Ain Shams University
Faculty of Science
Chemistry Department

UTILIZATION OF SOME NANO-MATERIALS IN THE IMPROVEMENT OF CEMENT QUALITY

Thesis submitted for
Ph.D. Degree of Science in Chemistry

By

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M.Sc. (2009)

Faculty of Science, Ain Shams University

To

Chemistry Department

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Cairo, Egypt

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FULL LENGTH ARTICLE

Pozzolanic and hydraulic activity of nano-metakaolin

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Abstract Nano-metakaolin (NMK) was prepared by firing of Nano-kaolin (NK) at different temperatures (750–825 °C) for 2 h. The pozzolanic activities of NMK samples were studied using hydrated lime as an activator. The optimum firing temperature of metakaolin (MK) was established from the results of hydration kinetics and differential scanning calorimetry (DSC) and found to be 750 °C; NMK, thus produced, is designated as NMK(750). This was based on the marked consumption of free calcium hydroxide by NMK fired at 750 °C as well as the highest values of chemically combined water at all ages of hydration. Therefore, NMK(750) was used for partial replacement of OPC and studying the physico–mechanical properties of OPC–NMK blended cement pastes. The optimum substitution of OPC by NMK was found to be 8–10%. This was based on the development of compressive strength of the various hardened OPC–NMK blended cement pastes having different NMK contents (0–16%), where the strength increases with NMK content up to 10% and then decreases. In addition, the SEM micrographs obtained for the hardened OPC (93%)–NMK (7%) blended cement paste displayed the formation of amorphous and microcrystalline CSH which fill the pores leading to a more dense structure with higher hydraulic activity as compared to neat OPC paste.

Introduction

The utilization of calcined clay as a pozzolanic material for mortar and concrete has received considerable attention in recent years. The effect of nano-clay on the mechanical properties and microstructure of Portland cement mortar was investigated [1]. The results showed that the compressive strength of the cement mortars with NMK was higher than the plain cement mortar with the same water/binder ratio.

Metakaolin (MK) which is a pozzolanic material, is a thermally activated aluminosilicate material obtained by firing kaolinite clay within the temperature range of 700–800 °C

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CHAPTER I
INTRODUCTION AND OBJECT OF INVESTIGATION

I.A. Introduction

In terms of volume used, cementitious materials, mainly in the form of concrete, are the most successful materials in the world. Every year more than 1 m^3 is produced per person worldwide. This success stems from the ease with which a mixture of grey powder and water can be transformed into a highly functional solid of readily manipulated shapes at room temperature. Furthermore it is a low cost, low energy material made from the most widely available elements on earth. Portland cement is the primary cementitious material that is used in the most widely construction in the world. Each year, the concrete industry produces approximately 12 billion ton of concrete and uses about 1.6 billion ton of Portland cement worldwide. Indeed, with the manufacture of one ton of cement approximately 0.8 ton of CO_2 are launched into the atmosphere. However, despite having a lower environmental impact than most alternative construction materials, the huge volumes of cement and concrete produced mean that cement production accounts for some 5–8% of manmade CO_2 emissions. Therefore there is increasing pressure to innovate to improve sustainability.

The need to reduce the environmental impact of cementitious materials is, and will continue to be, a major driver for innovation. The use of supplementary materials is now so well established that the average clinker content of cements in Europe is less than 80%.

Supplementary cementing materials have become an integral part of high strength and high performance concrete mix design. These may be naturally occurring materials, industrial wastes, or byproducts or the ones requiring less energy to manufacture. Some of the commonly used supplementary cementing materials are fly ash, silica fume (SF), granulated blast furnace slag (GGBS), rice husk ash (RHA) and metakaolin (MK), etc. Metakaolin is obtained by the calcination of kaolinite. It is being used very commonly as pozzolanic material in mortar and concrete, and has exhibited considerable influence in enhancing the mechanical and durability properties of mortar and concrete.

When mixed with calcium hydroxide and water, metakaolinite obtained by fixed-bed calcination of a commercial kaolinite at 730°C, hydrates and develops, at 28 days, compressive strengths (tests on minicylinders) of about 10–15 MPa. Hydration products are essentially C_2ASH_8 and CSH with some quantities of C_4AH_{13}. The influence of several factors e.g. curing conditions, metakaolinite/calcium hydroxide constitution and water/cement ratios, addition of sand to the mix, which can modify the hardening, has been investigated by **Murat (1983)**. From these investigations, it appears that metakaolinite-calcium hydroxide mixes react with water to form essentially hydrated gehlenite, CSH and small quantities of C_4AH_{13}. Compressive strength after curing at 28 days at 20°C in air-tight plastic boxes are higher than for natural calcium hydroxide activated pozzolana. Raising the W/S ratio or addition of sand to the mix diminishes strengths, but, in the case of pure paste, an increase of strength at 28 days can be obtained by increasing the theoretical MK/CH ratio.

Compressive strengths of calcium hydroxide-activated metakaolinite cements have been studied versus both calcination process of kaolinite (use of fixed-bed and stirred-bed or rotary kiln- Laboratory reactors) and calcination temperature **Murat and Comel (1983)**. Whatever the curing time from 7 days to 90 days, a maximum of strength is observed for calcination in the 700–850°C temperature range, but metakaolinite obtained in rotary kiln (process which realizes the dehydration of kaolinite in a shorter time, but can lead to a phenomenon of particle aggregation on the furnace wall) is less disordered and strengths of cements derived there from are some weaker than in the case of cements made with metakaolinite from fixed-bed calcination.

Serry et al. (1984) prepared four mixtures of weight ratios 80:20, 70:30, 60:40 and 50:50 of china kaolin/pure $Ca(OH)_2$. Each mix was activated for 2 hours at 800°C and then paste hydrated at room temperature and 100% RH for up to 28 days. The hydration products were studied by XRD as well as DTA and TG techniques. The chemically-combined water and $Ca(OH)_2$ contents were quantitatively determined from the TG curves. The results illustrated the formation of gehlenite hydrate (C_2ASH_8) as the main hydration product; its amount increases with the curing time. Hydrogarnet is also formed at the early stages of hydration in the mixes of lower lime content (e.g., mix 80:20) and increases on prolonged hydration; this is probably due to the lower pH of the reaction medium. CSH gel could not be easily detected by XRD because of its low degree of crystallinity. However, this phase was identified by DTA and gives the characteristic losses on the TG curves. $Ca(OH)_2$ is consumed gradually as the hydration proceeds and disappears nearly completely after long periods (28 days).

Five compositions with 10% to 50% metakaolin for cement substitution were studied **(Bredy et al., 1989)**. The rate of hydration was studied from the compressive strength after up to 6 months of curing and from the hydrates formed by DTA and XRD techniques. The metakaolin addition considerably reduced portlandite content in the hydrated cement and contributed to the formation of hydrated gehlenite which is not present in OPC paste. The microstructure study (SEM) showed that pozzolanic cement pastes were less crystallized than plain pastes. The porosity- measured by Mercury intrusion - with blended cements was higher than that with OPC, except for 10 and 20% metakaolin substitution. Evolution of the pore size distribution was studied indicating that the pozzolanic pastes enhance small diameters.

Considering Metakaolin as a supplementary cementitious material with pozzolanic properties; **Ambroise et al. (1994)** studied its activation by triacalcium silicate (C_3S), triacalcium aluminate (C_3A) and ordinary Portland cement. The early hydration period of pastes containing metakaolin was investigated using isothermal calorimetry and conductivity. Differential thermal analysis, X-ray diffraction, and Fourier transform infrared spectrometry were used to follow the consumption of calcium hydroxide (CH) and identify the products of reaction. Compressive strength and porosity were also determined. The results showed that CH is quickly consumed, the microstructure is rich in CSH and strätlingite (C_2ASH_8), and the pore size distribution is displaced toward smaller values.

Kaolins with fairly well crystallized kaolinite as the main component were calcined by **Changling He et al. (1994)** at respectively 550, 650, 800 and 950°C for 100 minutes. Both the raw and calcined samples, before and after being mixed with either ordinary Portland cement or with $Ca(OH)_2$ or after extended immersion in the simulated cement paste pore solution saturated with $Ca(OH)_2$, were studied by DTA (for raw kaolin), XRD, SEM and EMPA. The compressive strength, chemical shrinkage and alkali and acid solubility of samples were also investigated. The optimum calcination temperature from the combined scientific and economic standpoint is 550°C, corresponding to the culminating point of kaolinite dehydroxylation. Their study confirms that calcination is an effective approach to enhance the pozzolanic activity of kaolin. Most of kaolinite is destroyed and altered to an X-ray amorphous phase after heating at 550°C for 100 minutes. The amount of XRD amorphous metakaolin increases modestly during further calcination to 650°C and 800°C but starts to fall by 950°C when mullite appears. This amount is effectively measured by the background intensity of the XRD patterns. Results of chemical shrinkage for the mixtures of metakaolin-OPC or metakaolin- CH showed that the kaolins treated at 550°C and 650°C have the fastest reaction rate, slightly higher than the reference fly ash. They are followed by kaolin calcined at 800°C. The faster reaction rates are in agreement with the higher specific surface of 550-650°C metakaolin.

Zhang and Malhotra (1995) presented the results of the physical and chemical properties of a thermally activated alumino-silicate material (metakaolin), and the properties of fresh and hardened concrete incorporating this material that indicates that metakaolin (MK) material is highly pozzolanic and can be used as a supplementary cementing material to produce high-performance concrete. Although it requires a higher dosage of the superplasticizer and air-entraining admixture compared with that of the control concrete, the MK concrete can be produced with satisfactory slump, air content, and setting time. The concrete incorporating 10% MK had higher strength at all ages up to 180 days compared with the control concrete; in comparison with the silica fume concrete the MK concrete showed a faster strength development at early ages, but had lower strength after 28 days. At 28 days, the MK concrete had somewhat higher splitting-tensile and flexural strengths, Young's modulus of elasticity, and lower drying shrinkage compared with that of the control and the silica fume concretes. The resistance of the MK concrete to the chloride-ion penetration was significantly higher than that of the control concrete, but similar to that of the silica fume concrete. The MK concrete showed excellent performance in the freezing and thawing test. The performance of the MK concrete subjected to the de-icing salt scaling test was similar to that of the silica fume concrete, but marginally inferior to the control concrete.

Flash-calcination enables the dehydroxylation of powdered kaolinite clay within several tenths of a second, when traditional soak-calcinations require minutes at least has been presented by **Salvador (1995)**. Two different lime reactivity tests were thus necessary to assess the pozzolanic properties of products: the compressive strengths of minicylinders of (metakaolin – lime – water) after solidification, and the Chapelle test. Flash-calcined thin kaolin present high water absorption capacities, and thus require more water to gauge pastes or mortars. This makes comparison of mechanical strengths with soak-calcined products difficult, which makes it desirable to confirm them by Chapelle tests. By measuring compressive strengths of minicylinders verified, after a flash-calcination, the quality of the pozzolana increases with a value.