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Effect Mechanism of Corrosion Inhibition Additives on Cement Hydration

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Abstract. The addition of corrosion inhibition additives in reinforced concrete is the most common measure for the anti-corrosion of steel rebar. In a large number of traditional researches, scholars often pay more attention to the anti-corrosion effect and anti-corrosion mechanism of corrosion inhibition additives. However, various corrosion inhibition additives have significant effects on the properties of concrete, especially the hydration process of cement. This will further affect the performance of concrete. This paper takes the effect of corrosion inhibition additives on cement hydration as the main line, and systematically analyzes the influence of various types of corrosion inhibition additives on cement hydration heat release, hydration rate and hydration product generation, in order to provide certain reference for researchers in this field.

Keywords: corrosion inhibition additives, reinforced concrete, hydration process

1. Introduction

In Marine engineering, reinforced concrete structure is the most common component structure. In the service process of reinforced concrete structure, the corrosion of steel bars caused by chloride ion erosion, concrete carbonization and other factors has been an important reason to limit the long-term service of reinforced concrete [1, 2]. In response to this problem, scholars in the field of reinforced concrete corrosion protection have put forward a variety of protection methods, such as adding corrosion inhibition additives[3] to concrete, cathodic protection[3] and concrete coating[5]. Among them, the method of adding corrosion inhibition additives has made a lot of achievements in the field of engineering and theoretical research at home and abroad because of its good economy, excellent anti-corrosion effect and preventive effect. It should be pointed out that the corrosion inhibition additives referred to in this paper include reinforced concrete rust inhibitors and some concrete admixtures and nanomaterials with rust inhibition properties.

Generally, for most experts in the field of corrosion protection, they pay more attention to the anti-rust effect and anti-rust mechanism of corrosion inhibition additives, and pay less attention to its impact on the hydration process of cement-based materials. However, since most corrosion inhibition additives need to be incorporated into concrete at the mixing stage, they have different degrees of influence on the hydration process of cement, and then affect the macro properties of concrete such as mechanical properties, workability and so on. Therefore, it is of great practical significance to understand the influence of various corrosion inhibition additives on the hydration process of cement.

2. The effect of Corrosion Inhibition Additives on Cement Hydration Heat Release

Different kinds of corrosion inhibition additives have different effects on hydration heat release. The study found that: for hydrotalcite materials, it is possible to increase or decrease the hydration heat release of cement, which is closely related to the composition of the laminate elements, roasting temperature, particle size and interlayer ions. The smaller the particle size of LDH, on the one hand, provides more specific surface area, and then provides more active sites for the hydration of cement clinker, on the other hand, the smaller particle size also helps LDH to be more fully filled

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in the concrete pores, and then more fully in contact with cement clinker[6]. Other studies have shown that the addition of BTA-PBS microcapsule loaded rust inhibitor reduces the hydration heat release of cement, because the microcapsule particles are adsorbed on the surface3 of cement clinker C_3A, thus inhibiting the early hydration of cement. However, although BTA-PBS inhibited the early hydration of cement, it still effectively promoted the formation of C-S-H gel, because the micro-size characteristics of BTA-PBS helped it play the role of nucleation site[7].

In recent years, with people's attention to the concept of green environmental protection development, the research and development of green environmental protection rust inhibitor has been paid attention to by researchers at home and abroad. Such as corn protein rust inhibitor[8], ginger extract[9], Chinese parasol leaf extract[10] and so on have been proved to have good rust inhibition effect. Some scholars have found that before and after adding corn protein rust inhibitor into cement-based materials, although the hydration process includes five stages, such as initial hydration, induction period, acceleration period, deceleration period and stable period, the higher the content of corn protein rust inhibitor, the corresponding hydration heat release is significantly reduced[8].

Triethanolamine (TEA) is a common organic rust inhibitor. Recently, some scholars studied the influence mechanism of triethanolamine on the hydration process of cement[11]. It was found that the addition of TEA effectively changed the hydration state of cement, and could significantly promote the aluminate reaction and delay the silicate reaction. When the content of TEA is high, the hydration process of C_3A and C_4AF_3 is obviously faster than that of C_3S, and the hydration process3 is mainly controlled by aluminate reaction. Therefore, it can be predicted that the addition of TEA rust inhibitor will obviously change the setting and hardening process of cement slurry.

3. Influence of Corrosion Inhibition Additives on Hydration Rate

LDH materials have been shown to have a certain effect on the hydration process of cement, and this effect is closely related to its dosage and particle size[12, 13]. When LDH particle size is small, the hydration reaction of C_3S can be better promoted at low dosage, but when the dosage is large, the hydration reaction of C_3S will be inhibited. On the other hand, the larger LDH showed different rules. It had obvious promotion effect on the hydration3 reaction of C_3A at low content, but had little effect on the hydration3 reaction of C_3A at high content. At the same time, some studies have found that LDH has good water absorption characteristics, can absorb a certain amount of water in the mixing process, and release it in the late hydration period, which is conducive to the later hydration of cement. It is worth noting that some corrosion inhibition additives can cause the delay of cement hydration and reduce the formation of calcium hydroxide. Vitamin corrosion inhibitors have been found to compete with water molecules for adsorption, thereby delaying the hydration of C_3S and thereby reducing the workability of cement-based materials[14]. Therefore, in order to reduce the negative effects of adding corrosion inhibition additives, corrosion inhibition additives are usually loaded into zeolite, hydrotalcite, MOFs and other carriers[15-17].

In recent years, some studies have found that proper dosage of traditional concrete admixture can also play a good rust inhibition effect. Among them, the representative ones are fly ash, slag and red mud. The mechanism of these admixtures to improve the rust inhibition ability is mainly by introducing aluminum-containing compounds into the concrete, and then reacting with cement hydration products to form F salt, so as to achieve the ability of curing chloride ions[18-20].

Some scholars have found[11] that the addition of TEA has a significant acceleration effect on the initial dissolution of C_3S, C_3A, C_4AF and gypsum in cement. In addition, it can also be found that from the beginning of cement hydration, the concentration of S, Al and Fe increased significantly. In fact, some previous reports have found that TEA can accelerate C_3A reaction and delay C_3S reaction during cement hydration. For the silicate reaction, although TEA is beneficial to the initial dissolution of C_3S, it does not lead to the acceleration of subsequent C_3S hydration.

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4. Influence of Corrosion Inhibition Additives on Hydration Product Generation

The incorporation of zein rust inhibitor into cement-based materials can inhibit the formation of ettringite and calcium hydroxide in the early stage of cement hydration, mainly because the amino acids in zein rust inhibitor are composed of peptide bonds. At the same time, zein rust inhibitor can inhibit the hydration of C_3S and C_2S, thus delaying the whole cement hydration process. After the addition of corn protein rust inhibitor, the peak position of XRD diffraction peak has no significant change, but the peak type and the strength of the peak have significant changes, which indicates that corn protein rust inhibitor rust inhibitor will have a certain impact on the cement hydration process, but will not lead to changes in the type of hydration products[21].

It was found that nano-sized materials can provide an effective nucleation site for cement hydration, reduce the deposition of pre-generated hydration products on the surface of cement clinker, and then promote the generation of more C-S-H gel, and then improve the permeability resistance and mechanical properties of concrete structures. At present, nanomaterials commonly used in the field of concrete, such as nano silicon dioxide, carbon nanotubes, nano titanium dioxide, graphene oxide, etc., can play a good nucleation site effect and improve the performance of cement-based materials[22-24]. In addition, some scholars have found that some common rust inhibitors can also effectively promote the formation of C-S-H gels.

Electromigration rust inhibitor is a kind of highly practical corrosion inhibition additive. Under the influence of external current, rust inhibitor migrates to the surface of steel bar through the internal channels of concrete and plays the role of rust inhibition. Fei's research found[25] that before the electromigration rust inhibitor was energized, the cement-based material contained lamellar calcium hydroxide, needle-like ettringstone and C-S-H gel. After 28 days of electrization, the C-S-H gel in the cement-based material significantly decreased, while the ettringite basically disappeared. This indicates that ettringite and C-S-H gel in cement-based materials partially decompose under the influence of electric current.

5. Conclusions

Different types of corrosion inhibition additives have different effects on the hydration heat release in cement-based materials, which is closely related to the nucleation site effect and adsorption characteristics of corrosion inhibition additives. The smaller the particle size is, the more it can promote the hydration process of cement and improve the hydration heat release. When the corrosion inhibition additives adsorb too much on the surface of cement clinker, it is easy to cause the cement hydration delay. In addition, for some small-molecule corrosion inhibition additives, they often produce ion adsorption with water molecules near the cement clinker, which reduces the hydration rate and the workability of cement-based materials. In fact, for the vast majority of corrosion inhibition additives, generally only affect the hydration process of cement, and affect the amount of various hydration products, but will not cause changes in the type of hydration products. In the application process of electromigration rust inhibitor, the electrification process often leads to the decomposition of ettringite and C-S-H gel.

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