Over the last 20 years, the effects of using limestone in Portland cement (PC) have been well studied. The benefits of limestone as a partial replacement for PC are well established. Its economic and environmental advantages of reducing CO2 emissions are well known. For a long time, the limestone has been considered as an inert filler. Recently it has been concluded that limestone serves both as an inert filler and also reacts to a limited extend. The reactivity depends on its fineness (specific surface) [1] and content [2,3]. The question arose, whether a) it is the availability of excess carbonate ion in the hydration system, which determines the degree of influence on the hydration process or b) does the system have its internal capacity to include carbonate ions and the increased availability (more carbonate ions in the solution, embedding the hydrating particles) would not have a significant effect. So the question was if the more soluble carbonates would have more pronounced effect on the hydration of the Portland cement than the limestone, which is only slightly soluble. The influence of slightly soluble (CaCO3, MgCO3, dolomite), medium soluble (Li2CO3) and highly soluble (K2CO3 and KHCO3) carbonates on the hydration of Portland cement was studied using Rietveld analysis. The results indicated that the amount of reacted carbonate in cement hydration at a 15% addition of slightly or medium soluble carbonates does not exceed 5% and is not affected by their solubility; at a 15% addition of the highly soluble carbonate K2CO3 the amount of reacted carbonate is around 6% leading to the conclusion that the system behaves according to the option b). The figure presents the quantitative analysis of cement hydration at 3, 7, 28 and 90 days of hydration and temperatures of 25 and 40°C.


**Keywords:** Portland cement hydration, Carbonates, Rietveld refinement