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Determination of Moisture Adsorption Isotherm of Shale from Agbada Formation Using GAB Model

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Abstract

Shales are susceptible of different phenomena, including swelling, shrinkage and hydration (shale instability); hence are impacted by moisture content. Moisture adsorption isotherms of shales from Agbada Formation were determined at 27°C over a water activity (a_w) range of 0.30 to 0.96 using a Static gravimetric technique. Moisture adsorption isotherms of these two shale samples from well A and well B exhibited the sigmoid type II and V shapes respectively. The Guggenhein, Anderson, de-Boer (GAB) model was applied to fit the experimental data satisfactorily. A non-linear regression analysis method was determined to evaluate the parameters of GAB sorption equations. The criteria used to evaluate the goodness of fit to the model were Quadratic estimates, Central derivatives and Conjugate search of Microsoft Excel. The GAB model was used because it fit to the experimental adsorption data for a wide range of water activity (0.10 – 0.96) and the error square value calculated from Microsoft Excel was low. The estimated GAB parameters and constants were in good agreement with what the model dictates and with literature.

Keywords: Shale, adsorption isotherm, GAB model, water activity, monolayer moisture content.

Introduction

Shales are sedimentary rocks that have distinct laminated layers and moderate to high clay content. These distinct characteristics make them vulnerable to phenomena such as swelling, shrinking, hydration, strength reduction and ultimately failure[1]. Dzialowski mentions that over 90% of formations drilled worldwide are classified as shale formations. He further explains that about 75% of drilling operations' problems are related to shales. Drilling problems have often been approached on a trial and error basis. Chenevert points out that one of the most important factors that lead to shale failure is that shales contain a significant amount of clay[1]. Shales tend to hydrate when they come in contact with water. The transfer of water and ions from and to the shale alter the chemical and physical state of the shale [2]. Reactive clay minerals such as smectite have a higher number of active interlayers and increased isomorphic substitution than less reactive clays. Shales with higher reactive clays will therefore have more area for monolayer coverage by water molecules before multiple layers begin to form. Chenevert studied the effects of water adsorption on shale samples. He found out that all the shale samples tested were altered as a result of water adsorption, especially Montmorillonitic shales[1]. Adsorption isotherms provide information on a material's water content at certain equilibrium conditions. The behavior of a shale sample under these conditions can directly be related to its hydration and swelling potential. The isotherm can also give information on the expandable clay content of the shale. Chenevert studies shale preservation and testing techniques for borehole stability studies and found out that the controlled humidity desiccator technique, that is, the static gravimetric method, also known as the isopiestic method used to develop the shale adsorption isotherms is a convenient method for hydrating a sample without the risk of material loss; which is commonly associated with direct wetting in the presence of water [2]. Chenevert presented a shale control technique using the concept of "Balanced water activity" in solving drilling problems associated with shales[3]. He stated that the main reason for shale instability during drilling with water-based fluids is water adsorption and subsequent swelling of the wellbore. In other words, water adsorption could be prevented if the water activity of the drilling fluid is the same as the water activity of the shale pore fluid[4]. The moisture adsorption isotherm of this shale samples could be valuable information on solving the drilling problems encountered when tripping in or out of this shale formations since they give information about the humidity-water activity relation at a given temperature[5]. A number of models to describe moisture sorption isotherm have been proposed but the Guggenheim, Anderson and de Boer (GAB) model is considered to be the most versatile sorption model available in the literature[6].

The objectives of this study were, hence, to determine experimentally the equilibrium adsorption isotherm of this two Niger-Delta shale samples from Agbada formation and to model the adsorption characteristics using GAB equation.

Material and Methods

Shale samples from two wells in Agbada formation were used for this study. The first sample, Well A from Usan was cored at a depth of 2005 ft – 2006 ft. The second sample, Well B from

Obagi was cored at a depth of 3462.91 ft – 3464 ft and preserved. The Static gravimetric method, also known as the isopiestic method was used to develop the shale adsorption isotherms. In this method, weight measurements were taken of shale samples under varying relative humidity conditions at constant temperature and pressure. The relative humidity environments were created using saturated salt solutions in desiccators. The moisture adsorbed physically is the difference between the water content as expressed in initial weight and the water content at equilibrium known as the final weight of the sample. For this study, tests were carried out at ambient conditions. The adsorption isotherm curve is a plot of the amount of water adsorbed by the shale when placed in various desiccators versus the desiccator's water activity. To prepare these desiccators, various kinds of saturated salt solutions were used to provide and maintain different relative humidity environments. Six saturated salt solutions [KCl, $CaCl_2$, NaCl, K_2SO_4, KNO_3 and $Ca(NO_3)_2.4H_2O$] were used to provide constant water activity range from 0.3 to 0.96. These salt solutions were prepared with reagent grade salts and distilled water. The relative humidity data of the salt solutions were obtained from Greenspan. The shale samples were dried by placing them in an oven at 200°F for 24 hours, and then the weight of each dry shale sample was measured. Shale samples are placed in several desiccators with different relative humidity. A vacuum is pulled on the desiccators in order to remove the air and accelerate the test towards equilibrium. As the shale adsorbs water, a weight gain is observed. Each shale sample is weighted daily until there is no further weight gain observed. The shale sample is in equilibrium with the atmosphere inside the desiccators when the shale sample weight becomes constant. The final weight of each sample is taken. The amount of water absorbed by the shale sample is calculated as the difference between the final weight and the dried weight. The shale water activity is determined by matching the native moisture content of the shale with its respective water activity value from the adsorption isotherm curve.

Mineralogy: Mineralogy analysis indicates the relative quantities of compounds present in a rock. Clay and non-clay minerals are usually present in shales. The type of clay present is an indication of the degree of hydration experienced by the shale. It can be used to estimate the severity of wellbore instability issues that may arise. The mineralogy analysis for both Well A and Well B samples are presented in table-1. The Well A (Usan) cored at a depth of 2005 ft – 2006 ft, is made up of 20% quartz and 52% clay. It contains other non-clay minerals such as feldspar and carbonates in minimal amounts. The bulk of the clay content consists of illite and mixed clays with small amount of smectite. The existence of smectite indicates the probability of some swelling and dispersion in aqueous solution. Well B cored at a depth of 3462.91 ft – 3464 ft, is composed of 22% quartz and 51% clay. It also contains negligible amount non-clay minerals such as feldspar and carbonates. Zero smectite levels indicate low swelling tendencies.

Adsorption Isotherm Model: The experimental data obtained corresponding to the water activity, a_w and moisture content was adjusted to GAB (Anderson, 1946; de Boer, 1995; Guggenheim, 1995) equations in order to determine the best fit.

Data Requirements: At least 3 data points of a water activity, a_w / moisture measured at the same temperature, water activity, a_w may be entered as a value or a salt, moisture may be entered as a value (dry or wet basis) or as a set of pan / sample weights.

GAB Equation: This equation has a similar form of BET, but has an extra constant, K. BET is actually a special case of GAB, with K = 1. The GAB equation was used to model water adsorption of these shale samples as follows:

$$m = \frac{CKa_w M_o}{(1-Ka_w)(1-Ka_w+KCa_w)} \quad (1)$$

Where m is the amount of sorbate adsorbed by 1g of sorbant at sorbate activity a_w, M_o is the monolayer moisture content. C and K are GAB constants and are related to monolayer and multilayer properties[12]. The assumption of the GAB model over the BET (Brunauer, Emmett and Teller)[6] formulation stating that the sorption state of the sorbate molecules in the layers beyond the first is the same, but different to the pure liquid state, demands the introduction of the additional constant K[8]. C and K are related to the temperature effect being expressed by equation 2 and 3:

$$C = C_o \exp\left(\frac{\Delta h_c}{RT}\right) \quad (2)$$

$$K = K_o \exp\left(\frac{\Delta h_k}{RT}\right) \quad (3)$$

Where Δh_c is the specific bonding enthalpy of water monolayer (J/kg), Δh_k is the mean specific bonding enthalpy of the water multilayer (J/kg), R is the universal gas constant (J/kg/K), T is the absolute temperature (K), $\Delta h_{s,mono}$ is the specific sorption enthalpy of water monolayer (J/kg), Δh_{vap} is the specific vaporization enthalpy of water (J/kg), $\Delta h_{s,multi}$ is the mean specific sorption enthalpy of the water multilayer (J/kg), C_o and K_o are adjustable parameters accounting for temperature effect.

$$\Delta h_k = \Delta h_{s,multi} - \Delta h_{vap}$$

$$\Delta h_c = \Delta h_{s,mono} - \Delta h_{vap}$$

The GAB equation can be rearranged to polynomial expression:

$$\frac{a_w}{m} = \frac{K}{M_o}\left(\frac{1}{C-1}\right) a_w{}^2 + \left(\frac{C-2}{C*M_o}\right) a_w + \frac{1}{C*K*M_o} \quad (4)$$

The modified GAB equation replaces C with C/T, where T is the temperature in °C. This enables isotherms to be estimated for any temperature, based on data measured at one temperature. However, the accuracy of this is approximate only, as it assumes all materials are affected by temperature identically.

Model Validation: In this research, GAB equation was used to model the moisture adsorption isotherms for these shale samples. The experimental data were fitted to the model using a

non-linear regression. All calculations were performed using Microsoft Office Excel 2007 solver and analysis toolpac. The coefficient of determination, R^2, was calculated to give a measure of the proportion of variability attributed to the model. In addition to R^2, the criteria used to evaluate the fit of GAB model were quadratic estimates, central derivative, conjugate search and error square (E^2) method of the solverpac. It is calculated as follow:

$$E^2 = \sum_{i=1}^{N} \left(m_{exp} - m_{pre}\right)^2 \quad (5)$$

Where m_{exp} is the experimental value, m_{pre} is the predicted value, and N is the number of experimental data which is six (6). The lower the value of the error square, E^2 during the non-linear regression; the better the GAB model curve fitting.

Results and Discussion

Experimental characteristic of moisture adsorption isotherm: The experimental moisture adsorption data obtained corresponding to the water activity values of the salt solutions which ranges from 0.30 to 0.96 are presented in figure 1 and 2.

The adsorption isotherm for well A sample exhibited a shape similar to the sigmoid Type II as shown in figure 1. Type II sigmoid do not exhibit saturation limit. This type of isotherm indicates an indefinite multi-layer formation after completion of the monolayer and is found in adsorbents with a wide distribution of pore size. The intermediate flat region in the isotherm corresponds to monolayer formation, following which adsorption occurs in successive layers. Several authors including Chenevert and Osisanya have reported isotherms with similar Type II shape[9,10].

The adsorption isotherm for Well B sample exhibited a shape similar to the sigmoid Type V as shown in figure 3. Type V adsorption isotherm shows phenomenon of capillary condensation of gas. The saturation level reaches at pressure below the saturation vapour pressure; this can be explained on the basis of possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure of the gas. It can be deduce from figure 2 and 3 that Well A has higher adsorptive potential than Well B and a conclusion that more adsorption took place in Well A than in Well B can be made; therefore more expandable clays are present.

Modeling of Adsorption Isotherm: The Guggenheim, Anderson and DeBoer (GAB) model being the most commonly accepted model was used to fit the isotherms of Shale A and Shale B. The flexibility of the GAB isotherm has been attested through various literatures[4]. That is, it fits a wide variety of materials. Other shale adsorption isotherms developed by Osisanya for Mancos, Wellington and Pierre shales were also fitted. This was done to investigate any possible trend with shale type and GAB model parameters. The most important parameter in the model is the monolayer moisture content M_o. Reactive clay minerals such as smectite have a higher number of active interlayers and increased isomorphic substitution than less reactive clays. Shales with higher reactive clays will therefore have more area for monolayer coverage by water molecules before multiple layers begin to form.

The experimental adsorption isotherm of Well A and Well B samples were fitted to the GAB model (equation 1). The most important parameter in the model is the monolayer moisture content M_o. Reactive clay minerals such as smectite have a higher number of active interlayers and increased isomorphic substitution than less reactive clays. Shales with higher reactive clays will therefore have more area for monolayer coverage by water molecules before multiple layers begin to form. Thus, the M_o of reactive shale should be higher than that of less reactive shale. In our study, Well A and B have M_o values of 6.728 g/g (dry basis) and 2.999 g/g (dry basis). Thus, Well A is more reactive than Well B. Microsoft Office Excel solver was used to fit the curves to the model equation. It was programmed to uses a nonlinear regression-least squares method for curve fittings. The square of the correlation coefficient (R^2) for the fit should range between 0.9 and 1.00 to show a good fit for the model. The coefficients of determination (R^2) for fitting the GAB model was suitable and afforded the best fits to the experimental data because this model gave the best regression coefficient as shown in figure 3 and 4. Experimental data was inputted into the work sheet along with the model equation and the analysis of the nonlinear regression-least squares method for curve fitting carried out (tables 2-5). The square of the correlation coefficient (R^2) for the fit ranged between 0.95 and 0.98 showing a good fit by the model. Well B fitted more GAB model than Well A shale sample. Another application of adsorption isotherm modeling is the determination of properties at temperatures other than the ambient. Most shale isotherms have been developed under ambient conditions. This is however not representative of in-situ conditions; generally, increased temperature will reduce adsorption to some degree[10]. These isotherms can be obtained by placing samples in a constant environment chamber at various temperatures and relative humidities. The temperature dependent parameters, C and K can be evaluated based on their variations with temperature. If a trend is established, predictions can be made for downhole temperatures or desired range of temperatures. Table 2 estimated values of GAB model parameters and regression coefficient, R^2. It has also been recognized that the fit become better as the determination coefficient approaches 1 and this is evident for the GAB model. Therefore, the GAB equation is optimal to fit the moisture adsorption isotherms of the shale samples. The parameter *K is* in keeping with sorption on multilayer above the first layer and the heat of vaporization of water. Thermodynamically, *K'*s needs to be smaller than 1.000. The value of *K* provides a measure of the interactions between the molecules in the multilayer with the adsorbent, and it tends to fall between the energy value of the molecules in the monolayer and that of liquid water. The fitting

of the isotherms with this model was high ($R > 0.90$) and in all cases the results obtained in the present work for the adjustment of GAB model to the different shale samples are in accordance with the limit values for constants C and K suggested by Lewicki, based on the mathematical analysis of the model ($0.24 < K < 1$)[11].

The Monolayer Moisture Content: Modeling of adsorption data of the shale samples using GAB equation allows the determination of monolayer moisture content values, M_o, which are measure of adsorption possibility of the shale samples. The value of the monolayer moisture content indicates the amount of water that is strongly adsorbed to specific site at the shale sample surface, and this is a value that must be reached in order to assure shale stability. The monolayer moisture content calculated from the GAB model (table 2) were 6.7284 g/g (dry basis) for Well A and 2.9987 g/g (dry basis) for Well B. The low value of M_o reflects a reduction in the number of active sites due to chemical and physical changes. This can also be noticed in the experimental data isotherm where Well B exhibited a shape similar to the sigmoid Type V. Type V adsorption isotherm shows phenomenon of capillary condensation of gas.

Table-1
Shale Sample Mineralogy

Group Name : Well A
Data Name : SAMPLE-A
File Name : SAMPLE-A.PSE
Sample Name : AGBADA SHALE
Comment : DARK-SHALE

<Entry Card>

No.	Card	Chemical Formula / Chemical Name (Mineral Name)	S	L	Dx	d	WT%	I	S.G.	R
1	29-1488	Al2Si2O5(OH)4	0.142	0.714	(10/21)	0.590	-----	0.422		
		Aluminum Silicate Hydroxide (Kaolinite-1\			-----				--------	
2	26-1372	NaCa2Fe4Al3Si6Al2O22(OH)2	0.164	0.667	(10/15)	0.605	-----	0.403		
		Sodium Calcium Iron Aluminum Silicate Hydr			-----				--------	
3	36-0383	(Mg,Fe)CO3	0.273	0.625	(5/14)	0.632	-----	0.395		
		Iron Magnesium Carbonate (Magnesite, ferr			-----				--------	
4	52-1044	(Mg,Al)6(Si,Al)4O10(OH)8	0.139	0.625	(5/12)	0.597	-----	0.373		
		Magnesium Aluminum Silicate Hydroxide (Ch			-----				--------	
5	10-0446	Al2Si2O5(OH)4	0.170	0.564	(21/39)	0.592	-----	0.336		
		Aluminum Silicate Hydroxide (Dickite-2\IT			-----				--------	
6	13-0595	Mg4Si6O15(OH)2.6H2O	0.301	0.583	(21/39)	0.574	-----	0.335		
		Magnesium Silicate Hydroxide Hydrate (Sep			-----				--------	
7	29-1487	Al2Si2O5(OH)4	0.099	0.667	(4/ 7)	0.488	-----	0.325		
		Aluminum Silicate Hydroxide (Halloysite-7			-----				--------	
8	46-1045	SiO2	0.625	0.385	(5/42)	0.811	-----	0.312		
		Silicon Oxide (Quartz, syn)			-----				--------	
9	9-0432	Ca5(PO4)3(OH)	0.484	0.514	(18/42)	0.563	-----	0.290		
		Calcium Phosphate Hydroxide (Hydroxylapat			-----				--------	
10	26-0911	(K,H3O)Al2Si3AlO10(OH)2	0.504	0.471	(8/18)	0.607	-----	0.286		
		Potassium Aluminum Silicate Hydroxide (Il			-----				--------	
11	36-0426	CaMg(CO3)2	0.627	0.412	(7/41)	0.640	-----	0.263		
		Calcium Magnesium Carbonate (Dolomite)			-----				--------	
12	6-0263	KAl2(Si3Al)O10(OH,F)2	0.461	0.405	(17/42)	0.643	-----	0.260		
		Potassium Aluminum Silicate Hydroxide (Mu			-----				--------	
13	10-0495	KMg3(Si3Al)O10(OH)2	0.741	0.542	(13/26)	0.466	-----	0.253		
		Potassium Magnesium Aluminum Silicate Hydr			-----				--------	
14	31-0966	KAlSi3O8	0.333	0.405	(17/42)	0.614	-----	0.248		
		Potassium Aluminum Silicate (Orthoclase)			-----				--------	

Data Name : WELL B
File Name : SAMPLE-B.PKR
Sample Name : AGBADA SHALE
Comment : DARKISH-SHALE

<Entry Card>

No.	Card	Chemical Formula / Chemical Name (Mineral Name)	S	L	Dx	d	WT%	I	S.G.	R
1	27-1402	Si	0.270	1.000	(3/11)	0.569	0.728	0.414		
		Silicon (Silicon, syn)			-----				--------	
2	29-1489	Al2Si2O5(OH)4.2H2O	0.564	1.000	(5/ 7)	0.619	0.540	0.334		
		Aluminum Silicate Hydroxide Hydrate (Hall			-----				--------	
3	26-0911	(K,H3O)Al2Si3AlO10(OH)2	0.567	0.882	(15/18)	0.757	0.481	0.321		
		Potassium Aluminum Silicate Hydroxide (Il			-----				--------	
4	49-1057	K-Mg-Al-SiO2-H2O	0.629	0.909	(10/22)	0.690	0.498	0.313		
		Potassium Iron Magnesium Aluminum Silicate			-----				--------	
5	10-0357	(Na,K)(Si3Al)O8	0.632	0.941	(16/17)	0.716	0.460	0.310		
		Potassium Sodium Aluminum Silicate (Sanid			-----				--------	
6	13-0595	Mg4Si6O15(OH)2.6H2O	0.564	0.917	(33/39)	0.709	0.451	0.293		
		Magnesium Silicate Hydroxide Hydrate (Sep			-----				--------	
7	13-0135	Ca0.2(Al,Mg)2Si4O10(OH)2.4H2O	0.289	0.923	(12/17)	0.596	0.530	0.292		
		Calcium Magnesium Aluminum Silicate Hydrox			-----				--------	
8	29-1488	Al2Si2O5(OH)4	0.326	1.000	(14/21)	0.619	0.470	0.291		
		Aluminum Silicate Hydroxide (Kaolinite-1\			-----				--------	
9	5-0586	CaCO3	0.398	0.833	(10/42)	0.743	0.402	0.249		
		Calcium Carbonate (Calcite, syn)			-----				--------	
10	6-0263	KAl2(Si3Al)O10(OH,F)2	0.583	0.833	(35/42)	0.693	0.430	0.248		
		Potassium Aluminum Silicate Hydroxide (Mu			-----				--------	
11	10-0495	KMg3(Si3Al)O10(OH)2	0.603	0.833	(20/26)	0.719	0.386	0.231		
		Potassium Magnesium Aluminum Silicate Hydr			-----				--------	
12	19-1184	NaAlSi3O8	0.402	0.667	(28/42)	0.773	0.423	0.218		
		Sodium Aluminum Silicate (Albite, ordered			-----				--------	
13	9-0432	Ca5(PO4)3(OH)	0.500	0.886	(31/42)	0.619	0.393	0.215		
		Calcium Phosphate Hydroxide (Hydroxylapat			-----				--------	
14	24-1035	BaSO4	0.341	0.829	(34/42)	0.731	0.355	0.215		
		Barium Sulfate (Barite, syn)			-----				--------	

Table-2
Coefficients for GAB Isotherms for Shale A and Shale B

Model	Estimated Parameter	Well A	Well B
GAB	M_o	6.7284g/g (dry basis)	2.9987g/g (dry basis)
	K	0.7486	0.6410
	C	19.9324	18.7147
	R^2	0.95	0.98
	Standard Error	1.6890	0.3056

Table-3
Adsorption Isotherm Modeling for Shale A and Shale B

Well A			**Well B**		
m_o =	6.7284		m_o =	2.9987	
C =	19.9324		C =	18.7147	
K =	0.7486		K =	0.6410	
Aqueous Activity	Experimental Data	Model Data	Aqueous Activity	Experimental Data	Model Data
0.3	10.44	7.3962	0.3	2.55	3.0322
0.51	11.23	10.0663	0.51	5.09	4.0136
0.76	13.37	15.0383	0.76	5.17	5.5359
0.86	16.36	18.3807	0.86	6.38	6.4040
0.94	19.51	22.2396	0.94	6.93	7.2879
0.96	27.26	23.4574	0.96	7.8	7.5443

Table-4
Well A Regression Statistics Summary Output

Regression Statistics					
Multiple R	0.972494562				
R Square	0.945745674				
Adjusted R Square	0.932182092				
Standard Error	1.688980572				
Observations	6				
ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	198.9066425	198.9066425	69.72683923	0.001124419
Residual	4	11.41062149	2.852655371		
Total	5	210.3172639			

Table-5
Well B Regression Statistics Summary Output

Regression Statistics					
Multiple R	0.98853539				
R Square	0.97720222				
Adjusted R Square	0.97150277				
Standard Error	0.30556391				
Observations	6				
ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	16.00869531	16.00869531	171.45566	0.000196402
Residual	4	0.373477209	0.093369302		
Total	5	16.38217252			

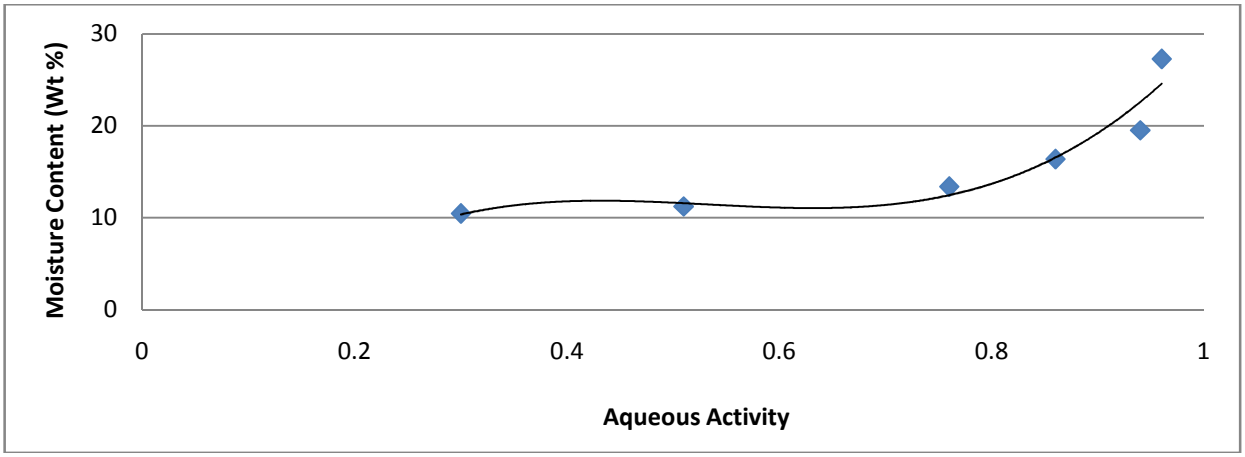

Figure-1
Adsorption Isotherm for Well A

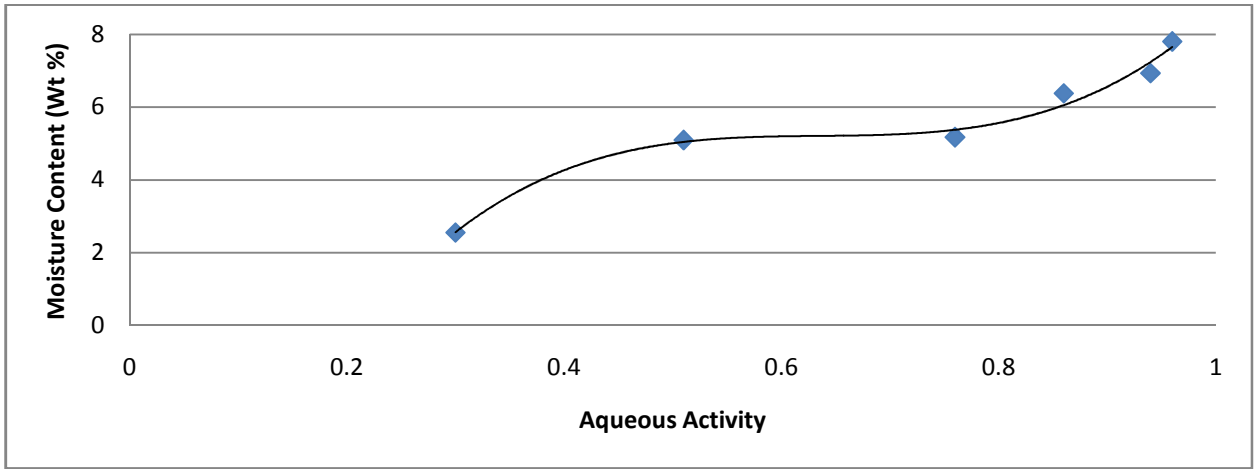

Figure-2
Adsorption Isotherm for Well B

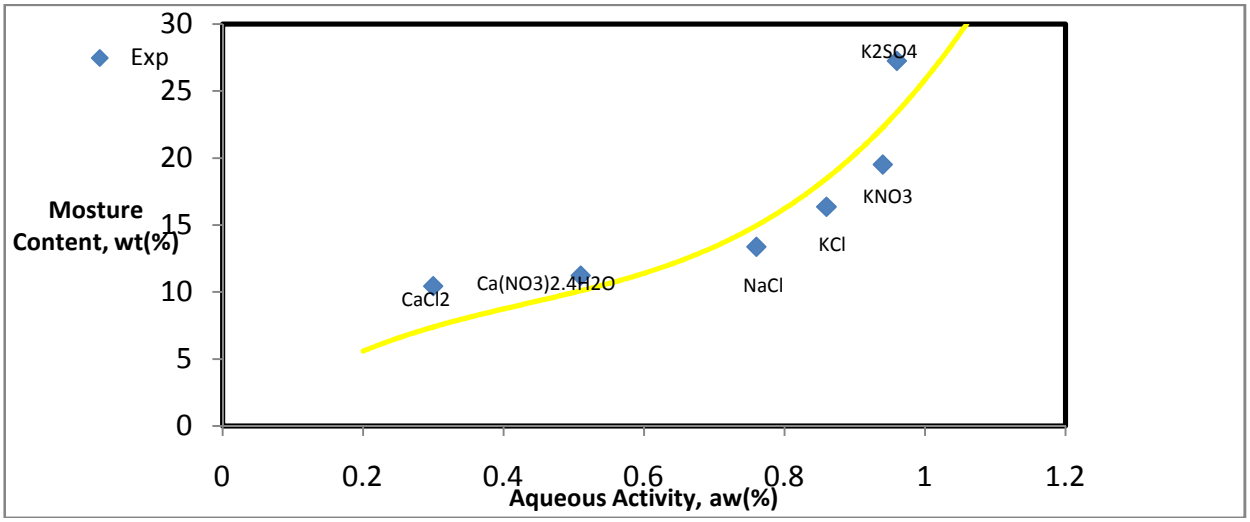

Figure-3
Adsorption Isotherm of Well A fitted to the GAB model

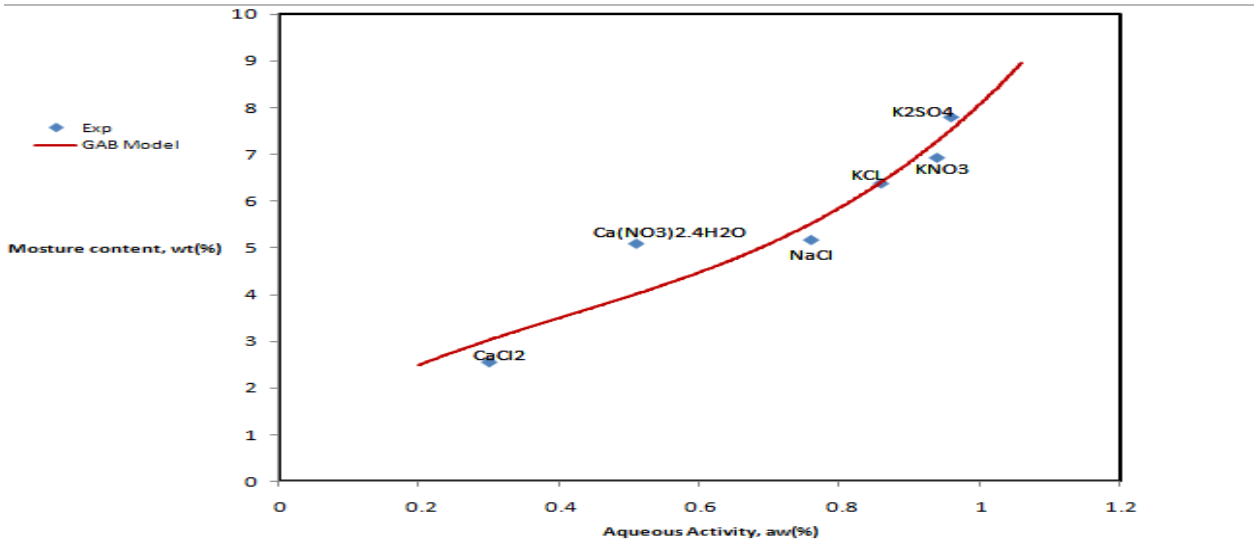

Figure-4
Adsorption Isotherm of Well B fitted to the GAB model

Conclusion

The adsorption isotherms of Well A and Well B exhibit the sigmoid Type II and V behavior respectively, which is a characteristic of a multilayer. Generally, increased temperature will reduce adsorption to some degree. Most shale adsorption isotherms have been developed under ambient conditions; hence, activity values claimed to correctly balance the aqueous phase of the drilling fluid may in fact be incorrect. The experimental data was modeled using GAB equation and estimated parameters and the correlation coefficients (R^2) indicate good accuracy with literature. Thus, it was demonstrated in this study that the GAB moisture adsorption isotherm model can be successfully applied to moisture adsorption by shale samples in the water activity, a_w range between 0.30 and 0.96.

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