

A Discussion of the Paper "ALINITE - CHEMICAL COMPOSITION, SOLID SOLUTION AND HYDRATION BEHAVIOUR" by J. Neubauer and H. Pöllmann*

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The authors (1) have made a very valuable study towards our understanding of precisely what alinite is and how it behaves upon hydration. Alinite has aroused considerable interest since it was first produced (2-4) on account of its energy saving low temperature synthesis in a calcium chloride salt melt at ca. 1100°C, its soft nature and hence the easier grindability of the alinite clinker and also the rapid-hardening properties of alinite cement. A number of investigations had earlier looked into the hydraulic behaviour of alinite (5-8). Gypsum addition has been reported as intensifying strength development rather than primarily functioning as a set regulator (2).

Controversy has surrounded the likelihood of reinforcement corrosion with alinite since it first entered commercial production at Astrakhan in Russia. Results have ranged from no corrosion in some cases to severe corrosion in other instances. Such variations are most likely due to the levels and ease of internal transport of labile (free) chloride present in individual consignments of alinite cement, upon hydration. Where chloride is entirely bound into the alinite structure, the potential for steel reinforcement corrosion should not normally arise. However, the presence of labile chloride in the alinite structure but not apparently bound to it chemically, as found by the authors in their preparations (1), does appear to have a strong potential for reinforcement corrosion.

Alinite cement has found some application in the former USSR as an oilwell cement. Here the question of its corrosion potential is not considered important in the well cementing context because of the lack of oxygen downhole. Alinite cement has been employed as a lightweight cement slurry extender on account of its rapid-hardening properties, akin to those of API Class C oilwell cement (9). However, batch-to-batch variability has often been a problem in such utilisation of alinite, which can be attributed to variations in labile chloride levels that influence hydraulicity considerably.

The authors (1) have demonstrated that, contrary to earlier reports (7,8), the hydration behaviour of alinites with different Si/Al ratios show no significant differences in hydraulic behaviour, because small amounts of free chloride accelerate the reaction to such a high degree that any intrinsic differences in reactivity due to different Si/Al ratios were not detectable. They have also confirmed that alinite does not have a fixed composition and is best represented by the formulation:

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$$Ca_{10}Mg_{1-x/2}\square_{x/2}[(SiO_4)_{3+x}(AlO_4)_{1-x}O_2Cl]$$

with 0.35 < x < 0.45 and \square representing a lattice vacancy. Alinite forms very well in impure systems containing different elements, but is not stable in a pure system CaO-SiO₂-Al₂O₃-CaCl₂. It was shown that hydration gives rise to an AFm phase represented as C₃A.CaY₂.10H₂O (where Y = Cl⁻, OH⁻, ½CO₃⁻²), calcium hydroxide (portlandite) and a calcium silicate hydrate (C-S-H) gel. Microprobe analysis of the C-S-H gel did not give any positive indications that Cl⁻ ions are incorporated within the C-S-H (1).

These investigations (1) have clearly shed more light upon the nature of alinite and its hydration products. Alinite could be more extensively utilised as a cement if the labile chloride content could ideally be removed, or at least rendered much less mobile. Also, the bound chloride needs to be examined, in order to see whether any significant exsolution of chloride from the hardened structure might take place over a period of years. This paper (1) is thus a very useful contribution to our further understanding of what alinite is and how it reacts with water, which are essential prerequisites to being able to control the mobility of the chloride ions that could allow a more extended usage for this type of cement in the future.

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