Thermally treated phlogopite as magnesium-rich precursor for alkali activation purpose

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ABSTRACT

Alkali-activated materials (AAMs), sometimes called geopolymers, have wide industrial relevance and are produced through alkaline activation of alumina and silica-rich precursors, including industrial side streams. It has been observed that MgO content in AAMs results in improved mechanical properties. However, most of the suitable MgO sources are either prohibitively expensive or carbonate-based, which leads to higher CO_2 emissions. Phlogopite is an attractive source of MgO as it is carbonate-free and locally abundant. Besides MgO, phlogopite also contains significant quantities of silica and alumina, making it a viable candidate for alkali activation. However, an alkaline solubility test in NaOH revealed phlogopite to be highly inert, with both silicon (Si) and aluminum (Al) solubility at around 1 wt% of the original material. In this work, thermal treatment was considered to improve the alkali activation potential of phlogopite. Thermal treatment was found to be successful; the resulting glassy material showed 45% Si and 33% Al release into the solution, on a par with highly soluble metakaolin (26% Si and 40% Al). During the solubility test, significant quantities of magnesium and iron were also released but they did not stay in the solution. Rather, they formed precipitated products, the main one of which was meixnerite ($Mg_6Al_2(OH)_{18} \cdot 4H_2O$), a hydrotalcite-like compound. The resulting alkali-soluble glass with phlogopite chemical composition can be used as a carbonate-free source of magnesium in alkali activation purposes. However, any commercial application should allow for due consideration of cost.

1. Introduction

Alkali activation is widely used for the synthesis of alkali-activated materials (AAMs), sometimes called geopolymers, from a variety of solid precursors rich in alumina and silica. Such binders are considered greener alternatives to conventional cementitious binders (Gartner, 2004) and their potential applications encompass a wide area, including construction (Duxson et al., 2007b), thermal insulation (Cheng and Chiu, 2003), waste immobilization (Van Jaarsveld et al., 1999) and water purification (Ge et al., 2015).

The structure of aluminosilicate AAMs consists of interconnected silicate and aluminate tetrahedra forming a 3-dimensional negatively charged framework, with pores filled with counter-balancing cations, Group I or Group II, and water molecules (Davidovits, 1991; Duxson et al., 2007a; Komnitsas and Zaharaki, 2007). Compared to Group I cations that usually perform the charge balancing function, Group II cations densify the structure, thereby enhancing their mechanical properties. A number of studies have investigated the incorporation of calcium into the structure of AAMs (Canfield et al., 2014; Chindaprasirt

et al., 2012; Chotetanorm et al., 2012; Li et al., 2013). Another Group II cation with equal potential to perform the structure-forming role in AAMs is magnesium.

Magnesium is an abundant alkali earth metal with considerably higher electronegativity than calcium, and is therefore a widely studied component in durable binders, including alkali-activated materials. Ben Haha et al. (2011) studied the effect of inherent MgO content on hydration and microstructure of alkali activated slag, while others have focused on external MgO addition during alkali activation of slag (Jin et al., 2014; Jin and Al-Tabbaa, 2015; Shen et al., 2011; Vandeperre et al., 2008). The general conclusion from these studies is that increased MgO content leads to improved strength. However, the practice of simply adding MgO lacks environmental credibility due to high CO_2 emissions in the MgO manufacturing process. The majority of MgO production worldwide at present uses $MgCO_3$ as a raw material (Ruan and Unluer, 2016) with inherently high CO_2 emissions ($MgCO_3 \rightarrow MgO + CO_2$). Furthermore, most of the sources of MgO are expensive (Walling and Provis, 2016). There is thus a need to focus on locally abundant and carbonate free sources of MgO.
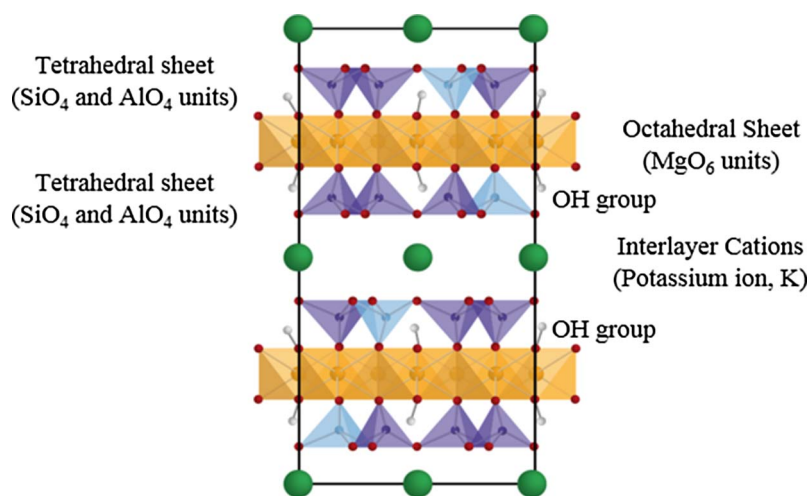
Fig. 1. Crystal structure of idealized phlogopite. The silicon (Si), aluminum (Al), oxygen (O), and hydrogen (H) atoms are shown as dark blue, light blue, red, and white spheres respectively. The potassium (K) atoms are shown as large green spheres.

Phlogopite is one such candidate; it is rich in magnesium and significant amounts can be found in mine tailings around the world, including Finland. The apatite mine in Siilinjärvi (Eastern Finland) has been producing apatite since 1979 (Airi et al., 1997), with a volume 0.85 tpa since 2010, which has resulted in over 220 Mt of phlogopite-rich mine tailings stored. Currently, only a fraction of the percentage of the yearly phlogopite side stream production is sold as a filler material in plastics, with some utilized as a potassium source to organic farming, and the rest stored in a tailings dam (Maier et al., 2015). Phlogopite is a clay mineral that contains large amounts of silica and alumina, making it a viable candidate for alkali activation. Phlogopite belongs to the mica subset of phyllosilicates (sheets silicates) and its unit structure consists of one octahedral sheet sandwiched between two tetrahedral sheets (Fig. 1). These sheets form a layer that is separated from adjacent layers by planes of inter layer cations. The ideal composition of phlogopite can be represented as $KMg_3AlSi_3O_{10}(OH)_2$, but in nature it is observable that the magnesium in phlogopite is usually replaced with ferrous iron, and the hydroxyl group with fluorine (Rayner, 1974).

Untreated phlogopite is known to have high stability (Condamine and Médard, 2014; Tutti et al., 2000) and it cannot be used for alkali activation directly. However, the pozzolanic activity of clays and clay minerals can be increased by thermal treatment. Thermal treatment leads to the removal of the hydroxyl group from the structure and favors the formation of amorphous phases leading to improved activity (Ambroise et al., 1987; Xu and Van Deventer, 2002). Previous studies indicate that there is an optimum activation temperature for each clay mineral to show considerable pozzolanic activity (Habert et al., 2009; He et al., 2000; Mcintosh et al., 2015; Taylor-Lange et al., 2015). However, there are no previous studies on thermal treatment of phlogopite for the purpose of alkali activation.

In this work, phlogopite was calcined to a series of temperatures and melted to produce a glassy material. All the treated materials were characterized by powder X-ray diffraction (XRD) to understand the phase changes during thermal treatment. The alkali activation potential of the treated materials was assessed using a solubility test in 6M NaOH, and the extent of elemental release into the solution was estimated with the help of ICP. The residue remaining after the solubility test was subjected to scanning transmission electron microscopy (STEM), XRD, and an acid solubility test to understand the process of alkaline dissolution.

2. Materials and methods

2.1. Materials

The phlogopite (P) used in the present study was obtained from

LKAB, Siilinjärvi, Finland. It was a by-product from the processing of apatite ore formed during early Proterozoic alkaline intrusion at the mine. Metakaolin (M), branded as Metastar 402 by Imerys Minerals, was used as a standard alkali activation material for activity comparison purposes. Sodium hydroxide with a purity > 99% was obtained from Merck (Germany) and nitric acid (64–66%) from Sigma-Aldrich. Deionized water was used whenever necessary.

2.2. Methods

The milling of the material was done using a vibratory disc mill (Retsch RS 200) for 1–5 min until the desired particle size was obtained. Particle size analysis of the powdered material was performed with a LS 13 320 laser diffraction particle size analyzer from Beckman Coulter, using air as a dispersion medium. The chemical composition of the material was determined with the help of a PANalytical AXios^{mAX} XRF spectrometer, equipped with a rhodium tube with a maximum power rating of 4 kW. Diffraction patterns were recorded using a Rigaku SmartLab 9 kW XRD machine. The analysis employed Co Kα radiation (Kα$_1$ = 1.78892 Å; Kα$_2$ = 1.79278 Å; Kα$_1$/Kα$_2$ = 0.5), a scan rate of 3°/min between 5° and 85° (2θ), and 0.02°/step. Phase identification was done using "X'pert HighScore Plus" (PANalytical software). Elemental concentration of the liquid sample was analyzed with a Thermo Fisher Scientific iCAP6500 Duo inductively coupled plasma optical emission spectrometer (ICP-OES), equipped with a Cetac ASX-520 auto sampler. Scanning transmission electron microscope (STEM) imaging was performed with a LEO 912 OMEGA EFTEM, with an energy-dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments, X-Max 80).

Phlogopite was milled to have an average particle size of between 1 μm and 10 μm. The milled phlogopite was then subjected to thermal treatment. This involved the calcination of the sample to a series of temperatures from 100 °C to 1300 °C in a Nabertherm high temperature furnace (HT 08/18), using a corundum crucible and 40 g batch size. A heating rate of 20°C/min was utilized and the sample was held at the maximum temperature for 30 min and then rapidly cooled to room temperature. The treated sample was labelled as Px, where x is the temperature of treatment. Heating to 1400°C and 1500°C produced partially melted samples with poor flow properties. These samples were discarded. In order to estimate the melting behavior of studied material, a thermodynamic simulation was performed using the chemical composition corresponding to phlogopite. Thermodynamic simulation was executed using commercial FactSage software version 7.0 and its FactPS and FToxid databases. The results of the calculations, i.e. the stability regions of different phases as a function of temperature and logarithmic partial pressure of oxygen, are shown in Fig. 2, in which the thick line