DETERMINATION OF POZZOLANIC ACTIVITY OF THERMALLY ACTIVATED BRICK LOAM

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Abstract. *Supplementary cementing materials (SCM) present of one of possible ways how to reduce the energy consumption and related CO_2 emissions from Portland cement production. There is number of more or less stablished SCM. These may be by-products of another production technologies (blast furnace slag, coal fly ash), natural materials (certain volcanic rocks) or produced materials (calcined clays).Metakaolin (MK) – thermally activated kaolin – belongs to the widely studied SCM. Its main drawback is relatively high price, caused partially by the rather "exclusive" raw material – kaolin. The research on thermal activation of more abundant clay raw materials to SCM may raise the application potential of clay-based SCM. This paper deals with thermal activation of a brick loam. The loam under study contains all principle clay minerals (kaolinite, illite, montmorillonite) accompanied by quartz and feldspars. The loam was characterized by thermogravimetry and XRD. Then it was activated at three temperature levels (500, 550 and 600 °C) and the pozzolanic activity was determined by Saturated Lime Test. It was found that all three materials are fixing considerable amount of Ca^{2+} ions, but probably not only by pozzolanic reaction, but also adsorption on clay minerals plays a role.*

Keywords

SCM, brick loam, pozzolanic activity, saturated lime test.

1. Introduction

The reduction of energy consumption and CO_2 emissions is currently a huge issue in (not only) cement industry [1]. Obviously there is number of possible ways how to achieve the goals, both on side of production technology as well as by using of alternative materials, such are e.g. alkali activated materials or calcium sulfoaluminate cements [2]. More conventional approach, providing the more or less identical resulting binder as Ordinary Portland Cement (OPC), lies in substitution of part of Portland clinker by Supplementary cementing materials (SCM). The SCM materials are usually amorphous alumino-silicates which are able to take part in pozzolanic reaction. In this process, SCM is reacting with $Ca(OH)_2$ to hydration products (C-S-H) responsible for the concrete strength. The mixture of Portland clinker and a SCM is called blended cement; the SCM addition is beneficial not only for environmental reasons but it can also improve the concrete durability measures [3].

There is broad range of technically used or just studied SCM materials. The Ground Granulated Blast Furnace Slag (GGBFS) and coal Fly Ash (FA) (especially Class F) are the most established and broadly used SCM. Obviously, these materials are by-products of iron and electricity production. Nevertheless the demand of building constructing industry for GGBFS and FA,, parallel to certain decline of the traditional industrial processes (at least in Europe), are promoting the possible application of less conventional SCM such are e.g. agricultural waste ashes or ashes from Municipal Solid Waste Incineration (MSWI) [4]. The thermally activated (calcined) clay minerals belong also to the well-established SCM. The most-known and used, of this group of materials, is metakaolin (MK) – calcined kaolin [5]. There seems to be general agreement that this material, produced at lower calcination temperature than Portland clinker (e.g. 650 °C for kaolin studied in [6]), is efficient SCM, reducing the environmental load of concrete production and improving the durability of concrete [7]. Currently high research attention is paid to approach called "LC^3 cements" – mixtures of Portland clinker, limestone and calcined clay [8]. LC^3 cements aim to have the same mechanical performance as OPC, but with higher durability and less CO_2 emissions (by 40%).

Metakaolin has one – but very important – drawback – it is relatively costly, because kaolin (raw material) is rather exclusive clay having number of applications in ceramic industry, paper making or refractories. Nevertheless kaolin is not the only clay possessing the pozzolanic activity when calcined [9]. There is a broad range of clay minerals found in nature. All of them can be thermally treated what results to the dehydration and dehydroxylation of the clay mineral, accompanied with collapse of crystalline structure to an amorphous matter [10]. The potential pozzolanic activity of the amorphous clay residuum is the key factor of its applicability in blended cements. The pozzolanic reactivity of three most common types of clay minerals (kaolinitic, illitic, smectitic), after thermal activation, were studied by Hollanders et al. [11]; the activated kaolinite was found to be the most effective pozzolana, while the others were performing worse. The same conclusion was made also by Tironi et al. [12].

There are several methods, how to assess the pozzolanic activity of a potential pozzolanic matter; mostly they are based on monitoring of $Ca(OH)_2$ depletion in the system by means of titration of residual solution or thermal analysis of hydration products [12, 13, 14]. Alternatively, the Strength Activity Index (SAI) may be determined which reflects the influence of pozzolana on the mechanical performance (strength) of the cementitious composite [12, 15]. These last two cited papers agreed on that the SAI index is the best indicator.

The present paper aims to investigate the potential applicability of Saturated Lime Test to the pozzolanity assessment of thermally activated brick loam. The brick loam was studied as an alternative clay raw material, which is highly abundant and less costly than kaolin.

2. Experimental

The brick loam (signed as BS) under studied was collected at Dolní Bukovsko locality, Southern Bohemia, where it is used as the raw material in the ceramic brick production. The chemical composition of the loam was determined by XRF spectrometry (Thermo ARL 9400 XP). The simultaneous thermal analysis TG/DSC (thermogravimetry – differential scanning calorimetry) was performed by Setaram LabsSys EVO under Argon atmosphere from ambient temperature to 1000 °C. The X-ray diffractometry (XRD; by means of PANalytical Aeris, Co(Kα) tube operating at 40 kV, 7.5 mA) was performed on brick loam before and after thermal activation. The diffractograms were evaluated by means of Profex software [16]. Thermal activation was performed at 500, 550 and 600 °C in electric furnace for 3 hours (ramp 10 °C/min; natural cooling). The pozzolanic activity was determined by means of Saturated Lime Test, modified on basis of [15]. In this test, the pozzolana (1 g) is reacting with saturated solution of $Ca(OH)_2$ (100 ml); the flasks were placed in orbital shaker incubator (40 °C). After a given time of reaction (1, 3, 7 days) the suspension was filtered and the OH^- and Ca^{2+} content in the filtrate was determined by titration. The OH^- were titrated by 0.1 M HCl with methyl-orange indicator, while Ca^{2+} by EDTA (0.03 M) at pH 12 and with calconcarboxylic acid as indicator. The pozzolanic activity was expressed as mg of $Ca(OH)_2$ fixed by 1 g of pozzolana.

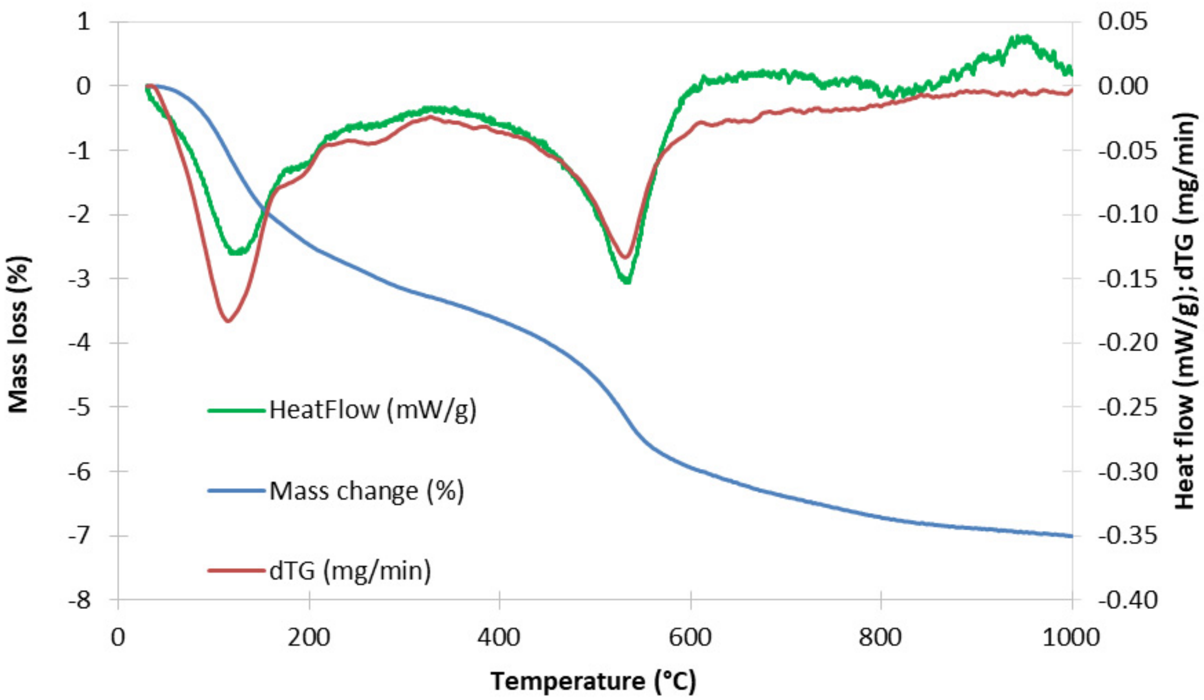

Fig. 1: Simultaneous thermogravimetry and DSC of brick loam BS.

3. Results and discussion

The chemical composition of the brick loam BS (Tab. 1) is not anything surprising; the high content of silica and alumina may be expected in this kind of material [17] The results of simultaneous TG/DSC (Fig. 1) are indication occurrence several endothermic processes; firstly the clay minerals dehydration is taking place from about 50 to 200 °C. The observed two-step dehydration is typical for clay minerals from Smectite group. The second endothermic peak, centred at 520 °C, is related to the dehydroxylation of clay minerals.

Tab. 1 Chemical composition of brick loam BS (% by weight; examined by XRF).

SiO_2	64.2
Al_2O_3	22.3
Fe_2O_3	5.7
CaO	0.9
K_2O	3.1
MgO	2.4
TiO_2	0.9

Nevertheless the phase with the highest abundance in BS loam is Quartz, which is further accompanied by small amount of Feldspars – probably Orthoclase and Anorthite. The quantification of the amount of individual phases in the loam by Rietveld refinement is not providing reliable results in the studied system with high amount of clay minerals. Nevertheless the "Smectite" seems to be the most abundant from the clay minerals present. To distinguish which specific clay mineral from Smectite group is present is not possible on the base of the presented experiments. Nevertheless the absence of dehydroxylation at about 700 °C (Fig. 1) indicates that the "Smectite" is not Ca nor Na-Montmorillonite but more likely Nontronite (or "unusual Montmorillonite") which dehydroxylation is taking place at lower temperature (454 °C) [18]. The final decision on the type of Smectite must be done by means of XRD of oriented samples treated by ethylene-glycol. The dehydroxylation of Illite and Kaolinite is centred at 532 °C.

The investigated temperatures of thermal activation of the loam were selected on the basis of these results: 500 °C as the beginning of the process and 600 °C as the temperature where the clay minerals decomposition was supposed to be completed. The XRD of the activated samples (Fig. 2) is documenting if the assumption was fulfilled. The Smectite structure was broken down already in the BSA 500 sample. The Kaolinite crystals were also already destroyed, what is in agreement with [19]. On the other hand, the Illite structure was partially preserved even in BSA 600 sample, even though Thermal analysis revealed that the decomposition should be completed. The results published in [20] confirmed that dehydroxylation of Illitic clay may took place even above the 600 °C. It should be noted, that diffractograms of

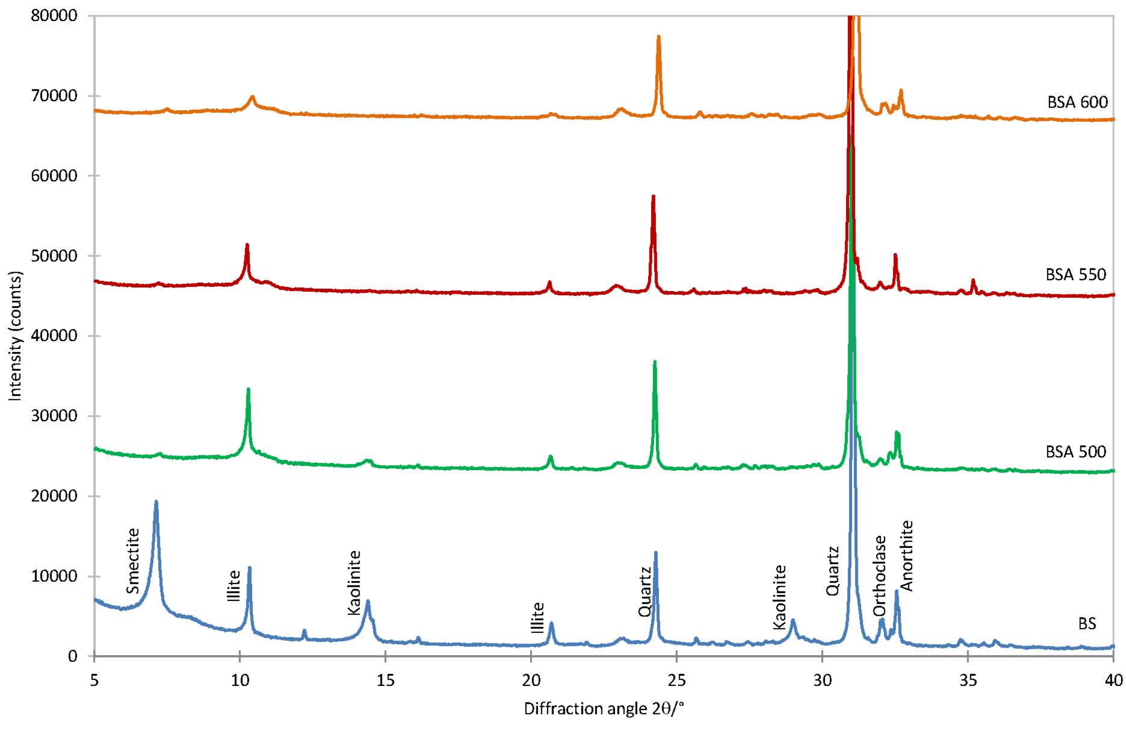

Fig. 2: X-ray diffractograms of brick loam BS before and after thermal activation.

To distinguish individual present clay minerals, the thermal analysis must be combined with XRD of untreated loam (Fig. 2). This method, performed so far with conventional pressed tablets, confirmed presence of Kaolinite, Illite and a mineral from Smectite group.

BSA 550 and BSA 600 in Fig. 2 are not shown complete – the highest Quartz diffraction is cut in order to emphasize the clay minerals residual diffractions (which are really low in “full scale” diffractograms). Not surprisingly Quartz and other anhydrous silicates were not influenced by the thermal activation.

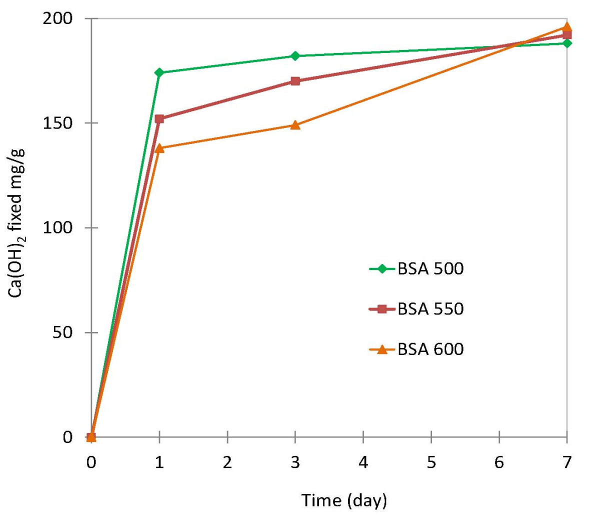

Fig. 3: Results of Saturated Lime test of activated brick loam.

The pozzolanic activity of thermally activated loam was tested by means of Saturated Lime Test (Fig. 3). All of the samples fixed considerable amount of Ca^{2+} ions already after 1 day of experiment. Interesting is the fact that BSA 500 featured the highest rate of Ca^{2+} sorption. It might be caused by presence of undehydroxylated Illite which may contribute to the Ca^{2+} fast removal from solution by its cation exchange capacity. Concerning the amount of Ca which may be adsorbed by illite – its Ca^{2+} exchange capacity is 5.6 mg/g [21], what is considerably lower than are the values measured in the test (Fig. 3). It means that most of the Ca^{2+} ions depleted from the solution (corresponding to about 90% of available $Ca(OH)_2$ in the starting saturated solution) were fixed in pozzolanic reaction taking place on the surface of BSA samples. The BSA 600 reactivity was somewhat slower, but after 7 days, the values were in fact equal. It means that all of the thermally activated samples are pozzolanic active and may be used as SCM in concrete. The final decision, if such SCM is feasible or not, must by obviously based on further tests (strength of concrete, effect of activated loam on durability etc.), which are beyond of the scope of this paper.

The obtained results are well comparable with that’s obtained in [12, 15] for various metakaolins and other activated clay minerals. On the other hand, Andrejkovičová et al [22] reported much higher values of fixed $Ca(OH)_2$ on metakaolins, but they used Chapelle test which is not fully identical with the Saturated Lime Test performed in this paper. Further one should consider that the used brick loam is not purely clay material but it contains significant amount of Quartz and other stable minerals, what obviously reduces its ability to take part “quantitatively” in the pozzolanic reaction.

Regarding the optimal temperature of the thermal activation, one has to consider not only the determined pozzolanic activity (Fig. 3). The BSA 500 seems to be the fastest “calcium absorber”, but it also contains the most distinct clay minerals residuals (see the clay minerals diffraction in Fig. 2) which are negatively influencing the concrete strength [23]. For this reason, the sample BSA 600 is more safe and this activation temperature is concluded to be the suggested for this type of brick loam. This relatively low calcination temperature (at least when compared to Portland clinker sintering at 1450 °C) is the main benefit of the brick loam used as SCM; the reason is obvious –the lower energy consumption. The drawback lies in lower content of reactive matter compared to conventional SCM due to content of residual minerals (Quartz and feldspars), resulting the lower ability to replace the clinker.

4. Conclusion

A sample of brick loam was thermally activated in order to be utilizable as SCM in concrete, as a less cost-intensive alternative to metakaolin. The activation temperature 600 °C seems to be sufficient to obtain reactive product. The Results of Saturated Lime Test were somewhat influenced by the presence of undehydroxylated illite in the “low-temperature” activated material. The future research will be focused on the testing of activated brick loam in the cementitious composites, as well as on more detail description of pozzolanic reaction and sorption taking place on its surface.

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