Cement Self-Healing

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Self-healing materials can repair corrosion, cracks, scratches, and other alterations independently and autonomously. This technology significantly benefits the economy, with direct consequences for social improvement in certain areas of science such as chemistry, energy, etc., by substantially increasing the life expectancy of structures and self-healing materials and significantly boosting the viability of industries as cracks and wear, in general, spontaneously disappear.

Keywords: bacteria ; cement ; self-healing ; nanocontainers ; superabsorbent polymers

1. Introduction

Self-healing materials can repair corrosion, cracks, scratches, and other alterations independently and autonomously. This technology significantly benefits the economy, with direct consequences for social improvement in certain areas of science such as chemistry, energy, etc., by substantially increasing the life expectancy of structures and self-healing materials and significantly boosting the viability of industries as cracks and wear, in general, spontaneously disappear. The application of this technology is effective in areas that are difficult to access, whereas their repair is difficult and expensive. Therefore, in recent years, the field of material science has begun to focus on "self-healing" technology rather than "improving" technology.

Although the use of materials with self-healing properties can prevent their damage, wear and tear during their service life is inevitable. This means continuous inspection of products and structures made of such materials is necessary to assess wear evolution. So far, the interventions carried out concern either the repair of the wear or the replacement of the product, which are both time-consuming and expensive procedures. Therefore, a self-healing material capable of carrying out these procedures without external intervention would be ideal [1][2][3].

For a material to qualify as a self-healing material, it must be able to eliminate cracks and other damage spontaneously after the appropriate stimulus. For this, it is required to fill the gap with "something" that will work through the self-healing process and restore the material to its original state. This filler should come from within the material itself. A small piece of the material will turn on and fill the crack. However, when these "activated pieces" approach the cracks, they should be able to "heal" the material (e.g., join the two surfaces of the damage together) and stabilize.

The phenomenon of self-healing was discovered through the use of polymers in 1969 [4]. After ten years, Wool observed the restoration of polymers to their original state using the self-healing phenomenon [5][6]. White stored a polymer in a container, in which the healing substance was released autonomously to restore the cracks [7]. Following these publications, scientists saw the potential of these new materials, and work in this area is ongoing [2][8]. Since the nineteenth century, the "self-healing capacity" of cement, i.e., its ability to heal itself, has been realized, and this property has taken on many different dimensions in recent years. The addition of substances offers stimulating or even mechanical functionality and is currently considered a viable method of increasing the durability of these structures to increase their service life. Many researchers have attempted to understand the mechanisms of these seals and healing cracks, which has led to several new self-healing technologies. These results have been certified both in the laboratory and in practice [9].

2. Cement Self-Healing

Cement is characterized as a technical stone and is a relatively cheap and durable material. In recent decades, the most used construction material's properties have depended on its initial components, such as water and various aggregates that can vary. However, the final product has high compressive strength but not tensile strength.

Cement is produced by burning raw materials at 1500 °C, releasing large amounts of carbon dioxide worldwide. Common materials used to manufacture cement include limestone, shells, and chalk or marl combined with shale, clay, slate, blast furnace slag, silica sand, and iron ore. Cement production must be reduced or replaced with materials that demonstrate the phenomenon of self-healing. In addition, some industrial wastes, such as fly ash, blast furnace slag, and iron silicates, can partially replenish or improve their properties.

A primary cause that activates the wear mechanisms of cement is its permeability, i.e., the microstructure of the cement pores under consideration, which includes isolated or interconnected pores. Interconnected pores let water and other chemicals into the concrete matrix, leading to chemical wear and tear. For example, the penetration of sulfate ions into the concrete leads to ettringite formation [10]. This conversion of a high-density phase into a lower-density phase creates internal stresses and the further expansion of cracks. In addition, ions entering the matrix through the networked pores destabilize the reinforcement's passive film, ultimately achieving concrete corrosion. Similarly, the diffusion of carbon dioxide occurs, which reacts with alkaline components in a process called carbonation. This results in a decline in pH and passivation of the protective film of the reinforcement.

The above brief description makes it clear that cracks in concrete must be reduced to limit the permeability of the matrix to attacking substances. Here, the method of healing is cost-effective [3]. The further hydration of cement particles and carbonation of dissolved calcium hydroxide guides the healing of concrete cracks. This was first observed by the French Academy of Sciences in 1836, and it was presented in a publication [3]. At that time, there was a differentiation between "self-healing" and "self-sealing". In one case, the original strength of the concrete is restored, while in the second case, when the cracks are filled, there is no improvement in the mechanical properties of the materials.

One observes self-healing in concrete samples exposed to freezing and thawing cycles [11][12][13][14]. In adverse climatic conditions near coastal areas, such as the Barents Sea, concrete undergoes multiple cycles of freezing and thawing. In winter, when the climate is heavy, concrete is damaged, while the properties are recovered due to self-healing during the year's warm months [12].

Recently, rigorous research has been carried out on the self-healing of concrete. These investigations can be classified into two categories: mixed materials (mineral mixtures, fibers, nanofillers, and curing agents); or self-healing technologies (capsules and bacteria).

2.1. Mechanisms

A substance used for self-healing cement must adhere to some characteristics. First, it must seal the crack zones to reduce the permeability of harmful substances. Additionally, the incorporation of these substances into the uterus must be continuous to ensure that the self-healing properties last for more than 50 years. Finally, this substance should be relatively inexpensive [15].

Various physicochemical processes contribute to the self-healing of cracks in cement. These can be the formation of calcium carbonate, the blocking of water from impurities resulting from the appearance of cracking, the complete hydration of unreacted cement, and, finally, the expansion of the hydration of the cement matrix with the formation of C-S-H sealing inside the crack [16].

From this brief discussion, one understands that the recrystallization of calcium carbonate is the primary mechanism implemented by cement hydration products dissolved in water and carbonate. $Ca(OH)_2$ is released and diffused along the cracks. Calcium ions react with dissolved carbon dioxide and form $CaCO_3$. In this way, they fill the gaps in the cement.

2.2. Self-Healing Methods of Cement

Recently, many studies have been conducted concerning the creation of containers added to cement that are suitable for self-healing. These materials have various forms and are charged with numerous substances, leading to cement "self-healing". Some of them are mentioned below.

Bacteria

Self-healing of cement can be accomplished by incorporating bacteria into the concrete [17]. The bacterium metabolizes urea and precipitates calcium carbonate into the crack environment. Microbial precipitation of calcium carbonate is evidenced by the concentration of dissolved inorganic carbonate ions, the concentration of calcium ions, and the presence of nucleation centered in the bacterium. Its walls act as centers of nucleation [18][19][20][21][22][23]. Using bacteria in concrete quickly reduces cracking and increases compressive strength and rigidity compared to those without bacteria. Applying microbial calcite helps reduce thawing and freezing due to the chemical process and reduces the permeability of substances, thereby reducing the freezing process. Because chemical ingress cracks are waterproof, this improves the service life of reinforced concrete [24]. On the other hand, using bacteria in concrete doubles the cost: In the application and growth of bacteria, it requires nutrients and metabolic products to develop microorganisms. Estimating the number of bacteria that should be used in concrete facilities for optimal performance is also tricky. Furthermore, the lifetime of this technology has not been fully certified [24]. Despite the various weaknesses of the technology, using bacteria to self-heal cement is becoming more popular in areas, such as in repairing limestone monuments and healing cracks in concrete in buildings with high strength, facilities near humid environments such as sea and rivers, and many other applications.

Bacillus sphaericus and Sporosarcinapastuerii were used in a study of the effect of bacteria on cement. After cultivation, they were planted in cement in different concentrations. The samples were cured in tap water and tested after 7 to 28 days. In cement, the increase in strength was 50% and 28% in mortar for Sphaericus and Sporosarcinapastuerii, respectively, compared to the conventional mixture. The XRD method proved the creation of calcite in cement samples produced in the presence of bacteria, which enhanced the strength and durability of cement [25]. Concrete reinforcement was accomplished using Bacillus subtilis. The addition of bacteria improved compressive strength in the order of 12 to 30%, tensile strength of about 13 to 19%, and tensile strength bending at values from 13 to 16% at different ages [26]. Bacillus subtilisaureolytic was used to enhance the self-healing properties of concrete. This bacterium produced calcium carbonate in an alkaline environment certified by scanning electron microscopy. The result of this method was to prove the sealing of concrete cracks [27]. B. sphaericus, protected by silicate gel, was incorporated into a cement matrix to study calcite precipitation, the self-healing mechanism of concrete. The protection of bacteria in this way from the pH of concrete leads to calcium carbonate precipitation into the uterus. For results of this biological treatment, it was evaluated with ultrasonic pulse and optical measurements that are particularly useful without contamination of the sample [28].

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