Gas capacity method to determine the content of bicarbonate and carbonate in sodium silicate sand

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Abstract. Because of the lack of test methods for each component, the performance of sodium silicate sand is generally evaluated by the total base amount. This paper establishes a method to measure the content of bicarbonate and carbonate in sodium silicate sand by means of gas capacity. The solution of calcium chloride was dropped into the sample of sodium silicate sand, and the reaction time was over 15 min. The volume of carbon dioxide produced by the measured amount of gas was measured and the content of bicarbonate was calculated by gas state equation. Drop the solution of hydrochloric acid into the sample and control the reaction time by more than 20 min. To measure the volume of carbon dioxide produced, the content of carbonate is calculated by gas state equation. The method was used to measure the content of bicarbonate and carbonate in sodium silicate sand samples. The measured value was consistent with the theoretical value, and RSD was less than 0.26.

1. Introduction
Sodium silicate reclaimed sand surface residual Na$_2$O can be divided into three parts: 5 ~ 10 % of Na$_2$O exists in glassy state of insoluble; 30 ~ 35 % of Na$_2$O exists in the form of salt; 55 ~ 65 % of the Na$_2$O exist in high water loss modulus sodium silicate [1, 3]. Sodium silicate sand after repeated use, not only in the reclaimed sand Na$_2$O content will increase, and the performance of the reclaimed sand is reduced [4,6]. Sodium carbonate, sodium acetate, etc., will deteriorate recycling sand available time and refractoriness. Sodium silicate sand after adding sodium bicarbonate, sodium carbonate, and sodium silicate sand of tensile strength increased slightly, sodium silicate sand a shorter time, maximum strength breakup sex improved significantly after high temperature heating [7, 8]. Sodium silicate, after blowing CO$_2$ hardening sodium bicarbonate is easy with the moisture migration outward, make type, core surface appear hoar, reduces the surface strength, pouring sand washing generating defects [9]. In order to guarantee the performance of the sodium silicate sand regeneration, it is necessary to accurately determine bicarbonate and carbonate in the reclaimed sand.

At present, in view of bicarbonate and carbonate analysis methods mainly include: weight method, titration method. Because there are a variety of alkaline substances in the sodium silicate sand regeneration, weight method and titration method cannot effectively distinguish between. In this paper, based on the experience of the gas volumetric method, to a mixture of sodium bicarbonate and sodium carbonate, drip into the CaCl$_2$ solution of measuring generates carbon dioxide, the volume of gas state equations, the content of sodium bicarbonate, in turn, drops into the HCL solution, volume
measurement generates carbon dioxide, the gas state equations, the content of sodium carbonate. This test method can accurately measure the content of sodium bicarbonate and sodium carbonate in the mixture; do set the stage for further sodium silicate sand regeneration study.

2. Experimental part

2.1. Main instruments and reagents
The test device is shown in figure 1. Digital display accurate to 0.001 g scales, digital display pressure meter resolution 0.1 kPa, and thermometer is accurate to 0.1 °C, sample preparation the JJ - 5 type cement mortar mixer.

![Fig. 1 Schematic diagram of Measuring sodium bicarbonate and sodium carbonate device](image)

(1) magnetic stirrer; (2) reaction bottle; (3) drain valve a; (4) drain valve b; (5) glass needle tube a; (6) glass needle tube b; (7) airway; (8) tee joint; (9) airway; (10) air pipe; (11) balance tube; (12) drain valve c.

2.2. Reagents and materials
CaCl₂ solution; Sodium bicarbonate powder; Sodium carbonate powder (270 ~ 300 °C drying). Casting raw sand (40 # ~ 70 #).

2.3. Experimental principles

2.3.1. CaCl₂ solution and sodium bicarbonate reaction. The CaCl₂ solution and the sodium bicarbonate of Sodium silicate were released to release CO₂, and the gas state equation (PV = nRT) was used to obtain the molar mass of CO₂ n₁. According to the chemical reaction, the molar mass of sodium bicarbonate is 2n₁, and then the mass m₁ of sodium bicarbonate is obtained. Its chemical reaction is as follows:

\[
2\text{NaHCO}_3 + \text{CaCl}_2 = 2\text{NaCl} + \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\]

\[
\text{Na}_2\text{CO}_3 + \text{CaCl}_2 = 2\text{NaCl} + \text{CaCO}_3 \downarrow
\]
Sodium bicarbonate quality calculation formula:

\[
m_1 = M_1 \times 2n_1 = M_1 \times 2 \frac{P \times (V_1 - V_2)}{1000 \times R \times T}
\]

In the formula: \(m_1\) is for the quality of sodium bicarbonate, g; \(M_1\) is the molar mass of sodium bicarbonate; \(P\) is the atmospheric pressure, kPa; \(V_1\) to measure \(CO_2\) volume, mL; The volume of \(CO_2\) in the blank sample was measured by \(V_2\), and mL; \(R\) is the gas constant, \(R=8.254 \text{ J} \times \text{K}^{-1} \times \text{mol}^{-1}\); \(T\) is the temperature in the tube, K.

2.3.2. HCL solution and calcium carbonate reaction. The HCL solution and calcium carbonate release \(CO_2\), and the gas state equation \((PV = nRT)\) gets the molar mass of \(CO_2\). The calcium carbonate is produced by the reaction of sodium bicarbonate and sodium carbonate and CaCl2. The molar mass of sodium carbonate is obtained by \(n_2 - n_1\), and then the mass \(m_2\) of sodium carbonate is obtained. Its chemical reaction is as follows:

\[
\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2
\]

Sodium carbonate quality calculation formula:

\[
m_2 = M_2 \times (n_2 - n_1)
= M_2 \times \left( \frac{P \times (V_3 - V_4)}{1000 \times R \times T} - \frac{P \times (V_1 - V_2)}{1000 \times R \times T} \right)
= M_2 \times \frac{P \times (V_2 + V_1 - V_3 - V_4)}{1000 \times R \times T}
\]

In the formula: \(m_2\) is for the quality of sodium bicarbonate, g; \(M_2\) is the molar mass of sodium carbonate; \(V_3\) is the volume of \(CO_2\) measured, mL; The volume of \(CO_2\) measured by \(V_4\) was blank sample, mL; \(P\) is the atmospheric pressure, kPa; \(R\) is the gas constant, \(R=8.254 \text{ J} \times \text{K}^{-1} \times \text{mol}^{-1}\); \(T\) is the temperature in the tube, K.

3. Test procedure

3.1. Connecting device
Said take 0.10 ~ 0.70 g sodium bicarbonate and sodium carbonate mixture or 10 to 50 g sodium silicate sand, together with the magnetic stir bar on reaction in a bottle, drip 5 drops of bromocresol green, methyl red indicator, tighten the reaction bottle stopper, the reaction on the bottle in the constant temperature magnetic stirrer. Connect the trachea, wait 5 min, adjust the liquid level, check the air tightness of the device. Record air pressure; read the airway surface and temperature.

3.2. Drop into CaCl2 solution
Open the drain valve to make the CaCl2 drop in the glass needle tube a bottle. The sample and CaCl2 react rapidly and have gas generation. Add CaCl2, with gas increases, the amount of tracheal drawdown, balance tube liquid level rise, should open the drain valve release sealing fluid, until the trachea and balance tube closed liquid level in the same height. Close the drain valve a, continue the reaction for 10 min, stop stirring, and hold the liquid surface of the tube and the balance tube to remain unchanged for 3 ~ 5 min. Record the initial readings of the tracheal liquid surface and the final reading of the reaction. The difference between the two is \(V_1\). Let's do a blank experiment and get \(V_2\).
According to the volume of carbon dioxide, the gas state equation is used to calculate the quality of bicarbonate.

3.3. Drop into HCL solution
Open the drain valve b to make the HCL solution drop in the glass cylinder b. The sample and HCL react rapidly and have gas generation. With HCL solution in the process, with gas increases, the amount of tracheal drawdown, balance tube liquid level rise, and open the drain valve c release sealing fluid, until the trachea and balance tube closed fluid is liquid level to level. Reaction after solution from green to red bottle, close the drain valve b, continue to reaction for 10 min, stop stirring, for volume balance and trachea tube liquid level remains unchanged within 3 ~ 5 minutes for the reaction end point. Record the initial readings of the tracheal liquid surface and the final reading of the reaction. The difference between the two is $V_3$. Do blank experiments to get $V_4$. The production of carbon dioxide from the gas state equation is obtained, and the content of carbonate is obtained.

4. Results analysis

4.1. Reaction times
When the mass of sodium bicarbonate was 0.05 ~ 0.25 g and sodium bicarbonate, the measured results were observed with the change of reaction time, as shown in FIG. 2 and FIG. 3. FIG. 2: at the beginning of the reaction of CaCl$_2$ solution and sodium bicarbonate, the measured value of sodium bicarbonate increased rapidly and after 15min, it tended to be constant and gradually approached the theoretical value. It can be obtained from FIG. 3: when the HCL solution drops in, the measured value of sodium carbonate at the beginning of the reaction increases faster, and after the response of 20min, it tends to be constant and gradually approaches the theoretical value.

![Fig. 2 The effects of reaction time on sodium bicarbonate test result](image1)

![Fig. 3 The effects of reaction time on sodium carbonate test result](image2)
4.2. concentration of solution
CaCl₂ solution reacts with sodium bicarbonate. According to the ion reaction conditions, there must be gas, precipitation or water generation. At least one of the three, the nature of the reaction is the difficult separation of the easy separation material. According to the test method, according to take 0.10 g (accurate to 0.001 g) powder, baking soda, using concentration were 0.5, 1.0, 1.5, 2.0 mol/L CaCl₂ solution experiment by studying the effect of CaCl₂ concentration on the determination results, the results are shown in table 1. Table 1 show that when CaCl₂ concentration is within 0.5 ~ 2.5 mol/L range, CaCl₂ concentration has a relatively small effect on the determination of sodium bicarbonate and its relative standard deviation (RSD). Considering the test efficiency and the amount of liquid needed to test the Sodium silicate sand, the test chose 1.0 mol/L of CaCl₂ solution.

| Sample NO. | CaCl₂ concentration /(mol/L) | theoretical value /g | Found /g  | RE /%  | RSD (n=5)/% |
|------------|-----------------------------|-----------------------|-----------|--------|-------------|
| 1          | 0.5                         | 0.1002                | 0.0995    | -0.7   | 0.25        |
| 2          | 1.0                         | 0.1004                | 0.0993    | -1.1   | 0.22        |
| 3          | 1.5                         | 0.1003                | 0.0993    | -1.0   | 0.26        |
| 4          | 2.0                         | 0.1006                | 0.0997    | -0.9   | 0.23        |
| 5          | 2.5                         | 0.1005                | 0.0993    | -1.0   | 0.25        |

5. Conclusion
The residual adhesives in sodium silicate regeneration sand are complex, and the residual Na₂O is divided into soluble, insoluble and insoluble three parts. Soluble parts contain sodium bicarbonate, sodium carbonate and sodium acetate. In this paper, based on the experience of the gas volumetric method, measurement of CaCl₂ solution and sodium bicarbonate reaction of carbon dioxide, the volume of gas state equations, the content of sodium bicarbonate, in turn, drops into the HCL solution; volume measurement generates carbon dioxide, the gas state equations, the content of sodium carbonate. The method can accurately measure the content of sodium bicarbonate and sodium carbonate in the mixture. The method is simple and feasible and suitable for production site application.

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