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Effects of ammonium chloride salt added to mixing water on concrete and reinforced concrete subject to atmospheric corrosion

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Abstract

Studied in this paper is the effect of SO_2 as a pollutant gas on concrete and reinforced concrete specimens at various relative humidity (RH) rates prepared with ideal mixing water (IMW) and IMW + 80 mg NH_4^+ (NH_4Cl) mixing water. The potential values of reinforcing steel were measured throughout 28 days and compressive strength values of concrete specimens in the same medium were determined at the end of the 28th day. SO_2 gas was observed to have a harmful effect at higher RHs on compressive strength of concrete and to make more negative the potential values of reinforcing steel. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Cement, aggregates and mixing water are the principal components of concrete and reinforced concrete, which are of great importance compared to the other building materials. Certain additives are added to these compounds depending on the area and conditions of the application to enhance the strength of the concrete against the physical, chemical, physico-chemical and mechanical effects.

The determining factor for the concrete to acquire a proper strength is the chain of chemical reactions between cement and mixing water. It is essential that concentration of ions in the mixing water should not exceed certain values. Ammonium ions in the mixing water should be as low as 30 to 60 ppm. Even relatively low concentrations are claimed to have the tendency to adversely affect the strength [1].

During the process of concrete hardening, the cement forms silicates with mixing water. If ammonium chloride salts are present in the mixing water, it interacts with $Ca(OH)_2$, which is included in the pores and forms $CaCl_2$ and volatile NH_3 [2]. Quick removal of NH_3 will adversely affect the concrete [3].

The equilibrium of NH_4^+/NH_3 depends entirely on the pH value of the medium. Following relations should be noted (Eqs. (2) and (3)):

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \qquad (1)$$

$$NH_4^+ \Longleftrightarrow NH_3 + H^+ \qquad (2)$$

The pK_a value at 25 °C is 9.3. NH_3 concentration in waters with pH >10 proportionally increases while NH_4^+ ion concentration decreases to a negligible level [4].

Reinforcing steel is known to be well protected against corrosion if embedded in the concrete properly compacted well and cured under favorable conditions [5]. Also, it is reported that the natural pH values (pH = 12.6–13.18) of concrete pores cause the passivation of the surface of the reinforcing steel [6]. However, the reinforcing steel, which must be passive under expected pore conditions, may lose its passivity if harmful ions such as NH_4^+, Cl^-, $SO_4^=$, etc., are present in the mixing water [7]. Passivity of the reinforcing steel can be determined by measuring its potential values. According to the ASTM C 876, if the measured potential, referenced to the copper–copper sulphate (CSE) is -0.20 V or higher, 90% or more of the reinforcing steel is passive. When the potential is in the range of -0.20 to -0.35 V CSE, the corrosion activity of the reinforcing steel

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is uncertain. If the potential is below − 0.35 V CSE, 90% of the reinforcing steel is active.

Aside from the properties of principal components of concrete and composition of mixing water, the medium surrounding the concrete is also important. The natural conditions, as well as industrial pollution, can result in the vulnerability of concrete subject to atmospherical effects. The most significant natural parameter is the relative humidity (RH). The gases emitted to the atmosphere by industrial plants such as SO_2 may affect concrete adversely. It is reported that the hazardous effect of SO_2 leading to corrosion of materials in the atmosphere occurs at higher rates in high RHs [8]. In literature, metal corrosion is not significant in atmospheric conditions below 70% RH which is called the critical point of RH [9]. It is known that a thin film layer forms on the material surface when the RH exceeds the critical point. Corrosive effect of SO_2 occurs due to dissolved gas within this thin layer of moisture, which results in formation of aggressive ions. The dissolution reaction of SO_2 in this layer is given below (Eqs. (3)–(7)):

$$SO_2 + H_2O \rightarrow SO_2{\cdot}H_2O \tag{3}$$

$$SO_2{\cdot}H_2O \rightarrow H_2SO_3 \tag{4}$$

$$H_2SO_3 \Longleftrightarrow H^+ + HSO_3^- \tag{5}$$

$$HSO_3^- \Longleftrightarrow H^+ + SO_3^= \tag{6}$$

$$SO_3^= + 1/2\,O_2 \rightarrow SO_4^= \tag{7}$$

In this study, the effect of SO_2 gas is investigated under laboratory conditions at 60%, 70%, 80%, 90% and 100% RH on the atmospheric corrosion of concrete and reinforced concrete samples prepared with two different mixing water.

2. Experimental

2.1. Materials

Chemical composition of cement used in the experiments is given in Table 1. Natural aggregate was used in the experiments. Ideal mixing water (IMW) was prepared with chemicals added to the distilled water. The chemical components of IMW are 10 mg/l NH_4^+ (NH_4Cl), 100 mg/l Mg^{2+} [$Mg(NO_3)_2$], 200 mg/l $SO_4^=$ (Na_2SO_4) and 100 mg/l Cl^- (NaCl) [10]. The steel rods composition used in the experiments were 0.13% of C, 0.65% of Mn, 0.030% of S, 0.013% of P and 0.017% of Si. Steel rods were embedded into the concrete as shown in Fig. 1.

Table 1
Chemical composition of cement

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
31.42	9.15	4.29	42.42	5.18	1.63

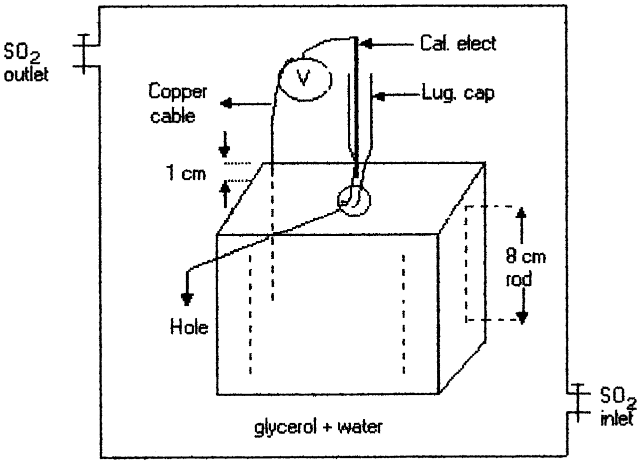

Fig. 1. Atmospheric corrosion experimental set-up.

2.2. Method

In these experiments, two different compositions of mixing water were used in concrete and reinforced concrete sample sets. One group was prepared with IMW and the other group was prepared with IMW + 80 mg/l NH_4^+. The concrete samples were prepared in 10 × 10 × 10 cm cubic shape embedding the steel into the concrete specimens having the same composition as given in Table 2. The atmospheric corrosion tests were performed on concrete and reinforced concrete samples mentioned above. The atmospheric corrosion test cell is shown in Fig. 1. Embedded plastic hooks were used to hang the specimens on wooden hangers in the cell. The RH was adjusted to desired values by means of a water–glycerol mixture placed in the cell [8,11]. Before the experiments, the samples were kept in the cell for a period of 1 day to ensure that the surface of the samples reached to the desired level of RH. The rate of gas flow in all experiments was 2 cm^3/s of SO_2, which was carefully measured and regulated throughout the exposure to obtain a constant SO_2 concentration. In laboratory conditions, the concentration of the gases were kept very high to accelerate the corrosion tests. The experiments were carried out at room temperature (~20 °C). The potentials of rod steel in reinforced concrete were measured

Table 2
Composition of the concrete

	Mass (kg)	Density (kg/dm^3)	True volume (dm^3)
Water	168	1.00	168
Cement	306	2.98	103
Air	–	–	20
0/4 Aggregate	878	2.48	354
4/16 Aggregate	868	2.45	355

once a day up to the 28th day by means of a multimeter. Measurements were made on the specimens in the cell. Compressive strength tests were carried out on concrete samples on the 28th day.

3. Results

3.1. Corrosion tests

Fig. 2a displays potential variations taking place in time after the concrete samples were prepared with IMW and were arranged in the corrosion test chambers with different levels of RH. Fig. 2b gives the potential variations obtained in time on exposing the specimens to SO_2 gas.

As can be seen in Fig. 2a, potential values vary depending on the RH. That is, the higher the RH is, the smaller the potential values are; however, the latter are observed to decrease in all levels of humidity during the first 3 days while the same tend to increase from then on up to the 15th day; after that they remain virtually constant. Potential values obtained at such RHs as 60% and 70% were approximately identical, whereas a notable decrease in potential was observed at 80% rate of RH. It has been determined that the decrease of potential values are very slow at 60–90% RH, whereas a sharp decrease at 100% RH has been observed.

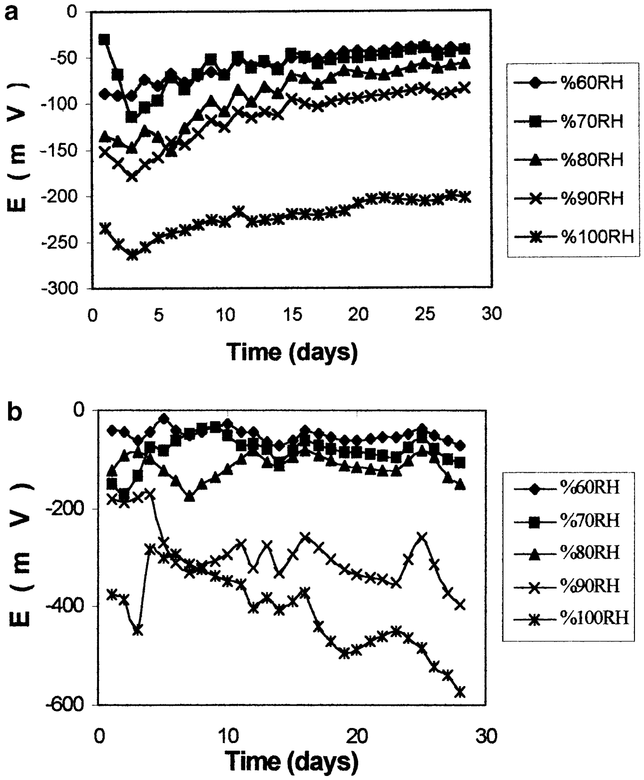

Fig. 2. (a) The potential variations of reinforcing steel vs. time at the different RHs gas-free (IMW). (b) The potential variations of reinforcing steel vs. time at the different RHs on SO_2 gas (IMW).

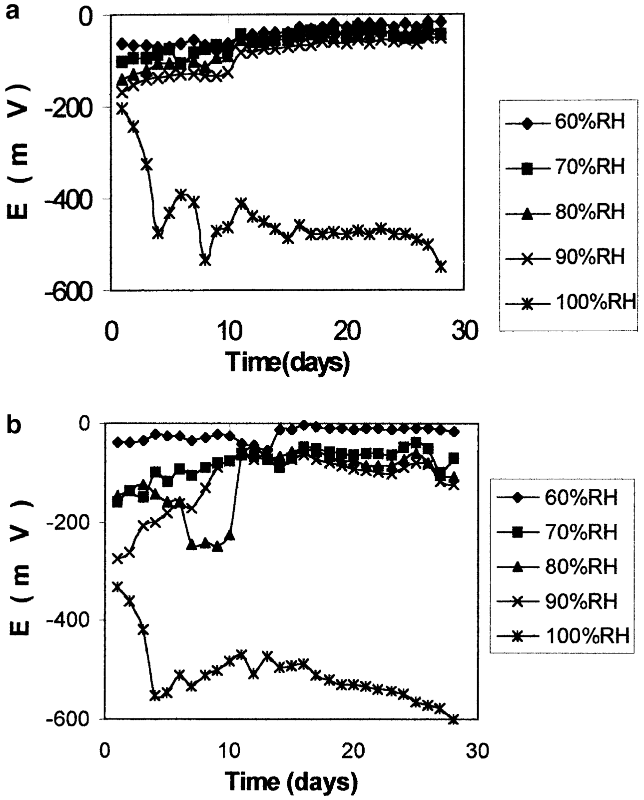

Fig. 3. (a) The potential variations of reinforcing steel vs. time at the different RHs gas-free (IMW + 80 mg NH_4^+). (b) The potential variations of reinforcing steel vs. time at the different RHs on SO_2 gas (IMW + 80 mg NH_4^+).

At 60% RH, for instance, the potential value measured on the 15th day was – 70 mV, whereas the same appeared to be – 105 and – 233 mV, respectively, at 80% and 100% RH rates. Potential values observed at 100% RH rates were 3.5 times as low as those obtained at 60% RH.

When reinforced concrete samples at different RH mediums were exposed to SO_2 gas (Fig. 2b), potential values at 60%, 70% and 80% RH were observed to be close to those obtained at gas-free mediums and remained unchanged throughout the measurement period (Fig. 2a–b). When the RH was 90%, the potential value, which was constant for the first 4 days, was observed to start to decrease continually after the fifth day. Variation in potential value at 100% RH depending on time, though observed similar to that at 90% RH, was indeed smaller in actual value. Comparing Fig. 2a with Fig. 2b, one will notice that the potential value on the 15th day at 90% RH in gas-free medium was – 95 mV, whereas it was – 233 mV under exposure to SO_2. The potential values at 100% RH on the 15th day were recorded to be – 230 and – 360 mV, respectively.

Given in Fig. 3a are time-dependent potential variations in reinforcing steel at different RHs in a medium where 80 mg ammonium ions were added to IMW. The figure reveals that potential varies depending on the RH. Potential values diminish in parallel with higher potential values.

These potential values diminish incrementally within 60% to 90% rates up to the 11th day thereupon they remain virtually constant. At 100% RH, the potential value starting from − 200 mV reached − 460 mV on the fourth day, when some fluctuations in potential values were observed and continued to the 10th day. On the other hand, the potential value was found to remain at approximately − 450 mV.

Given in Fig. 3b are time-dependent variations in potential values observed in the reinforced concrete samples exposed to SO_2 gas. As can be seen in the figure, within the range of 60% to 90% RH, potential values starting at various values on the first day increased with time and reached approximately − 100 mV at the 12th day, which was relatively the same among all. Potential values at 60% RH were approximately 0 mV from the 12th day to the 28th day while potential values at 70%, 80% and 90% RHs were observed to be close to one another, namely ∼ − 120 mV. On the first day, the potential value at 100% RH was recorded − 332 mV. This value reached to − 551 mV on fourth day. The potential values decreased by the time and were observed at − 612 mV on the 28th day. This means five times as low as those obtained at 70–90% RHs.

3.2. Compressive strength tests

Concrete samples which were prepared with IMW and IMW + 80 mg NH_4^+ were located in the atmospherical corrosion test chamber. These samples were kept in both gas-free conditions and SO_2 medium for 28 days before going under compression tests (Figs. 4 and 5).

Fig. 4 accounts for the results of compression tests (MPa) obtained with concrete samples prepared with IMW at gas-free conditions and SO_2 gas medium. Compressive strengths at 60% and 70% RHs seemed to be similar at both gas-free and/or SO_2 mediums. Obtained results at the 80–100% RH range proved to be lower under SO_2 exposure when compared with those at the gas-free medium. Compressive strength values at both mediums were found to be increasing with higher RHs.

Fig. 5 reveals variations in compressive strength of concrete samples prepared with IMW + 80 mg/l NH_4^+ at gas-free conditions as well as at SO_2 medium. While compressive strength values proved to increase under gas-free conditions with higher RHs, the same findings were not obtained under exposure to the SO_2 medium.

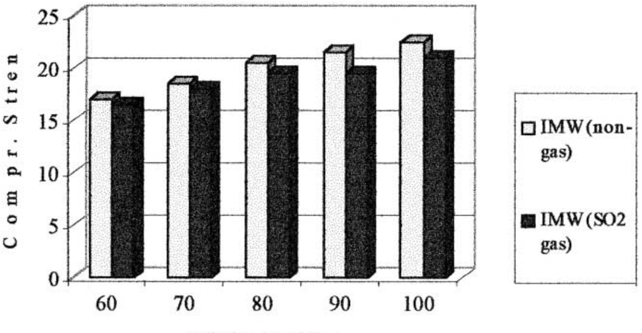

Fig. 4. Compressive strength of the concrete specimens prepared with IMW at different RHs, gas-free and SO_2 conditions.

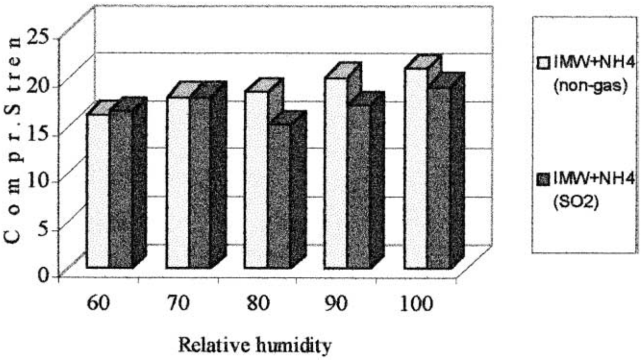

Fig. 5. Compressive strength of the concrete specimens prepared with IMW + NH_4^+ milligrams per liter at different RHs, gas-free and SO_2 conditions.

4. Discussion

Let us consider that reinforcing steel is passive when potential values measured across calomel electrode (SCE) are higher than − 322 mV [7]. Potential values obtained from reinforced concrete specimens exposed to certain RHs have more positive values than this. Even the smallest potential values measured under influence of 100% RH are not within the active potential range (Fig. 2a).

Given in Fig. 2b are potential values obtained by exposing reinforced concrete specimens at various RHs to SO_2 gas at 2-cm^3/s rate. The figure reveals that potential values at 60%, 70% and 80% RHs are within the passive region as in Fig. 2a, however, these potential values at 90% and 100% RH rates diminish in time. The last potential values obtained on the 28th day at 90% and 100% RHs are − 397 and − 572 mV, respectively, which shows that the reinforcing steel is active. It is known that a relatively thick film of moisture is formed on the surface of specimens under both 90% and 100% RH conditions [11]. In order to have corrosive effects on steel, SO_2 needs to be dissolved in the medium before oxidation. From the SO_2 dissolved on the moisture film formed on the specimen H^+, $SO_3^=$ and $SO_4^=$ ions are produced according to Eqs. (6) and (7). As a result of diffusion through pores in the concrete, these ions can participate in the reactions (Eqs. (8)–(10)):

$$Fe + 2H^+ \Longleftrightarrow Fe^{+2} + H_2 \qquad (8)$$

$$Fe^{+2} + SO_3^= \rightarrow FeSO_3 \qquad (9)$$

$$Fe^{+2} + SO_4^= \rightarrow FeSO_4 \qquad (10)$$

Particularly due to reaction (8), reinforcing steel will progressively dissolve. Potential values obtained from reinforced concrete specimens prepared with IMW + 80 mg/l

NH_4^+ at 60%, 70%, 80% and 90% RH levels are within the passive region (Fig. 3a) while those values taken at 100% rate of RH are in the active region from the fourth day. Hence, 100% RH condition can be considered as water medium [8,9]. Ammonium chloride salt is hydrolized in the pores by reactions (1) and (2) and produced chloride and hydrogen ions. The adverse effects of chloride ions on the reinforcing steel are well known [3,5–7,12,13]. Hydrogen ions also have adverse effects on the reinforcing steel as shown in reaction (8).

Potential values obtained from 60% to 90% RHs with SO_2 gas applied are in the passive region (Fig. 3b), although they are different from those for the gas-free medium. Potential values measured at 100% RH are, however, lower than those obtained in the gas-free medium. This should be due to the common effect of hydrogen ions formed by SO_2 gas externally applied and that of ammonium chloride salts contained in the IMW.

Concrete gains maturity and strength only in water condition. Since 100% RH condition can be considered as water medium, strength results taken in such medium are expected to be relatively high. This is also verified by the results of the experiment (Figs. 4 and 5) which reveals that compressive strength values increase proportionally with RH rate.

Compressive strength values taken from concrete specimens prepared with IMW exceeded 20 MPa at 90–100% RH (Fig. 4). The same values proved to be below 20 MPa under the same RH values on concrete specimens prepared with IMW + 80 mg/l NH_4^+ (Fig. 5). These results denote unfavorable effect of ammonium ions on concrete. Natural pH of concrete pores is greater than 10 (pH >10). NH_4^+/NH_3 equilibrium at this pH level increases in the direction of releasing NH_3 gas in concrete pores according to reaction (2), which may cause micro cracks.

Compressive strengths are observed to decrease (Figs. 4 and 5) when SO_2 gas is applied to concrete specimens prepared with both IMW and/or IMW + 80 mg/l NH_4^+ mixing waters at different RHs. The reason for this is that ions formed due to dissolution of SO_2 in the film layer of moisture on the surface of concrete specimen diffuse. Previous researches show that these ions forming large volumes of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) during the maturation of concrete cause expansion and cracking [3,14].

5. Conclusions

(1) Potential values of reinforced concrete specimens prepared with IMW decrease proportionally with an increase in RH in uncontaminated atmosphere medium. Potential values at all RHs remain in the passive region.

(2) Potential values of the same specimens exposed to SO_2 shift to the active region for 90% and 100% RH rates.

(3) Potential values of specimens prepared with IMW + 80 mg/l NH_4^+ at gas-free medium are quite low. The reinforcing steel is clearly in the active region for 100% RH. The same specimens exposed to SO_2 yields even lower potential values.

(4) Compressive strength of specimens prepared with IMW increases with RH. The same specimens exposed to SO_2 give lower values especially at 90% and 100%.

(5) Compressive strength of specimens prepared with IMW + 80 mg/l NH_4^+ is lower compared to those with IMW. The specimens exposed to SO_2 give significantly lower values at 80% and higher RHs. This effect is not noticeable at 60% and 70% RHs.

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