

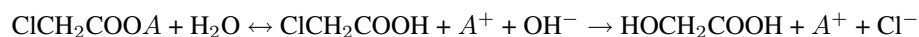
Phase Identification of Chloroacetate Salts and their Application as Cement Additives

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Organic as well as inorganic additives are used to control the setting behaviour of hydraulic binders. While LiCl and Li₂CO₃ typically act as accelerators [1,2], organic acids like citric, formic, benzoic, oxalic or tartaric acid and their Ca-salts retard the hydration reaction [1,3,4,5]. In a detailed report on the hydration behaviour of a CAC using Ca-salts of chlorinated acetic acids, calcium-monochloroacetate was pointed out as the strongest retarder [6]. Our present studies are focused on the influence of the cations of alkaline earth or lithium chloroacetates and occurring derivatives. However, for the phase identification of such compounds by XRD, appropriate database entries are lacking. Crystal-structural data are only available for NH₄-, Li-, Na-, Ca-, Ag-, Ni-monochloroacetates/hydrates [7,8,9,10,11,12]. Thus, the crystal structures, their thermal stabilities as well as their chemical behaviour and influence on a hydraulic binder system are objects of our investigation, starting with monochloroacetates.

Mg(ClCH₂COO)₂×4H₂O, Ca(ClCH₂COO)₂×H₂O, Sr(ClCH₂COO)₂, Ba(ClCH₂COO)₂×H₂O were crystallised from aqueous solution and found to form layered structures. Whereas, the high alkalinity of Li as well as of all other alkalis (A) leads to the hydroxylation of the relatively weak monochloroacetic acid, according to [13]:



Thus, after a longer storage over several weeks, from an aqueous solution of Li(ClCH₂COO) a new addition compound Li(ClCH₂COO)(HOCH₂COOH) with a chain like crystal structure crystallised. For all other alkalis a complete conversion into glycolic acid and chloride was observed.

The setting of a typical CAC (Secar51, W/Z = 0.5, T = 20°C) was retarded when a 0.025 molar solution of Ca-, Sr-, Ba- monochloroacetates was used (Ca > Sr > Ba) as revealed by isoperibolic heat flow calorimetry. For the magnesium monochloroacetate, the onset was slightly accelerated, whereas the hydration maximum is slightly retarded. In all cases the hydration product was found to be CAH₁₀. The lithium addition-compound strongly accelerates the setting, whereat two reactions occur. While C₂AH₈ was formed in the first sharp reaction, the second one leads to CAH₁₀, too.

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