Spot the Difference

P. Recchi, M. Magistri and P. Forni, Mapei Spa, Italy, discuss the development of an alkanolamine-based grinding aid with low iron-staining effect.

Abstract

Iron staining in concrete products is an unfavourable phenomenon, which is known by several names amongst cement manufacturers. Terms such as 'brown/yellow discolouration' and 'iron efflorescence' are synonyms for the same problem: the appearance of unwanted coloured spots (the colour range of which may vary from light yellow to deep brown/red) on the surface of concrete products. The addition of cement additives (especially alkanolamine-based ones) is known to be one of the possible causes of this problem. This article will present a novel alkanolamine-based grinding aid with a significantly reduced iron staining effect and unaltered performances, with respect to similar grinding aids that are already available.

Introduction

Factors leading to iron staining in concrete have been proposed and described in several publications. In particular, iron staining is known to be the consequence of the migration of iron ions (mainly in the Fe^{2+} oxidation state, due to its high solubility in water) from the inner pores to the surface of wet concrete. So far, several factors that can influence the extent of this migration have been identified. Curing conditions of concrete, average pore size, clinker composition, use of secondary components in cement and the use of cement additives are amongst the most critical of these factors. Furthermore, it seems that curing in high-humidity environments, small average pore sizes, scarcely mineralised clinker (low C_3S and high CaO) and addition of alkanolamine-based grinding aids are all factors that may promote iron staining.

Cement additives (a very broad definition that includes different products like grinding aids, performance enhancers, accelerators, retarders, etc.) have been extensively used in the cement industry since the 1930s. Alkanolamines are one of the most commonly used raw materials in the manufacture of these products. A possible problem lies in the fact that, in addition to clear benefits such as pack-set reduction and compressive strength increases, these molecules may – under specific circumstances – promote the solubilisation of Fe ions (through a chelating effect, for example) and hence their migration towards the concrete surface. The immediate result is the aforementioned iron staining phenomenon.

It has been observed that the extent of iron staining seems to be proportionally related to the dosage of cement additives (and thus the amount of alkanolamines introduced in the system): the more additive is used, the higher the risk of iron staining in the final product. One solution may therefore lie in significantly reducing the dosage. However, although this may minimise the iron staining effect, it could also reduce the positive effects related to the use of these products at the correct dosage. Another solution could lie in the use of alkanolamine-free grinding aids, but this usually translates into a less pronounced effect in terms of compressive strength increases and cement pack-set reduction.

As mentioned, this article will discuss a new cement additive, prepared with a carefully targeted blend of specific ethanolamines. The aim was to develop a product that would be able to deliver at least the same performance level as traditional grinding aids but with a low contribution to the iron staining phenomenon.

Figure 1. Iron release triggered by different alkanolamines.

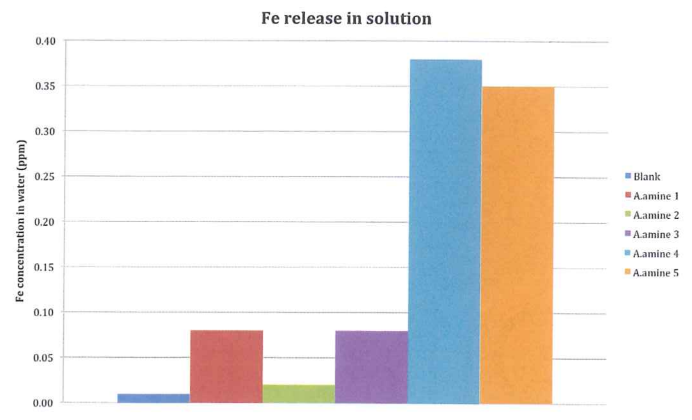
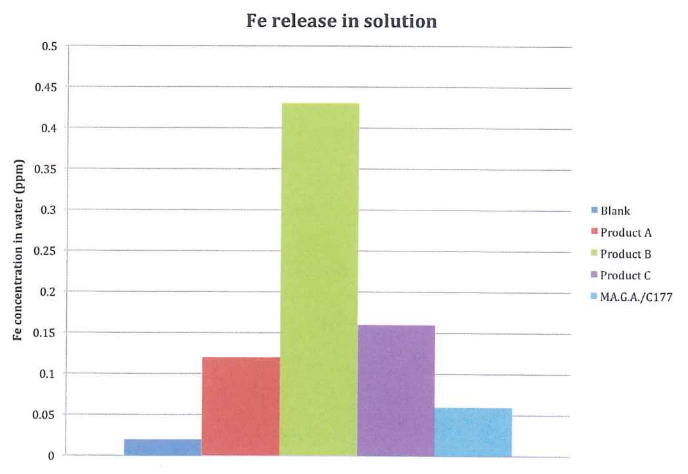


Figure 2. Iron release triggered by different cement additives.



Preliminary studies

Preliminary lab trials have shown that the tendency for iron staining is somehow related to the chemical structure of the considered alkanolamine. This tendency seems to become greater as the steric hindrance of the molecule is increased.

On a laboratory scale, the following internal method was used to measure a raw material's tendency to promote iron staining: standard mortars according to UNI EN 196-1 were cast using cement ground both in the absence (reference) as well as in the presence of a series of raw materials commonly used for the preparation of cement additives. Cement was reproduced on a lab-scale ball mill for an average of 45 minutes. The raw materials were added during the grinding process and the same dosage (200 ppm) was used for each raw material. A series of five different alkanolamines (commercial grade) were considered.

After seven days of curing, each prism was broken into three pieces of approximately the same size and weight. The prism pieces were put in a sealed plastic container, together with a certain amount of distilled water. The amount of water was calculated in each case in order to maintain the same water-to-cementitious matter ratio.

After an additional seven days, 20 ml of water was taken from each sample, acidified and analysed by means of an ICP-AES device. The results, expressed in total iron concentration (Fe), are reported in Figure 1.

As can be seen, different alkanolamines trigger different releases of Fe ions from the pores to the contact solution. When comparing these results with the chemical structure of each molecule,

Table 1. Effect of the considered cement additives on compressive strengths development

Product	Compressive strengths after 24 hours (MPa)	Compressive strengths after 2 days (MPa)	Compressive strengths after 7 days (MPa)	Compressive strengths after 28 days (MPa)
Reference (no additive)	14.9	21.4	44.8	57.5
Product A	17.1	24.3	44.9	56.5
Product B	16.2	22.9	47.2	61.4
Product C	17.3	23.2	46.2	58.4
MA.G.A./C177	17.5	23	45.9	59.6

Figure 3a. Blank sample.

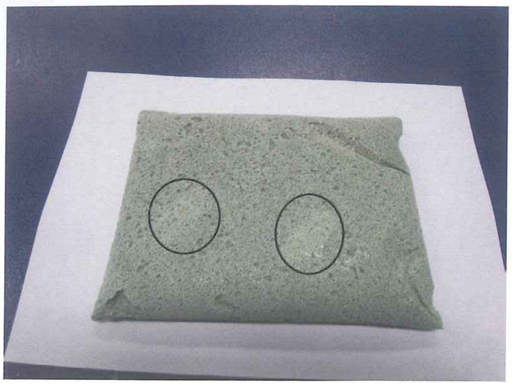


Figure 3b. Product A.

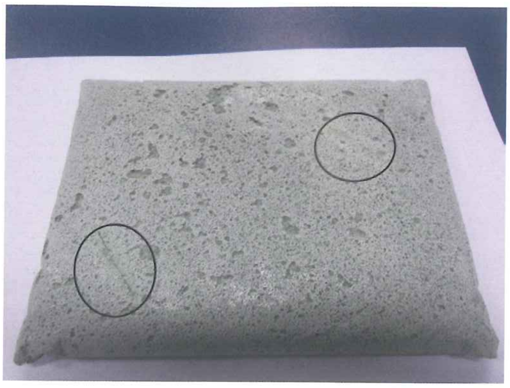


Figure 3c. Product B.

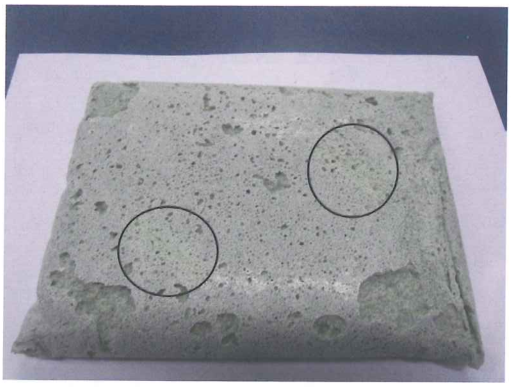
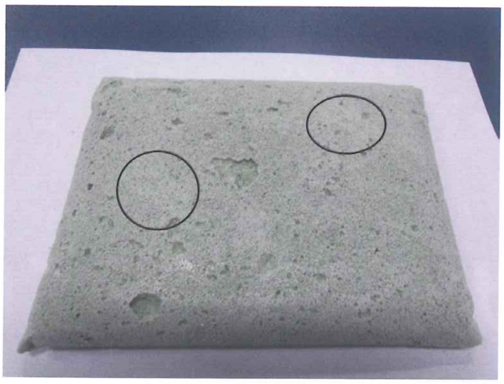


Figure 3d. MA.G.A./C177.



a clear and linear pattern emerges, where the amount of released Fe increases with the steric hindrance of the alkanolamine.

Product development

Using the information gathered in these preliminary evaluations, Mapei has formulated a new cement additive (commercially available under the name MA.G.A./C177) and repeated the test comparing the Fe release of this product against a variety of commercially available products. Products A, B and C are commercially available alkanolamine-based cement additives. The results of these second trials are reported in Figure 2.

These results are consistent with those obtained during the preliminary tests and the blend of alkanolamines on which MA.G.A./C177 is based seems to present a significantly reduced effect on the release of iron ions in the solution.

In order to determine the efficiency of the product MA.G.A./C177 in terms of compressive strength enhancement, a series of additional trials were performed adding the aforementioned products directly to the gauge water during the preparation of mortars of a standard OPC-type cement blend. The results of the physical-mechanical tests, performed according to the European Standard UNI EN 196-1 are shown in Table 1. As can be seen, the performance of MA.G.A./C177 is comparable to the performance delivered by the reference products.

Finally, in order to support the evidence found during these preliminary investigations, the company decided to perform a qualitative and 'practical' determination of the influence of the product MA.G.A./C177 on iron staining. For this purpose, Mapei used a slightly modified version of an internal method developed by a major global cement manufacturer. The method involves preparing a particularly 'porous' mortar (i.e. with a high sand-to-cement ratio and the addition of an air entraining agent), storing it in a sealed plastic bag for seven days, inscribing two cuts on the plastic surface (about 3 cm long) and waiting a further seven days for the (eventual) appearance of yellow spots around the cut area. The extent and intensity of these yellow spots are a good indicator of an additive's tendency to promote iron staining. The mortars were prepared both with and without the products described in the previous paragraph; addition took place directly in the gauge water and all the cement additives were dosed at 500 g/t (medium-high industrial dosage). Figure 3a is of a blank sample (i.e., no additives), Figure 3b shows cement treated with Product A, Figure 3c is cement treated with Product B, and Figure 3d shows cement treated with MA.G.A./C177.

As can be seen, Product A and Product B both cause a yellowish colouration in the spots (corresponding to the cut areas), while the blank sample only shows some sort of whitish efflorescence. MA.G.A./C177, on the other hand, shows no yellow colouration and a limited efflorescence.

Conclusion

This laboratory evaluation led to the development of a cement additive that is able to perform well as a grinding aid and strength enhancer (at all ages), and that is not prone to the promotion of iron staining. This could serve as a good amine-based performance enhancer, even in cases where yellow/brown discolouration is a problem due to a specific application or a given cement chemistry.