INFLUENCE OF THE RELATIVE MOLECULAR MASS OF VISCOSITY ENHANCERS ON CHLORIDE DIFFUSION IN MORTARS: A PERLIMINARY STUDY

Lixiao Zhao (1), Pan Feng(1)(2)

(1) School of Materials Science and Engineering, Southeast University, China

(2) State Key Laboratory of High Performance Civil Engineering Materials, China

Abstract

Chloride diffusion in concrete is one of the key parameters of durability design for structure. Existing methods of reducing the chloride diffusion such as decreasing water-cement ratio and adding mineral admixtures often lead to increase the risk of concrete cracking. In this study, we focused on mitigating the permeation of chloride ions in concrete by adding viscosity enhancers to improve the viscosity of concrete pore solution, without densifying the pore structure of concrete. A comparative study was conducted among the conductivity of KCl solutions with the addition of polyethylene glycol (PEG) with 11 different relative molecular masses. The results show that the chloride diffusion can be most effectively reduced when the relative molecular mass remains in the range of 400-1500.
Keywords: Viscosity enhancer, Chloride diffusion, Relative molecular mass, Conductivity

1. INTRODUCTION

As one of the most widely used building materials in the world, the durability of cement-based materials has attracted extensive attention. It is well known that steel corrosion is the biggest threat to the durability of reinforced concrete [1-2]. Corrosion of reinforcement is generally caused by electrochemical process which is triggered by chloride ions from the external environment to the surface of reinforcement passing through concrete matrix, which serves as the protective layer. Therefore, the permeability of chloride ions in concrete is one of the key parameters that affect the service life of reinforced concrete structures [3-4].

Currently, to reduce the permeability of chloride ions in concrete, we usually decrease the water-cement ratio or add mineral admixtures [5]. But these methods inevitably increase the compactness of concrete, accordingly, these will increase the risk of concrete cracking and the dead load of the structure. Is there a way to reduce the permeability of chloride ions without increasing the density of the structure? The literatures published in 2008 [6] and 2010 [7] proposed an innovative way to reduce the diffusion coefficient of chloride ions by increasing the viscosity of pore solution of cement-based materials, by adding nanomolecule viscosity enhancers. Kenneth et al. [8] extended for the research in [7], and through a year's exposure experiments, it was found that after adding small molecular viscosity enhancer, the effective diffusion of chloride ions in the mortar can be reduced by nearly a factor of two, and the method that adding prewetted fine lightweight aggregate with viscosity enhancer can achieve a better effect. Bentz et al. [9] clarified the influence of several different ways of adding viscosity enhancer on chloride ions penetration in concrete mixed with fly ash and slag, as well as its adverse influence on the strength development of concrete. Qiao et al. [10] explored the effects of shrinkage-reducing agent (SRA) on isothermal drying, ion diffusion and water permeability of concrete, and perceived that chloride ions permeation was reduced for concrete with higher SRA content. In fact, SRA is also one of the viscosity enhancers.

Almost all studies have shown that adding appropriate viscosity enhancer have the ability to restrain chloride ions diffusion in concrete. We can regard the diffusion rate of ions in solution as being inverse proportional to the viscosity of the solution based on the Stokes-Einstein equation [6, 11]. However, it is noticeable that, limited by the coverage of Stokes-Einstein equation [12-13], the key to whether a viscosity enhancer can effectively reduce chloride diffusion is the relative molecular mass, which must be small, as Bentz et al [6] also pointed out. In the previous studies, the appropriate range of relative molecular mass of viscosity enhancer used to reduce the diffusion coefficient of chloride ions has not been paid much attention, and most researchers have only used commercial shrinkage-reducing agent as viscosity enhancers for their projects.

In this paper, we used polyethylene glycol (PEG) with different relative molecular mass as viscosity enhancers to preliminarily study the resistance to chloride diffusion in aqueous solution. Here, the diffusivity of chloride ions was estimated by the conductivity of 0.1mol/L KCl solution, using the direct proportional relationship between solution conductivity and ion diffusion rate [14]. On trial, to get approximately equal viscosity, the dosage of PEG with different relative molecular mass was determined first, based on which, the conductivity of KCl solutions were tested. By the end, an appropriate range of relative molecular mass of viscosity enhancer for reducing chloride ion diffusion was given.

2.Materials and experiment

In this study, there were 11 kinds of PEG, corresponding to different relative molecular mass, PEG200, PEG400, PEG600, PEG1000, PEG1500, PEG2000, PEG4000, PEG6000, PEG8000, PEG10000 and PEG20000, respectively. Here, the number after PEG represents the relative molecular mass. As the monomer of PEG, we tested ethylene glycol as a minimum relative molecular mass viscosity enhancer. KCl, ethylene glycol and all PEG used in this test were analytical reagent and purchased commercially. And the water used was deionized water.

The viscosimeter used in this test was rotary viscosimeter, it works by driving a rotor to rotate continuously in the fluid through a verified spring. The rotating torque sensor measures the degree of torsion of the spring, namely the torque. The torque is proportional to the resistance caused by viscous drag of the rotor immersed in the sample, based on which the viscosity can be obtained. In this test, ultra-low viscosity adapter and rotor 0# were selected, and the rotation speed was set at 60 RPM. This collocation can accurately measure the viscosity range of 1-10 mpa·s. The two-plate conductance electrode was used in the conductivity test, and it's measuring range was 0-20000 uS/cm.

Since the temperature directly affects the viscosity and conductivity of the solution, all of our solution tests were carried out in the low-temperature thermostatic tank with the temperature constant at 20.2℃. Depending on the research results in literature [6], when the concentration of KCl in the solution is lower than 0.001mol/kg, the addition of additives will have a significant impact on the conductivity of the solution. The concentration of KCl solution used in this paper was 0.1 mol/L, so the influence of the viscosity enhancers on the conductivity of the solution was not considered in this test.

3.Results and discussion

3.1 Viscosity in solutions of different additive concentration

The mix proportions of ethylene glycol and its polymers (relative molecular mass range 200-20000) solution for 2, 3, 4, 5 (±0.05) mpa·s were determined through trial preparation. The mass fraction of PEG with different relative molecular mass and the viscosity of solutions are plotted in Figure 1. In Figure 1, it is clearly indicate that the solution viscosity increase exponentially with the increase of mass fraction of PEG under different relative molecular mass conditions. Further, with the increase of relative molecular mass of PEG, the increasing trend of the solution viscosity with the increase of mass fraction was more intense. In other words, as has been indicated in many literatures [6, 15], if it is only to increase the viscosity of the solution, then the viscosity enhancer with higher relative molecular mass would be the better choice.

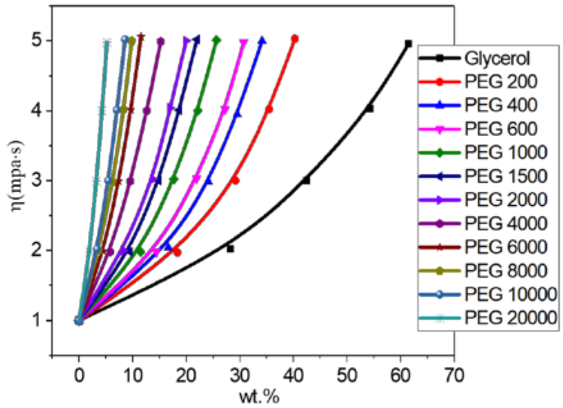

Figure 1: The relationship between mass fraction of PEG with different relative molecular mass and solution viscosity

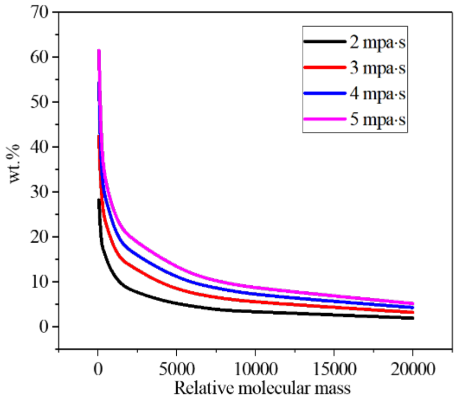

Figure 2: The relationship between relative molecular mass and mass fraction of PEG under different solution viscosity

As presented in Figure 2, the larger the relative molecular mass, the smaller the amount of PEG required to improve the viscosity. In Figure 2, we can also observe that the amount of PEG required to improve the unit viscosity (1 mpa·s) is decreasing under the same relative molecular mass. This might be due to the increasing possibility for molecules to attract or entangle with each other, under the condition of the increasing number of polymer molecules in a certain volume.

3.2 Conductivity of KCl in solutions of different viscosity

As recorded in Figure 3, we obtained the relationship between solution viscosity and solution conductivity with different relative molecular masses of PEG. Figure 3 shows that the conductivity of solution decrease with the increase of solution viscosity, indicating that PEG has the ability to improve solution viscosity and reduce chloride ions diffusion. It was explicit, however, that the PEG with lower relative molecular mass was much efficient in reducing the conductivity of KCl solution than that of the PEG with higher relative molecular mass. And our results also confirm that the size of the relative molecular mass proposed in the literature [6, 11] is the key to whether the viscosity enhancer can effectively reduce the ion diffusion in solution.

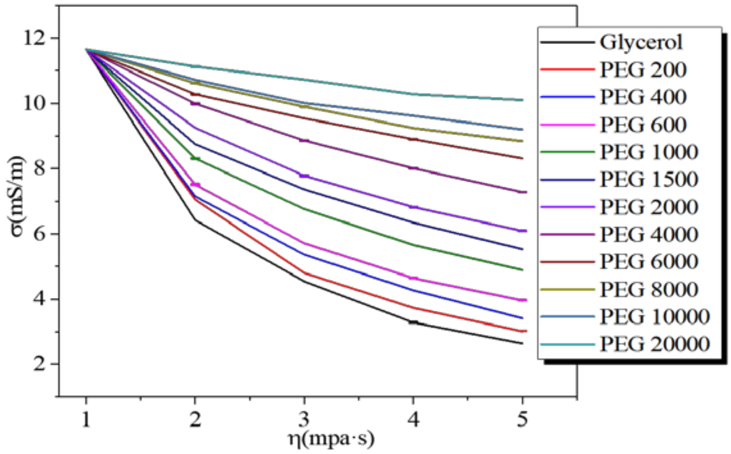

Figure 3: The relationship between viscosity and conductivity of PEG solutions with different relative molecular mass

3.3 The potential boundary of relative molecular mass for viscosity enhancer to reduce the conductivity

To further reveal the relationship between relative molecular mass of viscosity enhancer and solution conductivity, Figure 3 was deformed to obtain Figure 4, which is the relationship among relative molecular mass, mass fraction and conductivity of solution under different viscosity. Clearly, when the optimal limit is exceeded, excessive addition of admixture will reduce the properties of cement-based materials. In other words, too much added admixture may be not well. As exhibited in Figure 4, under different viscosity, the relationship curve among relative molecular mass, mass fraction and solution conductivity can be roughly divided into two parts. One part of it is a straight line, the other part of it is a curve, and all this inflection point occurs at a relative molecular mass of 400. In order to reveal the best solution conductivity reduction effect with the lowest dosage, the linear part of the curve in Figure 4 was taken as an ideal relationship curve between the relative molecular mass and the solution conductivity. Therefore, relative molecular mass 400 is regarded as the lower limit of the appropriate relative molecular mass range for the viscosity enhancer used to reduce ion diffusion.

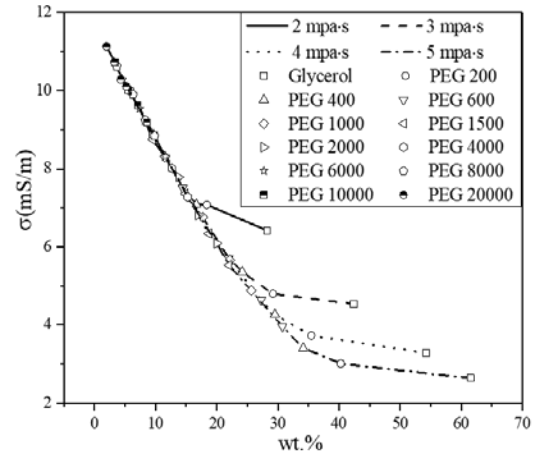

Figure 4: The relationship among relative molecular mass, mass fraction and conductivity of solution under different viscosity

Further treatment of Figure 3 is necessary to determine the appropriate upper relative molecular mass limit. Firstly, we need to define a parameter, as shown in Equation (1):

$$\varphi = \frac{\sigma_w - \sigma_r}{wt.\%} \qquad (1)$$

Where φ is the decrease in the conductivity of the solution with a unit mass viscosity enhancer; σ_w is the conductivity of KCl in pure water; σ_r is the conductivity of KCl in solution; $wt.\%$ is the mass fraction of the viscosity enhancer in solution.

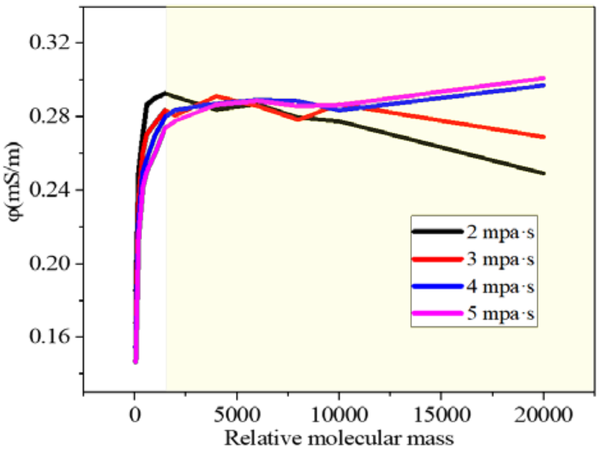

Figure 5: The relationship between the decrease of unit mass viscosity enhancer solution conductivity and the relative molecular mass under different viscosity.

In Figure 5, with the increase of the relative molecular mass of the viscosity enhancer, the decrease of the solution conductivity by unit mass viscosity enhancer will reach a plateau when the relative molecular mass reaches 1500. In other words, when the relative molecular mass of the viscosity enhancer is greater than 1500, the increase of relative molecular mass for viscosity enhancer at the same dosage will not cause the solution conductivity to decrease significantly. Whereas, as we have mentioned before, at the same dosage, increasing the relative molecular mass of the viscosity enhancer will increase the viscosity of the solution. In our original purpose, this type of viscosity enhancer was applied to reduce the diffusion of chloride ions rather than simply increase the viscosity of the solution. Hence, relative molecular mass 1500 is regarded as the upper limit of the appropriate relative molecular mass range for the viscosity enhancer used to reduce ion diffusion. Of course, if you want to greatly increase the viscosity of the cement paste while reducing the chloride diffusion, you can also increase the upper limit of the relative molecular mass appropriately.

4.Conclusions

In this study, by using PEG with different relative molecular mass as viscosity enhancer and KCl solution conductivity as a means of characterizing chloride diffusion, we preliminarily concluded that the appropriate relative molecular mass range of viscosity enhancer which used to reduce ion diffusion was 400-1500. At the same time, we also proved that the size of relative molecular mass is the key for viscosity enhancer to reduce the diffusion of ions.

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