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The Application of Organic Shale Inhibitor as A High Performance Water Base Mud (HPWBM) to limit hydration of shale/clays: A Laboratory Study

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Abstract

Adding additives such as inorganic shale inhibitor (NaCl, CaCl2, KCl and NaSiO3) and polyamine (MAL-SHALE HIB/MSH) reduce hydration in clay. Inorganic shale inhibitor only effective as long as water-based drilling fluids that contain these salts are in contact with the clays (temporary inhibition), the salt-containing fluid is displaced by fresh water, the clay will swell because hydration, and destabilizing the drilled formation. Inorganic shale is effective in shale formation where smectite is predominant clay mineral. Inorganic shale inhibitor is ineffective when clay contain a few cation or no exchangeable cation. A large quantity of salts such as brine (high salinity) or other electrolytes have been used to increase the ionic concentration of the water phase in order to retard osmotic hydration. Inorganic shale inhibitor adversely affect the chemical biological ecosystems above limits. This paper study about polyamine shale inhibitor/MSH to limit hydration shale/clay and to mitigate environment issue with salts. Polyamine/MSH is organic shale inhibitor that is permanent shale inhibitor because due high cationic exchange capacity and smaller hydrated ion radius compare to inorganic shale inhibitor. Single cation exchange mechanism that is shale matrix/surface reacting. Cationic source is cationic amine compounds. MSH is a persistent proprietary of mixture polyamine. Shale inhibitor material that is effective in preventing swelling of shale/clays. MSH properties are appearance clear yellowish to amber liquid, specific gravity around 1.12-1.17, pH: 7-9, and soluble in water that acts as a clay hydration suppressant, by intercalating and reducing the space between the clay platelets so that water molecules will not penetrate and cause shale swelling.

Keywords: High Performance Water Base Mud, Organic Shale Inhibitor, Swelling, Limit Hydration, Shale Stability.

Introduction

Obviously the drilling fluids industry has been trying to develop water based mud systems that achieve the performance of Oil Based Muds in terms of inhibition, lubricity etc. To this end, the major mud companies and chemical companies developed systems for High Performance Water Base Mud (HPWBM) to address the following issues, such as Control Clay Inhibition, Shale Stability, Improve Lubricity, Enhanced Rate of Penetration/ROP, and Anti Accretion. The presence of clay minerals which are present when drilling is a challenge for a mud engineer to penetrate clay without causing swelling that causes problems such as bit bailing. Clay has a very complicated property. Clay structure is non-stoichiometric ($2((Al_{1.67}Mg_{0.33})(Si_{3.5}Al_{0.5})O_{10}(OH)_2)$ with alumina and silica content of 70 % and fine crystals clays are less than 5 microns. Clay has a large surface area with 3 clay layers with a minimum of 1 aluminum oxide sheet surrounded by 2 silicon oxide sheets. Clay is a water strongly absorb because clay absorbed water is 10-20 nm. Bentonite clay thickness due to absorbed water is less than 1 nm. Hydration of clay is develop because of the ion exchange with water based mud. Some of chemical stabilization had tested on Oxford clay to test the hydration of oxford clay[(x)], shown at Fig.1. The phenomenon at ion exchange for KCL polymer system and Polyamine shown at Fig.1. Clay mineralogy factor effecting ion exchange are Replacement Power, type of clay, charge differential, cation concentration, and size/type cation.

Clay Mineralogy Ion Replacement Hierarchy

The ease of cation replacement depends on the: 1) Valence (primarily), higher valance can replace cations of lower valance, 2) Ion Size: cations with larger non-hydrated radii or smaller hydrated radii have greater replacement power, and 3) Relative amount: high concentration of Na^+ can displace Al^{3+}. Table-1 shown the clay mineralogy ion replacement hierarchy. According to point 1) and 2), the general order of replacement is $Li^+ < Na^+ < K^+ < NH_4^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Cu^{2+} < Al^{3+} < Fe^{3+}$.
Clay-rich rock samples, which exhibit strong interaction with freshwater and non-inhibited fluids, are usually selected to evaluate the inhibition performance of chemical additives. Table-2 shown the mineral composition by x-ray diffraction of these common clays and typical cation exchange capacity (CEC) of each clay, Gomez (2013).

Data and Method

A series of tests were conducted to obtain MAL-Shale HIB/MSH performance to limit hydration to control swelling of shale/clays. The test are polyamine performance test, MBT and Swelling test (Linier Swell Meter). MSH achieves is prevent swelling by inhibited and stabilized shale/clay create firmed and define cuttings, MSH deliver cuttings easily handling by rig shakers and solid control equipment. MSH deliver high Bottom Hole Hydraulic Horse Power, fast rate of penetration and Reduce Non-Productive Time because MSH are suppress MBT, reduce plastic viscosity/PV and contribute flat gel strength/GS to the mud system. MSH advantage are effective prevent swelling by inhibited and stabilized clay/shale, compatible to all inhibitive Water Based Mud chemicals, reduce Bottom Hole Assembly/BHA and bit bailing (anti accretion), suppress MBT, reduce PV, contribute flat GS, firmed and define cutting in shakers/surface, and un-weighted to base fluids (muds or completion).
MSH is a persistent proprietary of mixture poly-amine, shale inhibitor material that is effective in preventing swelling shales and clays. The properties of MSH are Clear yellowish to amber liquid, Specific Gravity 1.12-1.17, pH 7.0-9.0 and soluble in water. Application MSH up to 3.5% to the mud system, the density remains water density.

MAL-Shale HIB Lab Test Data

There are 4 scenario to analysis the polyamine performance/properties. Tabel-3 shown the polyamine performance test. Table-4 shown the result of MBT Test of Polyamine at 300 ^oF, 350 ^oF and 390 ^oF for 16 hours. The formulation to MBT test is Original fresh water, bentonite contaminant and MSH.

Result and Discussion

To comprehend the swelling process, the mud is tested by Linier Swell Test/LSM. There are 3 variation LSM test to analysis the performance of the mud test.
First, LSM test is done by 7% KCL and various of 2% polyamine in NT Bentonite core sample. Fig.3 shown the LSM test for 7% KCL and various of 2% polyamine. Fig 3 shown comparison of conducting LSM in NT Bentonite core for 7% KCl as base line with various 2% Polyamine in the market, MSH has given optimum (minimal) swelling index.
Second, LSM test is done with MSH in clay cutting sample (TPN-005 and TPN 006). Fig.4 shown the result of the LSM test. Fig 4 shown optimization LCM in TPN core samples for synergetic 7% KCl / 7% NaCl with various percentage MSH Polyamine, 7% KCl and 2% MSH Polyamine has given optimum (minimal) swelling index.
Third, LSM test is done with MSH in clay cutting sample from PMB-14 INF. Table-5 shown the concentration of mud for LSM test and Fig.5 shown the result of LSM test. Fig 5 shown comparison of conducting LSM in PMB core sample + mud formulation sample with various Polyamine sample. 2% MSH Polyamine has given optimum (minimal) swelling index.

Conclusions

Clay/shale structure is non-stoichiometric and water strongly absorb (highly swelling) due to meet water as Na+ ion in clay ease of cation replacement by H^+ in H_2O.
To prevent highly swelling in clay/shale formation requires optimum / collaboration inorganic and organic shale inhibitors base on mineralogy of clay and laboratory swelling test

for achieving optimum percentage of combination inorganic and organic shale inhibitors.
Simulated LSM core samples in combination and collaboration inorganic and organic shale inhibitors will be varying 4%-7% by weight KCl/NaCl and 2%-3% by volume Polyamine to give minimal swelling.
MSH/Polyamine advantages are effective prevent swelling by inhibited and stabilized clay/shale, compatible to all inhibitive Water Based Mud chemicals, reduce Bottom Hole Assembly/BHA and bit bailing (anti-accretion), suppress MBT, reduce PV, contribute flat GS, firmed and define cutting in shakers/surface, and un-weighted to base fluids (muds or completion).

References

[1] Gomes, S., Patel, Arvind., 2013, Shale Inhibition: What Works?, SPE 164108.
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Acknowledgements

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Table-1: Clay Mineralogy Ion Replacement

Cation	Ion Radius	Non Hydrated Radius	Hydrated Radius
	Å	Å	Å
Li^+	0.76	0.68	3.8
Na^+	1.02	0.95	3.6
K^+	1.38	1.33	3.3
NH_4^+	-	1.82	2.5
Cs^+	1.67	1.69	3.3
Be^{2+}	0.35	0.31	4.6
Mg^{2+}	0.72	0.65	4.3
Ca^{2+}	0.99	0.99	4.2
Al^{3+}	0.54	0.50	4.8

Table-2: XRD/CEC of clay-rich rock sample (Gomez, 2013)

	Oxford Clay	Arne Clay	Norway Shale	Wyoming Bentonite
Smectite* (%)	28	16	20	41
Kaolinite (%)	15	25	35	5
Illite (%)	15	25	10	-
Dolomite (%)	1	1	-	-
Calcite (%)	3	1	1	10
Halite (%)	-	-	3	-
Hematite (%)	-	-	1	-
Pyrite (%)	2	-	-	-
Siderite (%)	-	1	-	-
Feldspar (%)	1	1	-	9
Quartz (%)	35	30	30	35
CEC, meq/100g	23	13	19	33

*Includes Smectite/Illite mixed layers

Table-3: Polyamine Performance Test

Poly-Amine Performance Test *Formulation : Original FW/SW + MAL-SHALE HIB + NT-BENTONITE Contaminant*					
		Original Mud		MSH + NT Bentonite Contaminant	
Product Name		I	II	III	IV
Distilled/Fresh Water		306 cc	325 cc	306 cc	325 cc
NaCl (to simulate SW)		13 gr		13 gr	
MAL-SHALE HIB				7.0 cc (2%)	7.0 cc (2%)
NT-Bentonite		70 gr	45 gr	70 gr	45 gr
Properties:					
	Specs	Results	Results	Results	Results
YP, lb/100 sq.ft	≤ 3	45	253	0	1
MBT, ppb	≤ 7.5	25	30	5.0	5.0

Table-4: MBT Test Result of Polyamine

	MBT Result			
Sample	Initial	300 °F	350 °F	390 °F
2% MSH + 45 ppb NT Bentonite	5.0	5.0	5.0	25
2% MSH + 45 ppb NT Bentonite	N/A	2.5	2.5	N/A

Table-5. Concentration product used at LSM test with cutting sample PMB-14 INF

No	Product	Concentration (ppb, %)
1	Drill Water	322.3
2	Soda Ash	0.5
3	XCD Polymer	1.5
4	Polyamine (MSH) and others	2.0
5	PAC-L	2.0
6	MAL-ENCAP	2.0
7	MAL-ENHANCEX	2.5
8	BARITE	85.0

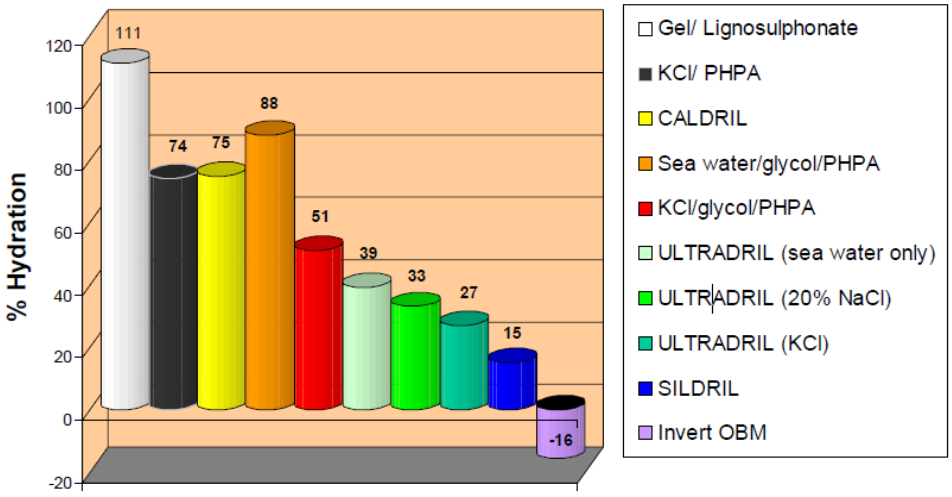

Figure 1: Hydration – Chemical stabilization of Oxford clay (Tertiary-Jurassic Era) (Ultradrill,2002)

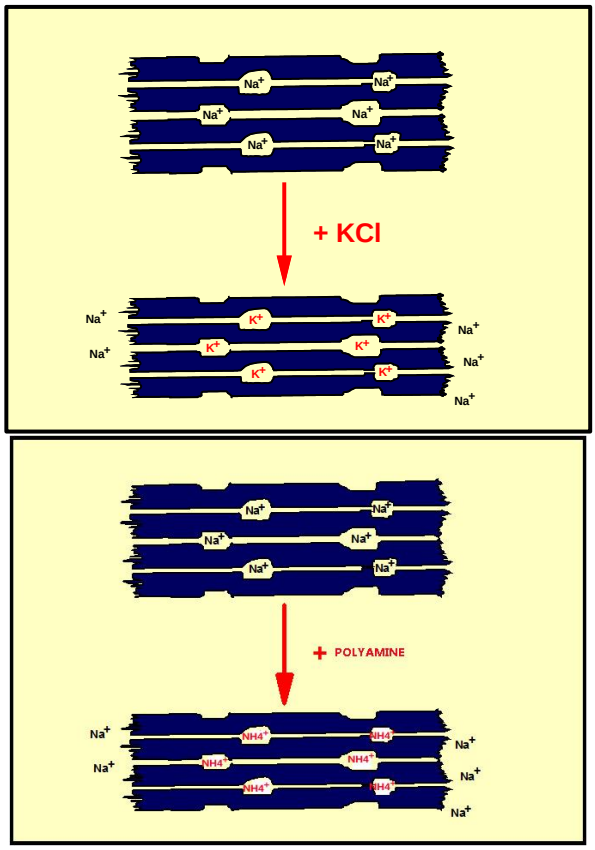

Figure 2: The Ion Exchange phenomenon to limit hydration using KCL Polymer system and Polyamine system

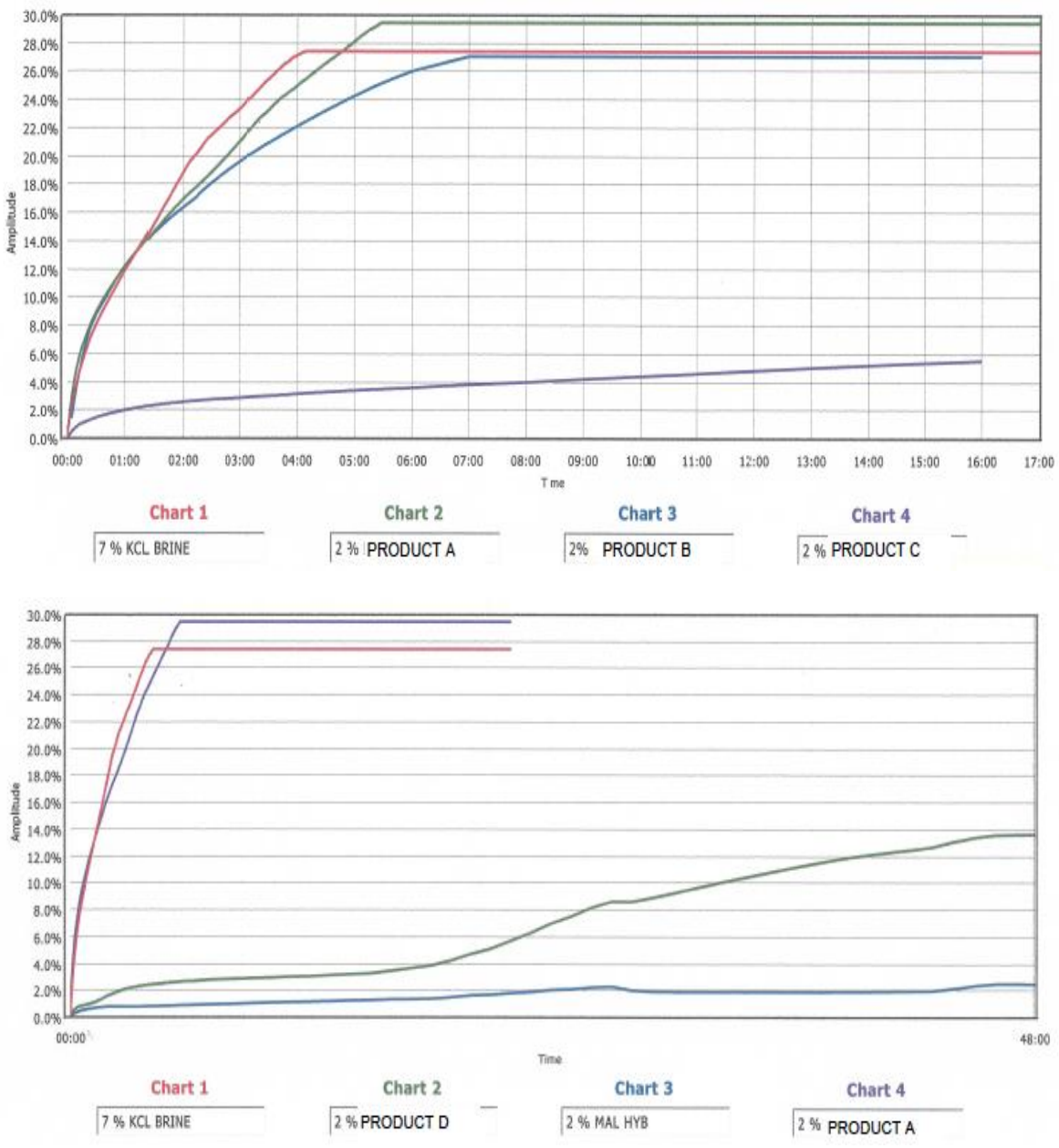

Figure 3: Linear Swell Meter for 7% KCl vs various 2% Polyamine in NT Bentonite core sample

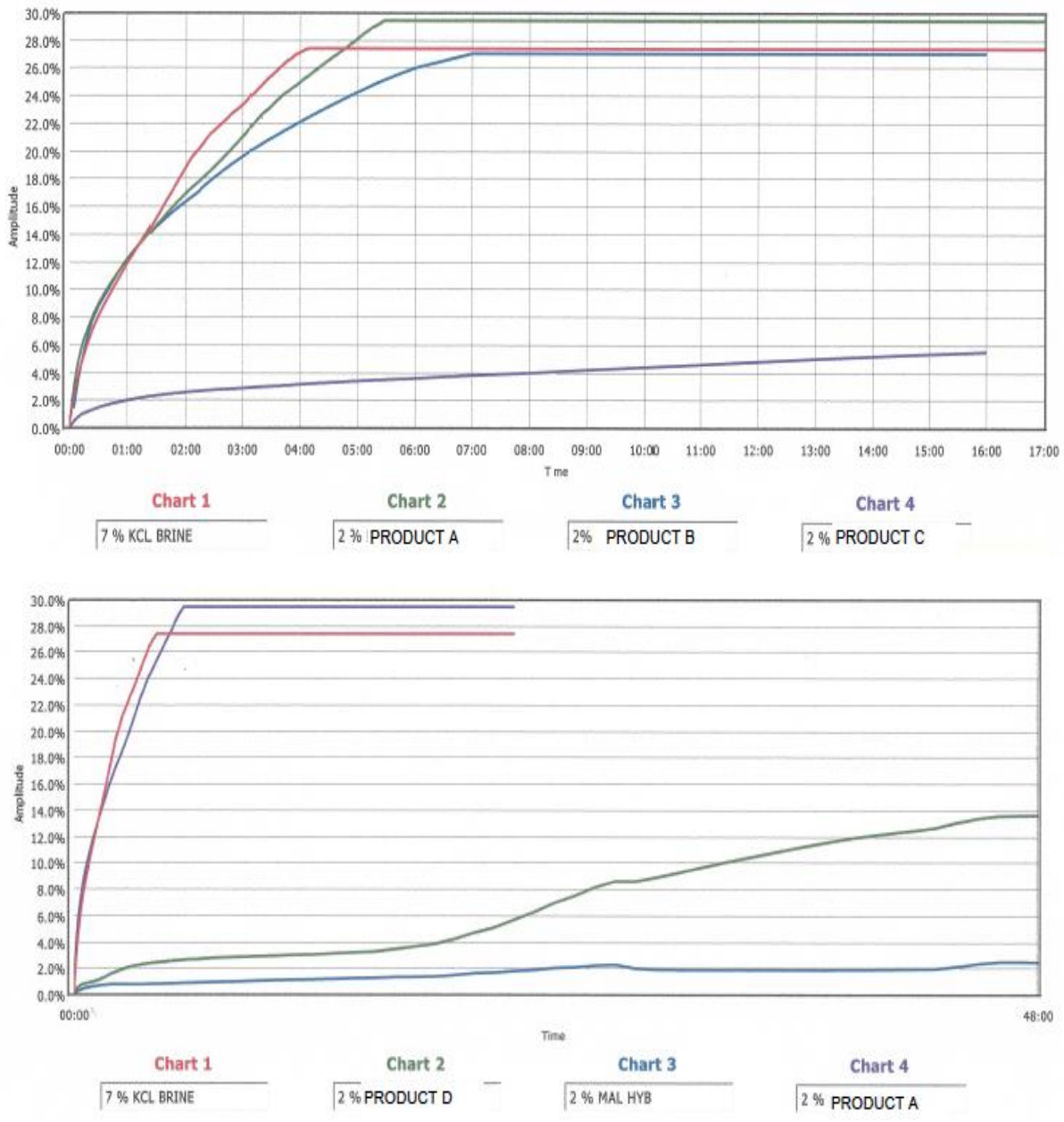

Figure 4: Linear Swell Meter with clay cutting sample (TPN-005 and TPN-006)

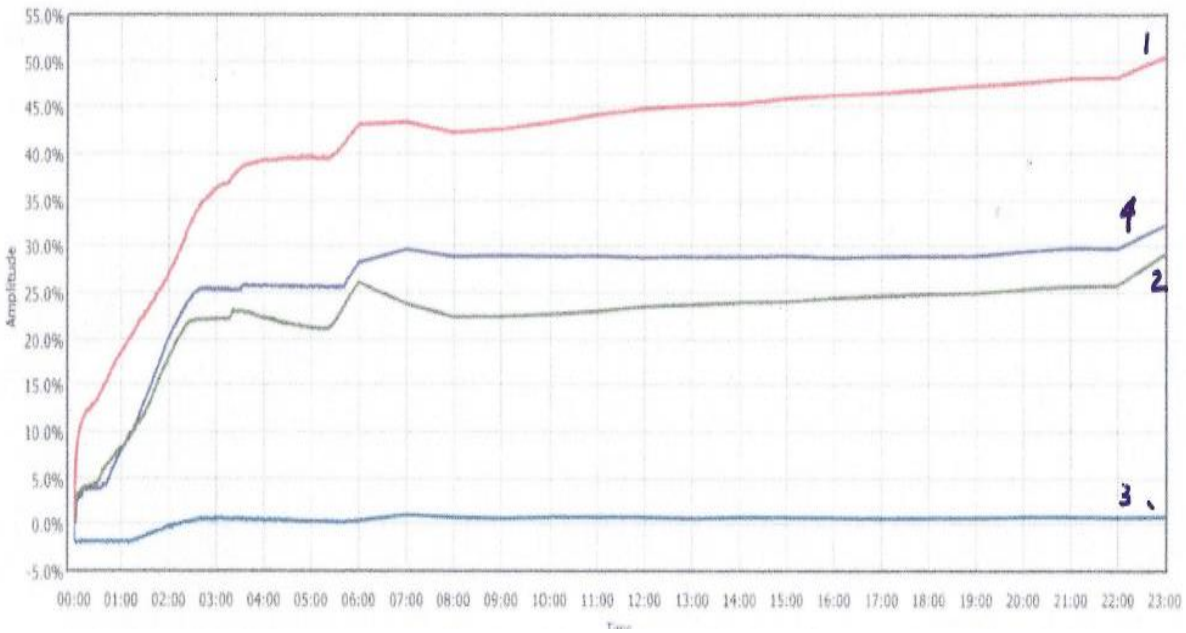

Figure 5: Linear Swell Meter with clay cutting sample from PMB-14 INF