

Survey of Polyamines as Prospective Shale Stabilizers

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Abstract

Polyamines are used in high performance water-based drilling fluids for their ability to stabilize clays when drilling through water-sensitive shales. Previous studies of polyamines have demonstrated that these compounds are indeed effective shale inhibitors. The primary focus of this paper is to explore the relationship between the compounds' inhibitive properties and the structural changes to the clay substrates. Three different types of polyamines are evaluated: straight short-chain compounds; angled short-chain compounds; and, a long-chain polyamine with modified functionality.

Oriented-aggregate mounts of sodium montmorillonite (Na-MMT) are prepared and analyzed via X-ray diffraction (XRD). The mounts are analyzed before and after application of the polyamine inhibitors to monitor the effect of the different compounds on the Na-MMT structure. In parallel, fluid imaging, a novel technology, is used to observe and quantify changes in the properties of Na-MMT slurries treated with the same polyamines.

XRD results indicate that polyamines intercalate within the interstitial layers of Na-MMT in either a mono-layer or di-layer arrangement depending on their size. XRD also demonstrates that shifts occur in the d-spacing of the Na-MMT when it is treated with the polyamines. This structural shift offers a strong correlation with the substrates' swelling and dispersive behaviors as measured by linear-swell meter testing and dynamic particle-size analysis. The link between all of these techniques provides the potential to establish a new screening approach for shale inhibitor selection and a further understanding into the polyamines' inhibition mechanism.

Introduction

Tightening environmental regulations and a drive towards more cost-efficient solutions are key factors in the drilling industry's effort to find suitable replacements for non-aqueous drilling fluids (NAF). NAFs are invert-emulsions for which the continuous phase is an oil (mineral oil, diesel) or a synthetic base-fluid (esters, olefins, etc.), and as such, offer enhanced inhibition for water-sensitive shale formations. Replicating or outperforming the highly inhibitive properties of NAF with high performance water-base drilling fluids poses a challenge for the industry.¹

Historically, wellbore stability has been a major concern during drilling operations due to the potential of water-

sensitive shale formations to hydrate when in contact with aqueous drilling fluid. The hydration of the clays present in water-sensitive formations leads to the degradation of the wellbore through two mechanisms: swelling and dispersion of the clays. Swelling of the clays from the formation often results in hole tightening and increased stuck pipe incidents, while dispersion often results in hole washout and weakening of the shale.²

In the field of clay stabilization, the use of inorganic salts, particularly potassium chloride (KCl), as effective shale inhibitors is well known. However, the resulting elevated salinity of the fluids treated with these inhibitor agents poses environmental concerns for disposal and higher waste management costs. Water-base fluids containing polyglycols offer an environmentally-friendly pathway for shale inhibition, but still require the addition of potassium ions to provide optimum efficiency.^{3,4} More current research in organic shale inhibitors centers around amine chemistry. The ammonium moiety of amine-based shale inhibitors is very effective for inhibition. Amongst these new compounds, polyamines are of particular interest because of the presence of multiple active sites in the molecule for increased performance.⁵

This work aims to examine the relationships between the changes in the properties of a water-sensitive clay substrate (Na-MMT) through the application of polyamine inhibitors. The three polyamines selected for experimentation exhibit distinct features: varying chain length, spatial arrangement (linear vs. angled molecule) and modified functionality through the addition of alkoxy groups on the carbon chain of the compound (polyetheramine, or PEA). The characterization of the clay substrate after interaction with the shale inhibitors takes place through a combination of techniques familiar to the drilling industry: X-ray Diffraction (XRD) and Linear-Swell Meter Testing (LSMT) coupled with recently introduced dynamic particle-size imaging.⁶

This study examines structural changes in the clay resulting from the addition of polyamines. The structural change analysis includes XRD measurements and correlation of the results with the swelling and dispersive properties of the clay substrate. The linear swell meter quantifies the swelling tendencies of the clay by measuring the increase in volume due to hydration of a reconstituted core sample exposed to a fluid. Monitoring dispersion tendencies occurs through examination of the particle-size distribution and shape factors of treated Na-MMT particles in a fluid suspension. Whenever

possible, inhibitive behavior comparison occurs against a KCl and ethylene glycol baseline. A comparison of results based on the structure of each polyamine provides further understanding of the shale inhibition mechanism. The techniques used in this work are also discussed in terms of their potential as screening tools for the selection of shale inhibitors.

Experimental Section

Materials

Polyamines:

The study analyzes three types of aliphatic polyamines: a small straight-chain polyamine (PA1), a small-chain polyamine with angled spatial arrangement (PA2), and a longer-chain compound with modified functionality (PA3). PA1 and PA2 are alkyl-polyamines with six carbon atoms per alkyl group. PA3 is a polyamine with a propoxylated backbone. All three polyamines readily disperse in water and have history of effectively achieving inhibition when drilling through water-sensitive shale formations. Samples of these materials are obtained from commercially available sources.

Substrate:

The source of sodium montmorillonite selected for experimentation is a finely ground premium grade, western bentonite. Mines located in the Big Horn Basin are the source of the composite sample used throughout testing. Careful substrate sample storage techniques ensure preservation of the active materials. With a CEC value of 69 meq/100g, as measured by the cobalt hexamine (CoHex) method, the substrate is categorized as highly sensitive to hydration. The bentonite disperses well in aqueous solutions and displays desirable swelling characteristics appropriate for this study. Figure 1 presents an in depth analysis of the Wyoming bentonite. The method of analysis used to generate these results is described elsewhere.⁷

XRD Analysis

The clay fraction of the material analyzed by XRD is separated from the bulk by homogenizing 2 g of the substrate in 35 mL of water and allowing the particles in suspension coarser than 2 μm to gravity settle. Preparation of an oriented aggregate mount is accomplished by carefully depositing a stream of the decanted colloidal suspension on a frosted silica slide with a pipette. The frosted glass slides dry at ambient temperature overnight. XRD analysis is performed before and after an aerosolized application of the aforementioned polyamines (PA1, PA2 and PA3) has saturated the surface of the substrate-mounted slides.

Measurements are made on a Bruker D8 Endeavor X-Ray Diffractometer using copper $K\alpha$ radiation. Before collecting diffraction patterns, the specimens are exposed to the following conditions:

- Ambient temperature air-drying
- Aerosolized Polyamine/Inhibitor Saturation
- Glycolation

Glycolation (the application of ethylene glycol) of the polyamine treated mounts uses the same aerosol method adopted for the preparation of the polyamine treated mounts. This tempering technique yields essentially the same basal spacings as a treatment with glycol in a sealed container overnight at 70°C.⁸ Glycol treatment of the polyamine-treated mounts verifies whether re-expansion of the intercalated layers is possible. By monitoring the shift of the 7.0⁰ (2 θ) bentonite peak (corresponding to the d_{001} lattice plane) throughout inhibitor application, a basis is established for characterizing an inhibition mechanism in tandem with other selected techniques.

Dynamic Particle Size Analysis

Under controlled flow conditions, dynamic imaging particle analysis shows the flocculation/dispersion behavior of the substrate/inhibitor slurry. A Na-MMT sample of 0.025 g is homogenized in a 3% v/v concentration inhibitor solution. A FlowCam fluid imager equipped with a 4X magnification lens and a 300 μm flowcell then measures the size distribution of the particles. A dynamic imaging particle analyzer captures real-time images of particles in solution under magnification as they pass through a flow cell and characterizes the magnified particles using a variety of measurements. The technique also allows for direct observation of the particles in situ (Figure 3).

Linear Swell Meter Analysis

An OFITE Dynamic Linear Swell Meter determines the swelling properties of Na-MMT. A pellet press produces core plugs from 12.0 g of ground Na-MMT. The plugs are then immersed into 3% v/v concentration inhibitor solutions. The hydration of the clay is monitored over a 24-hour period. The increase in height of the core plug during the exposure period relates directly with the level of interaction between the fluid and substrate. Industry uses linear swell meter testing (LSMT) to investigate the interaction between high clay content mineral samples and water-based fluids under simulated parameters in a circulating fluid.

Results and Discussion

Characterization of Substrate

The bentonite sample selected for testing is a mixture of sodium and calcium montmorillonite. The CEC data show that sodium dominates the exchangeable bases, but other ions such as calcium, magnesium and potassium are also present. The basal shift of the 7.0⁰ (2 θ) peak after glycolation illustrates the reactivity of the substrate. Subsequent heat treatments of the clay lead to the collapse of the expandable layers as shown in Figure 1.

XRD Data

Observation of montmorillonite subjected to amine sorption techniques shows the 2 θ shifting via XRD. PA1, PA2 and PA3 all follow a specific interlayer orientation mechanism

between the interstitial layers of Na-MMT. Table 2 compares the basal shifts of pre- and post-intercalated substrates and shows that both PA1 and PA2 have mono-layer orientations when aligned between adjoining montmorillonite layers. Na-MMT initially displays a basal spacing of 1.25 nm. Upon inhibitor application of PA1 and PA2, the basal shift yields a value of 1.32 nm and 1.34 nm, respectively. Conversely, PA3 exhibits formation of both mono-layer and di-layer complexes occupying basal spacings of 1.43 nm and 1.65 nm.

After the successive examination of amine saturated substrates, it is apparent that the interlayer area is being occupied in a discrete fashion based on the size of the compound. The mono-layer arrangement of both PA1 and PA2 on the planar surface of Na-MMT indicates that short-chain aliphatic amine cations have a higher affinity for parallel interlayer substitution than that of longer-chain amines with alkoxyate substituents. The positively charged ammonium sites on PA1 and PA2 balance the negative exchange sites on the substrates surface ceasing the expansion of the Na-MMT layers.⁹

PA1 and PA2's ability to intersperse freely between the inner layers of the substrate allows the polyamine to adjoin opposing lateral planes of Na-MMT by occupying negatively charged exchange sites with ammonium functionality. To confirm the layers of clay are impervious to re-expansion, the amine-saturated substrates undergo subsequent glycol solvation treatment. Figure 2 shows that glycol application to the amine saturated substrate does not produce any significant changes in basal shifting, further confirming the inhibitive stability of the short-chain polyamine complexes.

In contrast, PA3's sorption mechanism encompasses a different pathway. Being that the molecular chemistry of PA3 consists of a longer-chain length with alkoxyate groups, there is a difference in the orientation of the compound in the interlayer space. The mono-layer and di-layer of PA3 (Figure 2) are evidence that the orientation of the amine-cations is not linearly uniform on the planar surface of Na-MMT. This results from a steric interference by the larger amine cation PA3. After exposure to glycol, the previously formed monolayer and di-layer shift to collectively produce one di-layer, proving that a channeling effect is present from larger-chain amine cations. This promotes the invasion of glycol between the inter-pillar spacing of larger-chain amine saturated substrates and additional expansion of the interlayer space.¹⁰

Optical Imager Data

The width and shape of the particle size distribution conventionally characterize fine particles. Amongst these, the parameters most often cited to describe the distribution are the D10, D50 and D90. The D50 is the median particle size, defined as the diameter of the equivalent spherical particle under which half the particle population lies. Similarly, 10% and 90% of the population resides under the D10 and D90 limit, respectively. The benefit of using image analysis to characterize particles resides in the ability to access physical

parameters, such as shape factors, in addition to conventional information about the fine particle distribution. The following approach characterizes suspensions of Na-MMT after inhibitor treatment monitoring both particle size and selected shape factors. Results obtained during the course of this study are summarized in Table 3.

A dispersion of Na-MMT in DI (deionized) water, used as a baseline for testing, shows the lowest measured D50 at 15.06 μm . No effect on particle size distribution occurs by treating the substrate with glycol. However, an effect is apparent when the substrate undergoes polyamine treatment. The D50 for the Na-MMT treated with polyamines increases with decreased chain length of the polyamines investigated, indicating that the use of these compounds reduces the dispersive tendencies of the substrate, as illustrated in Figure 4. This trend correlates with data collected by XRD, leading to the observation that the decrease of the 2θ shift in basal spacing following inhibitor application is accompanied by the increase in D50 of polyamine-treated Na-MMT.

The addition of glycol to Na-MMT treated with PA1 and PA2 has little effect on the particle size distribution, while significant changes to D50 occur with the PA3/glycol mixture. These results are consistent with XRD data showing little alteration of the crystalline structure of the PA1 and PA2-treated Na-MMT after exposure to glycol and the significant structural shift with the PA3/glycol combination.

To further characterize the substrate properties after inhibitor treatment, the following shape factors are examined:

- Aspect ratio, a classification of the general form of the particles in suspension,
- Circularity, the degree to which a particle is similar to a circle,
- Mean geodesic length, a measure of the length of a curved particle, while following the curvature of the particle.

Results show that aspect ratio and circularity both decrease after application of inhibitor on the substrate, with this effect being most noticeable with PA1 and KCl. This result is consistent with reduced substrate dispersion and the formation of clay particle aggregates with more elongated shapes. The addition of glycol to the substrate does not modify the aspect ratio of the particles, but interestingly leads to an overall increase in circularity. The mean geodesic length, an alternative to D50, more accurately represents the size of the clay platelets in suspension. Variations observed in the mean geodesic length support the conclusion from the aspect ratio and circularity data pointing to the formation of elongated clay assemblies after inhibitor treatment.

Linear Swell Meter Data

Monitoring the swelling behavior of reconstituted Na-MMT core plugs immersed into aqueous solutions of polyamines, KCl and glycol further characterizes the interaction between Na-MMT and shale inhibitors. As a baseline, DI water shows directional swelling of nearly 99% after an exposure period of 24 hours (see Figure 5 and 6). The

core plug exposed to a 3% v/v solution of PA3 shows the highest swelling percentage (~109%), consistent with the intercalation of the large polyetheramine molecule and the resulting expansion of the montmorillonite lattice, as shown by the XRD data. Fluids prepared with PA1 and PA2 show a decreased amount of swelling compared to DI water or glycol alone, but fail to match the performance of KCl at the concentration selected.

In all samples, the subsequent addition of glycol to the fluid shows a synergistic effect and a further decrease of swelling during the exposure period. The most dramatic effect occurs in samples treated with PA3 and glycol, which leads to a decrease from 109% to 74%. This is consistent with glycol displacing water in the inter-pillar space between layers formed by the large PA3 molecules. This effect is less marked with PA1 and PA2, in which reduced size and mono-layer arrangement do not allow for a significant volume to be available for the intercalation of glycol molecules. Comparable effects are observed with monoamine compounds of various chain lengths.¹¹

Conclusions

This work demonstrates that low molecular weight short-chain polyamines demonstrate a higher inhibitive affinity in sodium rich smectites than that of its longer-chain analogues. The longer-chain polyamine PA3 appears to promote higher dispersion (lower D50) and higher swelling (higher Total Swell), while the shorter chain polyamines PA1 and PA2 show progressively more particle aggregation and reduced swelling. Moreover, PA1 and PA2's ability to integrate between the c-spacing of the interlayer of sodium montmorillonite does not permit inclusion of foreign macromolecules like glycol to enter the interlayer space, yielding a more stable mono-layer arrangement of molecules unlike PA3. After the careful examination of clay hydration, dispersion propensity and 2 θ shifting of Na-MMT via LSMT, dynamic particle imaging and XRD, respectively, establishes a fundamental correlation amongst these technologies. When Na-MMT is placed in a polyamine-abundant environment, an increase in D50 correlates to a decrease in the total swell percentage in addition to a smaller change in 2 θ shifting. This effect can potentially predict the swelling inhibition capacity of polyamine treated substrates when screening prospective polyamine shale inhibitors and reduce the need for lengthy LSMT runs.

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Table 1. Description of Polyamines Used in This Study

Inhibitor	Description
PA1	Linear, short-chain alkyl polyamine
PA2	Angled, short-chain polyamine
PA3	Long-chain polyamine with modified functionality (PEA)

Table 2. Effect of Inhibitor on Na-MMT Crystalline Structure

Inhibitor	2 θ Shift for d ₀₀₁ Plane (Basal Spacing in nm)				
	Initial	After Inhibitor Treatment		After Glycolation	
		Peak	Δ	Peak	Δ
PA1	7.03 (1.256)	6.67 (1.323)	-0.36 (0.067)	6.67 (1.324)	-0.36 (0.068)
PA2	7.04 (1.255)	6.62 (1.335)	-0.42 (0.079)	6.62 (1.335)	-0.42 (0.080)
PA3	7.06 (1.251)	6.18 (1.429) 5.34 (1.653)	-0.88 (0.178) -1.72 (0.402)	5.15 (1.715)	-1.91 (0.463)

Table 3. Effect of Inhibitor on Particle-Size Distribution and Particle Shape Factors

Treatment	DI	KCl	PA1	PA2	PA3	Glycol	KCl/ Glycol	PA1/ Glycol	PA2/ Glycol	PA3/ Glycol
D10, μm	4.04	22.67	31.25	14.10	10.62	3.90	19.90	26.56	12.86	24.79
D50, μm	15.06	50.13	65.73	41.49	30.89	15.22	46.15	77.01	46.39	70.15
D90, μm	44.79	95.18	150.39	108.35	73.66	44.37	95.02	179.90	121.12	172.49
Geodesic Length, Mean, μm	4.82	17.53	20.39	7.58	7.04	4.65	12.94	12.15	6.97	9.62
Aspect Ratio, Mean	0.76	0.70	0.71	0.74	0.70	0.70	0.70	0.72	0.74	0.70
Circularity, Mean	0.98	0.88	0.87	0.97	0.95	0.98	0.91	0.93	0.97	0.93

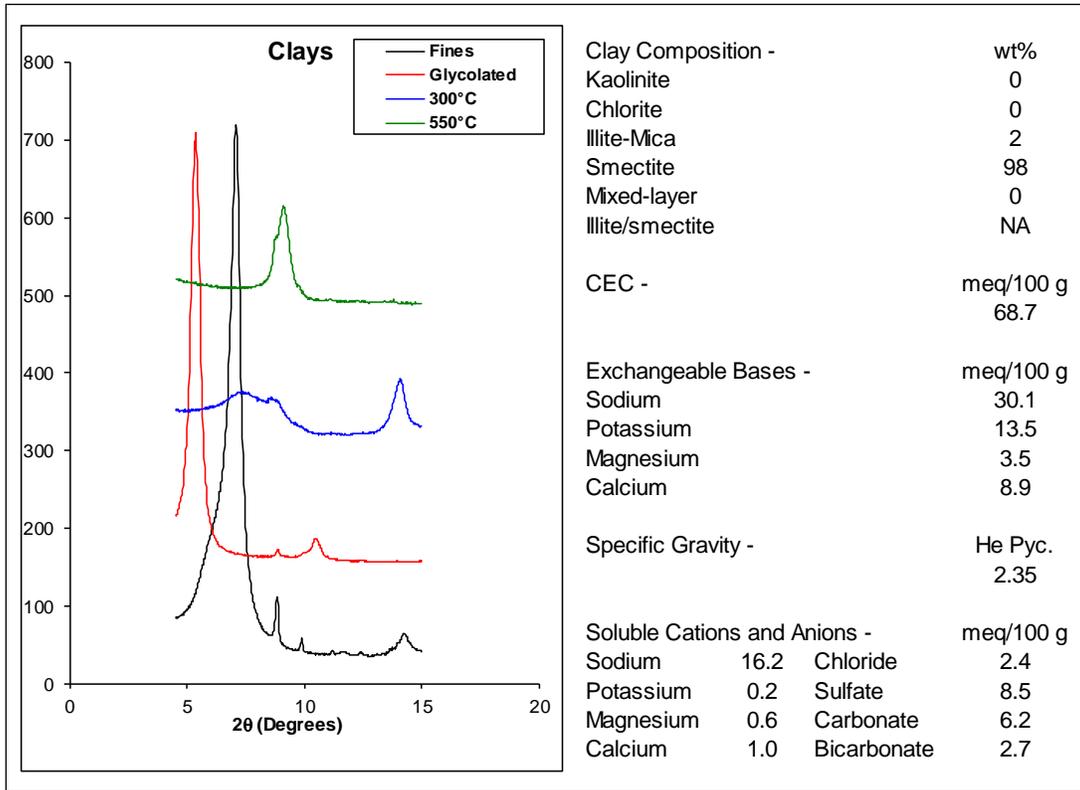


Figure 1. Clay Mineralogy of Na-MMT

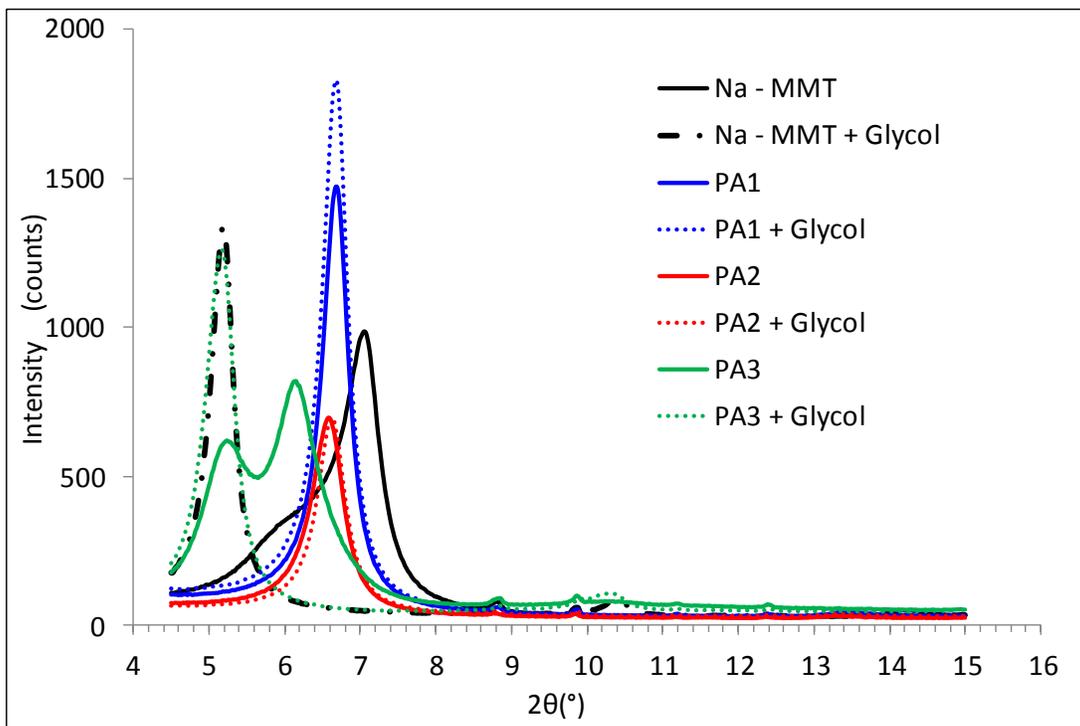


Figure 2. 2θ Shift Post Inhibitor Application

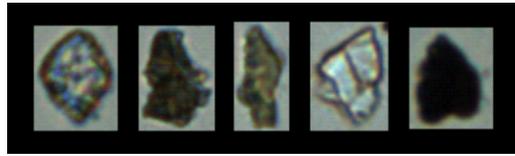


Figure 3. Selected Images of Na-MMT in DI Water

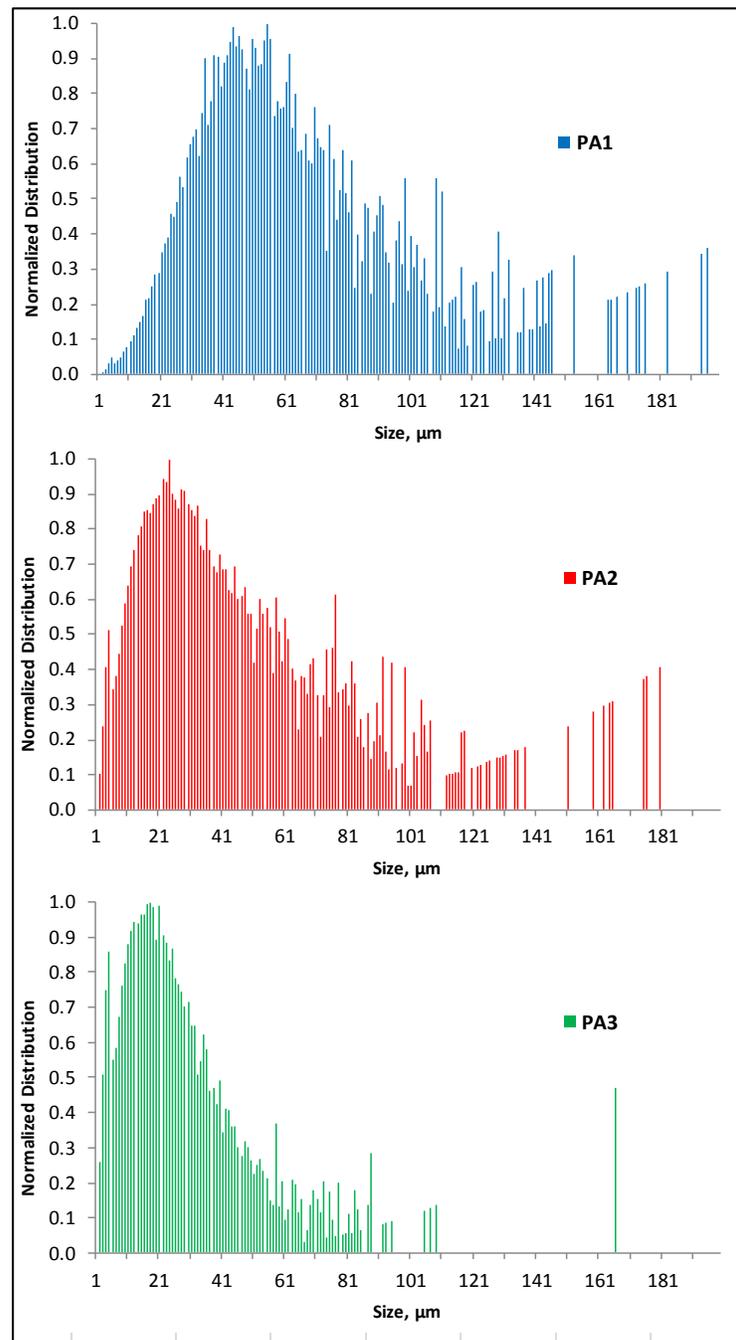


Figure 4. Particle-Size Distribution of Substrates Treated with Polyamines

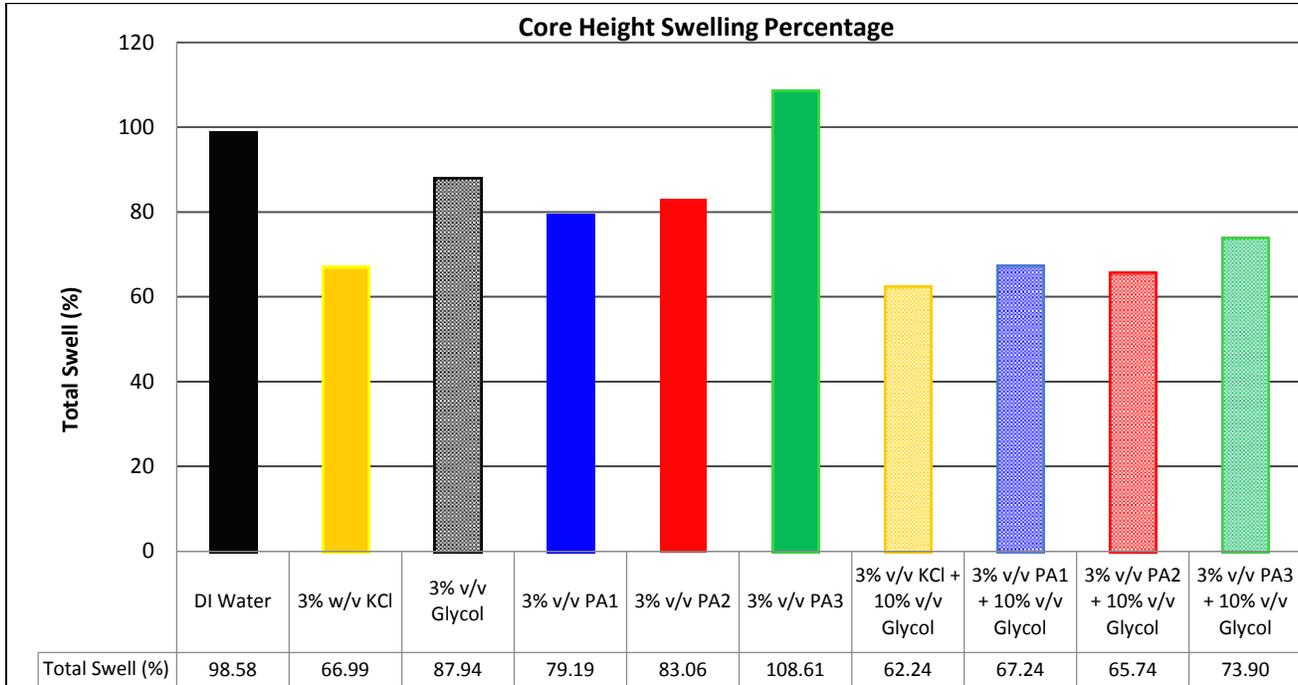


Figure 5. Na-MMT Total Swelling After 24-Hour Fluid Exposure

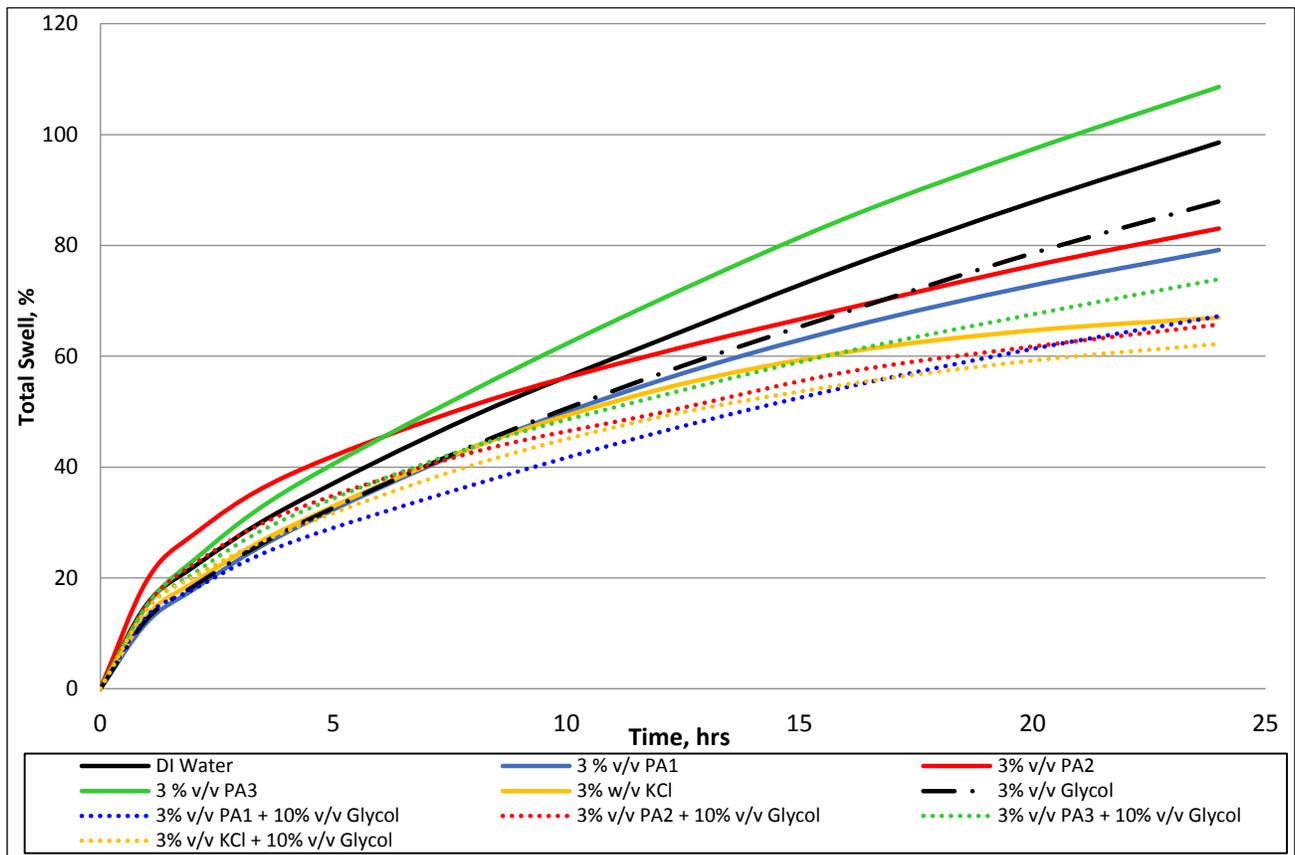


Figure 6. Swelling of Treated Na-MMT Core Plugs

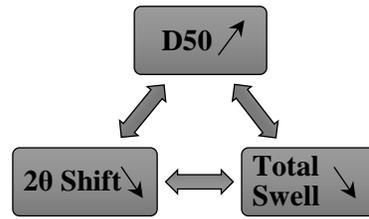


Figure 7. Correlation between Substrate Properties in the Presence of Polyamines