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DISCUSSION

A DISCUSSION OF THE PAPERS "INFLUENCE OF ZnO ON CLINKERIZATION AND PROPERTIES OF VSK CEMENT" BY D. BORDOLI, A.C. BAKUAH, P. BARKAKATI, AND P.C. BORTHAKUR,[1] AND "HYDRATION OF ORDINARY PORTLAND CEMENTS MADE FROM RAW MIX CONTAINING TRANSITION METAL OXIDES" BY G. KAKALI, S. TSIVILLS, AND A. TSIALTAS[2]

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Introduction

The role of minor elements in cement clinkering has long been a source of interest to investigators. Recent trends, especially the burning of secondary fuels in the kiln, could lead to increases in minor element concentrations. It is, however, difficult to deconvolute the role of minor elements on cement properties, partly because they are minor and partly because their behaviour in the kiln is not well documented. The distribution of a particular minor element during clinkering could affect the reactivity of the main phases (alite, belite) or of the minor phases (C_3A, ferrite), or it could form unique phases not present in normal clinkers. The two papers under discussion address the role of minor elements with varying degrees of success.

Discussion

Zinc oxide is a case in point. Barbanyagve (1) examined the system CaO-Al_2O_3-ZnO and reported the thermal synthesis, at ~1350°C, of two calcium alumino-zincates, $Ca_{14}Al_{10}Zn_6O_{35}$ (cubic, $a = 14.868$ Å) and $Ca_3Al_4Zn_6O_{10}$. Both phases were hydraulically active; 28 day strengths from 14 mm cubes were 43.2–47.9 mPa at water: solid ratios 0.25–0.40 ($Ca_3Al_4Zn_6O_{10}$) and in the same range for $Ca_{14}Al_{10}Zn_6O_{35}$.

Subsequent study of these phases (2) revealed that the cubic phase with $a_o = 14.9058$ Å was $Ca_6Zn_3Al_4O_{15}$ while the lower-symmetry phase had the most probable formula $Ca_3ZnAl_4O_{10}$: it was orthorhombic, $a = 16.7228$, $b = 10.7069$, and $c = 5.1355$ Å (2), and apparently isostructural with C_3MA_2 (3). The formula of a zinc-containing interstitial phase

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[1] Cem. Concr. Res. 28, 329–334 (1998).
[2] Cem. Concr. Res. 28, 335–340 (1998).

suggested by Kalki and Parisoakis, Ca_2ZnSiO_5, (4) is not confirmed by attempted preparations.

However, the real significance of these phases to clinker constitution and subsequent hydraulic behaviour arises from the fact that the solid phases present at clinkering temperatures, mainly alite and belite, cannot incorporate much ZnO. This was shown by electron microprobe studies of both synthetic preparations and real industrial clinker meals, to which ZnO had added (2). ZnO preferentially fractionated into the melt phase. This is corroborated by other studies (5,6). During cooling of the interstitial melt from $\sim$1450°C, again using industrial meals, $Ca_6(Zn, Mg)_3Al_4O_{15}$ was observed to crystallise (2). The practical limit of substitution of ZnO in the main clinker phases is certainly $<$1.0 wt % ZnO, perhaps only $\sim$0.2 wt%.

As a consequence of the appearance in Zn-containing clinkers of $Ca_6(Zn, Mg)_3Al_4O_{15}$, 1) magnesium, which might otherwise enter ferrite, alite and belite, is preferentially incorporated in the calcium zinc aluminate; and 2) Ca and Al are incorporated in the zinc phase. Both factors combine to alter the balance of other phases, especially C_3A and ferrite, and the effectiveness of zinc in altering these balances is enhanced by formation of a phase that supplements zinc with magnesium.

It is therefore not surprising that clinker properties are altered as a consequence of ZnO addition. Not only is bulk clinker mineralogy affected, but also the reactivity of the main minerals changes, and an interstitial phase, not normally present in cement, co-crystallises with C_3A and ferrite.

There are no shortcut solutions to determining the role of minor elements in clinkering; only a proper physiochemical investigation will elucidate the fundamental mechanisms whereby they alter clinker mineralogy and properties.

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