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Electrolytes' influence on foamability and foam stability of cement suspensions

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HIGHLIGHTS

- It was studied the influence of electrolytes on foamability of air-entraining agents.
- Al-anodizing waste was used as an adjuvant of air-entrainment.
- Ca and K electrolytes affect the air-entraining ability of the anionic agent.
- Foamability of the amphoterous agent is not affected.
- Al-anodizing waste act as an electrolyte sequester and assists the anionic agent.

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ABSTRACT

In this work, the foamability and foam stability of two Air-Entraining Agents (AEAs), an anionic and an amphoterous, were evaluated in cement suspensions. The anionic agents are the most used AEAs for cementitious materials, mainly due to their low cost. However, they may displays sensitivity in suspensions with high electrolytes concentration, as when mixed into cements. Amphoterous agents are known to be less sensitive, but their complex synthesis make them more expensive. Foamability and foam stability tests were performed in water and in aqueous suspensions with electrolytes from hydrated Ordinary Cement Portland (OPC) to investigate the air-entraining capacity of these AEAs. The AEAs performance were also tested regarding the addition of the alkali-catch Al-Anodizing Waste (AAW) as an air-entrainment adjuvant into cement suspensions. The AEAs were firstly characterized by FT-IR and surface tension tests. Chemical and physical features of AAW and OPC were determined by XRF, particle size and surface area analyzes. The electrolytes' influence and chemical interactions between materials were investigated by foaming tests, surface tension analysis, electrical conductivity and atomic absorption. The results demonstrated that the anionic agent is strongly affected mainly by Ca and also by K electrolytes. On the other hand, the amphoterous agents are unaffected. AAW showed high reactivity with electrolytes from hydrated cement and its alkali-catch ability may help sensitives AEAs to improve their air-entraining capacity.

1. Introduction

Air-entrainment is a technic in which an agent is added into cement admixtures to introduce small air bubbles (or voids) upon the cement paste [1]. The air-entraining occurs by the action of an agent which reduce the surface tension in the liquid medium. Thus, applying a stress, it is possible to introduce and stabilize air bubbles on the cement matrix producing aerated mortars or concretes [1–3]. The addition of an Air-Entraining Agent (AEA), also called surfactant, offer some advantages to fresh and hardened concretes and mortars, since it can improve the workability, avoid the exudation tendency, improve the thermal and sound insulation, improve the freeze-thaw resistance, decrease the charge over metallic structures and reduce the consumption of cement. However, many variables influence the air-entraining and stability of bubbles formed by entrapped air, such as the water content, temperature, type and content of the own agent and, as investigated in this work, the type and content of electrolytes present in the aqueous medium [4].

Many studies have made their contributions exploring fresh and hardened properties of cement-based materials and concretes

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with air-entraining agents [1,5–9]. However, little emphasis was given to the interactions between AEAs and electrolytes from cement phase's dissolution, since this relation can improve the air-entrainment process control. Thus, this work will contributes to fulfill this research gap by analyzing two AEAs, an anionic and an amphoterous, in cement suspensions. Beyond that, it will be demonstrated how the reduction on electrolytes concentration can improve the air entraining capacity of an AEA as by adding an alkali-catch adjuvant, i.e., the Al-anodizing waste.

Some authors have demonstrated that amorphous aluminum hydroxide or oxide has great reactivity in contact with hydrated cement since they show certain ability to catch alkalis dissolved into porous solution and forms new precipitated phases [10–12]. Aluminum hydroxide is the main component of the Al-Anodizing Waste (AAW) in which is generated in large quantities in aluminum industries. Although many applications have been proposed in the last two decades to reuse it [13–19], AAW continues to be disposed in landfills.

In this work it was demonstrated the influence of the main electrolytes present on porous solution (Na, K and Ca) and their correlations with the foamability and foam stability in cement suspensions as well as the influence of an alkali-catch material (AAW) as an adjuvant to support the AEAs.

Lightweight concretes takes high cement contents and, therefore, produces more portlandite than common concrete admixtures, leading to a strength loss and durability depletion [2]. Thus, the portlandite formation decay from the alkali-consumption by AAW, acting as a sequestering substance [1], it may also improve the chemical and mechanical durability of hydrated cements justifying, therefore, its addition. Al-rich materials influence the hydration reactions and are commonly used as set accelerators or expansive admixtures on products from cement Portland. However, possible chemical interactions between AAW and OPC will be not explored, only AAW as an adjuvant for air-entraining agents.

2. Aerated cement products

The air-entrainment in cement products is a common practice in the civil construction sector, especially in external places susceptible to low temperatures. By the way, when the water in the pores freezes, it expands and can generated cracks; but with air bubbles present in the cement matrix, there is space for ice expansion and thus the expansive stresses are prevented [2].

Normally, two different routes are employed for obtain these products, i.e., by chemical reactions or by foaming. In the first one, a chemical agent is added and mixed into an aqueous suspension of cement and the reactions generated release gases that remain trapped after curing. Aluminium metal powder is the most commonly used agent. It reacts with the alkaline medium, releasing hydrogen which is confined into the material, according to reaction 1. The pH of the medium for this reaction to occur should be approximately 12.5 [3].

$$2Al + 2(OH)^{-} + 4H_2O \rightarrow 2AlO(OH)^{2-} + 3H_{2(g)} \quad (1)$$

In the second route (the one used in this work), the air-entrainment can be carried out by stirring a preformed foam (AEA previously mixed with water) or AEA added directly into the cement paste. The production of porous cement materials may also involve both routes and the content of entrapped-air (voids) can be adjusted according to the desired application [3].

It's important to highlight that although AAW is mainly composed of Al, as will be seen below, it's not likely that the first route of air-entraining is involved with AAW addition since the Al present is in the hydroxyl form and the reaction expressed in Eq. (1) occurs with the elemental aluminium.

3. Types of surfactants, foaming mechanisms and foam stability

There are many types of AEAs, in which, its workability in cement admixtures can change considerably. Each type of AEA have different acting mechanisms and tend to behave in different ways. AEAs commonly show, in the same molecule, a hydrophobic tail (apolar) and a hydrophilic head (polar), see Fig. 1. The tail is usually composed by a hydrocarbon chain, and the head can be anionic, cationic, nonionic or amphoteric. Anionic AEAs are negatively charged and contain anionic functional groups at their heads (see Fig. 1a) [20,21]. The sodium can be dissociate and form free positive ions when in contact with water. This type of AEA is the most employed due to its low cost. However, it may be sensitive in suspensions with high electrolytes content, mainly those from calcium [22,23], resulting in a lower air-entraining capacity. Cationic AEAs are positively charged, but may be pH-dependent on amines dissociation, i.e., the ones with primary, secondary or tertiary amines are positively charged when pH is less than 10 (cement suspensions usually produce pH between 12 and 13). On the other hand, cationic ones with a quaternary ammonium cation are always positively charged regardless of pH. Amphoteric AEAs have both cationic and anionic centers attached to the same molecule and carry both a positive and a negative charge (see Fig. 1b). These surfactants are generally quite expensive, and consequently, their use is limited to special applications such as cosmetics where their high biological compatibility and low toxicity is of primary importance. Nonionic AEAs are adjuvants with no electrical charge and can promote retention of moisture [20].

Upon stirring, the air bubbles formation in pure water occurs even without the presence of AEAs. However, when stirring is stopped, the coalescence and collapse of the air bubbles is almost instantaneous. On the other hand, with the addition of AEAs, the surface tension of water decreases. Thus, the entrapped-air bubbles formed by stirring process become more stable, slowing down the coalescence process. Beyond, the anchoring of AEAs to the air bubbles surface, especially for ionic additives (positively or negatively charged), improves the foam stability due to the electrostatic repulsion mechanism. Thus, the coalescence and collapse of the entrapped-air bubbles are avoided (Fig. 1a) [20,21].

Likewise, the presence of electrolytes in the aqueous medium can compromise the foam stability of anionic AEAs since they can adhere to the hydrophilic head (Fig. 1b) and suppress the electrostatic repulsion mechanism (Fig. 1c). This mechanism has been investigated in this work [20,21].

4. Materials and methods

4.1. Raw materials preparation and characterization

The air-entraining agents (AEAs) tested were Sodium Lauryl Sulfate (SLS, $NaC_{12}H_{25}SO_4$, anionic, solid, Vetec) and Cocamidopropyl Betaína, (CB, $C_{19}H_{38}N_2O_3$, amphoterous, viscous liquid, Brenntag). Ordinary Portland Cement (OPC-type IV; 12 m^2/g, Supremo Cimento) and Aluminum Anodizing Waste (AAW; 65 wt % moisture, Alcoa) were also used.

Before previous water-separation by industries, AAW is a concentrated suspension (sludge). After sedimentation and filter-pressing process, AAW acquires the form of pellets. Therefore, before any characterization, AAW was dried at 110 °C/24 h in a laboratory dryer (SP Labor, model SP-100/27-A) and deagglomerated for 10 min in a planetary ball mill (Servitech, model CT-242/1). After this step, the surface area (Quantachrome Instrument NOVA