Continuous Detecting Device and Method for Ammonia Gas Release in Concrete Mixed with Denitrified Fly Ash

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Abstract: The ammonia gas released from concrete mixed with denitrified fly ash has a negative impact on the performance of concrete, and is also hazardous to the health of constructors in closed spaces such as hydraulic tunnels and subways. The study of ammonia gas releasing law of concrete mixed with denitrified fly ash can provide a solution to eliminate these adverse effects. Moreover, ammonia gas releasing is a continuous and slow process, and there is no effective detection method at present. In order to solve the problem that ammonia gas release from concrete mixed with denitrified fly ash cannot be absorbed and detected continuously, in this paper, a continuous testing device for ammonia gas release from concrete is developed, which can adjust the temperature and wind speed in the test box to simulate the construction environment, vibration and hardening process, and realize the real-time detection of ammonia gas release from pouring to curing of concrete. The ammonia gas releasing law of concrete mixed with denitrified fly ash in the process of vibrating and hardening was tested. The results show that vibrating can accelerate ammonia gas releasing in concrete, and ventilation is beneficial to ammonia gas dissipation. The ammonia gas concentration in the test chamber decreases gradually and tends to zero with the increase of ventilation time. The total ammonia gas release from concrete increases significantly in the early hardening stage and gradually increases with the time, and finally tends to be stable. The release rate of ammonia gas in concrete accords with the exponential decay law.

1. Introduction

With the higher and higher importance attached to the environmental protection, Chinese large-scale coal-fired power plants have completed their technological transformation of desulfurization and denitrification in order to reach the emission standard, and all of the fly ash (FA) generated by the power plants have been denitrified [1-3]. The residual ammonium salt in denitrified FA will experience chemical reactions in the cement hydration alkaline environment, and release ammonia gas. Consequently, various problems will take place during the use process of FA in concrete, e.g., increasing air content and viscosity of fresh mixed concrete, and degraded mechanical properties and durability of hardened concrete [4-6], but moreover, the irritant gases released from the concrete during the mixing, vibration, and hardening process may impact the workers’ health [7-9], and the intense smell is especially hard to accept in underground or sealed spaces.

The present domestic and foreign researches regarding denitrified fly ash mainly include the detection method of ammonia gas content in FA [10-12], influences of FA on the workability of fresh mixed concrete, and the macro-properties and micro-properties of hardened concrete, etc. [13,14], but a void has
been left with respect to continuous detection of ammonia gas release in the construction process, and ammonia gas release rules of concrete after being mixed with denitrified FA.

A continuous detecting device for ammonia gas release in concrete was developed and used to test the ammonia gas concentration, total release, and release rate during the vibration and hardening process of concrete mixed with denitrified FA, thus providing a test data basis for applying the denitrified FA, and determining the safety threshold of ammonia gas content in denitrified FA and concrete.

2. Test

2.1. Raw materials
The cement (C) and fly ash (FA) used in the test were 42.5 low-heat Portland cement and F-type grade I ash, respectively, where the ammonia gas content in FA was 350 ppm (350 mg NH₃/kg FA), and the fineness modulus of fine aggregate (S) was 2.61. The coarse aggregate (G) was broken limestone with continuous gradation at particle size of (5-40) mm, the admixtures were polycarboxylate superplasticizer (PCA) and rosin resin air entraining agent (AEA), and the chemical reagents were dilute sulphuric acid, salicylic acid, potassium sodium tartrate, sodium hydroxide, sodium hypochlorite, etc.

2.2. Concrete mix proportion
The construction mix proportion of the underground powerhouse in a hydropower station was used in this test as seen in Table 1. The absolute volume method was used to calculate the mix proportion.

| Sample No. | FA adulterate amount (by mass)/% | Ammonia gas content in FA (ppm) | Additive adulterate amount (by mass) | Mix proportion/(kg·m⁻³) | Initial setting time (h:min) |
|------------|---------------------------------|--------------------------------|-------------------------------------|------------------------|---------------------------|
| P-25-350   | 25                              | 350                            | 0.82 0.7                            | W 263 C 88 FA 786 G 1144 | 6:50                      |

3. Testing Method

3.1. Testing Device
The continuous detecting device of ammonia gas release in concrete is shown in Figure 1. This device consisted of data acquisition system, sealed experimental box, concrete vibrator, ammonia gas absorption apparatus, air supply system, temperature control system, automatic ammonia gas concentration detection system, etc., where the data acquisition system was the upper computer with its two ends connected to the temperature control system and automatic ammonia gas concentration detection system, and it could implement the real-time detection of temperature and ammonia gas concentration in the experimental box. The temperature control system included temperature controller and temperature sensor, and the automatic ammonia gas concentration detection system was composed of fixed-type ammonia gas detector and ammonia gas concentration sensor. Following the working principle of electrochemistry, the ammonia gas detector was featured by simple operation, high reaction speed, high accuracy, etc. The air inlet of experimental box was connected to the air supply system, the air outlet was connected to the ammonia gas absorption apparatus via a three-way valve, and the continuous ammonia gas absorption was realized through the conversion of this three-way valve. Determination of the ammonia gas concentration in absorption liquid based on Water Quality—Determination of Ammonia gas Nitrogen—Salicylic Acid Spectrophotometry (HJ 536-2009), the sum of ammonia gas concentration in the experimental box and that in the absorption liquid was the total ammonia gas release in the concrete mixed with denitrified FA.
The concrete construction environment and its vibration and hardening process were simulated by regulating the temperature, air speed, etc. in the experimental box, and in an effort to implement the real-time detection of ammonia gas release in the concrete from pouring to curing process.

![Figure 1: Continuous Testing Device of Ammonia gas Release in Concrete](image)

1-Data acquisition system, 2-Experimental box, 3-Vibrator, 4-Ammonia gas absorption apparatus, 5-Air supply system, 6-Temperature control system, 7-Automatic ammonia gas concentration detection system, 8-Three-way valve, 9-Stop valve

### 3.2. Calculation method

The calculation formula of total ammonia gas release in concrete is as below:

\[ C = C_1 + C_2 \]  \hspace{1cm} (1)

where \( C \) is total ammonia gas release in the concrete, \( \mu g \); \( C_1 \) is ammonia gas mass in the absorption liquid, \( \mu g \); \( C_2 \) is ammonia gas mass in the experimental box, \( \mu g \).

The ammonia gas mass \( C_1 \) in the absorption liquid is calculated through the following formula:

\[ C_1 = \rho_N \times 1.2143 \times V_p \times 1000 \]  \hspace{1cm} (2)

where \( C_1 \) is ammonia gas mass in the absorption liquid, \( \mu g \); \( \rho_N \) is mass concentration of ammonia nitrogen in the absorption liquid, and it is calculated by N, mg/L; 1.2143 is conversion coefficient, converting N into NH3; \( V_p \) is liquid volume in the absorption bottle; 1000 is unit conversion coefficient, converting mg into \( \mu g \).

The calculation formula of mass concentration \( \rho_N \) in ammonia nitrogen in the absorption liquid is as follow:

\[ \rho_N = \frac{A_s - A_b - a}{b \times V} \times D \]  \hspace{1cm} (3)

where \( \rho_N \) is mass concentration of ammonia nitrogen in the absorption liquid, calculated by N, mg/L; \( A_s \) is absorbance of the absorption liquid; \( A_b \) is absorbance of blank specimen; \( a \) is intercept of spectrophotometric calibration curve; \( b \) is slope of spectrophotometric calibration curve; \( V \) is volume of the absorption liquid, mL; \( D \) is dilution multiple of the absorption liquid.

The ammonia gas mass \( C_2 \) in the experimental box is calculated as below:

\[ C_2 = \frac{A_{V_{box}}}{V_m} \times 17.03 \]  \hspace{1cm} (4)
where \( C_2 \) is ammonia gas mass in the experimental box, \( \mu \)g; \( A \) is value displayed by the automatic ammonia gas concentration detection system, ppm; \( V_{\text{box}} \) is air volume in the experimental box, L; \( V_m \) is molar volume of gas, it is taken as 24.09 under 20°C and 101 kPa conditions, and it can be solved according to the ideal gas equation \( PV=nRT \) under other experimental conditions, L/mol; 17.03 is molar mass of ammonia gas, g/mol.

4. Ammonia Gas Release in Concrete Vibration and Hardening Process

According to the construction technology and environmental conditions, the starting time of vibration (from when the concrete was taken out of concrete mixer until the vibration was started) was selected as 30 min, the vibration lasted 45 s, and the aeration rate was 2.0 L/min. The ammonia gas concentration in the experimental box during the concrete vibration and before the initial setting is shown in Figure 2, and the total ammonia gas release and release rate in the hardening process are displayed in Figure 3 and Figure 4.

As shown in Figure 2, the ammonia gas release in the concrete could be accelerated by vibration. In the vibration process, the ammonia gas concentration in the experimental box was rapidly increased, and when the vibration was stopped, the ammonia gas was continuously released from the concrete, and its concentration reached the peak value before the ventilation, which could facilitate the dissipation of ammonia gas. As the ventilation was continued, the ammonia gas concentration in the experimental box was gradually reduced and tended to be zero, and the ammonia gas released from the concrete was totally absorbed by the absorption apparatus after being converted via the three-way valve.

![Figure 2](image)

Figure 2: Time-Dependent Change Curve of Ammonia Gas Concentration in Experimental Box

According to the test results in Figure 3, the total ammonia gas release in the concrete was significantly increased in the early hardening phase. As the time passed by, the total ammonia gas release was gradually increased, and slowly tended to be stable. The time-dependent change curve of ammonia gas release rate in Figure 4 was fitted through formula (5). The results show that the ammonia gas release rate in the concrete conform to the exponential attenuation law, and the correlation coefficient between measured curve and fitted curve was 0.9912.

The fitting formula for the ammonia gas release rate is: \( y=1700e^{-\frac{t-17}{30}} \) (5)
5. Conclusions

(1) A continuous testing device for ammonia gas release in concrete is developed. It can simulate the vibration process and hardening environment, and be applied to real-time detection of ammonia gas release during the concrete pouring and curing process.

(2) The total ammonia gas release is the sum of ammonia gas mass in the absorption liquid and that in the experimental box. The detection precision can be improved by correcting the measuring error of total ammonia gas release that is calculated only using the ammonia gas concentration in the absorption bottle.

(3) According to the detection results of ammonia gas concentration in the experimental box, the vibration will accelerate the ammonia gas release in the concrete, and the ventilation facilitates the dissipation of ammonia gas. As the ventilation time is lengthened, the ammonia gas concentration in the experimental box is reduced, and gradually tends to be zero. The ammonia gas released in the concrete can be totally absorbed by the absorption device after being converted by the three-way valve.
(4) From the ammonia gas release laws in the concrete hardening process, the total ammonia gas release in the concrete presents a significant rising trend, afterwards, it is gradually increased and then slowly tends to be stable, and the time-dependent change of ammonia gas release rate conforms to the exponential attenuation law.

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