Applied Clay Science 129 (2016) 35–39

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Note

Properties and pozzolanic reactivity of flash calcined dredging sediments

Ruben Snellings [a,*], Özlem Cizer [b], Liesbeth Horckmans [a], Paweł T. Durdziński [c], Philippe Dierckx [a], Peter Nielsen [a], Koenraad Van Balen [b], Lucie Vandewalle [b]

[a] Sustainable Materials Management, VITO, Boeretang 200, 2400 Mol, Belgium
[b] Department of Civil Engineering, KU Leuven, Kasteelpark Arenberg 40-2448, 3001 Leuven, Belgium
[c] Laboratory of Construction Materials, EPFL, Station 12, 1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 22 March 2016
Received in revised form 15 April 2016
Accepted 22 April 2016
Available online 9 May 2016

ABSTRACT

Dredging of ports, harbours and waterways generates vast amounts of sediments that find few applications and need to be disposed of. In the port of Antwerp, Belgium, each year 450,000 t (dry matter) of dredging sediments are mechanically dewatered and stockpiled. This paper investigates flash calcination of the clay-rich dredged sediments as a sustainable solution to develop novel pozzolanic supplementary cementitious materials (SCM) for blended cement.

1. Introduction

Maintenance and improvement of waterways by dredging of sediments in the Port of Antwerp (Belgium) generates each year about 450,000 t (dry matter) of material for which suitable disposal solutions or applications need to be found. For the whole of Europe the yearly volume of dredging sediments is estimated at 300 Mt. At present the use of dredging sediments as raw material has been explored for the production of bricks (Hamer and Karius, 2002; Lafhaj et al., 2008; Samara et al., 2009), lightweight aggregates (Chen et al., 2012), stabilised road-base (Siham et al., 2008; Zentar et al., 2008), Portland clinker (Aouad et al., 2012) and as supplementary cementitious materials (SCM) for blended cements (Beckstrom et al., 2014; Dang et al., 2013).

Key challenges that need to be addressed before the dredged sediments can be used as SCMs are 1) the dry matter (DM) typically accounts for only 15–20 mass% of the sludge, 2) the sludge may be polluted by heavy metals and organic contaminants and 3) the composition of the sludge may be variable. Point 1 can be dealt with by mechanical dewatering, point 2 by strict separation of polluted and non-polluted sediments, and point 3 by meticulous homogenization.

This paper investigates flash calcination as a means to activate the fine-grained clay minerals contained in the dredged sediments of the port of Antwerp. The effect of calcination on the physico-chemical characteristics and the pozzolanic reactivity of the dredged sediments is reported. The aim of this paper is to evaluate the potential of calcined dredged sediments as an alternative SCM.

2. Materials and methods

2.1. Materials

A representative sample of the filter cakes was selected for activation by flash calcination. The design and operation of the pilot-scale flash calciner are described by (Teklay et al., 2015). Three calcination temperatures were assessed: 820, 865, and 905 °C. Henceforth, the resulting samples are designated as “FC 820”, “FC 865” and “FC 905”, respectively. Before calcination the filter cake was dried at 110 °C until constant mass and subsequently ground in a vertical roller mill. The material feed to the flash calciner had a 13% residue on a 90 μm sieve. After calcination the material was cooled by ambient air, no post-calcination crushing or grinding was applied.

2.2. Characterisation methods

The dry matter content of the filter cake was determined by drying at 105 °C until constant mass. The samples were microwave digested in acid ($HCl/HNO_3/HF/H_3BO_3$) for the determination of the chemical composition by ICP-OES (Inductively Coupled Plasma—Optical Emission Spectrometry), the total sulphur content was analysed by anion chromatography. Total organic carbon was measured after acid dissolution of inorganic carbonates using ignition and CO_2 detection by IR spectrometry. Water-soluble chloride was determined by Cl extraction in boiling ultrapure water and measurement by anion chromatography.

The particle size distribution of both untreated and calcined materials was measured by laser diffractometry. The samples were dispersed in isopropanol prior to measurement. The specific surface area was

* Corresponding author.
E-mail addresses: ruben.snellings@vito.be (R. Snellings), ozlem.cizer@bwk.kuleuven.be (Ö. Cizer), liesbeth.horckmans@vito.be (L. Horckmans), pawel.durdzinski@epfl.ch (P.T. Durdziński), philippe.dierckx@vito.be (P. Dierckx), peter.nielsen@vito.be (P. Nielsen), koenraad.vanbalen@bwk.kuleuven.be (K. Van Balen), lucie.vandewalle@bwk.kuleuven.be (L. Vandewalle).

http://dx.doi.org/10.1016/j.clay.2016.04.019
0169-1317/

measured using multi-point BET N_2 adsorption. The samples were outgassed for 16 h at 40 °C.

The particle morphology of the calcined filter cake samples was studied by scanning electron microscopy (SEM). The powder samples were glued on a carbon stub and Pt-coated prior to microscopic investigation. A FEI Nova NanoSEM 450 electron microscope equipped with a field emission gun was operated at 5 kV acceleration voltage.

XRD data were collected using a X'Pert PRO diffractometer (Panalytical) equipped with a CuKα tube. Tube operating conditions were 40 kV and 40 mA. Diffraction scans were recorded from 7 till 70°2θ, step size 0.04°2θ, and a measurement time per step of 4 s. Rietveld analysis was performed using HighScore Plus software according to the procedures given in (Snellings, 2016).

Electron microscopy was used to determine the composition, distribution and morphology of the amorphous calcination products. The powder samples were embedded in a low-viscosity epoxy resin and gradually polished down to ¼ μm diamond powder grit size. The samples were carbon coated prior to microscopic analysis. A FEI Quanta 200 scanning electron microscope equipped with a Bruker XFlash 4030 EDS detector was used. The microscope was operated at 15 kV acceleration voltage and 12.5 mm working distance. Backscattered electron images and EDS full element maps of 8 frames of 252 × 189 μm were acquired. Subsequently the data were treated by image analysis procedures as detailed in (Durdziński et al., 2015) to determine the fraction of reactive phase and its composition.

2.3. Pozzolanic reactivity

The pozzolanic reactivity of the calcined filter cakes was determined by measuring the heat release of the exothermic pozzolanic reaction in a model mix of calcined filter cake and $Ca(OH)_2$ with additional alkalis and sulphate. Alkalis and sulphates are added to simulate the environment of Portland cement reaction. A hydration temperature of 40 °C was applied to accelerate the pozzolanic reaction. The heat release was measured up to 5 days of reaction using a TAM Air isothermal calorimeter The mix design and operational procedures are further detailed in (Snellings and Scrivener, 2016).

3. Results

3.1. Chemical composition

The mechanical dewatering of the dredged sediments produces filter cakes in which the measured dry matter content was 66 ± 3 mass%. The chemical and mineralogical composition of the filter cake is given in Table 1. Upon calcination the organic carbon compounds are decomposed and volatilised, reducing the total organic carbon level to 0.25 ± 0.06 mass%. Sulphur and chloride contents were relatively low initially and were not further reduced by flash calcination. The measured chloride contents were far below levels of 2.5–3.0 mass% (DM) reported by (Dang et al., 2013) for evaporation-dried marine dredged sediments and comply with the regulations for use in non-reinforced and normal reinforced concrete.

3.2. Physical properties and morphology

The calcination temperature had little effect on the particle size distribution (Table 1). However, compared to the untreated filter cake, all calcined filter cakes were significantly coarser. This indicates that irreversible particle agglomeration by sintering or melting occurred upon calcination as shown in the electron microscopy images in Fig. 1.

Significant changes in BET specific surface area values were noted amongst calcination temperatures (Table 1). The higher the calcination temperature, the lower the specific surface area. Given that the particle size distributions of the calcined filter cakes were practically identical, the observed decrease in BET specific surface area is indicative of a strong reduction in particle surface roughness. A decrease in particle surface roughness is generally favourable for fresh concrete as it lowers the water demand (Taylor, 1997).

Table 1
Chemical and mineralogical compositions of the dredged sediment filter cake. Mean particle size diameter (d_{50}) and BET specific surface areas are given as well. DM stands for Dry matter, TIC for Total Inorganic Carbon, TOC for Total Organic Carbon and LOI for Loss On Ignition.

Oxide	Mass% (DM)		Untreated	FC 820	FC 865	FC 905
Al_2O_3	10	Quartz	22	26	27	25
SiO_2	37	Plagioclase	3	5	5	6
Fe_2O_3	9	Alkali feldspar	2	2	3	3
CaO	12	Calcite	12	4	4	3
MgO	1.6	Aragonite	5	–	–	–
Na_2O	0.5	Pyrite	1	–	–	–
K_2O	2	2:1 clay (illite, smectite)	34	12	6	6
P_2O_5	1	Kaolinite	3	–	–	–
TiO_2	1	Fe-oxides (hem/mag)	–	2	3	3
S	1.1	Free lime	–	2	1	1
TIC	1.9	Anhydrite	–	2	2	2
TOC	3.6	Unidentified/amorphous	18	45	49	51
Cl	0.1	d_{50} (μm)	7.2	17.6	16.8	19
LOI	22	BET (m^2/g)	–	8.95	4.94	3.35

The effect of calcination temperature on particle morphology is illustrated by SEM images of powder mounts in Fig. 1. At the lowest calcination temperature of 820 °C the powders mainly consisted of irregular aggregates smaller than 30–40 μm. Fig. 1 shows remnant imprints of the membrane filters used in the dewatering step. These "imprints" are easily recognised by their characteristic regular hexagonal honeycomb patterns. Next to these features spherical particles were recognised. These are indicative of local melting processes and resemble typical fly ash cenospheres. The size of these spherical particles varied from a few microns up to 20 μm. At higher calcination temperatures spherical particles were more common. Features typical for sintering were observed at the particle surfaces: edges became more rounded and smaller particles were fused into aggregates. This trend compared well to the decrease in surface roughness derived from the BET data of specific surface area. Higher calcination temperatures thus led to 1) particle agglomeration and reduced surface roughness due to sintering, and 2) local melting and the formation of spherical glass particles.

3.3. Effect on mineralogy

The absolute content of crystalline materials was determined by XRD according to (Snellings, 2016). The remaining amorphous content was then determined by difference to 100%. Since the crystalline materials are known not to be reactive as SCM (Snellings et al., 2011), in a second step the properties of the amorphous phase were investigated in more detail by BSE-image analysis.

Excerpts of the XRD patterns of the untreated and calcined filter cakes are shown in Fig. 2. The quantitative results of the Rietveld analysis are given in Table 1. The XRD patterns clearly demonstrated a structural decomposition of the main clay minerals. At the lowest calcination temperature of 820 °C all kaolinite and more than half of the 2:1 clays (illite and smectite) were decomposed. At higher temperatures this decomposition was more complete as reflected by the decreasing content of 2:1 clays and the increasing amorphous fraction in Table 1. This amorphous fraction constituted about half of the calcined material and slightly increased with calcination temperature up to 905 °C.

Calcium carbonates (calcite, aragonite) were largely decomposed in the calcination process. A few percent of calcite remained after calcination. Part of the CaO released in the decomposition of the calcium carbonates reacted with sulphate to form anhydrite. A small amount