Reactivity and Microstructure of Calcined Marl as Supplementary Cementitious Material

Tone Østnor, Harald Justnes and Tobias Danner

Abstract The reactivity and microstructure of cement paste and mortar where cement is replaced by up to 65 vol.% calcined marl are discussed. It was found that the compressive strength evolution of mortar is following the same linear relation with amount of hydrate water at early ages for different cement replacements (35-65 vol.%), but that this deviates and give higher strength than predicted by the bound water at higher ages. Strength increases on a long term in spite of depleted calcium hydroxide at earlier ages and are discussed in terms of changes in CSH and CAH. XRD does not reveal any unusual crystalline products, but ettringite and hemi-/ mono-carboaluminate hydrate. SEM with WDS in a 2 year old mortar found pure CAH in a pore with atomic Ca/Al = 1.6 and some Si that might be a hydrogarnet.

1 Introduction

Marl, or calcareous clay, is considered "bad" clay for production of burnt clay products (e.g. bricks and light weight aggregate) since it is clay contaminated with substantial amounts of calcium carbonate that will form CaO after burning. This can lead to "pop outs" when calcium oxide reacts with water to calcium hydroxide during service.

Calcined marl has been proven earlier by Justnes et al. [1] to be an effective pozzolan in cementitious products. Thus, marl can be a large SCM resource that is not yet exploited to make blended cements or as mortar/concrete additive. Marl with 10-20 % $CaCO_3$, or rather calcareous mudstone, was calcined at 800 °C leaving 20 % of the original $CaCO_3$ intact.

T. Østnor (✉) · H. Justnes
SINTEF Building and Infrastructure, Trondheim, Norway
e-mail: tone.ostnor@sintef.no

H. Justnes · T. Danner
NTNU—Norwegian University of Science and Technology, Trondheim, Norway

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Calcined marl can be considered "industrial pozzolan" within the European cement standard (EN 197-1), and it may be feasible to make a pozzolanic cement with up to 55 % clinker replacement (CEM IV/B) considering the 28 day strength and sufficient early strength documented in this paper for mortar where cement is replaced by calcined marl.

2 Materials and Experiments

2.1 Materials

The marl was provided by Saint Gobain Weber who calcined it in a rotary kiln close to industrial conditions. The calcined marl were ground to d_{50} = 7 µm. Normal Portland cement (CEM I 42.5R according to NS-EN 197-1) produced by Norcem Brevik, Norway, was used for all the mortar and paste mixes. The super plasticizer used was Dynamon SP 130 supplied by Mapei AS, Norway.

2.2 Mortar and Paste Mixes

The mortars were made with 0, 20, 35, 50 and 65 vol.% replacement of cement with calcined marl to secure a constant volume of binder. The consistency of fresh mortar was determined using a flow table. The water-to-binder ratio (w/b) was 0.5 in all the mortars while the flow was maintained within ±5 % of the reference by varying the amount of super plasticizer; 0.0, 0.2, 0.3, 0.5 and 0.9 % (of binder weight) for the mortars with 0, 20, 35, 50 and 65 vol.%, respectively. The mortar mixes were cast in 40 × 40 × 160 mm moulds. After 24 h the prisms were removed from the moulds and stored in a cabinet at 90 % RH and 23 ± 2 ºC.

In the paste mixes was OPC replaced with 35, 50 and 65 % calcined marl with a w/b ratio of 0.5 and cured for 1, 3, 7, 28, 90 and 365 days at 90 % RH and 23 ± 2 ºC.

3 Results

3.1 Compressive Strength

The average compressive strength and flexural strength for all mortars as a function of time are given in Table 1 together with standard deviations based on 5 and 3 parallels, respectively.