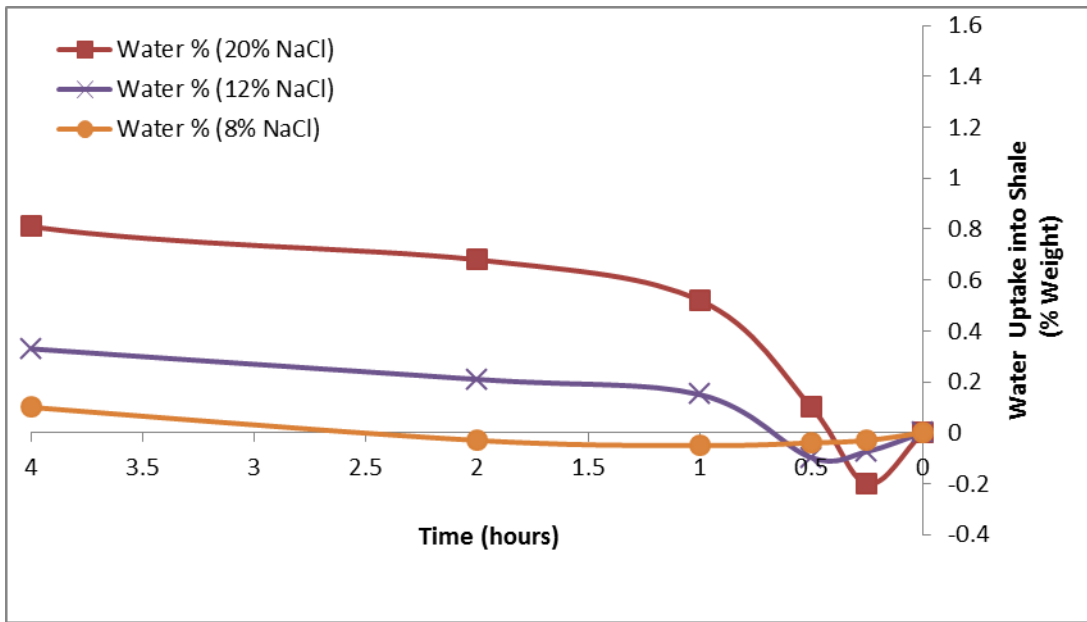


Figure 4: Early time water uptake into shale when immersed in NaCl solutions of 8%, 12% and 20% concentrations.

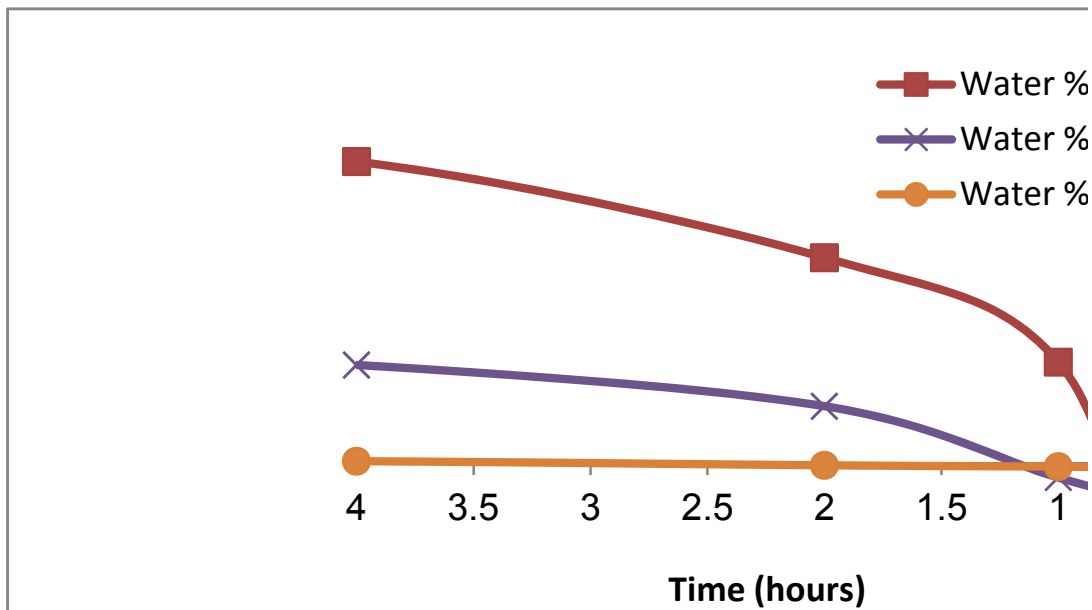
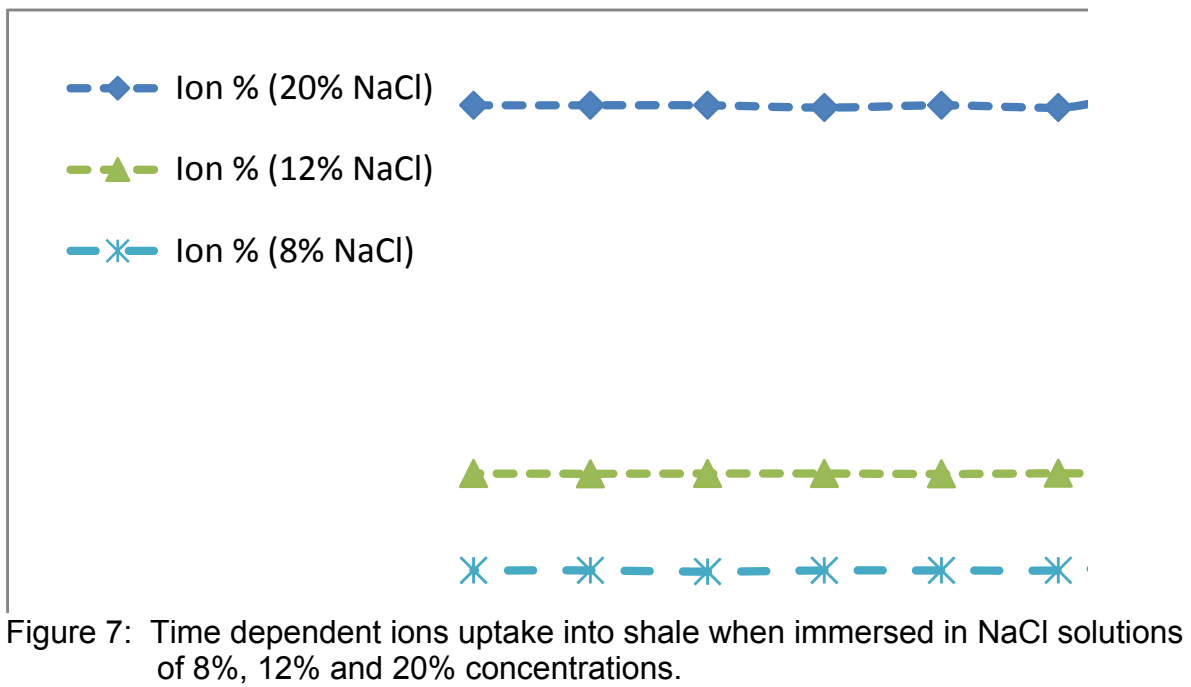
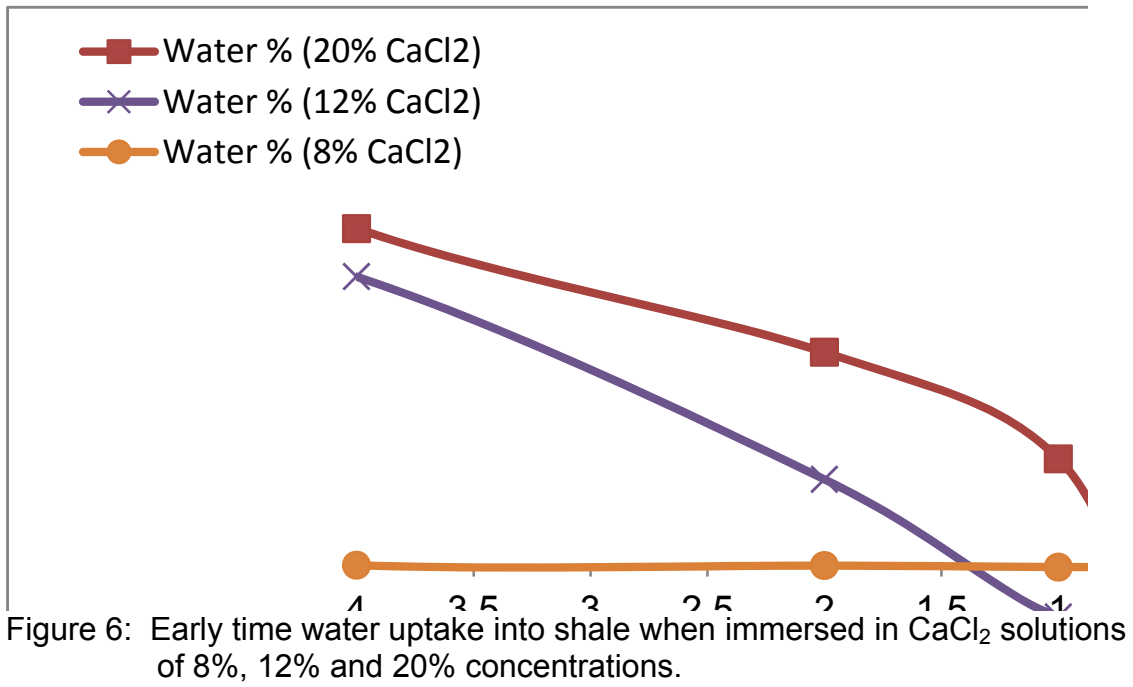


Figure 5: Early time water uptake into shale when immersed in KCl solutions of 8%, 12% and 20% concentrations.



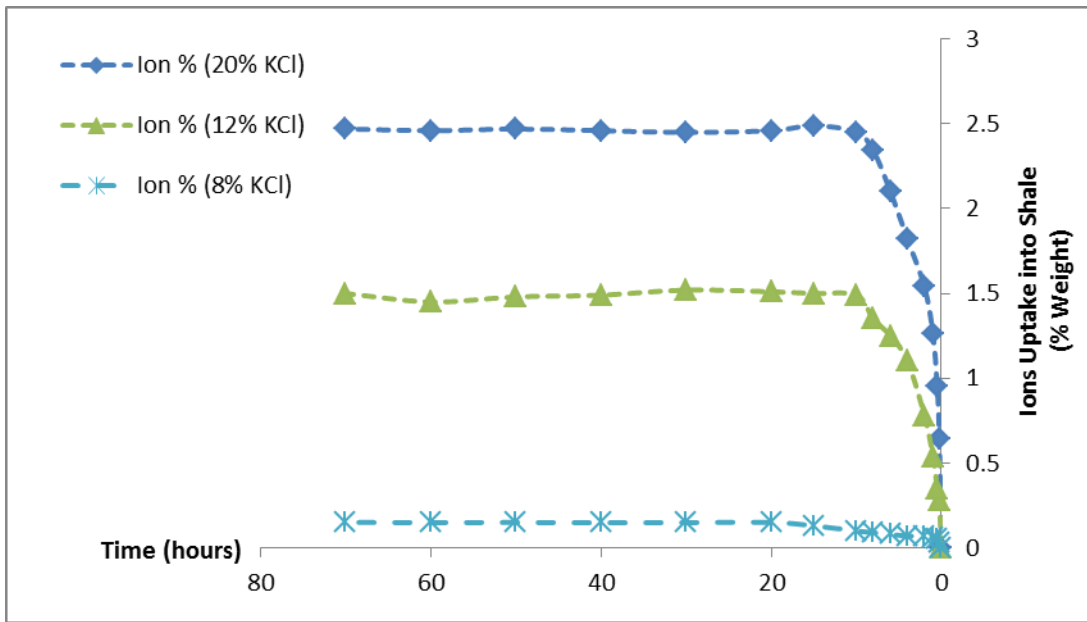


Figure 8: Time dependent ions uptake into shale when immersed in KCl solutions of 8%, 12% and 20% concentrations.

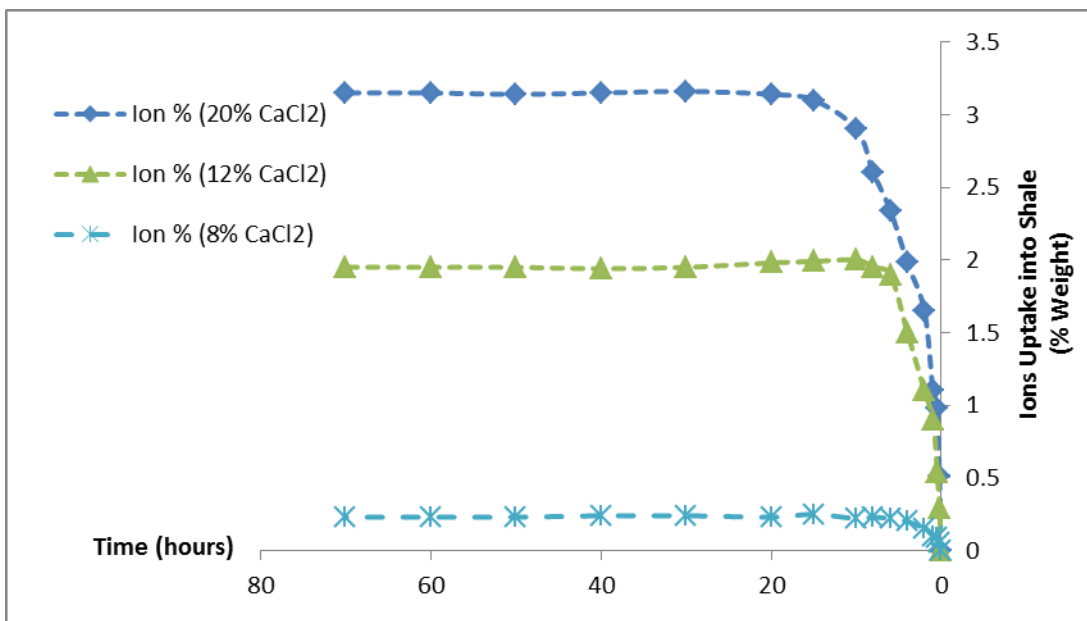


Figure 9: Time dependent ions uptake into shale when immersed in CaCl_2 solutions of 8%, 12% and 20% concentrations.

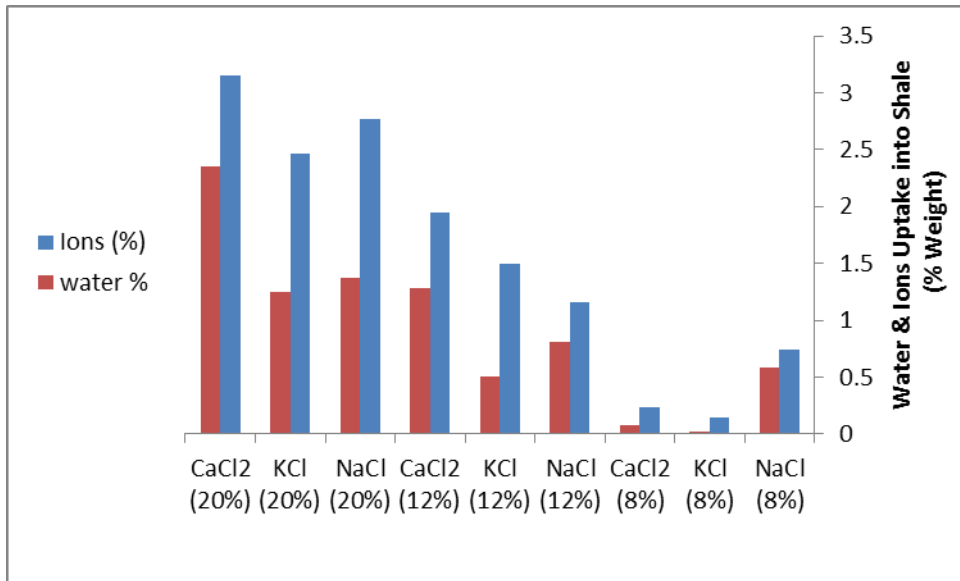


Figure 10: Equilibrium water and ions uptake when shale interacted with NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.

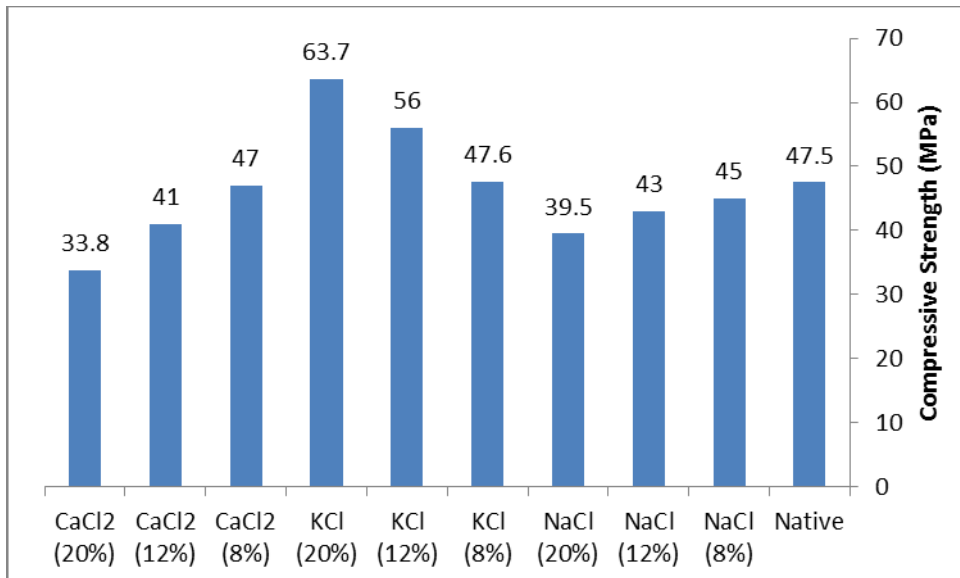


Figure 11: Native compressive strength of shale compared with the altered ones after immersion for 70 hours into NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.

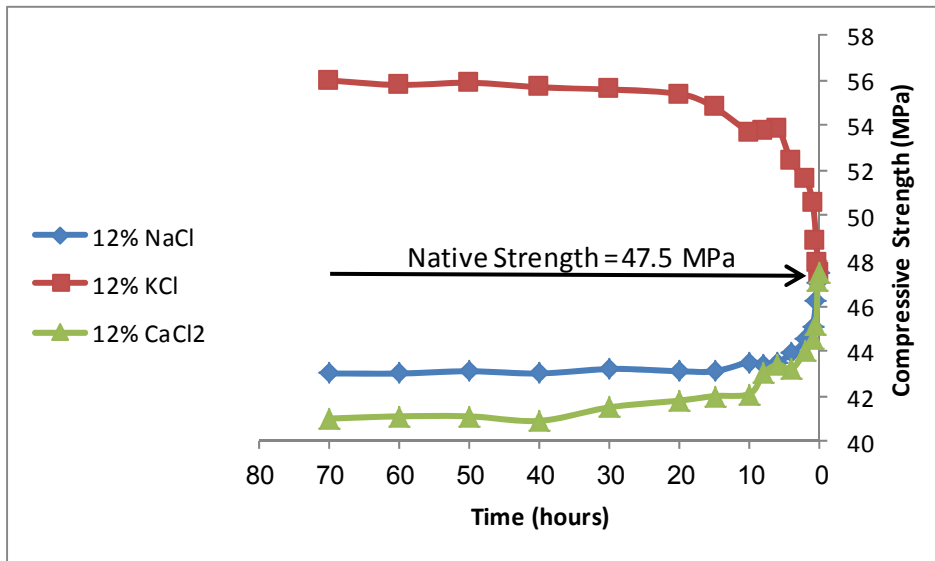


Figure 12: Compressive strength of shale after immersion in 12% NaCl, KCl and CaCl₂ solutions for 1/4, 1/2, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60 and 70 hours

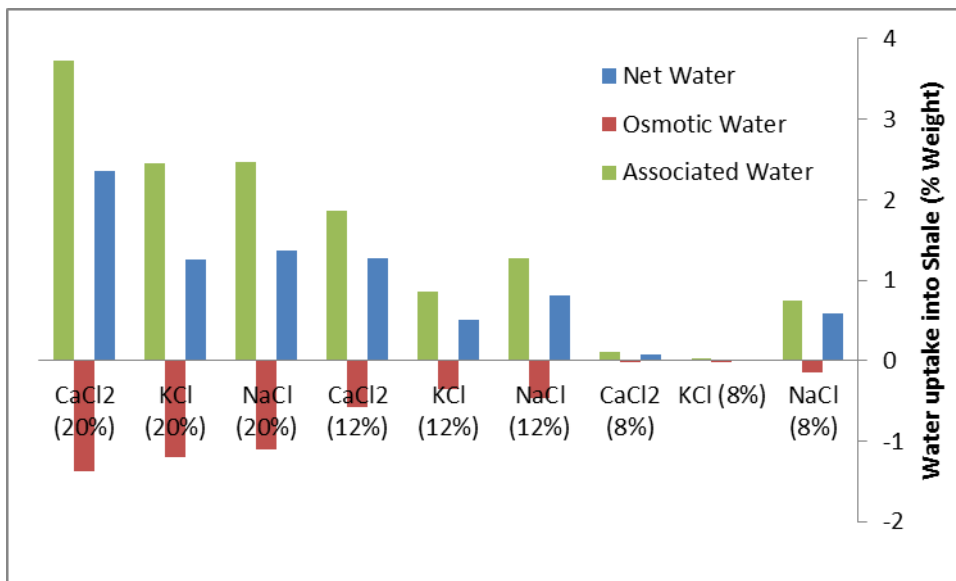


Figure 13: Osmotic water and associated water uptake into shale as it interacts with NaCl, KCl and CaCl₂ solutions of 8%, 12% and 20% concentrations.