

Study on Thermal Stability and High Temperature Gas Production of Silicate Concrete

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Abstract. In this paper, the thermal stability of ordinary silicate concrete is characterized by the synchronous thermal analyzer. Through the design of the heating gas extraction device, the gas production at elevated temperature of concrete is collected, and the gas composition and content were analyzed by gas chromatograph. The results show that the thermal loss of the concrete after drying is concentrated at 350~700 °C, the weight loss is about 6%, the gas production at high temperature is mainly CO₂, accompanied by a small amount of CO, SO₂ and H₂O, and the rate of gas production of concrete is about 33L/kg.

1. Introduction

Cement is one of the main raw materials for infrastructure construction. It is widely used in engineering fields such as industry, agriculture, national defense, transportation, urban construction, water conservancy and marine development^[1]. The common silicate concrete is made up of portland cement clinker, gypsum regulator and aggregate. The main chemical composition of portland cement clinker is CaO, SiO₂, Al₂O₃ and Fe₂O₃. The mineral composition of portland cement clinker is mainly composed of tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite, and a small amount of free calcium oxide, free magnesium oxide and alkali^[2]. After mixing portland cement clinker with water, the mineral and water of cement clinker are hydrolyzed or hydrated. In fully hydrated concrete, hydrated calcium silicate accounts for 70%, calcium hydroxide accounts for 20%, three sulfur type and single sulfur type calcium sulphoaluminate account for 7%, and others account for 3%.

In some closed space environment, the inner wall is often sprayed with cement mortar. During the high temperature test, the sprayed concrete will release the gas because of the heating process. This increases the pressure of confined space, increases the risk of gas leakage in confined space, and affects the safety of site construction workers and the whole high-temperature test^[3]. Therefore, the study of the high temperature gas production and gas components of concrete can provide data reference for the airtightness of the closed high temperature experimental environment system. Previous studies^[4,5] have pointed out that concrete will undergo different changes in the process of heating. At 250-300 °C, the hydration products containing aluminum and iron phases removed the bound water; the calcium hydroxide decomposed at 400-500 °C and formed calcium oxide; the C-S-H gel in 500-600 °C cement paste basically decomposed completely; at higher temperature, CaCO₃ decomposed into CaO and CO₂. Aiming at the most widely used silicate concrete, the stability of room temperature to 1200 °C high temperature and the composition and total amount of gas produced by the



decomposition of concrete are analyzed and characterized. The high temperature biogas production rate of ordinary silicate concrete is calculated.

2. Experimental procedure

2.1. Sample preparation

The common and widely used common silicate concrete is selected as the research object, which is mixed with Portland cement, aggregate and water. The cement uses standard 42.5R ordinary portland cement, its chemical composition as shown in Table 1. Laboratory tap water is used for mixing water and maintenance water, and ISO standard sand is selected for aggregate. In the process of mixing cement, a certain amount of standard type water reducing agent is added.

Table 1 The chemical and mineral composition of ordinary portland cement (wt.%)

| Chemical composition | Loss | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | Mineral composition in clinker | | | |
|----------------------|------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|--------------------------------|------------------|------------------|-------------------|
| | | | | | | | | C ₃ S | C ₂ S | C ₃ A | C ₄ AF |
| Wt.% (%) | 0.1 | 22.46 | 4.88 | 3.53 | 65.03 | 1.78 | 0.9 | 55.09 | 23.64 | 6.47 | 11.27 |

The cement mixing formula is shown in Table 2. The size of the concrete is 50mm×50mm×50mm. After molding, the mold was released after curing 24h in the curing room with a temperature of (20±2) and humidity > 90%, and it was continued to 28d under the same conditions. Then it was moved to drying chamber for 7d with the temperature of (20±2) °C and the humidity of (65±5)%. In order to reduce the influence of cement mixing water consumption and concrete water absorption on subsequent high temperature test results, before curing the high temperature test, the concrete after maintenance is placed in the electric heating drum dryer to remove the free water at 110°C for 3h.

Table 2 The formula of ordinary portland cement for experiment

| Water-binder ratio | Cement-sand ratio | The amount of concrete materials | | | |
|--------------------|-------------------|----------------------------------|------------|-------------------|-----------------------|
| | | Cement (g) | Water (ml) | standard sand (g) | Water-reduce agent(%) |
| 0.3 | 0.4 | 300 | 90 | 750 | 1 |

2.2. Analysis and characterization

The concrete was put into the STA-F4 synchronous thermal analyzer sample table after drying treatment. Under the protection of Ar gas, the thermal stability of concrete at high temperature was characterized by the heating rate of 10K/min to 1200 °C. A self-designed heating and gas extraction system is used to collect gas from the dry treated concrete at high temperature. The schematic diagram of the system is shown in Figure 1. The composition analysis of the high temperature gas production of the concrete in the gas cylinder is carried out by using the meteorological chromatograph.

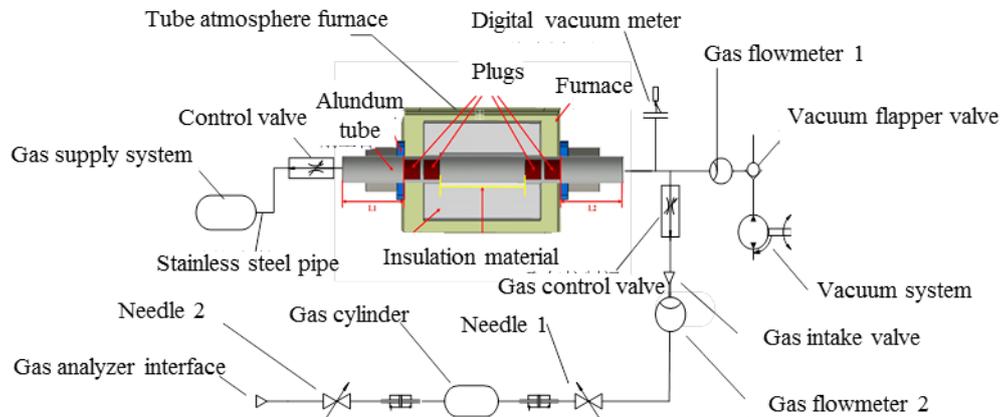


Fig. 1 Schematic diagram of gas heating system

3. Experimental results and analysis

3.1. Thermal stability

The thermal analysis curve of silicate concrete is shown in Figure 2. It can be seen from the TG curve in Figure 2 that the thermal stability of concrete has different characteristics at different temperature stages. After heating to 1200 °C, the weight loss of concrete is 6.3%, and there is a severe weight loss at the temperature stage of 650~750 °C. From the figure DSC curve, it is obviously that the portland concrete existence of a clear endothermic peak at 440 °C and 720 °C, on the TG curve showed that the weight loss of 1% and 3% at the temperature stage of 400~450 °C and 700~750 °C, respectively. This shows that the concrete has an obvious decomposition of gas production at the two temperature stages.

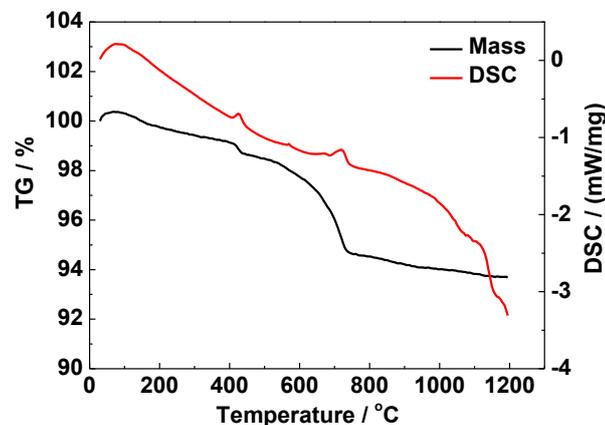


Fig. 2 Thermal analysis curve of concrete

3.2. Analysis of gas composition

The concrete was heated by the self-designed heating and gas extraction experimental device and gas production was collected. The gas supply system and vacuum system are used to realize the whole system cleaning, and high temperature system is responsible for the heating of concrete. The concrete is heated to 1200 °C in vacuum with the heating rate of 10K/min. The high temperature gas production of concrete is collected by gas cylinder, and the gas composition is analysed by meteorological chromatograph. The results are shown in Table 3.

Table 3 The gas composition of concrete after heating at 1200 °C

| Materials | Gas volume fraction in the cylinder (%) | | | Peak area of water vapor | | Air parameters | |
|-------------------|---|------|-----------------|--------------------------|------|------------------------|------------------|
| | CO ₂ | CO | SO ₂ | cylinder | Air | Relative humidity (RH) | Temperature (°C) |
| Silicate concrete | 85.4 | 3.52 | 5.57 | 6000 | 2600 | 42 | 29 |

It can be seen from the table 3 that the gas in the bottle is mainly CO₂ gas and a small amount of CO and SO₂, which indicates that during the heating process of concrete, the decomposition of silicate and a little sulphate are the main factors^[6]. Comparing the water vapor peak area in the cylinder and the area of the air sample water vapor peak, it can be seen that there is water release in the process of concrete heating.

3.3. Calculation of gas production rate

The total amount of gas production in concrete is calculated according to the results of the thermal weight loss of the material and the normalization of gas production. The content of water vapor in the sample is calculated according to the air sample. The following is the calculation process.

Relative humidity formula:

$$\varphi = P_w / P_s \quad (1)$$

Where: The φ is relative humidity and the unit is RH. P_w is the partial pressure of water vapor in the air and unit is Pa. P_s is a saturated vapor pressure at a certain temperature and unit is Pa.

According to the relationship between saturated vapor pressure and temperature, the vapor pressure of saturated water under the experimental conditions is calculated. The Antoine equation^[7] is the most commonly used formula of saturated water vapor pressure within the range of 10~168 °C, and the fitting formula is:

$$\lg P_s = 7.07406 - 1657.46 / (t + 227.02) \quad (2)$$

Where: P_s is saturated water vapor pressure and unit is KPa; T is temperature and unit is °C.

According to the formula (2), the saturated vapor pressure at 29 °C is calculated to be 3.98 KPa. Combined with the formula (1), the water vapor pressure in the air is calculated to be 1.67 KPa. According to the area of the sample water vapor peak and the reference air vapor peak area given in Table 3, the water vapor pressure in the sample was calculated to be 3.86KPa. The content of water vapor in the sample was calculated to be 4.39% by the experimental local pressure of 88 KPa. Combined with other gas contents in table 3, it can be seen that the cylinder contains 1.12% N₂ besides the four target gas. This may be caused by the use of the N₂ cleaning system and the residual vacuum residue before the experiment, but the content is minimal within the allowable range of the experimental error. It also shows that the method of calculating water vapor content in samples is feasible by comparing the air temperature and humidity, the peak area of air and water vapor and the peak area of water in the sample.

The result of normalization of the four target gases in the sample in proportion is CO₂: CO: SO₂: H₂O=86.37%:3.56%:5.63%:4.44%. According to the normalized result of gas production, the equivalent molar mass of the four gases is obtained.

$$M = M_1 * \varphi_1 + M_2 * \varphi_2 + M_3 * \varphi_3 + M_4 * \varphi_4 \quad (3)$$

Where: M is equivalent mole mass and unit is g/mol; M_1, M_2, M_3 and M_4 are four kinds of gas mole mass and unit is g/mol; $\varphi_1, \varphi_2, \varphi_3, \varphi_4$ are four kinds of gas volume fraction

For the silicate concrete, the equivalent mole of gas in the gas cylinder is calculated as follows:

$$M=44 \times 86.37\% + 28 \times 3.56\% + 64 \times 5.63\% + 18 \times 4.44\% = 43.4 \text{ g/mol}$$

The weight loss of ordinary concrete in TG-DSC is 6.3%, and the amount of gas material is produced after heating to 1200 °C per kilogram of ordinary concrete as:

$$n = 1000 * \gamma / M \quad (4)$$

Where: n is the amount of gas material per kilogram of ordinary concrete and unit is mol; γ is the weight loss rate of ordinary concrete. M is the equivalent mole mass of the cylinder and unit is mol.

So, the amount of gas material produced by the unit mass of ordinary concrete as follows:

$$n=6.32/100/43.4 \times 1000=1.456\text{mol}。$$

According to the ratio of four gases and the equation of ideal gas state, the volume is converted into a standard condition as shown in table 4.

Table 4 The gas production per unit mass of silicate concrete after heating to 1200 °C

| Materials | Gas production (L/kg) | | | | Total (L/kg) |
|-------------------|-----------------------|-----|-----------------|------------------|-----------------|
| | CO ₂ | CO | SO ₂ | H ₂ O | |
| Silicate concrete | 28.2 | 1.2 | 1.8 | 1.4 | 32.6 |

It can be seen from table 4 that the gas production after silicate concrete heated 1200 °C is mainly CO₂ gas due to the decomposition of silicate, and accompanied by a small amount of CO, SO₂ and H₂O. Through a gas volume under standard conditions, the unit mass of silicate concrete gas total volume is 32.6L/kg.

4. Conclusion

1. The weight loss of silicate concrete is concentrated at 350~700 °C, and the weight loss rate is about 6%.
2. The high temperature gas production of silicate concrete is mainly CO₂, with a small amount of CO, SO₂ and H₂O.
3. The gas production rate of silicate concrete is about 33L/kg.

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