Reduced pressure distillation method for determining the acetic acid salt in sodium silicate sand

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Abstract. The residual acetate in sodium silicate sand and regenerated sand has an important influence on the performance. This paper presents a method to separate and determine the residual acetic acid in the used sand. Using sulfuric acid solution as solvent, acetic acid generated by acetic acid was extracted by decompression distillation. The content of acetic acid was determined by titration, and the content of acetate was determined by titration. On the basis of single factor test, the extraction conditions were optimized by using four factors of orthogonal test, and the optimum extraction process was determined. The best extraction technology: distillation temperature 100 °C, 50 min distillation time, solvent concentration 1.0 mol/L, vacuum pressure 0.06 MPa. The method is used to determine the content of acetic acid in the sample of water sodium silicate sand, the measured value is consistent with the theoretical value, and RSD is less than 1.1 %. The determination of the content of acetic acid in the old sand and regenerated sand of sodium silicate was measured, and the measured value was in line with the measured value of the extraction method, and RSD was less than 1.3 %. This study lays the foundation for evaluating the performance of sodium silicate sand and recycled sand.

1. Introduction
Sodium silicate is colorless, tasteless, non toxic, in modeling, hardening and casting process, will not release the stimulating or harmful substances, so it is clean and pollution-free green sand binder [1, 2]. Residue of sodium silicate sand Na$_2$O quantity is higher, the more difficult the regeneration of sodium silicate sand. A large amount of waste sand put into environment alkaline pollution [3, 5]. The residual amounts of Na$_2$O in sodium silicate sand, the higher the recycling sex. Can be roughly divided into insoluble residue Na$_2$O (5 % ~ 10 %), soluble (30 % ~ 40 %) and solution (50 % ~ 65 %) of three parts, including soluble part with sodium acetate or scattered state of sodium carbonate in the waste Sodium silicate membrane [6,7]. Sodium acetate is strong electrolyte, can reduce the potential of colloidal particles and make colloidal particles condensed, deteriorating recycling sand available time, and thermal decomposition under the pouring temperature, erosion deterioration of silica sand and silica sand refractoriness [8]. The regeneration of sodium silicate sand, must to remove residual sodium acetate as far as possible, the determination of residual sodium acetate of sodium silicate sand analysis of reclaimed sand and equipment performance evaluation has important significance [9].
Based on the reduced pressure distillation, distillation temperature are discussed in detail, distillation time, solvent concentration and vacuum pressure influence on the determination results, in order to establish the analysis of residual acetic acid salt of sodium silicate sand laid a foundation. This method is easy to operate, high efficiency, low production cost, can be used in the laboratory and production site performance test of sodium silicate sand, convenient to guide the application of sodium silicate sand.

2. Test section

2.1. Main instruments and reagents
Distillation bottle; Distillate head; Capillary; Thermometers and condensing pipes; Receiver; Circulating water vacuum pump; Dhg-9030a type electric heating and temperature drying oven; Electric thermostatic water bath pan; Kl-up-uv-10 pure water machine; SHN roller mixer.

2.2. Test equipment
The vacuum distillation unit consists of four parts: distillation, extraction (decompression), safety protection and pressure measurement. The distillation is composed of distilling bottle, gram distillation head, capillary tube, and thermometer and condenser tube. Pump the air part with a vacuum pump. Safety protection is used in safe bottles. The pressure gauge adopts the manometer.

![Device of reduced pressure distillation](image)

**Figure 1.** Device of reduced pressure distillation

2.3. Experimental principles
Sodium acetate and sulfuric acid reacted with sodium sulfate and acetic acid, and the chemical reaction was as follows:

$$2\text{CH}_3\text{COONa}+\text{H}_2\text{SO}_4=\text{Na}_2\text{SO}_4+2\text{CH}_3\text{COOH}$$

Under normal atmospheric pressure, boiling temperature is 337 ℃ of sulfuric acid acetic acid boiling temperature is 117.9 ℃, when external pressure to reduce its boiling temperature decreases. The principle of vacuum distillation is the boiling point of using sulfuric acid and acetic acid, by heating the mixture of low boiling point of acetic acid in gasification, and the sulfuric acid with higher boiling point is still liquid gasification, so can have after gasification of acetic acid by condensation back into a liquid, the liquid mixture of sulfuric acid is still the high boiling point of liquid, so as to achieve the aim of sulfuric acid and acetic acid.

Under normal atmospheric pressure, water boiling temperature is 100 ℃, and acetic acid, compared to the boiling temperature of the boiling point were similar, their relative volatility is close to 1. A
mixture of acetic acid and water was obtained by decompression, and the presence of water did not affect the determination of acetic acid content.

The chemical reaction of acetic acid and sodium hydroxide is as follows:

\[ \text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} \]

According to the amount of sodium hydroxide, the content of acetic acid produced by reaction can be obtained, and the content of sodium acetate is obtained.

3. Results analysis

On the basis of single factor experiment, we studied has obvious effects on acetate measurements distillation time, solvent concentration, temperature, vacuum pressure, such as 4 factors in orthogonal experiment, the extraction conditions of L9(3^4) optimization. The horizontal table of orthogonal test factors is shown in table 1.

Table 1. Factors and levels of orthogonal test

| level | Factor | Temperature (℃) | Time (min) | Concentration (mol/L) | Pressure (MPa) |
|-------|--------|----------------|------------|-----------------------|---------------|
| 1     |        | 60            | 30         | 0.2                   | 0.04          |
| 2     |        | 80            | 50         | 1.0                   | 0.06          |
| 3     |        | 100           | 70         | 5.0                   | 0.08          |

Through the different test conditions, vacuum distillation get generated by sodium acetate reaction of sulfuric acid and sodium silicate bonded sand of acetic acid, and then measured the content of acetic acid with acid-base titration method, and can get the content of sodium acetate. The recovery rate is the ratio of the measured value and the theoretical value. The test results are shown in table 2 below.

Table 2. Compare different test method test result

| NO | Temperature (℃) | Time (min) | Concentration (mol/L) | Pressure (MPa) | Recovery rate (%) |
|----|----------------|------------|-----------------------|---------------|-------------------|
| 1  | 1(60)          | 1(30)      | 1(0.2)                | 1(0.04)       | 66                |
| 2  | 2(80)          | 2(50)      | 1                     | 2(0.06)       | 83                |
| 3  | 3(100)         | 3(70)      | 1                     | 3(0.08)       | 98                |
| 4  | 1              | 2          | 2(1.0)                | 3             | 78                |
| 5  | 2              | 3          | 2                     | 1             | 87                |
| 6  | 3              | 1          | 2                     | 2             | 96                |
| 7  | 1              | 3          | 3(5.0)                | 2             | 81                |
| 8  | 2              | 1          | 3                     | 3             | 82                |
| 9  | 3              | 2          | 3                     | 1             | 99                |
| K1 | 225            | 244        | 247                   | 252           |                   |
| K2 | 252            | 260        | 261                   | 260           |                   |
| K3 | 293            | 266        | 262                   | 258           |                   |
| R  | 68             | 22         | 15                    | 8             |                   |

3.1. Distillation temperature

The vacuum distillation process is a thermal separation process, and the distillation process needs to consume a lot of energy, and its energy consumption accounts for 50% ~ 70% of the whole separation process. The choice of temperature directly affects the test effect, reaction time and vacuum pressure. The distillation temperature is too low, the vacuum pressure is too high, the reaction is slow, the time is long; The distillation temperature is too high, the vacuum pressure is too low, the reaction is too intense, the interference factor increases, the test result is easy to produce the error. Acetic acid
and the boiling point of water is different, but the relative volatility is close to 1, so the vacuum distillation temperature limit is set to 100 °C. This method adopts the thermostatic digital water bath pot, and the temperature control system adopts microcomputer chip processor, with high temperature control accuracy and strong function. From table 2 shows, with the increase of distillation temperature, recovery rate increase gradually, when up to 100 °C, ideal distillation rate, test smoothly. The temperature is too low, the distillation speed is slow, the experiment result error is large.

3.2. Distillation time
In the process of vacuum distillation, distillation time is an important parameter and must be strictly controlled. The distillation speed is 2 ~ 4 mL/min until the volume of the solution of sulfuric acid (3 ~ 5 mL) of the sulfuric acid is added to the liquid product. Distillation time control mainly through judging standard addition recovery rate, sample at the temperature 100 °C, and under the condition of vacuum pressure 0.04 MPa, the test sample heating 30, 50, 70 min. With the increase of heating time, the sample standard addition recovery rate rising, high concentration (5.0 mol/L) sulfate solution sample heating recovery leveled off after 30 min, low concentration (0.2 mol/L) sulfate solution sample heating standard addition recovery rate after 50 min was satisfied. Therefore, the distillation time is 50 min after the distillation of all kinds of test samples.

3.3. Solvent concentrations
The concentration of sulfuric acid solution is too high, with strong corrosive and oxidizing properties. The concentration of sulfuric acid is too low, and the reaction is not sufficient. According to the test method, the concentration of sulfuric acid (0.2, 1.0, 5.0 mol/L) was tested to investigate the effect of sulfuric acid concentration on the measured value, and the results were shown in table 2. Table 2 shows that when the concentration of sulfuric acid is 0.2 mol/L, the concentration of acetic acid in the distilling bottle is low, the distillation process is long and the energy consumption is high. When the concentration of sulfuric acid is 5.0 mol/L, the concentration of acetic acid in the distilling bottle is large, the distillation process is short and the energy consumption is low. The test selection concentration was 1.0 mol/L of sulfuric acid solution, which was measured from the test of Sodium silicate sand sample and the test efficiency.

3.4. Vacuum pressure
The vacuum pressure is too high, the vacuum pump load increases, and the length of the distillation time affects the life of the vacuum pump. Selecting the right vacuum pressure is necessary to ensure the smooth operation of the test. Considering the maximum output power of the vacuum pump (0.098 MPa), the test of the standard sample and the recovery rate of standard samples under vacuum pressure is 0.04 MPa, 0.06 MPa and 0.08 MPa respectively. According to table 2 analysis, the recovery rate increases with the increase of vacuum pressure and heating temperature. Under the condition that the experiment is satisfied, the vacuum pressure of this test is 0.06 MPa.

4. Sample detection
To test and verify the feasibility of vacuum distillation - titration method, take five 500 g of new sand, add 50 g sodium silicate respectively, including four samples respectively, add 2, 4, 6, 8 g sodium acetate, remaining one without sodium acetate, made five samples of sodium silicate sand simulation. According to the test methods of adding sodium acetate four analog samples are measured and the results are shown in table 3, \( \omega_1 \) is sodium acetate mass fraction of sodium silicate sand sample; do not add sodium acetate was used to simulate the sample do the blank sample. Table 3 shows that the test value of sodium acetate is basically consistent with the theoretical value.
Table 3. The content of sodium acetate in simulation samples of sodium silicate sand

| Sample NO | theoretical value ω1/% | Found ω1/% | RSD(n=3) |
|-----------|------------------------|------------|----------|
| 1         | 0.363                  | 0.351      | 1.03     |
| 2         | 0.727                  | 0.702      | 1.09     |
| 3         | 1.454                  | 1.431      | 0.99     |

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 results of the determination of sodium acetate were shown in table 4, and ω2 was the quality fraction of sodium acetate in the sample of old sand glass. Table 4 is available: for determination of sodium acetate content in the old sand of Sodium silicate, the results of this method agree with the extraction method.

Table 4. The content of sodium acetate in used sodium silicate sand

| Sample NO | proposed method | titration method |
|-----------|-----------------|-----------------|
|           | Found ω2/%      | RSD(n=3)        | Found ω2/% | RSD(n=3) |
| 1         | 3.68            | 1.19            | 3.72       | 1.27     |
| 2         | 3.84            | 1.24            | 3.91       | 1.18     |
| 3         | 3.61            | 1.07            | 3.68       | 1.21     |

5. Summary
The residual adhesives in the old sand of Sodium silicate are complex and the residual Na₂O is divided into soluble, insoluble and insoluble parts. Soluble parts contain sodium acetate and sodium carbonate. Traditional distillation unit is cumbersome to operate, large energy consumption, easy to leak, influence measurement accuracy, and pollution to the laboratory environment. The separation and determination of residual acetate in the old sand of Sodium silicate were established. In this paper, acetic acid was extracted from sulfuric acid solution, and the content of acetic acid was determined by the neutralization titration method. The salt content of acetic acid was obtained by titration of acid base. Results show that on the basis of single factor experiment with four factors three levels orthogonal experiment of extracting conditions optimization, determines the best extraction technology: distillation temperature 100 °C, 50 min distillation time, solvent concentration 1.0 mol/L, vacuum pressure 0.06 MPa. The method can accurately measure the content of sodium acetate in the mixture, the method is simple and feasible, the equipment is easy to operate, energy-saving and environmental protection, and it is worth popularizing.

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