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Effect of hydroxyl ions on chloride penetration depth measurement using the colorimetric method

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ABSTRACT

In this paper, the effect of hydroxyl ions on chloride penetration depth measurement using the colorimetric method was studied. Equivalent silver nitrate solution (i.e. $Ag^+=Cl^-$) was added to the NaCl+NaOH solution with different concentrations, then the amount of precipitated silver chloride and silver oxide were determined by chemical methods, and the color of the precipitated products was examined. Results show that the amount of silver chloride formed decreases linearly as OH^- to Cl^- ratio (r) increases. Thus, the chloride concentration at color change boundary changes with the pH value of the concrete. AgCl has a white color, while Ag_2O has a dark brown color. When the value of r exceeds 4, the color of the mixture looks brown, and color change boundary cannot be easily distinguished.

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1. Introduction

The silver nitrate colorimetric method is a very easy and quick practice to measure the free chloride penetration depth in concrete. In this method, an aqueous silver nitrate solution with a certain concentration (normally 0.1 mol/l) is sprayed on the freshly fractured cross-section of concrete; consequently, the silver ions react with the chloride ions to form a white precipitate, i.e. silver chloride; in the chloride free or low chloride ion area, the silver ions react with the hydroxyl ions to form a brown precipitate. There is a very obvious boundary between the white and brown areas. Thus, many researchers have studied the chloride concentration at the boundary and noticed that it varies within a significant range.

Ostuki et al. [1] proposed to use silver nitrate to determine the depth of chloride penetration and quantify the chloride concentration at the color change boundary. They found that although the total chloride content at the color change boundary varied from 0.4–0.5% for paste, 0.8% for mortar and 0.5% for concrete, depending on not only the differences between internal or external values, but also on the differences between paste and concrete, the corresponding water soluble chloride content remains constant. This quantity is approximately 0.15% by the mass of cement. Collepardi [2] added different levels of chloride to concrete and studied the color change of concrete by spraying with silver nitrate solution at different ages. The results showed that 0.01%free chloride content by the mass of cement could be detected by colorimetric method. Andrade et al. [3] found that the value of total chloride concentration at which the color changed for concrete made with different types of binder was 1.13 ± 1.4% by cement mass or 0.18 ± 0.2% by concrete mass, with quite a high coefficient of variation of 62%. In another study [4], the concentration varied from 0.02% to 0.23% by the mass of concrete or from 0.28% to 1.41% by the mass of cement. The coefficient of variation was 40% for concrete and 30% for binder. The authors ascribed the high coefficient of variation to the method used to obtain the concrete powder at different depths for the chloride analysis.

As can be seen from the published data, the free chloride content at the color change boundary varies from 0.01% to 1.41% by the mass of cement. There are three possible reasons for the high variation. First, different testing methods are used for measuring the chloride concentration. Secondly, silver nitrate spraying test is a chemical reaction, which might be influenced by the chemistry of concrete pore solution. Different concretes, especially containing supplementary cementing materials, have different chemistry of pore solution, which is often not considered in the silver nitrate spraying test. Finally, since concrete is a heterogeneous material, and the color change boundary is an irregular line, sampling the boundary sample used for chloride analysis may also be responsible for the variation. However, no paper discussed the factors influencing chloride concentration at the color change boundary, except

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Table 1
The percentage of silver chloride in precipitate when equivalent silver nitrate ($Ag^+=Cl^-$) was added to NaOH+NaCl solution

Concentration of NaOH(mol/L)	Concentration of NaCl(mol/L)	WAgCl%			Average %	Standard deviation	Coefficient of variation %
		1	2	3			
0.5	0.5	98.84	98.49	98.34	98.56	0.21	0.21
0.5	0.2	93.82	93.90	94.73	94.15	0.62	0.66
0.5	0.1	93.40	95.40	94.70	94.50	0.83	0.88
0.5	0.05	94.06	95.30	92.55	93.97	1.12	1.2
0.5	0.01	67.93	69.01	67.48	68.26	0.65	0.96

Tang [5] recognized that hydroxyl ions have a great influence on the colorimetric method. In fact, silver nitrate can react with both chloride ions and hydroxyl ions to form white AgCl and dark brown Ag_2O. When aqueous silver nitrate solution was sprayed on the surface of splitted concrete, the precipitates formed on the surface of concrete may be a mixture of silver oxide (silver hydroxide is unstable, decompose to silver oxide instantaneously) and silver chloride. When the percentage of silver oxide is large enough, the color of white may be covered by brown. Consequently, the chloride cannot be detected by colorimetric method.

The objective of this paper is to study the effect of hydroxyl ions on the formation of AgCl and the colorimetric method. First, the effect of hydroxyl ions on the formation of silver chloride was studied by adding equivalent silver nitrate solution (i.e. $Ag^+=Cl^-$) to the NaCl+NaOH solution with different concentrations, then the amounts of precipitated silver chloride and silver oxide were determined by chemical methods. Secondly, excessive silver nitrate was added to the NaCl+NaOH solution with different concentrations, and the colors of the precipitates (Ag_2O+AgCl) were observed, which were compared to the color of concrete.

2. Experimental

Chemicals used in this study were chemical grades, and distilled water was used to prepare the solutions. Silver nitrate solution was added to the NaCl+NaOH solutions at the same equivalent concentrations of Ag^+ and Cl^-. The concentrations of NaOH solution ranged from 0.01 mol/l to 0.5 mol/l, and the concentrations of NaCl solution ranged from 0.002 mol/l to 0.5 mol/l. The procedure used to determine the percentage of AgCl in the precipitated mixture of Ag_2O+AgCl is described as the followings: (1) dry a porous stone filter at 105 °C to constant mass, and then get a mass of W_0; (2) add silver nitrate (the mole of silver ions equals to that of chloride ions) into the prepared solutions containing different concentrations of sodium chloride and sodium hydroxide, the solution was shaken manually for about 1 min, put aside for reaction for 1 min; (3) filter the solution and precipitated products using the porous stone, then rinse the filter with distilled water, followed by drying the filter and the precipitate (consisting of silver oxide and silver chloride) at 105 °C to constant mass, and then get a mass of W_1; (4) use diluted nitric acid to dissolve silver oxide in the precipitate, then rinse the filter with distilled water, and dry the filter and precipitate (silver chloride) at 105 °C to constant mass, and then get a mass of W_2. During the entire period of the experiment, intensive sunlight should be avoided. The percentage of silver chloride in the precipitate can be calculated as follows:

$$W_{\mathrm{AgCl\%}} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\% \tag{1}$$

where:

$W_{\mathrm{AgCl\%}}$ is the percentage of silver chloride in the precipitated mixture,
W_0 is the mass of the filter, g,
W_1 is the mass of the filter, silver oxide and silver chloride, g,
W_2 is the mass of the filter and silver chloride, g.

At the second stage, the percentage of AgCl in the mixture of Ag_2O+AgCl was controlled by the mole ratio of OH^- to Cl^-, and the colors of the mixtures, with 100%, 98.2%, 97.5%, 92.6%, 86.1%, 55.2%, 13.9%, 7.4%, 1.8% and 0% of AgCl, were observed and photos were taken with a digital camera (Cannon powershot A 550), at the same place with the same light intensity.

3. Results and discussion

Table 1 shows the percentage of silver chloride in precipitated mixture when equivalent silver nitrate ($Ag =Cl^-$) was added to NaOH+NaCl solution. The low coefficients of variation indicate that the method is reproducible. It can be seen that when the concentration of NaOH equals the concentration of NaCl, the formation of silver chloride is dominant, which means that chloride ions are more likely to react with silver ions rather than hydroxyl ions. This is because that the silver ions react with hydroxyl ions or chloride ions to form silver hydroxide and silver chloride, then silver hydroxide decompose to silver oxide. The solubility product of silver hydroxide is 2.6×10^{-8}, and is higher than that of silver chloride, which is 1.8×10^{-10} [6]. It can also be seen that the mole ratio (r) of OH^- to Cl^- has a great influence on the formation of silver chloride. In the three-phase-system of Ag^+–Cl^-OH^-, the mass percentage of the precipitates can be theoretically calculated

Table 2
Effect of r (mole ratio of NaOH to NaCl) on the percentage of silver chloride in precipitate when equivalent silver nitrate ($Ag^+=Cl^-$) was added to NaOH+NaCl solution

	Theoretical value	NaOH (mol/l)	NaCl (mol/l)	NaOH (mol/l)	NaCl (mol/l)	NaOH (mol/l)	NaCl (mol/l)	NaOH (mol/l)	NaCl (mol/l)
$r=1$		0.5	0.5	0.1	0.1	0.025	0.025	0.01	0.01
AgCl%	99.4%	98.56%		98.02%		98.47%		97.80%	
$r=10$		0.5	0.05	0.25	0.025	0.125	0.0125	0.1	0.01
AgCl%	94.3%	93.97%		92.91%		93.10%		93.33%	
$r=20$		0.5	0.025	0.2	0.01	0.1	0.005		
AgCl%	88.6%	87.77%		86.85%		87.60%			
$r=50$		0.5	0.01	0.25	0.005	0.1	0.002		
AgCl%	70.2%	68.26%		69.79%		68.58%			

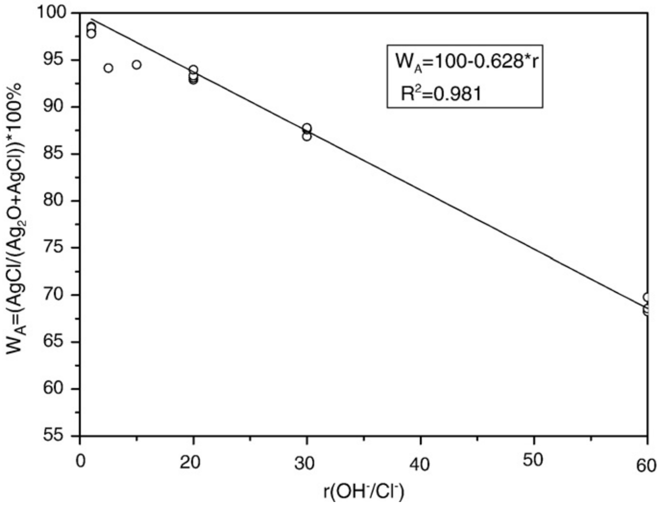

Fig. 1. The relationship between r and the percentage of AgCl in the precipitates.

based on the solubility products of silver hydroxide and silver chloride, as follows:

Solubility product of silver hydroxide:

$$M_{Ag} \times M_{OH} = 2.6 \times 10^{-8} \tag{2}$$

Solubility product of silver chloride:

$$M_{Ag} \times M_{Cl} = 1.8 \times 10^{-10} \tag{3}$$

Mass balance:

$$V_{Ag}M_{\mathrm{Initial-Ag}} - V_T M_{Ag} = VM_{\mathrm{Initial-Cl}} - V_T M_{Cl} + VM_{\mathrm{Initial-OH}} - V_T M_{OH} \tag{4}$$

Where M_{Ag}, M_{OH}, M_{Cl} are the mole concentrations of Ag^+, OH^- and Cl^- after reaction, respectively. $M_{\mathrm{Initial\text{-}Ag}}$, $M_{\mathrm{Initial\text{-}OH}}$, $M_{\mathrm{Initial\text{-}Cl}}$ are the mole concentrations of Ag^+, OH^- and Cl^- before reaction, respectively. V_{Ag} is the volume of $AgNO_3$ solution added to the NaOH+NaCl solution, V_T is the total volume.

Table 3
Effect of concentrations of hydroxyl ions on the chloride concentration at the color change boundary

r(OH−/Cl−)	OH− (mol/l)	pH value	Chloride concentration at the color change boundary (mol/l)
4	0.64	13.8	0.160
4	0.5	13.7	0.125
4	0.3	13.5	0.075
4	0.06	12.8	0.015
4	0.05	12.7	0.013
4	0.03	12.5	0.008

When equivalent silver nitrate ($Ag = Cl^-$) is added to NaOH+NaCl solution, the percentage of AgCl in the precipitate can be calculated according to Eqs. (2) to (4). Regardless of the concentration, when the value of r changes from 1 to 50, the percentage of silver chloride decreases from 99.41% to about 70.22%, as shown in Table 2.

To further experimentally study the effect of r on the percentage of silver chloride in the precipitate, equivalent silver nitrate ($Ag^+ = Cl^-$) was added to NaOH+NaCl solution with different concentrations, as shown in Table 2. Regardless of the concentration, when the value of r changes from 1 to 50, the percentage of silver chloride decreases from 98.56% to about 68.26%, and the color of precipitate changes from white to brown. The experimental data are slightly higher than, but fit quite well, theoretical values. Based on the experimental data, a plot of W_A vs r indicates that the percentage of silver chloride linearly decreases as the r increases, as shown in Fig. 1.

To study the color of the precipitated mixture of silver chloride and silver oxide, excessive silver nitrate was added to the NaCl+NaOH solutions with different concentrations. In this case, the mole ratio of to OH^- to Cl^- is two times as the mole ratio of Ag_2O to AgCl, and it is assumed that all the chloride and hydroxyl ions can react with silver ions to form precipitates. The mixture with different ratios of Ag_2O to AgCl could be obtained by controlling the ratio of NaOH and NaCl. The colors of the precipitated mixtures are shown in Fig. 2. When the percentage of silver chloride changes from 100% to 0%, the color changes from white to dark brown. From the pictures in Fig. 2, it can be seen that when the percentage of silver chloride equals around 97.5%, the color looks brown, and close to the color of concrete. When the

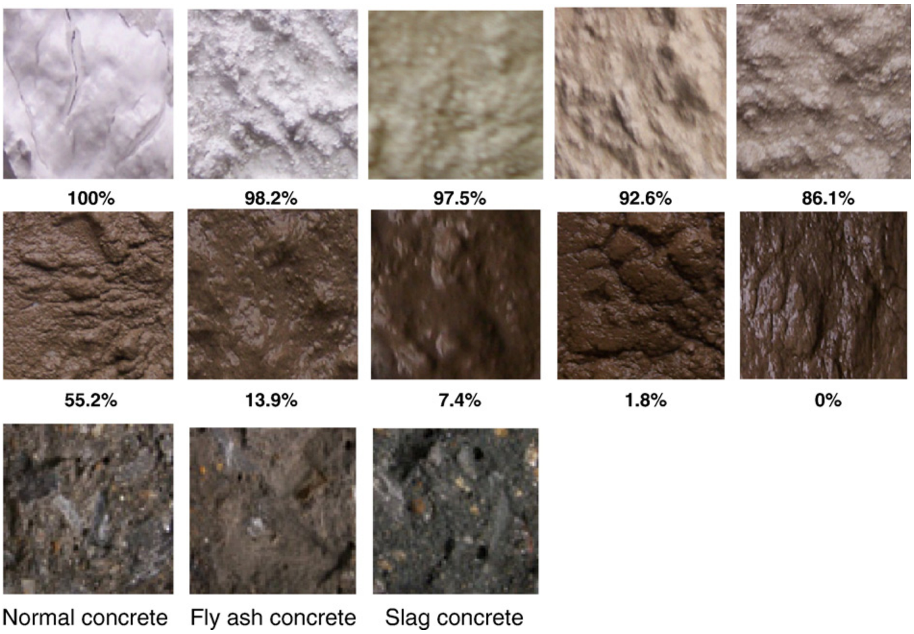

Fig. 2. The color of the mixture (Ag_2O+AgCl) containing different percentages of AgCl and the color of concrete.

silver chloride content is below that, it becomes very difficult to distinguish the color from concrete itself.

The critical percentage was assumed to be 97.5%, that is, when the percentage of silver chloride is lower than 97.5%, the color will look brown, and the chloride cannot be easily detected by spraying silver nitrate solution. According to Fig. 1, the critical value of *r* equals 4. Different concentrations of hydroxyl ions in the pore solution of concrete are assumed, their corresponding critical chloride concentrations for color change can be obtained, as shown in Table 3. As can be seen, the concentration of hydroxyl ions (or pH value) has a great influence on the chloride concentration at color change boundary.

Based on the above results, it can explain why Ostuki et al. found that 0.1 mol/l silver nitrate was the most appropriate concentration [1]. They sprayed 0.05, 0.1, 0.2, 0.3, and 0.4 mol/l silver nitrate solution onto the concrete surfaces. When silver nitrate solution is much lower than 0.1 mol/l (such as 0.05 mol/l), the color was not as bright as that of concrete surface sprayed with 0.1 mol/l silver nitrate, this may be ascribed to the amount of silver chloride formed on the concrete is small because of the low concentration of silver ions. When the silver nitrate solution is much higher than 0.1 mol/l (such as 0.4 mol/l), the color was also not as bright as that of concrete surface sprayed with 0.1 mol/l silver nitrate, this may be ascribed to the formation silver oxide, and the white color is covered. Thus, 0.1 mol/l silver nitrate solution is the most proper spraying solution.

It is well known that supplementary cementitious materials, especially silica fume, have a great influence on the hydroxyl ions in the pore solution of concrete. Silica fume can decrease the hydroxyl ions by almost one order of magnitude [7], which may result in a decrease of the critical chloride concentration for color change also by one order of magnitude. This can explain why Andrade et al. [3] found that the chloride concentration at the color change boundary of silica fume concrete was much lower than that of other concretes. Water to binder ratio also has an influence on the hydroxyl concentration, and it is not as significant as the incorporation of silica fume. The effect of supplementary cementing materials on chloride penetration depth measurement using the colorimetric method needs further study.

4. Conclusions

When the silver nitrate colorimetric method is used to measure the chloride penetration depth, the precipitate formed on the surface of concrete may be a mixture of silver oxide and silver chloride. The amount of silver chloride formed decreases linearly as the *r* increases.

Since silver chloride is white and silver oxide is dark brown, it will be very difficult to distinguish the color of precipitated products from concrete when *r* is greater than 4.

For a given *r*, the concentration of hydroxyl ions (or pH value) in concrete pore solution has a great influence on the critical chloride concentration at the color change boundary.

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