Extraction and Determination of Residual Ester in Ester Hardened Sodium Silicate Sand

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Abstract. The residual ester in sodium silicate sand and recycled sand has an important influence on the performance of recycled sand. In this paper, a new method to extract and detect residual esters in water sodium silicate sand and regenerated sand is established. The residual ester of ester hardened water sodium silicate sand was extracted by the extractor using petroleum ether, ethanol, acetone and other solvents. After hydrolysis of residual ester in extracts, the content of acid was determined by means of neutralization titration. The content of the residual ester was determined by using acid base titration test. The experimental results are obtained through the study of extraction solvent, extraction temperature, extraction time and liquid solid ratio. Based on the single factor experiment, the optimum extraction process was determined by using the four-factor three-level orthogonal test to optimize the extraction conditions. The best extraction technology: extraction solvent for petroleum ether, extraction temperature is 80 °C, extracting time 1.5 h. This study lays the foundation for evaluating the performance of sodium silicate regeneration sand.

1. Introduction
Ester hardening sodium silicate sand good rolled and better dispersed, small gas evolution, non toxic tasteless, to the environment pollution-free, low production cost, is to realize the casting of the 21st century green industry clean production new technology [1-3]. Because organic ester curing agent mixed with sodium silicate, sodium silicate in sodium silicate in the alkaline medium, the organic ester hydrolysis, decomposition of alcohol and acid, organic acid react with sodium silicate and hardening stage by stage, in fact, the organic ester hydrolysis could not have reached 100%, and part of the residue [4-6]. In the ester hardening regeneration recycle process of sodium silicate sand, sand in the residual organic ester has a great influence on performance of reclaimed sand, residual ester and Sodium silicate can produce chemical reaction, the ester hardening sodium silicate dry reclaimed sand can use shorter time, bond strength decreased [7-8]. Visible, the determination of residual ester analysis of sodium silicate sand ester hardening of reclaimed sand and equipment performance evaluation is important, but also did not see the analysis method of residual ester in research of sodium silicate sand [9].

In this paper, using organic solvent extracted by extraction method of sand residual ester, then extract after rotary evaporation residue ester, by acid-base titration analysis to determine the saponification value in the evaluation of residual ester extraction effect and the amount of residual ester. In detail the effects of different solvents and extraction conditions were studied, in order to establish ester hardening
residual ester method lays the foundation of sodium silicate sand, this method can be used in the lab and production field and the performance test of reclaimed sand work of sodium silicate sand, convenient guidance of sodium silicate sand and the application of reclaimed sand.

2. Experimental part

2.1. Main instruments and reagents
DHG-9030a type electric heating and temperature drying oven; RE-52AA rotary evaporator; Electric thermostatic water bath pan; KI-up-uv-10 pure water machine; Extraction device; SHN roller mixer.

0.362 mol/L sodium hydroxide solution; 0.665 mol/L hydrochloric acid solution; Phenolphthalein indicator; Pure water; Low, the boiling point of solvent oil, acetone and petroleum ether and so on are analytically pure.

2.2. Experimental methods
The sand of ester hardened Sodium silicate, the sample method: the original sand is the local foundry sand, and the MDT- series organic ester is used as Sodium silicate. The organic ester is in accordance with standard and is slightly yellow and transparent liquid, slightly soluble in water. Boiling range: 180 ~ 290 °C, has general chemical properties of the resin, under the condition of alkali hydrolyzed easily into alcohol and acetic acid. The amount of Sodium silicate was 3.5% of the original sand, and the organic ester was 12% of the Sodium silicate. According to the conventional sand mixing process in a rolling wheel sand mixing machine mixing, sand hardening after 24 h, 105 °C drying. Set aside.

During the test, 100 g (accurate to 0.1 mg) of the above Sodium silicate samples were taken respectively, and the sample was loaded into pre-prepared filter cartridge, and the residual ester in the sand was extracted by the soxler extraction method. By adjusting the temperature (80 ~ 100 °C), the extraction time was 0.2 ~ 0.5 hours. The extraction of residual ester is carried out according to the following process.

Analysis of saponification value of residual ester of liquid extract: the saponification value of residual ester was determined by titration of acid base, thus the content of organic acid of residual ester hydrolysis was obtained. The saponification values were determined according to the literature. Analysis procedure:

Transfer the residual ester into a conical bottle and add a proper amount of pure water as titration test sample. Use pipette to 10.0 mL potassium hydroxide or sodium hydroxide standard solution to add to the sample, connects the reflux condenser pipe and conical flask, and put the conical flask on the heating device and simmer, maintain boiling state 10 to 30 min, carries on the saponification reaction:

\[
\begin{align*}
C_3H_5(OCOR) _3 + H_2O & \rightarrow 3RCOOH + C_3H_5(OH) _3 \\
RCOOH + NaOH & \rightarrow RCOONa + H_2O
\end{align*}
\]

Then, add 0.5~1mL of phenolphthalein indicator in the hot solution, and titrate excessive alkali with standard hydrochloric acid solution, titration to the indicator pink just disappear:

\[
NaOH + HCl \rightarrow NaCl + H_2O
\]

The saponification value is calculated by the amount of acid base consumed and the quality of the sample. The arithmetic mean of the two parallel measurement results is determined by the error: the absolute difference between the two parallel measurement results is not greater than 0.30%.

According to the previous test results, the calculation can be done.

\[
\text{Saponification value} = \frac{C \times (V_0 - V_1) \times k_{mNa} \times G}{m_{Na}} \text{ (mg / g)}
\]

Form medium:

\[
V_0—\text{the volume of hydrochloric acid consumed by blank test, mL;}
V_1—\text{the volume of hydrochloric acid consumed by the sample, mL;}
C—\text{the actual concentration of hydrochloric acid, mol/L;}
G—\text{Sample quality, g;}
k_{mNa}=40—\text{Using sodium hydroxide standard solution, g / mol;}
\]
kmK=56.1—Use the standard solution of potassium hydroxide, g / mol.

3. Experimental results and analysis
Orthogonal experiment on the basis of single factor experiments, selecting has obvious influence on the residual ester extraction yield of extraction solvent, extraction temperature, extraction time, liquid-solid ratio and other four factors in orthogonal experiments, the extraction conditions into the L₉ (3⁴) line optimization. The orthogonal experimental factors are shown in table 1.

| Table 1. Factors and levels of orthogonal test |
|----------------|----------------|----------------|----------------|
| Level |
| Factor |
| Solvent | Temperature (°C) | Time (min) | Liquid-solid ratio (mL / g) |
| 1 | ethanol | 60 | 30 | 2.0 |
| 2 | Petroleum ether | 80 | 60 | 2.5 |
| 3 | acetone | 100 | 90 | 3.0 |

The residual ester of the old sand was extracted separately according to different conditions, then the analysis was titrated and the results were shown in table 2.

| Table 2. Compare different test method test result |
|----------------|----------------|----------------|----------------|
| NO |
| Solvent | Temperature (°C) | Time (min) | Liquid-solid ratio(mL / g) | Saponification value(mg / g) |
| 1 | 1 (ethanol) | 1 (60) | 1 (0.5) | 1 (2.0) | 0.066 |
| 2 | 2 | 2 (80) | 2 (1.0) | 2 (2.5) | 0.083 |
| 3 | 3 | 3 (100) | 3 (1.5) | 3 (3.0) | 0.095 |
| 4 | 2 | 2 | 3 | 0.086 |
| 5 | 2 | 2 | 3 | 1 | 0.099 |
| 6 | 2 | 3 | 1 | 2 | 0.090 |
| 7 | 3 (acetone) | 1 | 3 | 2 | 0.087 |
| 8 | 3 | 2 | 1 | 3 | 0.082 |
| 9 | 3 | 3 | 2 | 1 | 0.085 |
| K1 | 0.244 | 0.239 | 0.238 | 0.25 |
| K2 | 0.275 | 0.264 | 0.254 | 0.26 |
| K3 | 0.254 | 0.27 | 0.281 | 0.263 |
| R | 0.031 | 0.031 | 0.044 | 0.013 |

3.1. Selections of solvents
According to the properties of dissolved hardening sodium silicate ester and the nature of the regeneration of sodium silicate sand residue, select 95 % ethanol and petroleum ether (60 - 90 °C b.p.), acetone as solvent, respectively study the extracting efficiency of various solvents. According to the result of experiment shows that this experiment adopts the petroleum ether (60 - 90 °C b. p.) as solvent to extract the residual ester effect is best.

3.2. Extraction temperature
Petroleum ether and acetone are easy to volatile organic compounds and easy to burn, the average extraction temperature was 60 °C, should not be infinite in order to speed up the return rate and raise the temperature (reflux rate generally 5 ~ 10 times per hour), extraction temperature can appropriate increase in winter, generally is 80 °C. 95 % ethanol is the boiling point of 78.4 °C, 60 °C were used in this
experiment, 80 °C and 100 °C to experiment, found 100 °C for the extraction of residual ester effect is best.

3.3. Extraction time
When the liquid color is transparent, it can be tested and confirmed. The test method is to extract the droplet on the filter paper under the drop of the lower mouth of the lipid pipe, and the removal of the liquid leaves no trace after evaporation. During the experiment, the residual ester was found to be 1.2-1.5 h.

4. Sample detection
To verify the feasibility of the determination of residual ester method, take 500 g of new sand, add 50 g sodium silicate, respectively, in one of the four samples respectively, add 2, 4, 6, 8, 10 g ester, 1 remaining without ester, made five samples of sodium silicate sand simulation. According to the test method, four simulated samples of the ester were measured, and the results were shown in table 3, and \( \omega_1 \) was the quality fraction of the ester in the sample of Sodium silicate sand, and the samples were blank samples with the simulated samples without the ester. Table 3 shows that the determination of ester content is basically consistent with the theoretical value.

| Table 3. the content of ester in simulation samples of sodium silicate sand |
| --- |
| NO | theoretical value \( \omega_1 \) / % | Found \( \omega_1 \) / % | RSD(n = 5) |
| 1 | 0.363 | 0.351 | 1.03 |
| 2 | 0.727 | 0.702 | 1.09 |
| 3 | 1.090 | 1.068 | 0.97 |
| 4 | 1.454 | 1.431 | 0.99 |
| 5 | 1.851 | 1.833 | 0.98 |

Take 1 kg of sodium silicate sand foundry ester hardening, into the DHG - 9030 type a thermostatic drum wind drying oven, adjust the temperature to 108 °C, drying to constant weight. According to the test method, the content of ester was shown in table 4, and \( \omega_2 \) was the quality fraction of the ester in the old sand sample of the Sodium silicate. Table 4 can be obtained: the determination of the ester content in the old sand of the Sodium silicate is obtained, and the method is consistent with the extraction method.

| Table 4. The content of ester in used sodium silicate sand |
| --- |
| NO | proposed method | RSD(n = 5) | titration method | RSD(n = 5) |
| 1 | 2.67 | 1.12 | 2.72 | 1.21 |
| 2 | 2.84 | 1.22 | 2.91 | 1.15 |
| 3 | 2.61 | 1.05 | 2.68 | 1.21 |
| 4 | 2.68 | 1.13 | 2.72 | 1.22 |
| 5 | 2.62 | 1.04 | 2.68 | 1.20 |

Take a foundry ester hardening sodium silicate sand regeneration 1 kg, into the DHG - 9030 type a thermostatic drum wind drying oven, adjust the temperature to 108 °C, drying to constant weight. According to the test method, the results of the determination of ester are shown in table 5, and \( \omega_3 \) is the quality fraction of ester in the old sample of Sodium silicate. Table 5 is available: for determination of ester content in the old sand of Sodium silicate, the results of this method agree with the extraction method.
### Table 5. The content of ester in reclaimed sodium silicate sand

| NO | proposed method | titration method |
|----|----------------|-----------------|
|    | Found $\omega_3$ / % | RSD (n = 5) | Found $\omega_3$ / % | RSD (n = 5) |
| 1  | 0.79           | 1.19           | 0.76           | 1.24           |
| 2  | 0.80           | 1.23           | 0.71           | 1.29           |
| 3  | 0.78           | 1.15           | 0.68           | 1.23           |
| 4  | 0.79           | 1.18           | 0.75           | 1.26           |
| 5  | 0.78           | 1.13           | 0.69           | 1.22           |

### 5. Conclusion

Casting production using organic ester are mixed ester, hydrolysis rate is different, so the extraction solvent, extraction temperature, extraction time, liquid-solid ratio sets the threshold respectively, and a large number of experiments. Based on the single-factor experiment, the optimum extraction process was determined by using the four-factor three-level orthogonal test to optimize the extraction conditions. Soxhlet extraction and sand in the residual ester, saponification value as the evaluation indexes, through orthogonal experiment the optimum process conditions for: petroleum ether as extraction agent, the extracting time 1.5 h, the temperature is 80 °C, liquid-solid ratio 3:1 mL / g, saponification value is 0.099 mg / g.

Compared with the results of gas chromatograph, the method of determination of residual ester in the old sand of Sodium silicate by instrument has the characteristics of high accuracy and stable reliability. Moreover, this method can be used in the lab and production field and the performance test of reclaimed sand work of sodium silicate sand, convenient guidance and the application of the reclaimed sand of sodium silicate sand, in order to establish residual ester of sodium silicate sand ester hardening method laid a foundation.

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