



Adsorption Morphology of Nano Scale Inhibitors for Oilfield Mineral Scale Mitigation

Open
Access

Fatin Najihah Mat Ali¹, Siti Ujila Masuri^{1,*}, Lingeswaran Kaniappan¹, Radhiyatul Hikmah Abu¹, Nur Ismarrubie Zahari¹

¹ Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

ARTICLE INFO

ABSTRACT

Article history:

Received 29 December 2019

Received in revised form 1 February 2020

Accepted 9 February 2020

Available online 25 March 2020

Formation of mineral scales is a major issue in oil and gas industry which requires the use of scale inhibitors via squeeze treatment to mitigate the problem. Unfortunately, the retention ability of the existing scale inhibitor is low due to low adsorption of scale inhibitors onto the mineral surface, resulting in less efficient performance of scale inhibition. Recent advancement shows that nano scale inhibitors are believed to be able to migrate deep into reservoirs and adsorb onto the mineral surface during the shut-in period. Since the adsorption ability of scale inhibitors onto the mineral surface is an important characteristic, in this work adsorption morphology of several nano scale inhibitors onto mineral surface was investigated. For this purpose, this paper first describes the synthesis of these nano scale inhibitors which are nano Ca-DTPMP, nano Si-Zn-DTPMP, and nano Si-Ca-DTPMP. Results from Transmission Electron Microscopy analysis indicate the particle size of these nano scale inhibitors in comparison to the commercial DTPMP and Ca-DTPMP. To investigate the adsorption morphology of these nano scale inhibitors onto mineral surface, static adsorption tests were done using Kaolinite as the selected mineral. Results from Field Emission Electron Microscopy analysis show the morphological changes of the Kaolinite surface after application of the scale inhibitors. Nano Si-Zn-DTPMP scale inhibitor exhibits smallest particle size of 31 nm to 37 nm based on the TEM image. As supported by the FESEM image on the adsorption morphology, this small particle size contributes to better adsorption of this scale inhibitor than its counterparts.

Keywords:

Mineral scale; nano scale inhibitor; adsorption; DTPMP

Copyright © 2020 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

In oil and gas industry, mineral scale refers to precipitation of sparingly soluble salts resulted from the mixing of incompatible formation water and water injection [1]. The mineral scales are precipitated in the production tubing due to the changes in pressure and temperature as two

* Corresponding author.

E-mail address: ujila@upm.edu.my (Siti Ujila Masuri)

<https://doi.org/10.37934/arfmts.68.1.2233>

incompatible waters such as brine water and formation water mixed together [2]. In general, the formation of scale usually occurs in sequence from nucleation to crystal growth and finally to precipitation [3]. It is apparent that in scaling problem, the main ions that cause scaling problem are Calcium and Magnesium and their scale deposits are Calcium Sulfate (CaSO_4), Barium Sulfate (BaSO_4), Calcium Carbonate (CaCO_3), Calcium Fluoride (CaF_2), Calcium Phosphate ($\text{Ca}_3(\text{PO}_4)_2$), Magnesium Hydroxide ($\text{Mg}(\text{OH})_2$) and Magnesium Carbonate (MgCO_3) [4]. The precipitation of insoluble or slightly soluble salts in the water-intensive processes equipment such as steam generators, boilers, cooling towers and pipes is a critical problem [5]. In the worst cases, the scale precipitation can block the tubing completely and lower the throughput of the pipeline extremely [6].

Scale deposition can be moderated via chemical, physical or biological methods. These methods can be divided into three main categories which are through affecting the salt solubility, changing the roughness of the surfaces on which scales are deposited and finally a method that can alter the growth mechanism of crystals by addition of the chemical inhibitor [7]. The use of chemical scale inhibitors is known to be the best approach to inhibit the mineral scales formation since its role is to prevent deposition of the scales, delay the growth of the scale and scale dispersion for the nucleation inhibition [8]. The chemical scale inhibitors which consist of polyphosphates, phosphonates or polycarboxylates are referred as threshold scale inhibition agents which are highly effective in scale inhibition due to their lower inhibitive dosage requirement for specific stoichiometric scale quantities and their workability at peak levels of saturations indexes for certain scales such as CaCO_3 and BaSO_4 [9].

In addition, the squeeze treatment process is a widely used scale prevention method in oil production site due to its high cost effective factor to inhibit the scale formation [10]. In this process, the scale inhibitor solution is injected into the well above the formation pressure. Consequently, the scale inhibitor solution will be pushed into the near well formation rock pores. The well is then shut in for a given period in order to allow the inhibitor to be retained in the rock matrix. When the well is set back on-stream, produced water will pass through the pores dissolving some of the retained chemical. The disintegration of the retained chemical includes the mechanism of Brownian diffusion that influence particles migration and reaction with base fluid compounds and mineral surfaces [11]. Unfortunately, the retention ability of the existing scale inhibitor is low due to the low adsorption of scale inhibitors onto the mineral surface, resulting in less efficient performance of scale inhibition [12]. Thus, the adsorption of the scale inhibitors has direct influence on the efficiency of the adsorption squeeze treatment [13].

In recent advancement, nano scale inhibitors are believed to be able to migrate deep into reservoirs and adsorb onto the mineral surface during the shut-in period and release phosphonates into the production water at a concentration higher than the minimum inhibitor concentration (MIC) required to inhibit scale formation for a longer period of time [14]. It must be considered that the scale removal techniques should be economical, fast, non-damaging to the wellbore tubing and formation as well as ability to prevent the precipitation [15]. Since the application of nanotechnology turns out as the new focus in the innovation of scale inhibitor, the adsorption ability of nano scale inhibitors with different particle size needs to be further investigated. In this work, several nano scale inhibitors were considered, which are nano Calcium Diethylenetriamine Pentamethylene Phosphonic (nano Ca-DTPMP), nano Silica Zinc Diethylenetriamine Pentamethylene Phosphonic (nano Si-Zn-DTPMP), and nano Silica Calcium Diethylenetriamine Pentamethylene Phosphonic (nano Si-Ca-DTPMP). After the syntheses of these nano scale inhibitors, the particle sizes were analyzed followed by the study on their adsorption morphologies onto mineral surface. The results were compared between the different types of nano scale inhibitors as well as with the commercial counterparts in an effort to develop more efficient scale inhibitor with better adsorption ability.

2. Methodology

In this work, the nano scale inhibitors were first synthesized, which are nano Ca-DTPMP, nano Si-Zn-DTPMP, and nano Si-Ca-DTPMP. The products obtained from the synthesis processes were used for Transmission Electron Microscopy (TEM) analysis to determine the particle size ranges for all synthesized scale inhibitors. Comparisons were made between these nano scale inhibitors as well as with the commercial DTPMT and Ca-DTPMT scale inhibitors. To investigate the adsorption morphology of these nano scale inhibitors onto mineral surface, static adsorption tests were done using Kaolinite as the selected mineral. For this purpose, the solid products obtained for each scale inhibitors were kept for morphological studies before and after undergoing static adsorption test. Results from Field Emission Electron Microscopy (FESEM) analysis show the morphological changes of the Kaolinite surface after application of the scale inhibitors. The following describes the details.

2.1 Synthesis of Nano Ca-DTPMP

The following describes the synthesis process of nano Ca-DTPMP [16]. First of all, 0.1385g Calcium Chloride (CaCl_2) was weighed, transferred into an empty 50ml volumetric flask and diluted with deionized (DI) water until it reached 50ml. Next, 1.5g of Tetradecyltrimethylammonium Bromide (TTAB) surfactant was prepared. The Calcium Chloride (CaCl_2) solution was titrated about 40ml and added to the 1.5g TTAB in a beaker while constantly stirred. The solution was left to stir for additional 15 minutes to let it be well-dispersed and the solution was expected to have pH 6.5.

Next is description for the preparation of DTPMP acid solution. Firstly, 2.08ml of DTPMP was measured with pipette and the DTPMP was diluted with DI water until the 25ml volume was reached by using the volumetric flask. In order to obtain pH 9.0 DTPMP solution, Potassium Hydroxide (KOH) was added slowly to the solution. When the two solutions were successfully acquired, the DTPMP solution was drop by using burette into the mixture of CaCl_2 with TTAB while the solution was constantly stirred. A white milky precipitate was formed instantaneously. As soon as the drop wise process was done, the solution was stirred for another hour before transferred into the conical flask and the lid of the conical flask was covered using Aluminium foil. Afterward was the aging process, where the conical flask that contained the white slurry was placed in the 75°C oil bath for 12 hours.

Moving onto the next stage, the solution was equally divided into two different test tubes and centrifuged for 23 minutes at 4000 rpm. The separated white precipitate was filtered using 2 μm filter and left to dry in the oven at 100°C for 6 hours. Lastly, both the liquid and solid products were set aside for the TEM and FESEM analysis, respectively. Similar procedure was repeated for synthesizing Ca-DTPMP except that the 1.5g of TTAB surfactant was not added during the Ca-DTPMP synthesis procedure. However, for the preparation of the commercial DTPMP, the only required procedure is that the pH of the DTPMP solution is adjusted to pH 9 by using the 10M KOH.

2.2 Synthesis of Nano Si-Zn-DTPMP

The following describes the synthesis process of nano Si-Zn-DTPMP scale inhibitor. First and foremost, silica stock slurry was diluted with deionized water and as a result the silica nano-slurry (5% wt/wt) was obtained. Then, the pH of the slurry was adjusted to 4 by adding 1N Hydrochloric acid (HCl). Also, 0.3M Zinc Chloride (ZnCl_2) was prepared in deionized water and the solution pH was adjusted to 4.5 by adding 1N HCl. After being done with the preparation, the 16ml ZnCl_2 solution was put on dropwise to the 50ml nano-slurry of silica while stirring the solution with the aid of magnetic

stirrer. The resultant Zn-silica slurry was subjected to heating in 70°C water bath with subsequent stirring for 15 minutes.

Next, the stock solution of DTPMP was diluted with deionized water to prepare 0.1M DTPMP solution. Then, the solution pH was adjusted to 9 by adding KOH. By using burette, 12ml DTPMP was added to the Zn-silica slurry while stirring. The formation of white Zn-DTPMP precipitates took place immediately after the DTPMP injection into the slurry of Zn-silica. After the addition of DTPMP was completed, the resultant mixture was slowly added with surfactant formed from the combination of Sodium Dodecyl benzenesulfonate (SDBS) solution (10% wt/wt, 3ml) and 1g Piperazinediethanesulfonic (PIPES) powder while constantly stirred [17]. The pH of the solution and the concentrations of dissolved Zn^{2+} and DTPMP were left to stabilize for 15 minutes and remain constant. The Zn-DTPMP slurry was stabilized by sonication for about 5 minutes which allows the precipitates to further disperse. The Nano Si-Zn-DTPMP solids were separated by centrifuging the nano-fluid at 8500rpm for 15 minutes. Finally, the solids product obtained were put in oven overnight at 100°C to increase the efficiency of interstitial water removal process [14]. The products obtained underwent transmission electron microscopy (TEM) for further investigation on the particle size ranges whilst the solid products obtained for each scale inhibitors were kept for morphological studies of before and after undergoing static adsorption test.

2.3 Synthesis of Nano Si-Ca-DTPMP

The following describes the synthesis process of nano Si-Ca-DTPMP scale inhibitor. The silica nano-slurry (5% wt/wt) was prepared by diluting silica stock slurry with deionized water. The pH of the slurry was then adjusted to 4.5 by adding 1N HCl. Afterward, 0.4M $CaCl_2$ was prepared in deionized water and the solution's pH was adjusted to 4.5 by adding 1N HCl. Next, 15ml $CaCl_2$ solution was dropwise to the 10ml nano-slurry of the silica while stirring the solution with magnetic stirrer at room temperature. The resultant Ca-silica slurry was subjected to be left in 70°C water bath and followed by stirring for about 15 minutes.

Proceeding to the next step, the acidic DTPMP stock solution was diluted with deionized water and the pH of the solution was adjusted to 9 by adding 10M KOH to acquire 0.1M DTPMP solution. Then, 15ml of DTPMP solution was added to the Ca-silica slurry under constant stirring at 70°C by using a burette. White precipitates, in this case, Ca-DTPMP formed immediately once the DTPMP added into the Ca-silica slurry. Once completed, the resultant mixture was gradually added with surfactant formed with respect to the combination of SDBS solution (10% wt/wt, 3ml) and 0.5g PIPES powder under constant stirring [17]. The pH of the solution and the concentrations of the dissolved Ca^{2+} and DTPMP were stabilized for 30 minutes until it remained constant. The resultant nano-suspension was preserved for 30 min at 70°C. The nano-fluid was subjected to sonication for about 15 minutes. The Si-Ca-DTPMP solids were separated by centrifuging the nano-fluid at 8500rpm for 20 minutes. To sum up, the resultant solids were put in oven overnight at 60°C to aid the interstitial water removal process [14]. The products obtained underwent transmission electron microscopy (TEM) for further investigation on the particle size ranges. Furthermore, the solid products obtained for each scale inhibitors were kept for morphological studies of before and after undergoing static adsorption test.

2.4 Static Adsorption Test

Following is the detailed procedure for preparing the essential material for static adsorption test. Adsorption or desorption isotherms provide crucial information on water solid interactions and the

present solid porous structure [18]. In this study, synthetic Nelson Forties Formation Water (NFFW) replicates the formation water in real oil production system was prepared. Thus, the synthesized scale inhibitor was allowed to mix with NFFW and the Kaolinite as mineral rocks was introduced into the mixing to fully imitate the squeeze treatment operation in oil production system. As shown in Table 1, the NFFW was prepared by dissolving appropriate quantities of salts in deionized water with appropriate compositions.

Table 1
NFFW brine composition [17]

Ion	Concentration (ppm)	Composition	Mass (g/2000ml)
Na ⁺	31275	NaCl	159
Ca ²⁺	2000	CaCl ₂ 6H ₂ O	21.86
Mg ²⁺	739	MgCl ₂ 6H ₂ O	12.36
K ⁺	654	KCl	2.5
Ba ²⁺	269	BaCl ₂ 6H ₂ O	0.96
Sr ²⁺	771	SrCl ₂ 6H ₂ O	4.7
Li ⁺	50	LiCl	0.61

In order to let the brine became homogenous, the prepared NFFW was stirred and left for 24 hours. The formation water (FW) brine was filtered to remove any dirt and physical impurities. A blank sample without any scale inhibitor was prepared with 100ml of FW brine solution. Then, 100ppm stock of nano Ca-DTPMP scale inhibitor in FW brine solution was prepared in a 100ml conical flask and 10mg of scale inhibitor powder with FW solution was transferred into a 100ml conical flask until the total volume reached 100ml and stirred thoroughly for 30 minutes. 100ml of FW with 10mg of nano scale inhibitor were added into a glass bottle. Plus, 10g of Kaolinite was weighed and transferred into the glass bottle. The bottle containing the minerals and scale inhibitor stock solution were shook well for thorough mixing and transferred into a 95°C pre-heated oven. The sample was taken out from the oven after 24 hours and filtered through a 10µm pore size filter paper. Filtration process was done at room temperature soon after it was taken out of the oven and left to complete approximately for an hour. The filtrate was transferred onto a petri dish and the filtered sample was placed for an overnight to dry in a 60°C oven. The sample which was Kaolinite with adsorbed or precipitate scale inhibitor was examined under Scanning Electron Microscope (SEM) to observe any morphology changes and the results were discussed. Furthermore, the steps were repeated by using commercial DTPMP, Ca-DTPMP, nano Si-Zn-DTPMP and nano Si-Ca-DTPMP scale inhibitors.

3. Results

To obtain the results in term of the particle size characterization of the synthesized scale inhibitors, the Transition Electron Microscopy (TEM) technique was utilized. In general, nanofluids can be defined as fluids with particle size of less than 100nm [19]. Additionally, Field Emission Scanning Electron Microscopy (FESEM) technique was utilized to examine and analyze the adsorption performance of the synthesized scale inhibitors in the static adsorption test.

3.1 TEM Characterization of Scale Inhibitors

Figure 1 to 5 shows the TEM images of the scale inhibitors considered in this work. From Figure 1, it can be seen that the particle size of the commercial DTPMP was found to be in the range of 263nm to 504nm. Such a range of particle size convinces that the commercial DTPMP is not a nano-

size scale inhibitor. The introduction of Ca in DTPMP was able to reduce the particle size to the range of 164nm to 169nm as seen in Figure 2 for Ca-DTPMP. This shows a great improvement in terms of particle size characterization by introducing Ca element. However, it is worthy to note that the resulting scale inhibitor is still not a nano-size solution since the range of particle size is still larger than 100 nm. On the other hand, it can be seen from Figure 3 that this range drops to 74nm to 108nm for nano Ca-DTPMP which indicates the attainment of nano particle size of this scale inhibitor. Additionally, the result for nano Si-Zn-DTPMP is even better as demonstrated in Figure 4, whereby the particle size of this scale inhibitor ranges from 31nm to 37nm. From the results obtained, it can be seen that the effect of surfactant is significant for nano-synthesis formation [20]. The nano Si-Ca-DTPMP, however results in particle size ranged from 130nm to 135nm as seen in Figure 5. Although it is slightly bigger than the scale for nano-size particles, it is still smaller than the commercial DTPMP.

Based on the results obtained via TEM technique, it can be confirmed that nano Si-Zn-DTPMP yields the smallest particle size among the nano scale inhibitors considered in this work, which is ranged from 31nm to 37nm. Therefore, in terms of particle size characterization, the nano Si-Zn-DTPMP represents the best scale inhibitor among all the scale inhibitors synthesized in this work as it exhibits the smallest particle size which constitutes to higher diffusion coefficient whereby the diffusivity of the particles is inversely proportional to the particle radius [12,21].

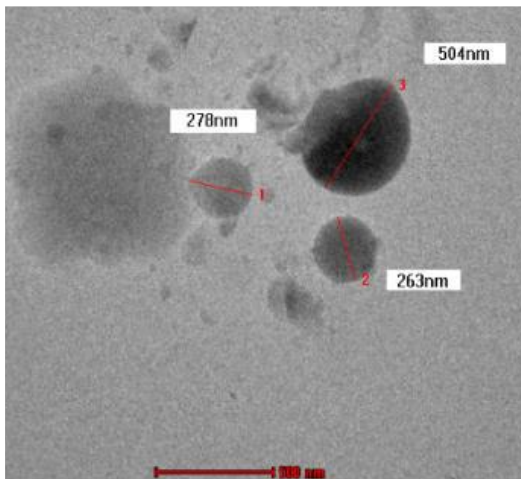


Fig. 1. TEM image of Commercial DTPMP

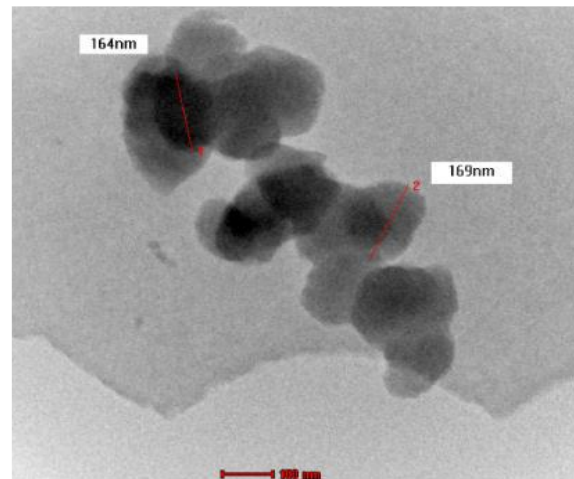


Fig. 2. TEM image of Ca-DTPMP

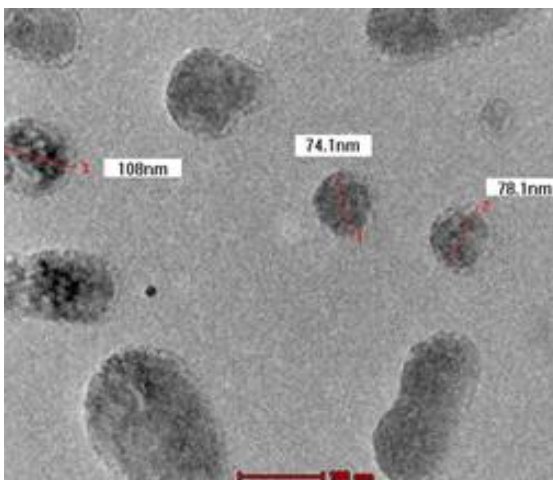


Fig. 3. TEM image of nano Ca-DTPMP

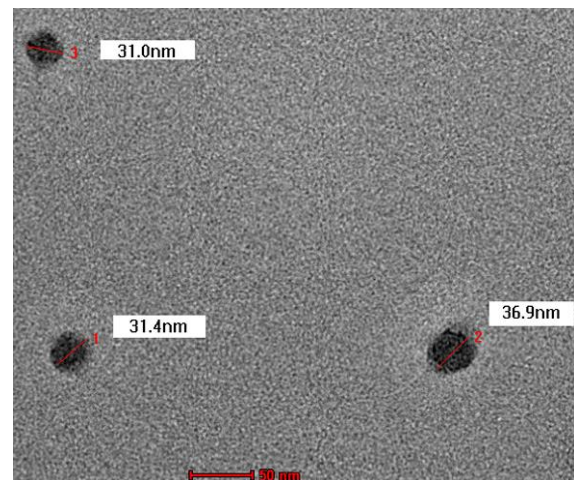


Fig. 4. TEM image of nano Si-Zn-DTPMP

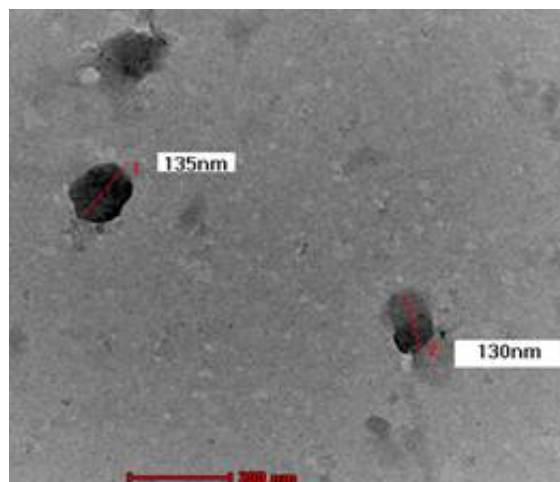


Fig. 5. TEM image of nano Si-Ca-DTPMP

3.2 FESEM Analysis on Static Adsorption Test

As mentioned earlier, static adsorption tests were undertaken to investigate the adsorption morphology of the synthesized nano scale inhibitors onto a selected type of mineral surface that can normally be found in a sandstone mixture. Precisely, sandstone is a mixture of different types of minerals such as quartz, feldspar and Kaolinite [14]. In this study, Kaolinite was the selected mineral surface as it is the most abundant member of the Kaolin group, and also one of the most abundant clay minerals on Earth. Thus, it is one of the common and simplest clay minerals [22]. For the purpose of investigating the adsorption morphology of the synthesized nano scale inhibitors onto Kaolinite surface, the solid products obtained for each scale inhibitors were kept before and after undergoing static adsorption test. Results from Field Emission Electron Microscopy (FESEM) analysis show the morphological changes of the Kaolinite surface after application of the scale inhibitors to determine the effect of such scale inhibitors.

Figure 6 shows the FESEM image of Kaolinite surfaces in the absence of any scale inhibitor, which is referred to as 'blank scale inhibitor'. In this case, only Kaolinite minerals are presented and therefore no adsorption of scale inhibitor has taken place. This figure is important as it indicates the morphology of such surface prior to any adsorption of scale inhibitors. This result acts as a reference to differentiate the initial morphology of the Kaolinite surfaces against the Kaolinite surfaces with adsorption of any type of scale inhibitors. Meanwhile, Figures 7 to 11 present the FESEM results of Kaolinite surfaces upon the adsorption of commercial DTPMP, Ca-DTPMP, nano Ca-DTPMP, nano Si-Zn-DTPMP, and nano Si-Ca-DTPMP, respectively, after undergoing the static adsorption test. From these figures, comparison on how the scale inhibitors adsorb onto and affect the Kaolinite surfaces can be investigated.

Observation to Figure 6 (blank scale inhibitor) reveals that the Kaolinite surfaces have plate like structure which is stacked on top of each other which replicates the mineral rocks in the real process of squeeze treatment in oil production site. This Kaolinite surfaces represents the adsorbent while the synthesized scale inhibitors represent the adsorbate which will be adsorbed onto the Kaolinite surfaces during the static adsorption test [14].

Figure 7 presents the FESEM image of the adsorption of commercial DTPMP onto the Kaolinite surfaces. Based on this figure, it can be seen that most of the Kaolinite surfaces are still visible even with the presence of commercial DTPMP. This shows that the commercial DTPMP is not adsorbed effectively into the spaces available on the Kaolinite surfaces due to its larger particle size which is

affected by the absence of surfactant. However, the shape of the Kaolinite surfaces has become somewhat irregular due to the effect of such adsorption.

Figure 8 presents the FESEM image of the adsorption of Ca-DTPMP onto the Kaolinite surfaces. From this result, it can be seen that the Ca-DTPMP scale inhibitor is not able to be well-adsorbed onto the Kaolinite surfaces especially into gap between the stacks of the Kaolinite structure but its adsorption performance is found to be better than the commercial DTPMP as the plate-like structure of the Kaolinite surfaces are less visible with the adsorption of the Ca-DTPMP.

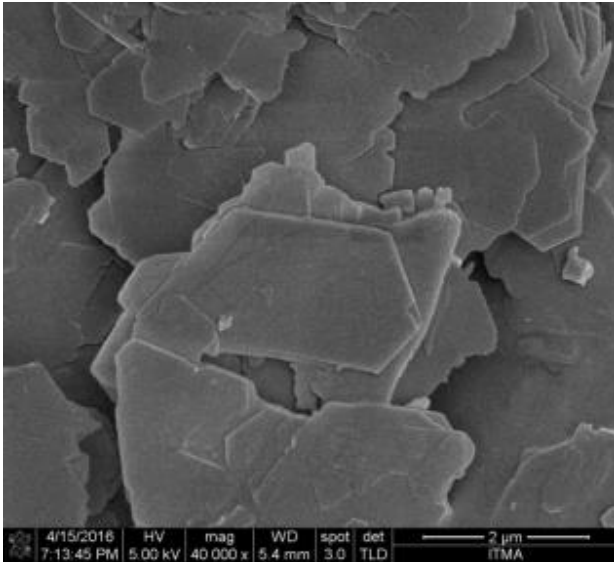


Fig. 6. FESEM image of Kaolinite surfaces without adsorption of any scale inhibitor (blank scale inhibitor)

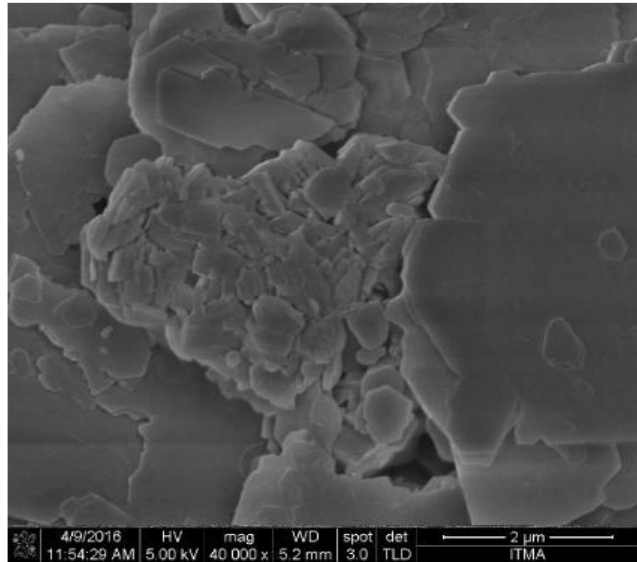


Fig. 7. FESEM image of Kaolinite surfaces with the adsorption of commercial DTPMP

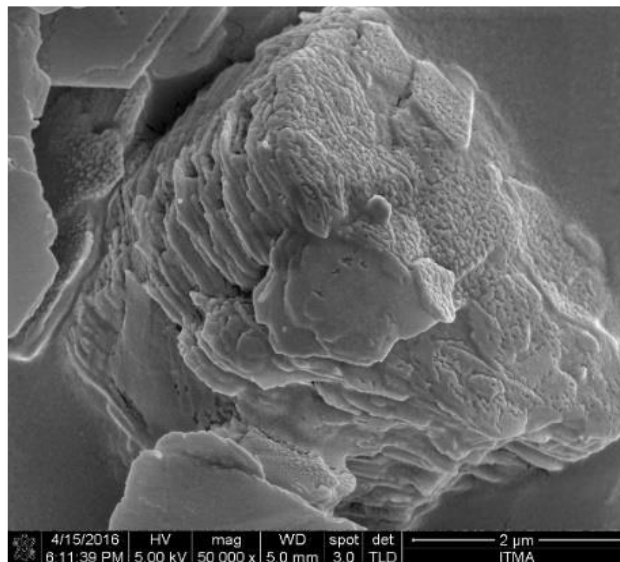


Fig. 8. FESEM image of Kaolinite surfaces with the adsorption of Ca-DTPMP

On the other hand, Figure 9 to 11 demonstrate the adsorption effect of the nano scale inhibitors (nano Ca-DTPMP, nano Si-Zn DTPMP, and nano Si-Ca DTPMP, respectively) onto the Kaolinite surfaces. Observations to these figures indicate differences in morphology of Kaolinite surface with the adsorption of these nano scale inhibitors in comparison to those seen previously for the

commercial and Ca DTPMP scale inhibitors. With adsorption of nano scale inhibitors, the Kaolinite surfaces can be seen to be more uniformly covered by the scale inhibitor particles. Looking at the morphologies in Figure 9 to 11, the nanoparticles have certainly adsorbed onto the Kaolinite surfaces and between the stacking gaps of the plate-like Kaolinite structures. Such morphologies are seen to demonstrate consistency between the three different types of nano scale inhibitors. Additionally, these morphologies can be seen to differ from those for commercial and Ca DTPMP whereby most of the Kaolinite surfaces are still visible and the gaps between the stacks of the Kaolinite structure still exist. This demonstrates the effectiveness of adsorption by the nano scale inhibitors in comparison to the commercial and Ca DTPMP counterparts due to the nano-size particles which result in better adsorption onto the mineral surfaces.

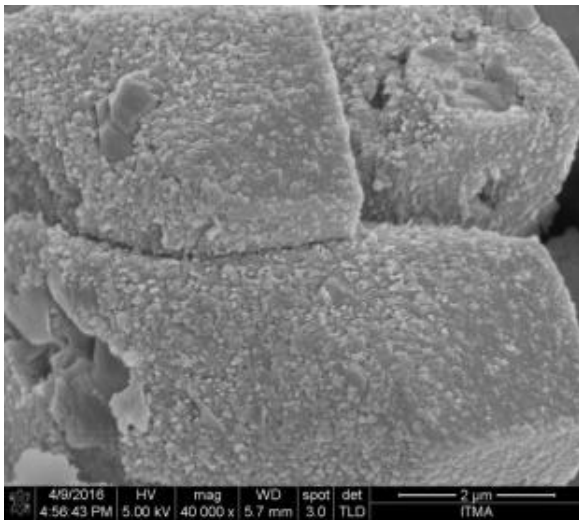


Fig. 9. FESEM image of Kaolinite surfaces with the adsorption of nano Ca-DTPMP

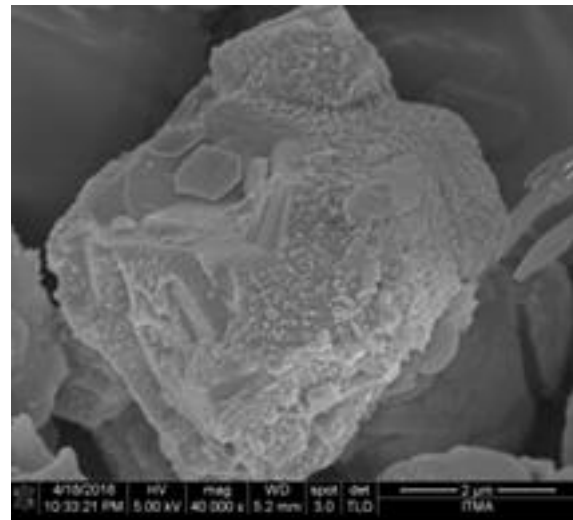


Fig. 10. FESEM image of Kaolinite surfaces with the adsorption of nano Si-Zn-DTPMP

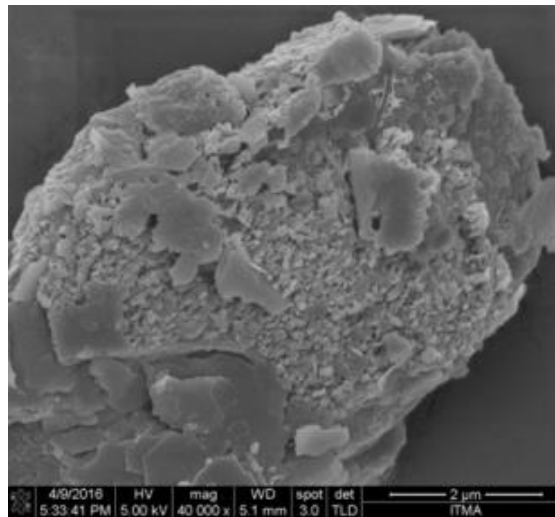


Fig. 11. FESEM image of Kaolinite surfaces with the adsorption of nano Si-Ca-DTPMP

Furthermore, a comparison between the adsorption morphologies of the three different nano scale inhibitors reveals that the nano Si-Zn-DTPMP has covered the Kaolinite surfaces more uniformly as compared to the other two synthesized nano scale inhibitors. This is because nano Si-Zn-DTPMP has the smallest particle size as indicated in TEM analysis. The size of particles for nano Si-Zn-DTPMP

obtained from TEM analysis ranges from 31nm to 37nm; whereas the particle size for the other nano scale inhibitors range from 74nm to 135nm. As a result, this causes the adsorption morphology for nano Si-Zn-DTPMP to be smoother, showing the least plate-like structure of the Kaolinite surfaces as seen in Figure 10. Although the morphology of the Kaolinite surface due to adsorption of nano Ca-DTPMP shown in Figure 9 seems to be smooth, the plate-like structure of the Kaolinite surface is still much noticeable in comparison to those for nano Si-Zn-DTPMP shown in Figure 10, whereby the Kaolinite surface is seen to be much rounder with the least appearance of plate-like structure. This demonstrates that the smaller particles size of the nano Si-Zn-DTPMP results in better adsorption, as supported by the relationship of diffusion coefficient to the particle size [12, 21], whereby the diffusion coefficient increases as the particle size decreases.

4. Conclusions

This paper presents the syntheses and discusses the adsorption morphologies of five phosphonate based scale inhibitors which are commercial Diethylenetriamine Pentamethylene Phosphonic (DTPMP), Calcium Diethylenetriamine Pentamethylene Phosphonic (Ca-DTPMP), nano Calcium Diethylenetriamine Pentamethylene Phosphonic (nano Ca-DTPMP), nano Silica Zinc Diethylenetriamine Pentamethylene Phosphonic (nano Si-Zn-DTPMP) and nano Silica Calcium Diethylenetriamine Pentamethylene Phosphonic (nano Si-Ca-DTPMP). Transmission Electron Microscopy (TEM) analyses were undertaken to determine the particle size ranges for all synthesized scale inhibitors. Results show that the three nano scale inhibitors namely nano Ca-DTPMP, nano Si-Zn-DTPMP, and nano Si-Ca-DTPMP exhibit smaller, nano particle size as expected due to the effect of surfactant presence during the synthesis execution. In specific, nano Si-Zn-DTPMP yields the smallest particle diameter which is ranged from 31 nm to 37 nm. Furthermore, to investigate the adsorption morphology of these nano scale inhibitors onto mineral surface, static adsorption tests were done using Kaolinite as the selected mineral. Results from Field Emission Electron Microscopy (FESEM) analysis indicate the effectiveness of adsorption by the nano scale inhibitors in comparison to the commercial and Ca DTPMP counterparts due to the nano-size particles which result in better adsorption onto the mineral surfaces. In particular, the nano Si-Zn-DTPMP results in smoother adsorption morphology, showing the least plate-like structure of the Kaolinite surfaces due to its nano-size quality. Thus, it can be concluded that nano Si-Zn-DTPMP exhibits the smallest particle size and best adsorption morphology which constitutes to promising scaling inhibition performance to mitigate mineral scale. Whilst, other nano scale inhibitors namely nano Ca-DTPMP and nano Si-Ca-DTPMP also exhibit smaller particle size which is crucial in mitigating oilfield scales better.

Acknowledgement

This research was funded by a grant from Ministry of Education Malaysia (MOE Reference Code FRGS/2/2013/SG06/UPM/02/3).

References

- [1] Azizi, Jaber, Seyed Reza Shadizadeh, Abbas Khaksar Manshad, and Amir H. Mohammadi. "A dynamic method for experimental assessment of scale inhibitor efficiency in oil recovery process by water flooding." *Petroleum* 5, no. 3 (2019): 303-314.
<https://doi.org/10.1016/j.petlm.2018.07.004>
- [2] Kelland, Malcolm A. *Production chemicals for the oil and gas industry*. CRC press, 2014.
<https://doi.org/10.1201/b16648>
- [3] Wang, Qiwei, Feng Liang, Waleed Al-Nasser, Faez Al-Dawood, Tawfiq Al-Shafai, Hameed Al-Badairy, Shouwen Shen, and Hassan Al-Ajwad. "Laboratory study on efficiency of three calcium carbonate scale inhibitors in the presence of EOR chemicals." *Petroleum* 4, no. 4 (2018): 375-384.

- <https://doi.org/10.1016/j.petlm.2018.03.003>
- [4] Cruz, Constanza, Luis A. Cisternas, and Andrzej Kraslawski. "Scaling problems and control technologies in industrial operations: Technology Assessment." *Separation and Purification Technology* 207 (2018): 20-27.
<https://doi.org/10.1016/j.seppur.2018.06.023>
- [5] Issabayev, Yerzhan A., Galina I. Boiko, Nina P. Lyubchenko, Yerengaip M. Shaikhutdinov, Hervé Muhr, Ludovic Colombeau, Philippe Arnoux, and Céline Frochot. "Synthesis of unexplored aminophosphonic acid and evaluation as scale inhibitor for industrial water applications." *Journal of water process engineering* 22 (2018): 192-202.
<https://doi.org/10.1016/j.jwpe.2017.12.007>
- [6] Zhang, Ping, Zhang Zhang, Yuan Liu, Amy T. Kan, and Mason B. Tomson. "Investigation of the impact of ferrous species on the performance of common oilfield scale inhibitors for mineral scale control." *Journal of Petroleum Science and Engineering* 172 (2019): 288-296.
<https://doi.org/10.1016/j.petrol.2018.09.069>
- [7] Sheremetov, L., A. Cosultchi, J. Martínez-Muñoz, A. Gonzalez-Sánchez, and M. A. Jiménez-Aquino. "Data-driven forecasting of naturally fractured reservoirs based on nonlinear autoregressive neural networks with exogenous input." *Journal of Petroleum Science and Engineering* 123 (2014): 106-119.
<https://doi.org/10.1016/j.petrol.2014.07.013>
- [8] Kalpakjian, Serope. *Manufacturing processes for engineering materials*. Pearson Education India, 1984.
- [9] Zeino, Aasem, Muhammed Albakri, Mazen Khaled, and Maan Zarzour. "Comparative study of the synergistic effect of ATMP and DTPMPA on CaSO₄ scale inhibition and evaluation of induction time effect." *Journal of Water Process Engineering* 21 (2018): 1-8.
<https://doi.org/10.1016/j.jwpe.2017.11.013>
- [10] Tavakoli, Hossein Manzari, Mohammad Jamialahmadi, Shahin Kord, and Amin Daryasafar. "Experimental investigation of the effect of silica nanoparticles on the kinetics of barium sulfate scaling during water injection process." *Journal of Petroleum Science and Engineering* 169 (2018): 344-352.
<https://doi.org/10.1016/j.petrol.2018.05.077>
- [11] Muhammad, Nura Mu'az, and Nor Azwadi Che Sidik. "Utilisation of Nanofluids In Minichannel For Heat Transfer and Fluid Flow Augmentation." *Journal of Advanced Research Design* 50, no. 1 (2018): 18-45.
- [12] Teck, John Kia Yu. "Numerical Study of Adsorption Enhancement by Nanoparticles Scale Inhibitor." In *Advanced Materials Research*, vol. 1119, pp. 43-48. Trans Tech Publications Ltd, 2015.
<https://doi.org/10.4028/www.scientific.net/AMR.1119.43>
- [13] Khormali, Azizollah, Anar R. Sharifov, and Dmitry I. Torba. "Increasing efficiency of calcium sulfate scale prevention using a new mixture of phosphonate scale inhibitors during waterflooding." *Journal of Petroleum Science and Engineering* 164 (2018): 245-258.
<https://doi.org/10.1016/j.petrol.2018.01.055>
- [14] Zhang, Ping. "Synthesis and application of phosphonate scale inhibitor nanomaterials for oilfield scale control." PhD diss., Rice University, 2011.
- [15] Kamal, Muhammad Shahzad, Ibnelwaleed Hussein, Mohamed Mahmoud, Abdullah S. Sultan, and Mohammed AS Saad. "Oilfield scale formation and chemical removal: A review." *Journal of petroleum science and engineering* 171 (2018): 127-139.
<https://doi.org/10.1016/j.petrol.2018.07.037>
- [16] Mat A., Fatin N., Siti U. Masuri and Azmah H. M. Ariff. *Synthesis of Nano Calcium Diethylenetriamine Pentamethylene Phosphonic (nano-Ca-DTPMP) Scale Inhibitor and Characterization against Ca-DTPMP Counterpart and Commercial DTPMP in Basic Methodology: Sample Preparation and Characterization*, 2018.
- [17] Ibrahim, Jamal Mohamad Bin Mohamad. "Establishing scale inhibitor retention mechanisms in pure adsorption and coupled adsorption/precipitation treatments." PhD diss., Heriot-Watt University, 2012.
- [18] Arlabosse, Patricia, Élisabeth Rodier, J. H. Ferrasse, S. Chavez, and Didier Lecomte. "Comparison between static and dynamic methods for sorption isotherm measurements." *Drying Technology* 21, no. 3 (2003): 479-497.
<https://doi.org/10.1081/DRT-120018458>
- [19] Abubakar, S. B. and N. A. Che Sidik. "Numerical Prediction of Laminar Nanofluid Flow in Rectangular Microchannel Heat Sink." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 7, no. 1 (2015): 29-38.
- [20] Loh, Boon Hao, Siti Nur Fadhilah Zainudin, Lih Jiun Yu, and Khang Wei Tan. "Water-in-Diesel Nano-Emulsion: A Preliminary Study on Its Formation and Short Term Physical Stability." *Progress in Energy and Environment* 3 (2017): 7-13.
- [21] Abdul K., Muhamad S., Radhiyatul H. Abu, Siti U. Masuri and Abdul A. Hairuddin. "Effect of Initial Concentration and Solution Temperature on Adsorption of Calcium HEDP Scale Inhibitor." *Australian Journal of Basic and Applied Sciences* 9, no. 23 (2015): 376-379.

-
- [22] Detellier, C., and S. Letaief. "Kaolinite–polymer nanocomposites." In *Developments in Clay Science*, vol. 5, pp. 707-719. Elsevier, 2013.
<https://doi.org/10.1016/B978-0-08-098258-8.00022-5>