Utilization of recycled chemical residues from sodium hydrosulfite production in solid lubricant for drilling fluids

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ABSTRACT

The chemical residues from sodium hydrosulfite production contain complex chemical composition and give out a bad odor posing a grave threat to the environment and public health. The organic residues containing thiodiglycol, 2,2′-dithiodiethanol, and 1,4-thioxane are suitable for high pressure lubrication applications. In this paper, the chemical residues were recycled and used to prepare the solid lubricant for drilling fluids. The lubricity of solid lubricant was illustrated and the experimental results indicated that the solid lubricant could improve lubricity of drilling fluids, which had met the requirement of industrial applications. Experimental studies were also performed on its salt resistance, temperature resistance, and compatibility. The solid lubricant had passed pilot experiments and been used in the Changqing and Dagang oil fields in China. This study not only enables recycling of industrial products but also makes the clean production come true, which contributed to environment protection.

Keywords: Recycled chemical residues; Solid lubricant; Clean production; Lubricity; Drilling fluids

1. Introduction

Sodium hydrosulfite (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}) is a strong reducing agent as an important raw chemical in industry \cite{1,2}. One of the two conventional approaches to produce sodium hydrosulfite is based on the sodium formate (NaCOOH), and the main stoichiometry of the reaction is:

\[ 2\text{HCOONa} + \text{Na}_2\text{S}_2\text{O}_5 + 2\text{SO}_2 \rightarrow 2\text{Na}_2\text{S}_2\text{O}_4 + 2\text{CO}_2 \uparrow \text{+H}_2\text{O} \]

Sodium formate approach is the popular method with the following side reactions:

\[ \text{HCOOH} + \text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 + \text{H}_2\text{O} \]

\[ 2\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaHSO}_3 \]

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Now, the annual output approximates to 600,000 tons all over the world, but for the production of 3 tons of sodium hydrosulfite, 1 ton of the chemical residues is produced which is chemically complex and gives out a bad odor. According to European Waste Catalogue, the organic residues are absolute hazardous. Therefore, proper treatment and recycling of the chemical residues are important to environmental protection and public health [3]. At present, landfill is the main disposal method [4,5], but since this method leads to high economic pressures, it is restricted in industry. Incineration is practiced by some manufactures to reclaim a small number of sodium sulfite but owing to of the large amounts of organic sulfur, sulfur dioxide is emitted to the environment causing acid rain and other issues. However, the chemical residues contain thiodiglycol, 2,2’-dithiodiethanol, and 1,4-thioxane with lubrication and permeation [3,6]. Hence, it could be said that the chemical residues were not only the waste but also the potential raw material for lubricant.

How to deal with the residues is a thorny problem and the safe disposal is critical for public health? According to the reported, the more effective approach to waste management is clean production, a strategy for addressing the generation of pollution as well as efficient use of resources at stages of the production process [7,8]. The clean production is commonly understood as positive economic benefits arising from efficient use of materials and energy. The aim of this paper is to recycle and reuse the chemical residues from sodium hydrosulfite production based on the theory of clean production. In this paper, the chemical residues containing thiodiglycol, 2,2’-dithiodiethanol, and 1,4-thioxane were recycled and used as the lubricating additive in solid lubricant. The solid lubricant named slube based on graphite was prepared by mechanical kneading. The lubricity was investigated from the adhesive coefficient and friction coefficient, and the experimental results indicated the lubricity was so excellent that could achieve the request of industrial applications.

2. Materials and experimental methods

2.1. Materials

The chemical residues from sodium hydrosulfite production were supplied by Shandong Shuangqiao Chemical Co., Ltd. (China). The graphite including flake graphite (FG) and expanded graphite (EG) were obtained from Shandong Province, China. The recycled asphalt was provided by Shijiazhuang Yongfa Asphalt Factory (Hebei, China). All the other lubricating additives, the filtrate reducer and emulsifier were all commercially available. High-quality sodium bentonite was provided by the Tianyu bentonite factory (Henan, China).

2.2. Preparation of bentonite dispersion

The preparation of bentonite dispersion for the experiments was carried out following the American Petroleum Institute (API) standard [9]. High-quality sodium bentonite (26 g) was added into distilled water (500 mL) and the mixture was continuously agitated for 20 min using a high speed mixer at 10,000 rpm. The bentonite dispersion was left in a covered container for 24 h at room temperature for complete hydration. The solid lubricant was stirred for 5 min prior to the lubricity measurements.

2.3. Experimental method

2.3.1. Characterization of material surface

The surface features of the materials were characterized by scanning electron microscopy (FEI-XL30) at the International Centre for Bamboo and Rattan after gold coating.

2.3.2. Test method of slube stability

The thermal stability of slube was analyzed by the thermo-gravimetric analyzer (Netzsch TG209). The heating rate was 10˚C/min. The temperature was set from room temperature to 550˚C.

The rolling oven (BGRL-2) was used to evaluate the temperature resistance of slube. Slube was mixed with bentonite dispersion at the concentration of 1.0%, and then the mixture was rolled in rolling oven at different temperatures (100, 120, 140, 160, and 180˚C) for 16 h, respectively. The lubricity was measured when the temperature of mixture returned to room temperature.

When the salt resistance of slube was determined, sodium chloride (NaCl) was used and its concentrations were determined at 4 and 20%, while the concentrations of slube were 1.0, 1.5, 2.0, 2.5, and 3.0%, respectively. Slube and NaCl was added into bentonite dispersion and continuously agitated for 5 min. Then, the lubricity of bentonite dispersion with slube and NaCl was also measured by the HTD NF-1 differential sticking tester and extreme pressure (EP) lubrication tester, respectively.

2.3.3. Characterization of lubrication

The lubrication of slube was evaluated from the adhesive and friction coefficient. The adhesive
coefficient describing the lubricity of filter cake and imitating the static friction between the drill and borehole wall was measured using the HTD NF-1 differential sticking tester. Slube was mixed with bentonite dispersion according to the ratio of 1/100 and stirred at 10,000 rpm for 5 min. The pressure difference was 3.5 MPa and the filtration time was 30 min. After compacting for 5 min, the torque was monitored for every 5 min and the largest torque was used to calculate the adhesion coefficient by below equation:

\[ K_f = 0.845 \times M \times 10^{-2} \]  

(1)

where \( M \) is the torque. The reduced ratio in adhesion coefficient was calculated by below equation:

\[ \Delta K_f = (K_f - K_{f1})/K_f \times 100\% \]  

(2)

where \( K_f \) and \( K_{f1} \) are the adhesion coefficients of bentonite dispersion before and after slube was added, respectively, while \( \Delta K_f \) was the reduced ratio in adhesion coefficient.

The friction coefficient describing the lubricity of drilling fluids was measured on an EP lubrication tester. Initially, the friction coefficients of distilled water and bentonite dispersion were determined, respectively. Slube was mixed with bentonite dispersion at a ratio of 1/100 and stirred at 10,000 rpm for 5 min. The pressure difference was 150 psi and the EP lubrication tester was rotated at the speed of 60 rpm. Readings were recorded in 5 min and used in the calculation of friction coefficient as:

\[ f = 0.01 \times N \times 34/T \]  

(3)

where \( f \) is the friction coefficient, \( N \) is the reading of bentonite dispersion with slube, while the \( T \) is the reading of distilled water. The reduced ratio in friction coefficient was calculated according to equation:

\[ \Delta f = (f_0 - f_1)/f_0 \]  

(4)

where \( f_0 \) and \( f_1 \) are the friction coefficients of bentonite dispersion before and after slube are added, respectively, while \( \Delta f \) is the reduced ratio in friction coefficient.

Based on the reduced ratio in adhesion and friction coefficient, the total lubrication index (TLI) was calculated according to equation:

\[ TLI = 1.3 \times \Delta K_f + \Delta f \]  

(5)

Normally, the lubricity is described by the reduced ratios in adhesion and friction coefficient, intuitively. According to the enterprise standard (Table 1), the lubricant could be applied in drilling when the reduced ratio in adhesion or friction coefficient is more than 50%.

2.3.4. Characterization of compatibility

According to API standard, the compatibility of slube in bentonite dispersion was evaluated from the density, rheological properties, filtrate loss (FL), and lubricity. The density of drilling fluids was measured by mud balancer at room temperature, and rheological properties were measured by ZNN-D6S-type rotating viscometer. The rheological properties included plastic viscosity (PV), yield point (YP), and gel strength (Gel). FL was measured after 30 min by using an API filter press under a pressure of 100 psi.

3. Design and preparation of solid lubricant

The lubricant including the liquid and solid ones could improve the lubricity of drilling fluids and prevent the pipe-sticking accident [10]. The liquid lubricant is difficult to transport and use, which make the application under restrictions, especially in some remote and freezing areas. In order to ensure the dispersion of solid lubricant in water-based drilling fluids, the solid lubricant should be sufficiently dried without aggregation. Therefore, the solid lubricant should be made from the load materials, lubricating additive, separant, and surfactant.

According to the previous report [11,12], graphite was used as the load material in order to absorb each component for lubricant. Taking the cost and performance into consideration, FG and EG were selected as the load materials. FG with the lamellar structure could cause the sliding friction easily, and provided excellent lubricity. The lamellar structure of FG could be found in Fig. 1(a). EG prepared from graphite intercalated compounds was a kind of hydrophobic carbon materials with macro and mesopores [13–15]. Due to the porous structure of EG, it had a surprising sorption capacity [16] which could render the lubricant drier. The lamellar and porous structure of EG was shown in Fig. 1(b). The lubricity of FG and EG was represented in Table 2. The experimental results indicated that the graphite could hardly provide the lubricity, and the lubricating additive was essential. The chemical residues from sodium hydrosulfite production included inorganic and organic compounds, and the organic residues consisting of mainly...
Table 1
The enterprise standard of solid lubricant for drilling and main property indication of slube

<table>
<thead>
<tr>
<th>Items</th>
<th>Enterprise standard</th>
<th>BIEE&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CBDECL&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Black solid particle or powder</td>
<td>Black solid powder</td>
<td>Black solid powder</td>
</tr>
<tr>
<td>Weight of screen residue (0.90 mm), %</td>
<td>≤10</td>
<td>8.0</td>
<td>7.3</td>
</tr>
<tr>
<td>Moisture, %</td>
<td>≤15</td>
<td>10.0</td>
<td>9.2</td>
</tr>
<tr>
<td>pH value</td>
<td>7.0–9.0</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Level of florescence</td>
<td>≤5.0</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Filter loss</td>
<td>Reduced or unchanged</td>
<td>Reduced</td>
<td>Reduced</td>
</tr>
<tr>
<td>Increment of apparent viscosity, mPa s</td>
<td>≤5.0</td>
<td>4.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Reduced ratio in adhesion coefficient (ΔK&lt;sub&gt;f&lt;/sub&gt;), %</td>
<td>≥50</td>
<td>51.2</td>
<td>56.5</td>
</tr>
<tr>
<td>Reduced ratio in friction coefficient (Δf), %</td>
<td>≥50</td>
<td>53.1</td>
<td>50.9</td>
</tr>
</tbody>
</table>

<sup>a</sup>Beijing Institute of Exploration Engineering.<br><sup>b</sup>CNPC Bohai Drilling Engineering Company Limited.

![SEM micrographs: (a) −100 mesh FG; (b) EG; (c) recycled asphalt; and (d) slube.](image)

Table 2
The lubricity of graphite and residues<sup>*</sup>

<table>
<thead>
<tr>
<th>Items</th>
<th>Flake graphite</th>
<th>Expanded graphite</th>
<th>Residues</th>
<th>Organic residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion coefficient (K&lt;sub&gt;f&lt;/sub&gt;)</td>
<td>0.190</td>
<td>0.207</td>
<td>0.169</td>
<td>0.156</td>
</tr>
<tr>
<td>Reduced ratio in adhesion coefficient (ΔK&lt;sub&gt;f&lt;/sub&gt;), %</td>
<td>8.21</td>
<td>–</td>
<td>18.4</td>
<td>24.5</td>
</tr>
<tr>
<td>Friction coefficient (f)</td>
<td>0.446</td>
<td>0.477</td>
<td>0.417</td>
<td>0.384</td>
</tr>
<tr>
<td>Reduced ratio in friction coefficient (Δf), %</td>
<td>8.43</td>
<td>2.16</td>
<td>14.3</td>
<td>21.18</td>
</tr>
</tbody>
</table>

<sup>*</sup>The addition of samples is determined at 1.0%.
thiodiglycol and 2,2’-dithiodiethanol could be used as the lubricating additive with the formation of thiolate species on the surface from S-S bond cleavage [17]. It could be seen that the inorganic residues are not suitable for lubricant clearly. The inorganic residues were removed by heating the chemical residues at 100˚C for 2 h [3], which permeated and polluted the stratum during the process of drilling. The lubricity of chemical residues was also measured and shown in Table 2. The experimental results indicated that the organic residues could provide the better lubricity, and were more suitable for preparing the solid lubricant. In addition, the animal/vegetable oil was also selected to improve the lubricity.

One of the advantages of solid lubricant is that they are powdery and convenient to transport. As a result, they must be sufficiently dried otherwise they can become pasty and prone to agglomeration. Here, the recycled asphalt was chosen as the separant due to the environmental issues, good performance, low cost, and good sealing characteristics [12]. The structure of recycled asphalt is shown in Fig. 1(c). The fibrous structure could be found in recycled asphalt, and it was a benefit for reducing the filter loss of drilling fluids. In additional, the surfactants with good lubricity and compatibility were used to modify the hydrophilicity of solid lubricant. Other additives such as filtrate reducer and emulsifier were also required in order to enhance the overall performance.

All the raw materials including the load materials FG (50 g), EG (2 g), organic residues (25 g), recycled asphalt (5 g), surfactant (2 g), and other auxiliaries (13 g) are proportionately added to the reactor and

Fig. 2. The lubricity of slube/GD-2 in water-based drilling fluids, (a) the ratio in adhesion coefficient; and (b) the ratio in friction coefficient.

Fig. 3. The TLI of slube/GD-2 in water-based drilling fluids.

Fig. 4. The fluid loss of slube/GD-2 in water-based drilling fluids.
stirred for 30 min to obtain the product (named slube). It should be noted that very little byproducts are produced from this process which is environmentally green. The solid lubricant named slube was prepared according to a suitable formulation and the structure of slube was shown in Fig. 1(d). The surface of graphite was very rough allowing the organic residues and other additives to adsorb effectively. The lamellar graphite absorbed the organic residues and other additives could adhere to the surface of drilling tool fast and realize sliding easily resulting in the low-friction during drilling.

Fig. 5. The evaluation of salt resistance of slube, (a,c) the ratio in adhesion coefficient; and (b,d) the ratio in friction coefficient.

Fig. 6. The evaluation of salt resistance of slube in DTI.
4. Results and discussion

4.1. The lubricity of slube in water-based drilling fluids

After conducting a large number of experiments and adjusting the compounds, the solid lubricant slube was achieved. In order to make a comparison, the commercial solid lubricant GD-2 was introduced. In order to make a comparison, the commercial solid lubricant GD-2 was introduced. The experimental results of lubrication test were shown in Figs. 2 and 3. Compared with the lubricity of slube and GD-2, it could be clearly seen that slube provided the better lubricity in the adhesion coefficient. Though the lubricity of slube in friction coefficient was a bit poor, the lubricity of slube in TLI was significantly better than that of GD-2 (shown in Fig. 3). After the filtrate for 30 min, slube was embedded into the filter cake, and the soft and lamellar structure of graphite adsorbed chemical residues and other lubricating additives could availably reduce the friction between drill pipe and borehole wall, and improve the lubricity of filter cake. Besides the excellent lubricity, slube could provide the less fluid loss than GD-2 (shown in Fig. 4), which was due to the recycled asphalt with fibrous structure. The recycled asphalt was also embedded into the filter cake and the formation of the network structure reduced the fluid loss availably. According to the enterprise standard (Table 1), when the reduced ratio in adhesion or friction coefficient was more than 50%, the additive could be used as the lubricant. Though the reduced ratio in friction coefficient of slube was lower, it could still achieve the requirement of industrial applications.

4.2. The evaluation of salt resistance of slube

During drilling, a large number of inorganic salts including sodium chloride (NaCl), potassium chloride (KCl), and calcium chloride (CaCl₂) penetrate into drilling fluids from the stratum, rendering the additives useless. On the other hand, these inorganic salts are necessary for drilling fluids, and they could be used as the antifreeze agent [18], shale inhibitors, and so on. Hence, the salt resistance of slube was evaluated in detail. The results of lubricating experiments were shown in Figs. 5 and 6. The influence of NaCl and CaCl₂ on the lubricity of slube was obvious. With the increasing concentration of NaCl and CaCl₂, the lubricity became poor, including the adhesion coefficient and friction coefficient. It can be

### Table 3
The compatibility of slube in drilling fluids system

<table>
<thead>
<tr>
<th>Slube (%)</th>
<th>ρ (g/cm³)</th>
<th>PV (mPa s)</th>
<th>YP (Pa)</th>
<th>Gel (Pa/Pa)</th>
<th>FL (mL)</th>
<th>pH</th>
<th>ΔKₜ (%)</th>
<th>Δf (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.06</td>
<td>48</td>
<td>10</td>
<td>2.0/10.0</td>
<td>5.0</td>
<td>9.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>1.06</td>
<td>48</td>
<td>10</td>
<td>2.5/10.5</td>
<td>5.4</td>
<td>9.5</td>
<td>53.06</td>
<td>60.92</td>
</tr>
<tr>
<td>2</td>
<td>1.06</td>
<td>48</td>
<td>11</td>
<td>2.5/10.5</td>
<td>5.3</td>
<td>9.5</td>
<td>56.10</td>
<td>67.21</td>
</tr>
<tr>
<td>3</td>
<td>1.06</td>
<td>49</td>
<td>12</td>
<td>2.5/11.0</td>
<td>5.5</td>
<td>9.5</td>
<td>57.51</td>
<td>75.72</td>
</tr>
<tr>
<td>4</td>
<td>1.06</td>
<td>50</td>
<td>13</td>
<td>2.5/11.0</td>
<td>5.0</td>
<td>9.5</td>
<td>58.19</td>
<td>77.65</td>
</tr>
<tr>
<td>5</td>
<td>1.06</td>
<td>53</td>
<td>13</td>
<td>2.5/11.0</td>
<td>4.8</td>
<td>9.5</td>
<td>59.02</td>
<td>78.14</td>
</tr>
</tbody>
</table>

*6% bentonite + 1% Slube + 0.3% CMC + 0.2% SM-1 + 0.3% HMS + 0.3% FT-3 + 0.2% NaOH.*
explained that the inorganic salt invaded drilling fluids, and destroyed the function of additives. However, the lubricity of drilling fluids could be improved with the increasing content of slube. Consequently, the lubricity of drilling fluids could be controlled by adjusting the concentration of slube during the process of drilling.

4.3. The evaluation of temperature resistance of slube

With the rapid development of drilling technique, the well was drilled deeper and deeper which results in an increase in the wellbore temperature, continuously. When the depth of well is 7,000 m, the bottom-hole temperature is about 180°C, and the additives become invalid possibly. As a result, the temperature resistance of slube should be evaluated comprehensively. In this section of experiments, slube was added into the bentonite dispersion at the concentration of 1.0%, and then the bentonite dispersion with slube was rolled at different temperatures (100, 120, 140, 160, and 180°C) for 16 h, respectively. The lubricity of mixture was determined until the temperature was cooled to the room temperature, and the results were shown in Fig. 7. The lubricity of slube showed a slight decrease with the increasing temperature. When the temperature reached 180°C, the reduced ratio in adhesion coefficient decreased to 48.98% from 53.06%, while the reduced ratio in friction coefficient was 55.60%, which still fulfilled the requirement of industrial application. In order to analyze the thermal stability of slube, thermo-gravimetry (TG) was applied, and the result could be seen in Fig. 8. The decomposition temperature of slube was about 195°C. The loss capacity of slube was mainly related to the

Table 4
Comparative evaluation data of lubrication for different water-based drilling fluid systems

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula of drilling fluids</th>
<th>ΔKf (%)</th>
<th>Δf (%)</th>
<th>DTI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyalcohol drilling fluid</td>
<td>H₂O + 4%bentonite + 2% SYP-1 + 0.2% KPAM + 1% LY-1 + 2%HFT-301 + 3%SMP + 1% Slube</td>
<td>53.6</td>
<td>52.8</td>
<td>122.48</td>
</tr>
<tr>
<td>Organic salt drilling fluid</td>
<td>H₂O + 0.3% Na₂CO₃ + 0.1% KOH + 0.1% XC + 2% NFA-25 + 2% NPAN + 1% Slube</td>
<td>46.7</td>
<td>42.6</td>
<td>103.31</td>
</tr>
<tr>
<td>Solid-free drilling fluid</td>
<td>H₂O + 0.15% PAM-3 + 0.1% KPAM-1 + 1% KCl + 1% Slube</td>
<td>51.7</td>
<td>54.9</td>
<td>122.11</td>
</tr>
<tr>
<td>Polysulfide drilling fluid</td>
<td>H₂O + 3% bentonite + 0.1% FA-367 + 3% SMC + 3% SMP-2 + 3% SPNH + 1% Slube</td>
<td>54.8</td>
<td>53.1</td>
<td>124.34</td>
</tr>
</tbody>
</table>

Table 5
Feedback results in field applications (times of pipe-sticking accidents)

<table>
<thead>
<tr>
<th>Well #2</th>
<th>Well #3</th>
<th>Well #4</th>
<th>Well #5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twice</td>
<td>None</td>
<td>Three times</td>
<td>None</td>
</tr>
</tbody>
</table>

*6% bentonite + 0.10% CMC + 0.02% XCD + 0.06% PAC + 2% Slube + 2% FT-1 + 0.1% NaOH.

explained that the inorganic salt invaded drilling fluids, and destroyed the function of additives. However, the lubricity of drilling fluids could be improved with the increasing content of slube. Consequently, the lubricity of drilling fluids could be controlled by adjusting the concentration of slube during the process of drilling.

Table 6
The evaluation indexes of heavy metals and biological toxicity test

<table>
<thead>
<tr>
<th>Name</th>
<th>Item</th>
<th>Limit value (mg/kg)</th>
<th>Detection value (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy metals test⁵</td>
<td>As</td>
<td>2.5</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td></td>
<td>Ba</td>
<td>10</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>5</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td></td>
<td>Cr⁶</td>
<td>5</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>5</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>5</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>5</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>5</td>
<td>&lt;5.0</td>
</tr>
<tr>
<td>Biological toxicity test⁶</td>
<td>LD₅₀ for acute oral toxicity</td>
<td>200</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>LD₅₀ for acute dermal toxicity</td>
<td>1,000</td>
<td>879</td>
</tr>
</tbody>
</table>

⁵Detection method: ASTM F963 method.

water before 100°C. The loss capacity of slube showed a sharp decrease from 195°C, which was due to the decomposition of organic residues and lubricating additives in slube. As a result, it can be stated that the decomposition temperature of slube was about 195°C. Taking the results into consideration, slube could provide the excellent temperature resistance, and be applied in the ultra deep well (about 7,000 m). In addition, slube contained graphite and asphalt, which was a benefit for improving the sealing ability and sloughing prevention under the environment of high temperature.

4.4. The compatibility of slube in drilling fluid system

As slube was used in drilling fluid system, its compatibility among the various additives was important. The compatibility of slube was characterized and the experimental results were shown in Table 3. From the results, it can be seen that there were no obvious change in the rheological properties and filter loss, and the lubricity of drilling fluids were improved with the increasing concentration of slube. Hence, slube could provide the excellent compatibility in drilling fluids.

In order to evaluate the lubricity of slube all-sidedly, four kinds of water-based drilling fluid system was applied, including the polyalcohol drilling fluid, organic salt drilling fluid, drilling fluid solid-free drilling fluid, and polysulfide drilling fluid. The experimental results (shown in Table 4) indicated that slube could provide the good lubricity properties, except the organic salt drilling fluid. Now, slube had been adopted by the Changqing and Dagang oil fields in China, and the feedback results were shown in Table 5. Slube was used in the #3 and #5 wells in the oil field, respectively. From Table 5, compared to the #2 and #4 wells without adding slube, pipe-sticking accidents didn’t occur in #3 and #5 wells, confirming the enhanced efficacy of the new materials in the field.

4.5. Benefit analysis

The evaluation indexes of slube including heavy metals and biological toxicity test was measured, and the test results were shown in Table 6. It could be clearly seen that the lubricant contains few heavy metals and weak biological toxicity, which could avoid the secondary pollution of the environment. According to market research, the lubricant for drilling fluids includes two primary types, the liquid and the solid. Compared to the oil-based liquid lubricant (≥12 CNY/kg), the water-based liquid lubricant (≥6.5 CNY/kg) with inferior lubricity could provide the large cost advantages. However, the liquid lubricant not only becomes restricted by environmental regulations with more serious environmental problem, but it is difficult to transport and use, which make the application under restrictions, especially in some remote and freezing areas. Consequently, the solid lubricant has become the hot research in the drilling field, mainly including graphite (≥5.5 CNY/kg), plastic pellet (≥8.5 CNY/kg), slube (≥5.2 CNY/kg), et al. Besides the high added-value lubricant, utilization of recycled chemical residues in solid lubricant could reduce the waste handling costs for enterprise, and eliminate environmental pollution and threat to public health, which conforms to the requirements of clean production perfectly.

5. Conclusion

The chemical residues from sodium hydrosulfite production could be recycled and converted to the usable industrial products, which could make the clean production come true and bring the positive environmental and economic profits. The solid lubricant named slube based on the chemical residues was prepared by optimization of residues, choice of load materials, and lubricating additives. Slube could provide the excellent lubricity, salt resistance, temperature resistance, and compatibility, and it could be used for drilling in ultra deep well.

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