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Emission characteristic of ammonia in cement mortars using different sand from area of production

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ABSTRACT

This paper discusses the influence of organic matter contained in aggregate on the emission characteristic of ammonia (NH_3) from cement mortar. NH_3 can be released to indoor-outdoor environment through diffusion in mortar (or concrete) and have resulted in the increasing air pollution, and especially well known as a harmful gas for the human body. The concentration of NH_3 released from cement concrete was then compared to the contents of organic matter contained in the aggregate. The result indicates that the contents of organic matter in the aggregate significantly differ with types of aggregate from different areas of production. The organic matter becomes organic nitrogen through the process of microbial breakdown for a certain period and pure ammonium ion (NH_4^+) is produced from the organic nitrogen. The NH_4^+ was reacted with alkaline elements in the cement and released as NH_3 from cement concrete through a volatile process. The released NH_3 was proportional to the contents of NH_4^+ adsorbed in the aggregate from different areas of production and the concentrations of NH_3 emission from cement mortar according to the aggregate differ by more than 4 times.

Keywords: Ammonia, Aggregate, Ammonium, Cement hydration, Mortar, Organic matter

1. Introduction

Indoor air pollution is an important topic in modern times. People in western countries spend approximately 90% of their time indoors, so exposure to indoor air has a major impact on the overall intake of potentially hazardous air pollutants [1]. Air pollution has been associated with the induction or exacerbation of allergic conditions and asthma as well as with fatigue, headache, cough, and nasal, eye, throat or skin irritation [2].

Especially one recent study from Japan has shown that NH_3 and VOC can be emitted from concrete [3]. And when visiting underground spaces that have poor ventilation or building that are surrounded by cement concrete, we can detect a pungent odor as the unique smell of concrete. This odor is caused by the various gases occurring by the hydration process of cement concrete (or mortar), while the amount and types of gas depend on the composite materials and environmental factors such as moisture, temperature etc. Among these gases, NH_3 can be released to indoor-outdoor environment through diffusion in concrete wall and have resulted in the increasing air pollution, and especially well known as a very harmful gas for the human body and it is easily released as NH_3 in the high pH environment of concrete [4]. NH_3 is a colorless, flammable alkaline gas with a pungent odor and is produced by the decomposition of nitrogenous organic matter [5]. The US Department of Health and Human Services has reported on the hazardous properties of NH_3 and presented an occupational safety and health guideline for NH_3 [6]. According to the Occupational Safety and Health Administration (OSHA), continuous exposure to above 25 ppm of NH_3 in the air can cause headaches, nausea and even serious burning of the eyes, nose, throat and skin. Exposure to very high levels of NH_3 can cause serious burns and permanent damage to the eyes, lungs and skin [7]. Therefore, OSHA recommends that the level of NH_3 in workroom air should be limited to 50 ppm for 5 minutes exposure [8]. Various studies have been carried out to investigate NH_3 emission sources [9-11] and NH_3 concentration in indoor air [12-15]. Kobayashi reported that NH_3 generated from aggregates and cement contained in cement concrete cause the deterioration of linseed oil in oil paintings in newly constructed art museums [16]. It has also been reported that the addition of amines to antifreezing agents in cold regions also causes large amounts of NH_3 to be generated in cured cement concrete in the same manner as the

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case of amides [17]. Sisovic et al. investigated the relationship between indoor and outdoor NH_3 concentration in selected office buildings and reported that the NH_3 concentration of indoor air exceeded several times that of outdoor air [18]. Bai et al. examined the effect of temperature, relative humidity and air exchange rate on the emission of NH_3 from experimental samples of concrete wall in an environmental chamber [17]. They reported that a high air exchange rate leads to a decreased NH_3 concentration, while an elevation of temperature increases the NH_3 concentration and volatilizing rate in the chamber. Puhakka et al. suggested remedial measures against high concentrations of NH_3 in buildings [19]. Recently, the cases of damage of residents or workers on construction sites due to an excessive concentration of indoor NH_3 have significantly increased, and reducing the risk caused by NH_3 in indoor air becomes a significant issue in Korea. However, only a few investigations on NH_3 released from cement concrete have been carried out.

The focus of this paper is to measure the emission of NH_3 from cement concrete using different aggregate according to the area of production and to investigate the relationship between the amount of organic matter and NH_4^+ contained in the aggregate as well as the emission of NH_3 from cement concrete using different aggregate from area of production.

2. Materials and Methods

2.1. Materials

Ordinary Portland Cement (OPC) as specified in KS L 5201 (Portland cement, 2006) was used in the manufacture of all concrete. For the purpose of this study, 4 types of aggregate sample were collected from different areas of production as shown in Table 1, and the material from Chonbuk Jeonju and Gunsan which is used in building and infrastructure construction, Jeonju and Gunsan are district of Chonbuk, located in Korea. We carried out the experiment (organic matter, ammonium ion, CEC) for 3 times and the each value was expressed as an average of these measurements. And the chemical compositions and characteristics are shown in Table 2 and 5.

The aggregate samples were dried in a dry oven and then washed with running water after sorting with 40 sieves. As shown in Table 1, cement mortar was made using 4 types of aggregate collected from different areas of production by means of a 2.5:1 ratio of aggregate to cement according to KS L 5105 (Testing method for compressive strength of hydraulic cement mortar, 2007), and with a water-cement ratio (W/C) fixed at 0.5. The size of cement mortar for analyzing the emission of NH_3 was 150 × 150 × 50 mm and the mortar has been placed into the environmental chamber, as shown in Fig. 1. The environmental chamber was then immediately sealed and cured for 24 hours in a constant temperature and humidity chamber at 20 ± 2°C. Three mortar specimens were used for sampling of gases and the value was expressed as an average of these measurements.

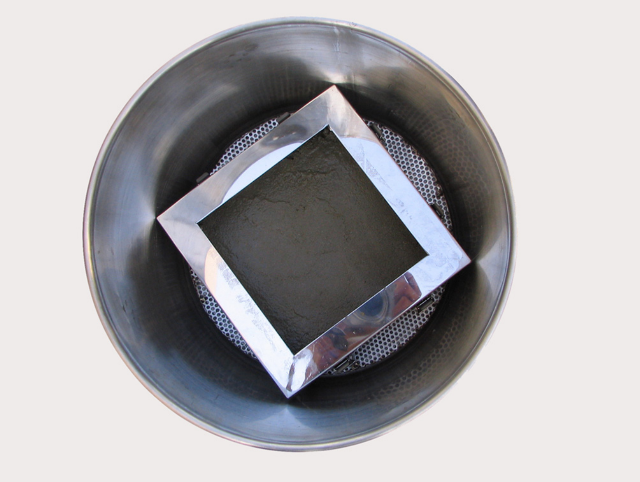

Fig. 1. Placing concrete into the environmental chamber.

2.2. Sampling of Gases from Cement Concrete

The environmental chamber sampling system used in this study was especially designed and consists mainly of a 0.02 m^3 stainless steel environmental chamber and cement mortar holder as shown in Fig. 2, and gas sampling system as shown in Fig. 3. Sampling of gases was performed by collecting the gases directly in an impinger using an MFC pump for gases released from cement mortar within the early hydration stage of 24 hours. Although the load factors of samples generally used in the environmental chamber

Table 1. Types of Aggregate and Mortar

Marks	Types of Aggregate	Marks	Types of Mortar
A-1	Sea aggregate (Gunsan-Bieung island)	M-1	mortar used sea aggregate
A-2	Land aggregate (Jeonju)	M-2	mortar used land aggregate
A-3	River aggregate (Jeonju)	M-3	mortar used river aggregate
A-4	Crushed aggregate (Jeonju)	M-4	mortar used crushed aggregate

Table 2. Chemical Compositions and Characteristics of Aggregate

	Oxide composition (%)											NH_4^+ (mg/kg)	pH
	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	Fe_2O_3	BaO	P_2O_5	MgO	TiO_2	MnO		
A-1	84.72	8.23	4.42	1.33	0.27	0.29	0.09	0.56	-	0.05	-	0.265	7.21
A-2	34.94	16.84	0.54	0.52	38.80	0.54	0.12	0.41	4.70	0.52	0.26	0.359	6.59
A-3	70.16	16.46	4.31	1.91	0.86	3.49	0.08	0.74	1.29	0.45	-	1.078	5.96
A-4	70.14	14.59	4.18	4.50	2.28	2.07	0.09	0.61	1.05	0.34	0.02	0.284	7.45

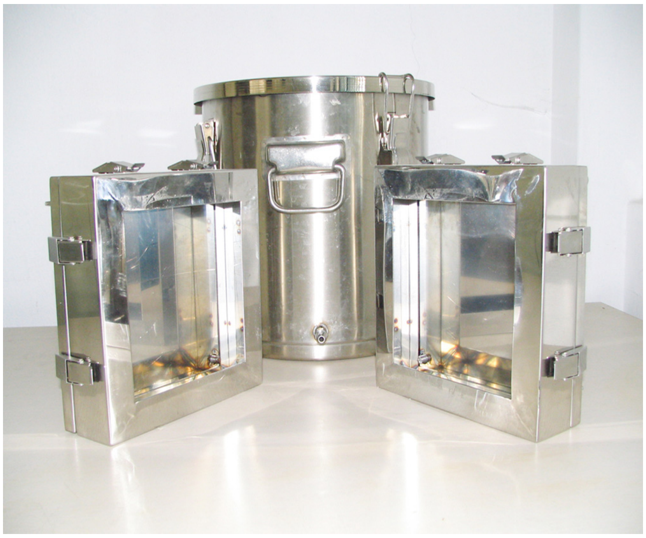

Fig. 2. Environmental chamber and cement mortar holder.

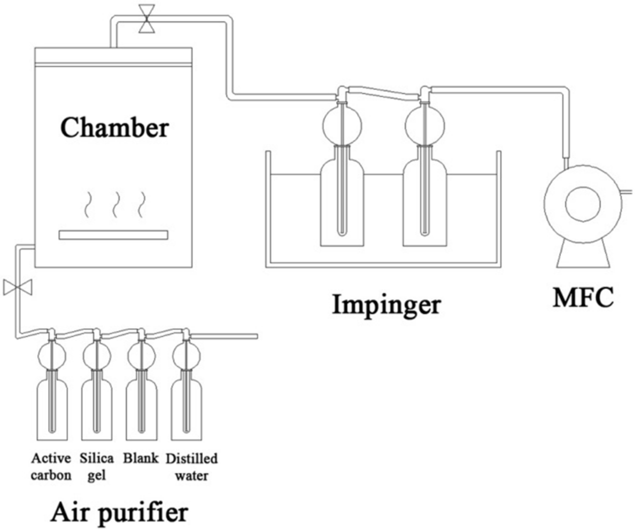

Fig. 3. Gas sampling system.

are 2.0 m^2/m^3 (± 10%) for solid and 0.5 m^2/m^3 (± 10%) for liquid, the load factor of 1.0 m^2/m^3 (± 10%) in this work was used because cement concrete is in the semisolid state before hardening by the hydration of cement.

2.3. Measurement of Ammonia

NH_3 concentration was determined via spectrometric method. The NH_3 in gas stream should be first absorbed in boracic acid (H_3BO_3) solution, in which NH_3 reacts with hypochlorite to form chloramines. Chloramines then react with phenol to form the intermediate, named monochloro quinoimine. Finally, this intermediate couples with a second phenolic molecule to form indophenols blue (Fig. 4). NH_3 was then determined by measuring light absorbance at 640 nm with a spectrophotometer. The 1 mol of NH_3 reacts with 2 mol of phenate and 3 mol of OCl^- to form 1 mol of indophenols.

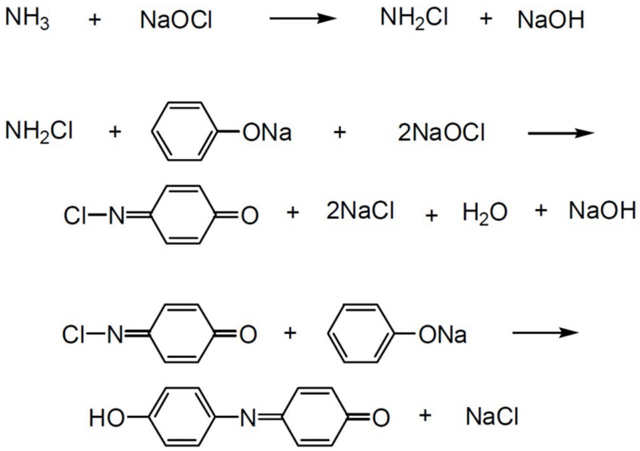

Fig. 4. Ammonia analysis by the phenate method.

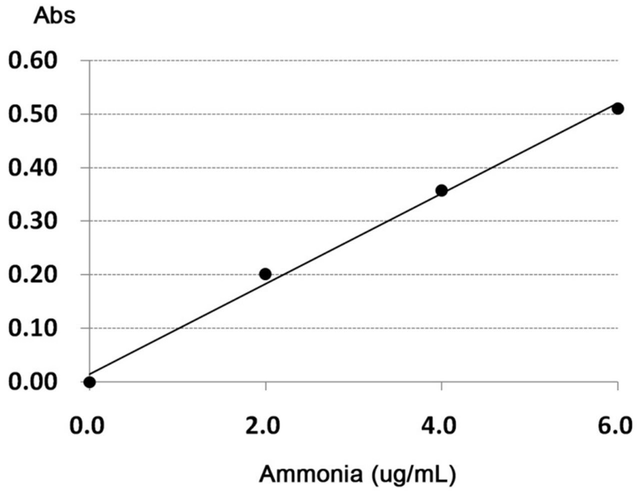

Fig. 5. Ammonia calibration curve.

Absorbance of indophenol in each experiment was measured and the calibration curve was obtained by plotting absorbance against ammonia concentration. The slope of linear correlation is defined as 'absorbance sensitivity' and the slopes of experiment groups were compared to discuss the quality of ammonia analysis (Fig. 5).

$NH_3 = W/V_o$
Where W= μg NH_3 from standard curve.
V_o = Volume of air sample in m^3 at 25°C

$$V_o = A \times \frac{273}{273+T} \frac{\times P}{760}$$

Where A = MFC volume air
P = atmospheric pressure at sampling point
T = temperature, °C at sampling point.

2.4. Measurement and Calculation of Organic Matter

The organic matter in the aggregate was measured in accordance with KS F 2104 (Testing method of organic matter in soils by ignition loss, 2008). The samples were collected according to KS F 2301 (Practice for preparing disturbed soil samples for soil testing,

2005) and particles of more than 2mm were eliminated in the samples. The samples were dried for about 24 hours at 110 ± 5˚C in a dry oven, and the sample of 2~10 g was then placed in a crucible of 50 mL. The concentration of organic matter was measured by ignition loss (I_{loss}) using the following equation:

$$Ignition\ loss(I_{loss}) = (W_a - W_b)/(W_a - W_c) \times 100(\%) \qquad (1)$$

Where W_a is total mass of sample and crucible (g), W_b is total mass of sample and crucible after heating (g) and W_c is Mass of crucible (g).

2.5. Measurement and Calculation of Ammonium Ion

The concentration of NH_4^+ in the aggregate was measured in accordance with KS I ISO 14256-1 (Soil quality - Determination of nitrate, nitrite and ammonium ion in field-moist soils by extraction with potassium chloride solution - Part 1: Manual method, 2009). In general, NH_4^+ of aggregate exists in soil solution and it is desorbed by priority from the surface of the soil by soil extraction liquid. If there are strong alkaline and hypochlorous acid ions in the soil, the NH_4^+ forms a monochloroamine (NH_2Cl) and indophenol blue compound by reacting with the phenol. An extinction of the compound is generally measured at the wavelength of 630 nm. The concentration of ammonia nitrogen was calculated using the following equation:

$$W(NH_4 - N) = 2 \times (\alpha_{SE} - \alpha_{BE})/(\alpha_{NAS} - \alpha_{ZS}) \times D \times R \qquad (2)$$

Where 2 is mg (NH_4-N/L) as a weight concentration of ammonia nitrogen standard solution, α_{SE} is extinction of soil extraction liquid, αBE is extinction of blank solution, α_{NAS} is extinction of ammonia nitrogen standard solution, α_{ZS} is extinction of water. D is a coefficient used when diluting soil extraction liquid and a value of the volume of the diluted soil extraction liquid divided by the volume of soil extraction liquid used in dilution. R is a coefficient considered volume ratio of solution to weight of soil dried in dry oven after extraction.

2.6. Measurement of Cation Exchange Capacity (CEC)

The concentration of cation exchange capacity in the aggregate was measured in accordance with KR10-03976281 (Measuring method of soil cation exchange capacity using methylene blue indicator). The aggregate was dissolved in methylene blue solution (soil : solution = 1 : 10, % by mass) at 25˚C during 1 hour, and then measurement of chromaticity by spectrophotometer (wavelength – 609 nm).

3. Results & Discussion

3.1. Emission of Ammonia from Cement Mortar

Table 3 shows the concentration of NH_3 released from cement mortar cured for 24 hours in the environmental chamber using a spectrometric method. It can be seen from Table 3 that the concentration of NH_3 of the M-3 using river aggregate is about 58.80 ppm, which was more than 4.7 times that of the M-2 using land aggregate. However, the NH_3 concentrations of the M-1 using sea aggregate and M-4 concrete using crushed aggregate were about 1/3 times lower than those of the M-2 using land aggregate.

According to the report of the US Department of Health and Human Services, exposure to household NH_3 above 1ppm can cause irritation of the eyes, nose and throat and exposure to very high levels of NH_3 can cause serious burns and permanent damage to the eyes, lungs and skin. The OSHA has set a short-term (15 min) exposure limit of 35 ppm for NH_3. The National Institute for Occupational Safety and Health recommends that the level in workroom air should be limited to 50 ppm for 5 minutes of exposure.

3.2. Mechanism of Ammonia Volatilization

In general, NH_4^+ in soil is released into the atmosphere by the chemical reaction of NH_4^+ and alkali (OH^-) as presented in Eq. (3) and this is called ammonia volatilization [20].

$$NH_4^+ + OH^- \rightarrow NH_3(gas) + H_2O (3)$$

On the same principle, the emission of NH_3 from cement concrete

Table 3. Ammonia from Cement Mortar Using Different Sand from Area of Production

	Abs	Average Abs	Ammonia(mg/ml)	ppm/hour (load factor : 1.0 m^2/m^3)
M-1	0.111 0.111 0.107	0.110	1.299	4.48
M-2	0.210 0.204 0.205	0.206	2.350	12.44
M-3	0.722 0.715 0.715	0.717	8.469	58.80
M-4	0.101 0.100 0.101	0.101	1.193	3.67

occurs by the chemical reaction of NH_4^+ adsorbed into the aggregate and alkali produced by the hydration of cement. Hence, NH_4^+ adsorbed into the aggregate is a primary source of NH_3 released from cement concrete. The concentration of NH_3 released from cement concrete within 24 hours was practically similar to the content of NH_4^+ contained in the aggregate from different areas of production.

3.3. Creation of Ammonium Ion and Adsorption

The contents of NH_4^+ in the aggregate are significantly related to the organic matter contained in the aggregate. Generally, part of the organic matter in the soil becomes organic nitrogen through the process of microbial breakdown for a certain period and pure NH_4^+ is produced from the organic nitrogen. However, the contents of NH_4^+ and organic matter in soil are not in direct proportion because the pure production of NH_4^+ is determined by the relation of complex factors such as habitat factor of soil, carbon-nitrogen (C/N) ratio and other biological elements etc.[20]

Usually, the surface of the soil has a negative charge; various cations that are dissociated among the soil solution are adsorbed on the particle surface by electrostatic interactions. The main cations that are adsorbed in the soil are H, Ca, Mg, K, Na etc. Other cations (Al_3^+, NH_4^+, Fe_3^+, Mn_2^+ etc.) are also adsorbed on the surface and constantly change according to the environment.

Strength of adsorption
1) As charge of cation increase
2) As ionic radius of cation decreases
3) As negative charge of exchanger increase
And then
$Na < K = NH_4 < Mg = Ca < Al(OH)_2 < H$

Adsorbed NH_4^+ does not leach easily by water, but is exchanged with other cations and come out in soil solution.

3.4. Characteristic of CEC and Organic Matter

The adsorption of cation and cation exchange interaction is determined by the cation exchange capacity (CEC), which is the absorbable and exchangeable ability of the cation. CEC of the soil is determined by the composite of the soil, quantity of clay and organic matter. Table 4 presents a typical CEC of soils and it is expected that the CEC of soils might be increased with an increase of organic matter contents [21].

Table 4. Cation Exchange Capacity of Soils (Brady & Weil, Gardiner & Miller, 2004)

Types of soil	CEC cmol(+) kg^{-1}
Pure organic matter	200
Pure smectite	100
Pure kaolinite	8
Typical sandy soil	5
Typical loamy soil	15
Typical clayey soil	30
Typical loamy sand	3

(Brady&Weil, Gardiner&Miller, 2004)

Table 5. Organic Matter, CEC and Ammonium in Different Aggregate Specimen

Type	Organic matter (%)	CEC mol(+)/kg	Ammonium (mg/kg)
A-1	0.62	2.46	0.34
A-2	1.31	9.35	0.46
A-3	1.92	15.55	1.39
A-4	0.53	0.19	0.37

Table 5 shows the contents of organic matter and CEC in the aggregate from different areas of production. In the cases of river aggregate (A-3) and land aggregate (A-2) containing high contents of organic matter, the CEC were higher than in other aggregate.

The special quality of the charge of organic matter plays an important part in strengthening the cation exchange capacity of soil. According as pH increases, the cation exchange capacity of organic matter increases remarkably. Table 2 presents the pH of soils of this study. The pH of river aggregate (A-3) is lower than that of other aggregates and sea aggregate (A-1) and crushed aggregate (A-4) have a pH of more than 7. However, the pH did not have a large influence on CEC. Because the pH difference was not significant in each aggregate sample, it is believed that the content of organic matter relates more to the CEC than to the pH of aggregate.

3.5. Relationship between Ammonium Ion and Organic Matter in Different Aggregate

Table 5 shows the contents of organic matter and NH_4^+ in the aggregate from different areas of production. In the cases of river (A-3) and land (A-2) aggregate containing high contents of organic matter, the NH_4^+ was higher than in other aggregate. Hence, the composition possibility of NH_4^+ in soil was increased with increasing organic matter content and the increase of organic matter leads to the increase of NH_4^+ due to the high CEC of the aggregate.

The organic matter in soil adsorbs cation due to high CEC. Hence, the produced NH_4^+ is absorbed into the aggregate by cation exchange interaction without spill.

4. Conclusions

The various gases occurring by the hydration process of cement concrete, among these gases, ammonia gas can be released to indoor-outdoor environment through diffusion in cement concrete. The emission of NH_3 from cement concrete using 4 types of aggregate according to the different areas of production was investigated using a gas-detecting tube test and the concentration of NH_3 released from cement concrete was compared to the contents of organic matter and NH_4^+ contained in the aggregate. It is found that NH_3 released from cement concretes is produced by the reaction of NH_4^+ adsorbed into the aggregate with a strong alkali in cement concrete, as a process of ammonia volatilization. The concentrations of NH_3 emission from cement concrete according to the aggregate used from different areas of production differ by more than 4 times. And the differences depend on the content of NH_4^+

adsorbed into the aggregate.

The content of NH_4^+ in sand is strongly related to the content of organic matter. This is because the composition possibility of NH_4^+ in soil was increased with increasing organic matter content and the increase of organic matter leads to the increase of NH_4^+ due to the high CEC of the aggregate.

Therefore, it is recommended that aggregate containing low organic matter is used in the manufacturing of concrete in order to reduce the emission of NH_3 from cement concrete building.

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