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Degradation of Water-based Mud Filter Cakes using Environmental Friendly Pullulanase Enzyme

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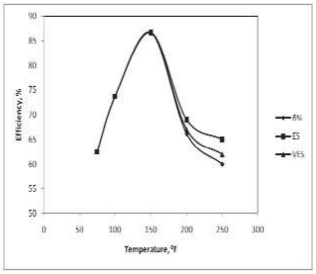
Graphical abstract



Abstract

The filter cake removal is of primary concern in a horizontal oil producer. It has been highlighted in many publications that the cleanup process in long horizontal and multilateral wells is a challenging task. Many chemical solutions have been used to remove the polymeric and bridging agents in oil producers. Due to their nonspecific characteristics, the chemical solutions have their limitations and in some cases have affected the well productivity. Thus an enzyme treatment using Pullulanase had been applied to degrade the mud filter cake of drill-in fluids, which comprised starch and xanthan gum. In this research work, static fluid loss and soaking tests were performed at temperatures ranging from 75^{o}F to 250^{o}F. The experimental results revealed that the efficiency of the cleaning solution comprising Pullulanase in degrading starch and xanthan gum was influenced by solution temperature and its concentration. For 6% concentration of Pullulanase, the highest degrading efficiencies experienced were 63%, 74%, 87%, 66% and 59% at temperatures of 75^{o}F, 100^{o}F, 150^{o}F, 200^{o}F, and 250^{o}F respectively. In terms of concentration, it was found that 6% of Pullulanase gave the optimum efficiency as compared to 7% and 8% concentrations at temperature of 150^{o}F. The experimental results also proved that enzyme stabilizer and viscoelastic surfactant could prevent the deactivation of enzyme activity at temperatures above 150^{o}F.

Keywords: Enzyme activity; enzyme stabilizer; filter cake degradation; Pullulanase; viscoelastic surfactant

Abstrak

Penyingkiran kek turas menjadi perhatian utama dalam pengeluar mendatar minyak. Permasalahan ini telah diketengahkan dalam banyak penerbitan yang menyatakan bahawa proses pembersihan telaga mendatar yang panjang dan telaga berbilang sisi ialah suatu tugas yang mencabar. Pelbagai larutan kimia telah digunakan untuk menyingkir agen polimer dan agen penitian dalam pengeluar minyak. Berikutan ciri-cirinya yang tak khusus, larutan kimia mempunyai penggunaan yang terbatas dan dalam kes tertentu telah menjejaskan kebolehpengeluaran telaga. Sehubungan itu, rawatan enzim yang menggunakan Pullulanase telah diaplikasi untuk menurunkan kek turas bendalir gerudi yang mengandungi kanji dan gam xantan. Dalam penyelidikan ini, ujian kehilangan bendalir statik dan ujian rendaman telah dilaksanakan pada suhu yang berjulat dari 75^{o}F hingga ke 250^{o}F. Hasil kajian membuktikan bahawa kecekapan larutan pembersih yang mengandungi Pullulanase dalam menurunkan kanji dan gam xantan adalah dipengaruhi oleh suhu larutan dan kepekatannya. Untuk kepekatan 6% Pullulanase, kecekapan penurunan tertinggi yang dialami ialah 63%, 74%, 87%, 66%, dan 59% masing-masing pada suhu 75^{o}F, 100^{o}F, 150^{o}F, 200^{o}F, dan 250^{o}F. Dari segi kepekatan, Pullulanase dengan kepekatan 6% telah memberikan kecekapan optimum yang lebih baik berbanding kepekatan 7% and 8% pada suhu 150^{o}F. Hasil kajian turut membuktikan bahawa penstabil enzim dan surfaktan likat-anjal berupaya mencegah daripada berlakunya penyahaktifan aktiviti enzim pada suhu yang melebihi 150^{o}F.

Kata kunci: Aktiviti enzim; penstabil enzim; penurunan kek turas; Pullulanase; surfaktan likat-anjal

■1.0 INTRODUCTION

The technology relating to horizontal, high angle, multilateral, and open hole completion continues to develop from time to time as the oil industry pursues more efficient and cost effective method to drain oil and gas from a reservoir. The success of the technology is closely associated to the type of drilling fluid used in the drilling operation. Drilling fluids, as the first line of defense when drilling an oil well, are designed to form a filter cake on the borehole wall of a permeable formation—a result of filtration into the porous rock. Drill-in fluids (DIF) have been developed as one of the key components in successful horizontal well drilling. These DIF are relatively clean compared to the conventional drilling fluids. They are generally utilized to minimise the effect of formation damage by drilling fluids across a horizontal or high angle open hole completion [1, 2, 3].

The drill-in fluids are generally seawater based system containing polymer loading of starch or cellulose, xanthan gum, and sized calcium carbonate or salt particulate. The starch polymer provides viscosity, friction reduction, and leak-off control. Xanthan is used to provide solids suspension properties for drill cutting removal. The calcium carbonate helps to control lost circulation and it also acts as weighting agent. It has a high solubility in acid in the filter cakes removal process. Generally DIF is typically formulated to deposit a high quality, relatively impermeable filter cake.

Drill-in fluids form a relatively impermeable filter cake on the wellbore wall. A filter cake serves many useful purposes in a drilling operation. The main function is to limit the leak-off of drilling fluid and filtrate into formation. The damage associated with the filter cake is the area of the hole that is closest to the vertical which is also the section that has been exposed to the DIF for the longest period. Filter cake must be removed to achieve the desired production rate. Otherwise, left in place, the filter cake can significantly impede production capabilities causing reduced flow rates, increased near wellbore drawdown, poor production profiles, and ineffective completion process [4].

Filter cake deposited on the formation must be removed prior to running completion and releasing well to production. It can be removed using mechanical and chemically approaches. Past experience revealed that mechanical technique includes circulation of completion brine at relatively high velocity is used to induce sufficient erosion to external filter cake. However, it will create a problem such as to well productivity loss through sanding and water blockage. Conventional chemical treatments, such as aqueous solutions of oxidizers and hydrochloric acid, however, are very reactive and non-specific species. Thus enzyme solution is believed to be capable of complement the weaknesses of those two techniques [1, 5, 6]. In this research work, Pullulanase, an enzyme solution, with degrading capability has been used to degrade starch and xanthan polymer found in drilling mud filter cake. The use of Pullulanase enzyme provides better health, safety, and environment profile than chemical catalysts and oxidizers. Generally it has higher in molecular weight than oxidative breakers, so it tends not to leak-off into the surrounding formation and can also be less susceptible to dramatic changes in activity by trace contaminants.

■2.0 MATERIALS AND EXPERIMENTAL PROCEDURES

This part describes the apparatus and procedures which were used for flow visualization experiments. The experimental system was designed to ensure the drill-in fluids generated filter cake as required for the cleaning process which simulated the real situation.

2.1 Mud Formulation

The water-based mud was used as the laboratory sample. The components that were used as the drill-in fluids are shown in Tables 1 to 3. Cleaning fluids which contained specific enzyme were used to degrade the starch and xanthan gum in drilling fluid filter cake that deposited on a core sample.

Table 1 Composition of water-based mud

Materials	Quantity	Function
Fresh water	1 bbl	Base fluid
Defoamer	0.02-0.04 gal/bbl	Reduce forming action
Biocide	0.01-0.02 gal/bbl	Prevent bacterial degradation
Xanthan gum	1.0-1.2 Ib/bbl	Viscosifier
Starch	2.0 Ib/bbl	Fluid loss control
KCI	97.7 Ib/bbl	Water activity and density
KOH	0.25-0.5 Ib/bbl	pH modifier
$CaCO_3$ fine (8-10 microns)	5.0-8.0 Ib/bbl	Bridging and weighting agent
Sodium sulfite	0.2-0.25 Ib/bbl	Oxygen scavenger
Lubricant	0.4-0.84 gal/bbl	Reduce torque

Table 2 Composition of basic water-based mud

Materials	Quantity	Function
Fresh water	1 bbl	Base fluid
Bentonite	0.75 – 1.0 lb/bbl	Viscosifier
Barite	As required	Weighting agent

Table 3 Composition of industrial-water based

Materials	Quantity	Function
Fresh water	1 bbl	Base fluid
Salt (KCl)	±30 lb/bbl	Water activity and density
Caustic soda (NaOH)	to pH 9.0	pH modifier
Bentonite	0.75 – 1.0 lb/bbl	Viscosifier
Hydro-PAC	1 – 3 lb/bbl	Filtration control agent
Hydro-STAR	4 – 8 lb/bbl	Filtration control agent
Barite	As required.	Weighting agent

2.2 Treatment Solution

Pullulanase enzyme [7] was used to formulate the treatment solution. Three types of treatment compositions were produced as shown in Table 4.

Table 4 Types of treatment solution

Treatment Solutions	Components
1	Pullulanase
2	Pullulanase + Enzyme stabilizer
3	Pullulanase + VES

The enzyme was obtained from Science Technics Sdn. Bhd., Petaling Jaya, Selangor. The enzymes they supplied were manufactured by Novozymes and the product complied with the recommended purify specifications by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) and the Food Chemical Codex (FCC).

The Pullulanase or Promozyme D2 is obtained from Bacillus subtilis organism. It has been declared that the activity unit of the enzyme is 1350 NPU/g. The enzyme was supplied in the form of liquid and yellow in colour. It operated at 65°C as optimum temperature at pH 6.

2.3 Procedures and Apparatus

The procedures started from formulating the water-based mud, testing the rheological properties of the mud, generating the filter cake specifically in static conditions, analysis of the filter cake before, during, and after the treatment processes. Figure 1 shows the flow of the whole experiment.

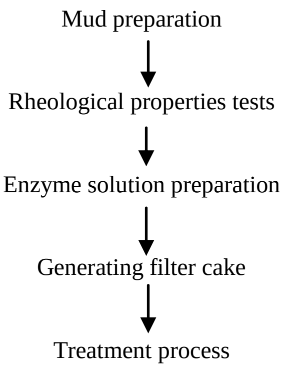


Figure 1 Flow chart of filter cakes degradation process

2.4 Rheological Properties Tests

Rheological properties for industrial samples were obtained by conducting laboratory test in Drilling Engineering Laboratory. All methods were conducted as per API-RP-13B (1) (*American Petroleum Institute-Recommended Practices for Field Testing Water-based Drilling Fluids*, 2009) [8]. The rheological properties for the samples were benchmarked against the industrial water-based mud presented in Table 5.

Table 5 Rheological properties of industrial water-based mud

Properties	Quantity
Density	9.7 ppg
Plastic viscosity	20 cp
Yield point	> 20 Ib/100 ft^2
Gels	7/10/12 Ib/100 ft^2
Filtrate	< 5 cm^3/30 min

2.5 Enzyme Solution Preparation

The enzyme solution was used as the treatment solution to degrade the filter cake. In this research work, the enzyme solution was prepared into two samples. The first sample was according to the percentage of concentration. In addition, the enzyme stabilizer and VES were added in the treatment solution concentration [9]. The typical composition of the treatment fluid is shown in Table 6. The effect of the treatment was measured based on the differences in thickness of the filter cake before and after the treatments. Five samples of treatment fluids were used for each degradation experiment.

Table 6 Typical composition of treatment solution

Components	Concentration
Fresh water	As required to make up the volume
Enzyme	6% – 10% vol
Buffer (KCI)	2% wt/vol
Enzyme stabilizer	0% – 2% vol
VES	0% - 2% vol

Filter cake deposited from each temperature was soaked in every sample up to 48 hours treatment time. The outcome of the treatment solution towards the filter cake degradation was observed at 6 hours, 12 hours, 24 hours, 36 hours, and 48 hours treatment time. The thickness of filter cake before and after treatments was measured prior to calculating the efficiency of degradation in the form of percentage to determine the effectiveness of each sample of the treatment solution in degrading the filter cake. The efficiency of the filter cake degradation was calculated based on the following formula [10]:

where

DE = Degradation efficiency
Tf = Filter cake thickness after soaking
Ti = Filter cake thickness before soaking

2.6 Measurement of Surface Tension

Surface tension is the tension between liquid phase and gas surface. In liquids, van der Waals attraction force within the molecules is the same except for molecule in surface area. The unbalanced attraction force will cause the surface tension happened on that liquid surface. In this research work, the surface tension of treatment fluids was measured using a Du Nouy tensiometer. The measurement unit is in mN/m or dyne/cm. Du Nouy Ring method is the simplest method used to measure the surface tension. However, ring method is very sensitive to the steel size and ring dimension that are being used. The true value of surface tension cannot be obtained without doing the correction. The measurement of surface tension can be divided into three sections, namely the early preparation, measurement procedure, and correction of measurement reading values.

2.7 Measurement of Apparent Viscosity

The main objective of adding viscoelastic surfactant to enzyme was to increase the viscosity of the cleaning fluids [11]. The main function of cleaning fluids was to degrade polymeric material in the filter cake. The apparent viscosity of cleaning fluids was measured at different temperatures using a rheometer. The experiment was conducted as per the API-RP-13B (1) (*American*

Petroleum Institute-Recommended Practices for Field Testing Water-based Drilling Fluids, 2009) [8].

■3.0 RESULTS AND DISCUSSION

The discussion of the experimental results was divided into: soaking process for basic mud, soaking process for industrial mud, effect of ES and VES, apparent viscosity, and surface tension.

3.1 Soaking Process for Basic Mud

Filter cake deposited from basic mud formulation was soaked with different samples of cleaning solution as shown in Table 7. The reaction of cleaning solution in degrading the filter cake was observed until 48 hours at temperatures ranging from 75°F to 250°F. The thickness of the filter cake before and after soaking was measured.

Table 7 Formulation of cleaning solution

Component	Concentration
Fresh Water	As required
Enzyme	6, 7, 8 (%)
Buffer KCl	7.5 gm/1000 ml

It is found that the thickness of the filter cake did not change after soaking process. The results were found to occur in every stage of temperature tested. This is because the enzyme solution could not degrade the filter cake as there was no polymer available in the basic mud.

As mentioned earlier, enzyme works only on targeted substrates. In this case, the Pullulanase enzyme only attacks polymer-based structure. Since the basic mud formulation only consisted of fresh water, bentonite, and barite, thus it did not experience degradation due to the absence of polymer components.

3.2 Soaking Process for Industrial Mud

Filter cakes deposited at temperature ranging from 75°F to 250°F were soaked with three different concentrations of Pullulanase cleaning solution, as shown in Table 8. The thickness of the filter cake before and after soaking was measured. To determine the effectiveness of cleaning solution of each sample, the percentage of efficiency in degrading filter cake was calculated.

Table 8 Sample of cleaning solution

Sample	Cleaning solution (Pullulanase)
1	6%
2	7%
3	8%

At 75°F, the highest value was given by Sample 2 (7% enzyme) which was 66%, followed by 63% from Sample 1 (6% enzyme) and 58% by Sample 3 (8% enzyme). At this temperature, the enzyme degraded the filter cake effectively because of no interruption of its activity.

Next, the experiment was conducted at 100°F. The results for this temperature were presented in Figure 2. Sample 1 (6% enzyme) was found to have given the highest efficiency in degrading the filter cake. The efficiency of filter cake degradation at this temperature was much higher than temperature at 75°F, which was 74%. The second highest efficiency in degrading the filter cake was Sample 2 and followed by Sample 3. The percentages of filter cake removal for the samples were 72% and 65% respectively.

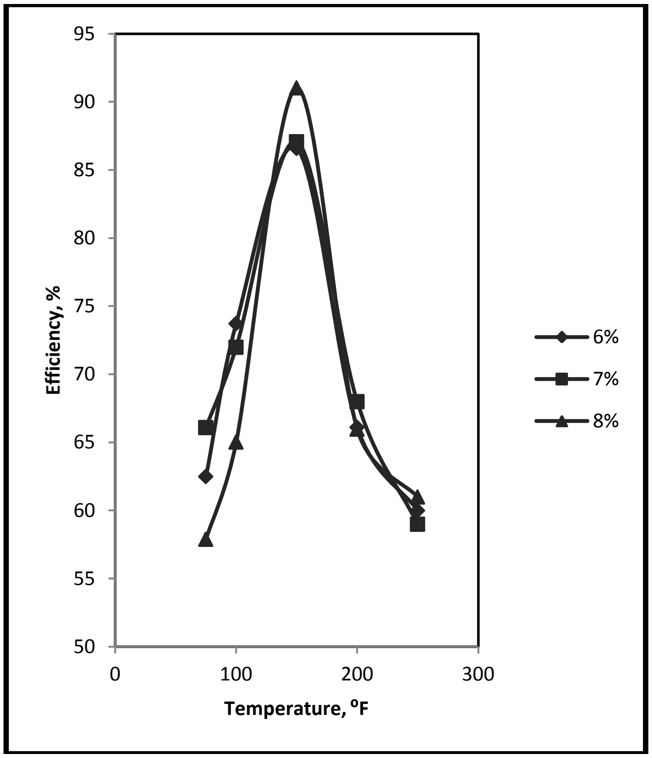


Figure 2 Degrading efficiency versus temperature for different concentrations

The experimental work was continued with soaking the filter cake at 150°F. It was shown that Sample 3 (8% enzyme) gave the highest efficiency in filter cake removal which was 91%. It was followed by Samples 2 (87%) and 1 (87%) respectively. It was noted that at this point of temperature, the degrading activity reached the highest value. The Pullulanase enzyme was found to have worked effectively because it was the optimum environment for the enzyme to do its activity.

However, experimental result at 200°F showed that the degrading activity started to decrease. The highest value obtained by Samples 1 and 2 were 66% and 57% of efficiency, as the enzyme started to reach its point of denaturing because the temperature is no longer optimum for the enzyme to work. The enzyme was coagulated because the secondary and tertiary structures within the enzyme were altered and the enzyme could not return to its original conformation [12].

Based on these values, it could be stated that 150°F was the the best temperature environment for the enzyme to degrade the filter cake. Within its activity range, an enzyme can speed up a reaction as the temperature increased. However, higher temperatures can also denatured the enzyme, so there must be an optimum temperature for a given enzyme [12].

From the aspect of concentration, the results revealed that those three enzyme concentrations (6%, 7%, and 8%) have given higher value of degradation of filter cake which was more than 50%. These provide an evidence that the enzyme concentration used was more than enough to degrade the filter cake. Therefore the optimum concentration of enzyme that best applied in the oilfield was 6% enzyme.

The enzyme activity started to reach a lower point at 200°F. This is because the temperature level was too high for the enzyme to react with the substrate. Thus, at this temperature, the treatment solution started to coagulate as the protein in the enzyme denatured. The temperature edge for use of a given enzyme depends critically on the kinetic turnover, deactivation, and transport. The faster an enzyme can be brought to treatment downhole location, the higher the maximum temperature at which it can be used. Thus, wells with higher bottomhole temperature may still be treated, depending on temperature gradient and the process design. Field treatment procedures must be tuned to bring enzyme to the desired cleanup location downhole at a sufficiently low temperature and for a sufficient time to enable it to degrade the polymer, before the enzyme itself is deactivated by heat along the transportation from surface to downhole location [12].

As shown in the graph, it can be seen that an increase in enzyme concentration caused an increase in degradation efficiency. Higher concentration of enzyme could degrade more polymers in the filter cake. The degradation mechanism occurs where the enzyme binds with the polymer strand in the filter cake and cleave the strand into smaller fragments. As a result, the polymer can be easily removed since the structure of the filter cake has been disturbed.

It could be justified that the optimum temperature for Pullulanase to degrade the filter cake efficiently is at 150°F. As the temperature increases, the speed of the enzymatic reaction also increases. When it reaches 150°F, the maximal reaction of Pullulanase is achieved. Then, the degradation efficiency declines significantly as temperature rises more than 150°F due to the denaturation of protein by heat [13].

3.3 Effect of ES and VES

As stated before, Pullulanase enzyme was actively degrade polymer at temperature of 150°F which is its optimum temperature. As temperatures were increased, the efficiency of degradation became lower due to the deactivation of Pullulanase enzyme. Therefore, ES and VES were introduced in treatment solutions to sustain its activity at temperature above 150°F.

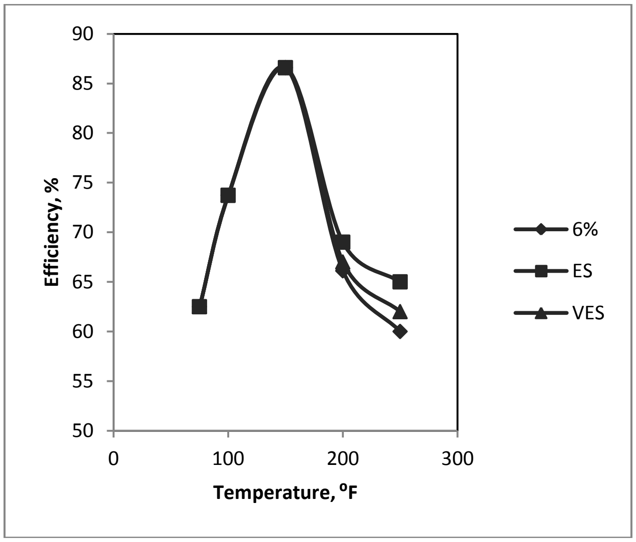


Figure 3 Degrading efficiency in the presence of ES and VES

Figure 3 shows the efficiency of degrading drilling fluid filter cake with and without ES and VES. The efficiency of degradation in the presence of ES gave higher efficiency, i.e. 65%. It increased by 5% as compared to sample without ES. The component of ES used was calcium ion. Most thermostable enzyme gave higher activity at high temperature in the presence of calcium ion. In this research work, it was proven that the presence of calcium ion has increased the efficiency of enzyme at high temperature. The binding of calcium ion can stabilize the special geometry of the enzyme molecule, which makes it more active [14]. At relatively low temperatures, the influence of calcium ion is not significant, but at high temperature, the enzyme will be more thermostable which would lead to higher activity at those temperatures [12].

The graph also showed the effect of VES on degradations efficiency. The presence of VES has succeeded in increasing the degradations efficiency by 2% to 62%. However, it was less by 3% from ES. Generally VES comprises low molecular weight surfactants that form elongated micelle structures. It exhibits viscoelastic behavior that has the ability to increase fluid viscosity. The solution treatments of VES gave a uniform distribution in the whole reaction that has succeeded in improving the speed of starch degradation and could sustain its activity at high temperature [1].

This study proved that the presence of ES and VES were significant in order to sustain the enzymes activity at temperature above 150°F. Both of them are the main components to prevent deactivation of enzyme at high temperature and thus increase the degradation efficiency.

3.4 Apparent Viscosity

This experimental work was conducted to determine the effect of VES on apparent viscosity of cleaning solution. It was compared with the apparent viscosity of cleaning solution without the presence of VES. From Table 9, it could be seen that Sample 1 (with VES) showed the highest apparent viscosity compared with Sample 2 (without VES). Sample with VES gave 5.0 cp of apparent viscosity compared to the solution without VES that only experienced 2.5 cp of apparent viscosity. The experimental result showed that the addition of VES could increase the viscosity of cleaning solution. High value of apparent viscosity is required to increase carrying capacity of the cleaning solution and reduce the fluids invasion into formation [15].

Table 9 Apparent viscosity of cleaning solution

Sample	Cleaning solution	Apparent viscosity (cp)
1	Pullulanase enzyme	2.5
2	Pullulanase enzyme + VES	5.0

3.5 Surface Tension

During the filter cake cleaning, it is expected that some of the fluids used will leak into the formation. These aqueous fluids may be trapped in tight formation by the capillary forces. Therefore, it is very important to determine the surface tension of the cleaning fluids.

Table 10 Surface tension of cleaning solution

Cleaning solution	Surface tension (Mn/m)
6% Pullulanase enzyme	49
6% Pullulanase enzyme + VES	54
6% Pullulanase enzyme + ES	50

Table 10 shows the surface tension of cleaning solution. The surface tension of cleaning solution containing only Pullulanase enzyme was 49 Mn/m. The surface tension was found to have increased marginally after adding VES (54 mN/m) and ES (50 mN/m). The addition VES increased the surface tension especially at high temperature. Low surface tension values are required to minimize formation damage due to water blockage [16]. However, it also depends on the surface tension of reservoir fluids itself. For example, if the surface tension of reservoir fluids higher than cleaning fluids, more cleaning fluids will invade into reservoir formation resulting further formation damage.

■4.0 CONCLUSIONS

Based on the experimental results, there were several conclusions could be framed out accordingly:

(1) The Pullulanase enzyme gave a satisfying value of degradation which was more than 50%.
(2) The optimum concentration of enzyme was 6% at 150°F.
(3) The use of ES and VES was found to have increased the efficiency of degradation of water-based mud cake by 5% and 2% respectively.
(4) The Pullulase enzyme has the potential to be used in water-based mud filter cake removal.

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