**AADE-24-FTCE-033**

# Successful Field Deployment of Nano-Silica Based Shale Inhibitors

Tulio Olivares, Rafael Pino, Saudi Aramco; Ashok Santra, Nicolas Osorio, Aramco Services Company.



## Abstract

Water based mud (WBM) usually contain shale inhibitors during drilling of water sensitive formations. Formations rich in Kaolinite can lose integrity when exposed to KCl through cation exchange with potassium ion. In the United States, environmental regulations prohibit the disposal of greater than 3,000 ppm chloride on lease or 1,000 ppm chloride off lease. The hazardous nature of choline chloride (a very cost-effective option) restricts its use as shale inhibitor for water-based muds. Shale inhibitor presented herein is environmentally friendly and highly effective.

Functionalized Nano-Silica Based Shale Inhibitor (NSBSI) has been developed in this work to overcome the difficulties in clay stabilization in particularly challenging formations. NSBSI can be used in low solids non-dispersed (LSND) muds, such as polymer and Polyanionic cellulose (PAC) muds. It can also be used as an alternative to polyamine-based and silicate-based shale inhibitors. For field trials, commercially available poly-amine based shale inhibitors were replaced by NSBSI in the mud formulations, resulted in a trouble-free drilling through problematic shale sections with no changes in mud properties, and no indications of lack of inhibition.

A facile synthetic approach was developed to synthesize and scale up of NSBSI from lab-scale to field trials quantity. The crystal structure and other materials characterization were done using powder X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) to evaluate production of anticipated product reproducibly. Shale stabilization efficiency of NBSSI were tested in comparison with other commercial shale inhibitors those were replaced during field trials. Clay swelling and clay dispersion tests were performed to evaluate the effectiveness of the impermeable coating of nano-platelets on to the clay-rich shales rock surface. The NSBSI demonstrated >85% recovery of swellable shales in dispersion tests. The linear swelling measurements were also performed to understand and compare the effectiveness of NSBSI over 24, 48 and 72 hours. The test demonstrating NSBSI inhibitor hydration and subsequent swelling rate was relatively lower compared to other incumbents on clay-rich shales.

The novel inhibitor (NSBSI) presented in the current study has outperformed conventional shale inhibitors wherein the presence of inorganic constituents results in stronger film formation compared to other organic or polymeric inhibitors. Field trials have been successfully conducted in two different wells and results are presented here.

## Introduction

Water based muds (WBM) are popular options when it comes to environmental sustainability, however, conventional WBM consistently struggle to match the drilling performance of non-aqueous invert emulsion-based muds. Today about half of the drilling fluids used are water based. Non-aqueous drilling fluids has inherent advantages like rheological robustness, fluid loss control and non-interactive nature against clay-rich formation. Rocks composed of water sensitive clay minerals are susceptible to swelling in presence of water-based fluids (van Oort, 1997 and 2003; Saleh et al., 2019; Akpan et al., 2019; Wang, 2020; Quainoo et al., 2020; Xie et al., 2019; Patel and Santra, 2020; Yang et al., 2019), leading to wellbore stability issues like borehole collapse and stuck pipe events and non-productive time (NPT). Formation rocks with higher amount of smectite type clays like montmorillonite (a layered aluminosilicate with high cationic exchange capacity) contributes to its troublesome water swelling behavior. Clays like Kaolinite, Illite or Chlorite are less susceptible to swelling because of their low cation exchange capacity (Figure 1).

Swelling issues during drilling with water-based fluids can be controlled by the use of proper shale inhibitors or clay stabilizers. Swelling happens due to water-clay interaction – which is a hydration phenomenon of smectite clays leading to spatial separation (also known as house of cards effects) of the aluminosilicate’s layers wherein (1) Osmotic swelling: due to osmotic pressure difference and (2) Crystalline swelling: due to electrical double-layer effects are the two major driving forces behind it.

One of the popular mechanisms of shale stabilizers work is by adsorption of inhibitor molecules on the clay surfaces through electrostatic attraction forces forming a hydrophobic barrier that inhibits or delay the penetration or diffusion of water molecules (Li et al., 2018; Ni et al., 2019; Xu et al., 2018; Rana et al., 2019; Shettigar et al., 2018; Ahmad et al., 2018; Chen et al., 2017; Ahmed et al., 2019; Ferreira et al., 2016; Arfaj et al., 2019; An and Yu, 2018; Boul et al., 2016; Huang et al., 2018; Ahmad et al., 2021; Zhang et al., 2019; Qiu et al., 2018; Li et al., 2020; Ibrahim and Saleh, 2021; Patel et al., 2020; Wang, 2020). Second mechanism utilizes potassium chloride (KCl) at higher concentrations providing inhibition through cation exchange. However, use of large amount of KCl (>3%) is an environmentally sensitive issue. Polyamines, quaternary ammonium salts, dendrimers, graphene oxide derivatives, functionalized carbon nanotubes, polyethyleneimines, functionalized Nano-silica, laponite, biopolymer derivatives have been proposed for shale inhibition. This paper demonstrates performance of our novel functionalize Nano-silica based shale inhibitors (NSBSI) and its success in field trials.

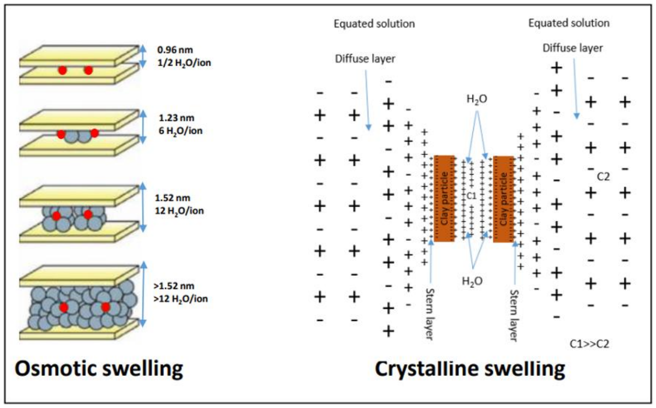


**Figure 1 -** Shale welling mechanism.

**Materials**

The novel amine functionalized Nano-silica (NSBSI) we have developed is spherical in shape (Figure 2) with a mean particle size distribution of 30-50 nm. In addition to making a hydrophobic adsorption layer on the rock surface, chemically being $SiO_2$, it reacts in the cementation on formation surface forming a permanent impervious Calcium-Silicate-Hydrate type of layer. We have compared its performance against 3 commercially used materials.

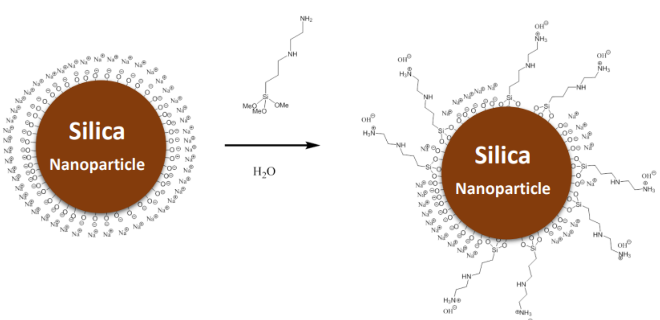


**Figure 2 -** Shape and structure of the amine functionalized Nano-silica inhibitor (NSBSI)

**Dispersion test**

The dispersion tests were conducted on Pierre II Shales. Mineralogical composition of Pierre II both in fresh water (de-ionized water) and seawater. Fresh water-based and seawater-based fluids containing inhibitors, xanthan gum (0.2ppb), and de-ionized or seawater were formulated. Pierre II shale was added to the fluids and the dispersion in glass jars was rolled at 25°C for 16 hours in an oven. Commercial shale inhibitors (Choline Chloride, Commercial A, and KCl) were used to prepare fresh water-based and seawater-based fluids to compare the shale recovery in the dispersion tests. After 16 hours of dispersion tests, the dispersion was passed through #8 mesh to recover shales that remained unaffected from hydration and swelling. Table 1 summarizes the % shale recovery for each test. Amine functionalized Nano-silica inhibitor performed very well compared to the commercially used materials.

**Table 1 -** Shale recovery test

| Materials | Test conditions | % Recovery |
|---|---|---|
| FNSBSI (3ppb) | Sea water | 91% |
| Choline Chloride (3ppb) | Sea water | 82% |
| None | Sea water | 25% |
| None | Fresh water | 0.4% |
| Choline Chloride (3ppb) | Fresh water | 57.9% |
| Commercial A (3ppb) | Fresh water | 53.4% |
| KCl (3%) | Fresh water | 50.3% |
| Choline Chloride (3ppb) | Sea water | 81.6% |
| Commercial A (3ppb) | Sea water | 72.2% |

**Linear Swell meter Test**

Linear swell meter measurements measure the capacity of inhibitors to prevent hydration and swelling are conducted to quantify the changes in the volume of bentonite pellets/ wafers. The bentonite wafers were prepared by pressing dry bentonite powder at 41.4 MPa for 30 minutes. The drilling fluids were circulated around the wafers and the changes in the height of compressed wafers with respect to time were used as swelling percentages. The results are summarized in Figure 3 demonstrate both NSBSI performs very well in comparison to the three commercial products tested herein. Amine functionalized Nano-silica inhibitor not only provide lower overall swelling after 72 hours, but also provide very low % swelling after 24 hours. Early stage of swelling is very detrimental for drilling operation, lower swelling at 24 hours indicate the slower swelling kinetics, therefore, indicating better inhibiting layer formation.

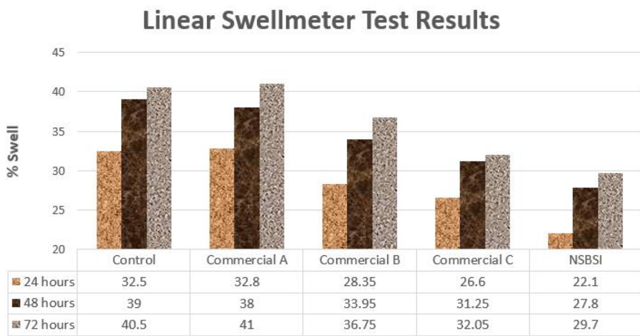


**Figure 3 -** Linear Swell meter results comparison

## Field Deployment

After the extensive lab testing, the functionalized Nano-silica Based Shale Inhibitor was field implemented in two wells (Well A & Well B). In order to establish a proper evaluation, several key performance indicators (KPI) were established prior the field trial. Those KPI were:

- Successful and trouble free drilling the entire hole section containing shale with adequate fluid density in use.
- Maintained drilling fluids properties as per programmed and reasonably within the estimated product consumption.
- Supply two highly qualified and experience mud engineers to supervise the system 24 hrs/day.
- No problem while initial or maintenance mix of the fluid, homogeneous mixture.
- No drastic or significant changes in mud properties attributable to inadequate mixing, poor maintenance of the drilling fluid or lack of supervision.
- No hole stability issues due to lack of shale inhibition.
    - Good cuttings integrity: dry and inhibited cuttings observed at shakers.
    - Clean BHA & Stabilizers: no balled-up events on BHA and stabilizers.
    - No stuck pipe due to lack of inhibition.
- No issues running the liner or casing to bottom related to shale inhibition.

Well A was identified and the functionalized Nano-silica Based Shale Inhibitor was mixed without any issues at 3% by volume in a 76 pcf (10.1 ppg) NaCl Polymer mud. The mixture of the functionalized Nano-silica Based Shale Inhibitor was very homogeneous during the whole drilling phase. The section drilled using the mentioned shale inhibitor was 12-1/4” hole from 3,319 ft to 5,061 ft passing through sandstone, reactive shale and limestone formations. During the drilling phase mud properties such as Plastic Viscosity (PV), Yield Point (YP), API Fluid Loss (API FL) and pH were within the proposed range given in the drilling program. Functionalized Nano-silica Based Shale Inhibitor has no detrimental effect on basic mud properties as we can observe in Figure 4.

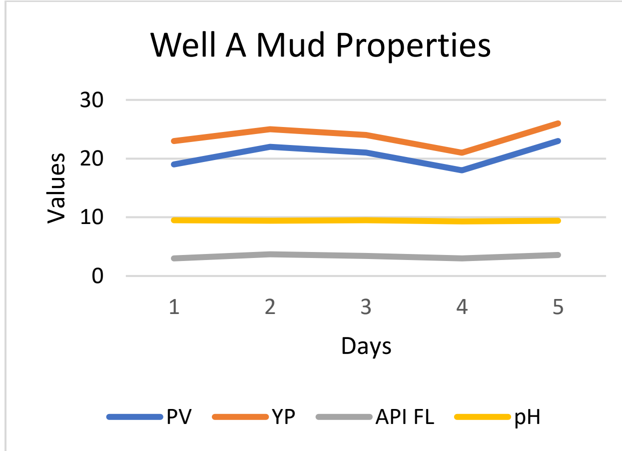


**Figure 4** - Mud Properties on Well A after functionalized Nano-silica Based Shale Inhibitor

Comparing the performance of the functionalized Nano-silica Based Shale Inhibitor with proposed KPI for the field evaluation, we observed that mud rheological properties, cutting quality and Bit/BHA after pull out of the hole (POOH) looked satisfactory within drilling program specifications. Cutting quality can be observed in Figure 5 and Bit/BHA after POOH in Figure 6. Both looked standard in comparison to previous wells where an alternative product was used instead of functionalized Nano-silica Based Shale Inhibitor. No formation deposit was observed on the drill bits; therefore, we concluded there was no bit balling occurred in this case. Observation of some mud residue as shown by the arrow (Figure 2) is normal, it comes from the scraping of hole sides while pulling out the bottom hole assembly (BHA), and it is due to the fact that hole shape is not perfectly vertical and even. Drilling was performed without problems, ROP was achieved as programmed, cutting quality was good (dry and stable), minimal accretion, there were no other issues while drilling this section and running the casing.

**Figure 5** - Inhibited cuttings after functionalized Nano-silica Based Shale Inhibitor additions (Well A)

**Figure 6** - BHA after pull out of the hole

As summary for Well A:

- Functionalized Nano-silica Based Shale Inhibitor didn't alter the original mud properties.
- Shale cuttings were in good shape and dry inside.
- No issues experienced with ROP and Torque while drilling.
- No issues experienced like tight spot while back reaming and tripping. Hole was in good condition.
- No bit balling was experienced.

Based on the above, we did conclude the trial on Well A was fully successful.

Well B was identified in a different studied area than Well A and functionalized Nano-silica Based Shale Inhibitor was mixed at 3% by volume in a 78 pcf (10.4 ppg) NaCl Polymer mud. The section drilled using the mentioned shale inhibitor was 12-1/4" hole from 4,519 ft to 6,659 ft passing through sandstone, reactive shale and limestone formations. Similarly, during the drilling phase mud properties such as Plastic Viscosity (PV), Yield Point (YP), API Fluid Loss (API FL) and pH were within the proposed range given in the drilling program. Functionalized Nano-silica Based Shale Inhibitor has no detrimental effect on basic mud properties as we can observe in Figure 7.

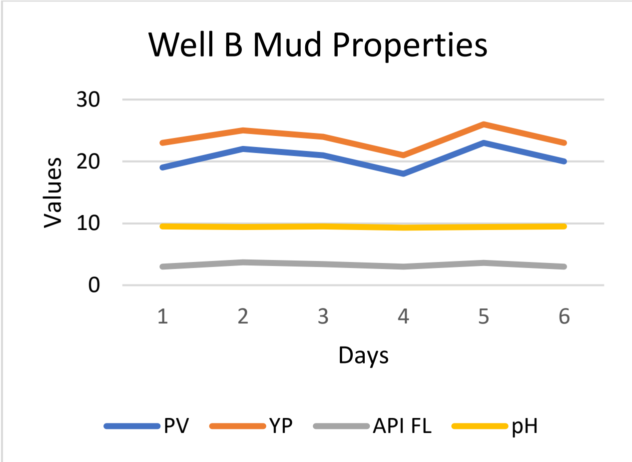


**Figure 7** - Mud Properties on Well B after functionalized Nano-silica Based Shale Inhibitor

Comparing the performance of the functionalized Nano-silica Based Shale Inhibitor with proposed KPI for the field evaluation, we observed that mud rheological properties, cutting quality and Bit/BHA after pull out of the hole (POOH) looked suitable. The drill bit after POOH can be observed in Figure 8 and Cutting quality in Figure 9. No formation (shale) accretion was observed on the drill bits; therefore, we concluded there was no bit balling occurred in this case. Drilling operation executed as planned, expected ROP was accomplished without issues, cutting were dry and there were no other issues while drilling this section or even running the casing.

**Figure 8** - Bit after pull out of the hole

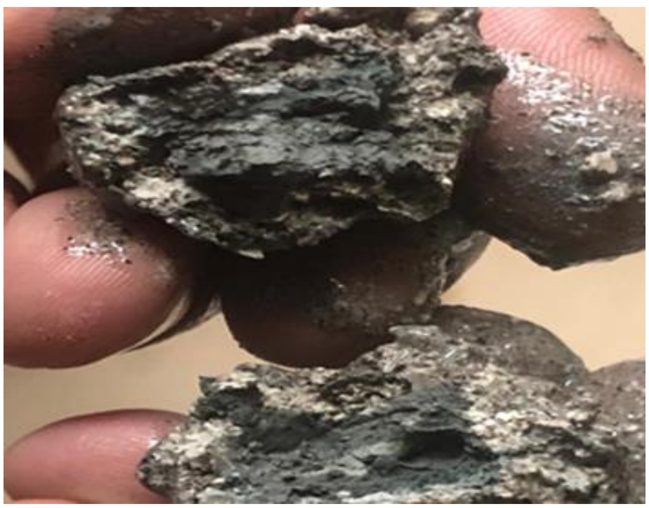

**Figure 9** - Inhibited cuttings collected after Nano-silica Based Shale Inhibitor additions (Well B)

As summary for Well B:

- Functionalized Nano-silica Based Shale Inhibitor didn't alter the original mud properties.
- Shale cuttings were in good shape and dry inside.
- No issues experienced with ROP and Torque while drilling.
- No issues experienced like tight spot while back reaming and tripping. Hole was in good condition.
- No bit balling was experienced.

Based on the above, we did conclude the trial on Well B was completely successful and we were ready to approve this technology to be extensively used in our operations.

## Results:

- There was no issue while adding/mixing FNSBSI to the active mud system.
- There were no issues while drilling such as hole cleaning observed.
- The cuttings integrity was good due to inhibition of swelling provided by NSBSI.

## Conclusions

- Two novel nanomaterials-based shale inhibitors have been developed.
- Both demonstrated superior performances in laboratory-based dispersion and linear swell meter test when compared with commercially used materials.
- Both novel inhibitors developed here perform very well in comparison to the commercially used materials.
- Novel amine functionalized Nano-silica based shale inhibitor (NSBSI) has been successfully field trialed.

## Nomenclature

*KCl: Potassium chloride*
*FNSBSI: Functionalized nano-silica based shale inhibitor*
*LSND: Low solids non-dispersed*
*XRD: X-ray diffraction*
*TGA: thermogravimetric analysis*
*WBM: Water based mud*
*NPT: non-productive time*
*$SiO_2$: Silicon dioxide*
*°C: Centigrade degree*
*nm: Nanometer*
*Mpa: Megapascal*
*KPI: Key performance indicator*
*BHA: Bottom hole assembly*
*ppg: Pounds per gallon*
*ft: feet*
*PV: Plastic viscosity*
*YP: Yield point*
*API: American petroleum institute*
*POOH: Pull out of the hole*
*ROP: rate of penetration*
*NaCl: Sodium chloride*
*ppm: parts per million*

## References


1. Ahmed, H. M., Kamal, M. S., and Al-Harthi, M. 2019. Polymeric and Low Molecular Weight Shale Inhibitors A Review. Fuel vol. 251, pp. 187-217.
2. Ahmad, H. M., Kamal, M. S., and Al-Harthi, M. A. 2018. High molecular weight copolymers as rheology modifier and fluid loss additive for water-based drilling fluids. J. Mol. Liq. vol. 252, pp. 133-143.
3. Ahmad, H. M., Murtaza, M., Kamal, M. S., Hussain, S. M. S., and Mahmoud, M. 2021. Clay Swelling Mitigation During Fracturing Operations Using Novel Magnetic Surfactants. J. Mol. Liq. 2021, 325, 115164.
4. Akpan, E. U., Enyi, G. C., Nasr, G., Yahaya, A. A., Ahmadu, A. A., and Saidu, B. 2019. Tannin-Based Deflocculants in High Temperature High Pressure Wells: A Comprehensive Review. J. Petrol. Sci. Eng., vol. 175, pp. 1028-1038.

5. An, Y., and Yu, P. 2018. A strong inhibition of polyethyleneimine as shale inhibitor in drilling fluid. J. Petrol. Sci. Eng. Vol. 161, pp. 1-8.
6. Arfaj, M. K., Rana, A., and Saleh, T. A. 2019. Improvement in Rheological Features, Fluid Loss and Swelling Inhibition of Water-Based Drilling Mud by Using Surfactant-Modified Graphene presented. at the Abu Dhabi Int. Petroleum Exhibition & Conf., Abu Dhabi, UAE, 111-14 November.
7. Boul, P. J., Reddy, B. R., Zhang, J., and Thaemlitz, C. 2016. Functionalized nanosilicas as shale inhibitors in water-based drilling fluids. SPE Drilling and Completion vol. 19. Pp. 98-105.
8. Chen, G., Yan, J., Lili, L., Zhang, J., Gu, X., and Song, H. 2017. Preparation and performance of amine-tartaric salt as potential clay swelling inhibitor. Appl. Clay Sci. vol. 138, pp. 12-18.
9. Ferreira, C. C., Teixeira, G. T., Lachter, E. R., Nascimento, R. S. V. 2016. Preparation and Performance of the Hyperbranched Polyamine as an Effective Shale Inhibitor for Water-Based Drilling Fluid. Appl. Clay Sci. vol. 132–133, pp. 122-132.
10. Huang, X., Shen, H., Sun, J., Lv, K., Liu, J., Dong, X., and Luo, S. 2018. Nanoscale laponite as a potential shale inhibitor in water-based drilling fluid for stabilization of wellbore stability and mechanism study. ACS Appl. Mater. Inter. vol. 10, 33252-33259.
11. Ibrahim, M. A., and Saleh, T. A. 2021. Synthesis of efficient stable dendrimer-modified carbon for cleaner drilling shale inhibition. Journal of Environmental Chemical Engineering 2021, 9, 104792-104799.
12. Li, X., Jiang, G., Shen, X., and Li, G. 2020. Poly-l-arginine as a High-Performance and Biodegradable Shale Inhibitor in Water-Based Drilling Fluids for Stabilizing Wellbore. ACS Sustain. Chem. Eng. Vol. 8, pp. 1899-1907.
13. Li, X., Jiang, G., Yang, L., and Peng, S. 2018. Study of gelatin as biodegradable shale hydration inhibitor. Colloid. Surface. A vol. 539, pp. 192.
14. Ni, X., Jiang, G., Li, Y., Yang, L., Li, W., Wang, K., and Deng, Z. 2019. Synthesis of superhydrophobic nanofluids as shale inhibitor and study of the inhibition mechanism. Appl. Surf. Sci. vol. 484, pp. 957-965.
15. van Oort, E. 1997. Physico-Chemical Stabilization of Shales. SPE International Symposium on Oilfield Chemistry, Houston. SPE-37263-MS. https://doi.org/10.2118/37263-MS
16. Van Oort, E. 2003. On the physical and chemical stability of shales. J. Petrol. Sci. Eng., vol. 38, pp. 213–235.
17. Patel, H. A., and Santra, A. 2020. Organically modified layered magnesium silicates to improve rheology of reservoir drilling fluids. Sci. Rep. vol. 10, pp. 13851.
18. Patel, H. A., Santra, A., and Thaemlitz, C. 2020. Functionalized Layered Nanomaterials: A Next-Generation Shale Inhibitor. Presented at the Int. Petroleum Technology Conf., Dhahran, Kingdom of Saudi Arabia, IPTC-20014-MS.
19. Quainoo, A. K., Negash, B. M., Bavoh, C. B., Idris, A., Shahpin, H. B. A., and Yaw, A. D. 2020. Inhibition Impact of Amino Acids on Swelling Clays: An Experimental and COSMO-RS Simulation Evaluation. Energ. Fuel. Vol. 34, pp. 13985-14000.
20. Qiu, Z., Xu, J., Yang, P., Zhao, X., Mou, T., Zhong, H., and Huang, W. 2018. Effect of Amphiphilic Polymer/Nano-Silica Composite on Shale Stability for Water-Based Muds. Appl. Sci. vol. 8, pp. 1839-1853.
21. Rana, A., Arfaj, M. K., and Saleh, T. A. 2019. Advanced developments in shale inhibitors for oil production with low environmental footprints–A review. Fuel vol. 247, pp. 237-249.
22. Saleh, T. A., and Ibrahim, M. A. 2019. Advances in functionalized Nanoparticles based drilling inhibitors for oil production. Energy Reports, Vol. 5, pp. 1293-1304.
23. Shettigar, R. R., Misra, N. M., and Patel, K. 2018. CTAB grafted PAM gel and its application in drilling fluid. J. Petrol. Sci. Eng. Vol. 160, pp. 129-135.
24. Wang, K., Jiang, G., Li, X., and Luckham, P. F. 2020. Study of graphene oxide to stabilize shale in water-based drilling fluids. Colloid. Surface. A vol. 606, pp. 125457-125467.
25. Wang, L. 2020. Clay stabilization in sandstone reservoirs and the perspectives for shale reservoirs, Adv. Colloid Interface, vol. 276, pp. 102087.
26. Xie, G., Huang, D., Deng, M., and Luo, P. 2019. Investigating the Role of Alkyl Chain Length of the Inhibitors on Its Intercalation Inhibiting Mechanism in Sodium Montmorillonite. Energ. Fuel. Vol. 33, pp. 5182-5190.
27. Xu, J., Qiu, Z., Zhao, X., Mou, T., Zhong, H., and Huang, W. 2018. A polymer microsphere emulsion as a high-performance shale stabilizer for water-based drilling fluids. RSC Adv. Vol. 8, pp. 20852-20861.
28. Yang, L., Yang, X., Wang, T., Jiang, G., Luckham, P. F., Li, X., Shi, H., and Luo, J. 2019. Effect of alkyl chain length on shale hydration inhibitive performance of vinylimidazolium-based ionic liquids. Ind. Eng. Chem. Res. Vol. 58, pp. 8565-8577.
29. Zhang, F., Sun, J., Chang, X., Xu, Z., Zhang, X., Huang, X., Liu, J., and Lv, K. 2019. Novel Modified Styrene-Based Microspheres for Enhancing the Performance of Drilling Fluids at High Temperatures. Energ. Fuel. Vol. 33, pp. 7118-7132.