



## Research paper

# Effects of processing on the mineralogy and solubility of carbonate-rich clays for alkaline activation purpose: mechanical, thermal activation in red/ox atmosphere and their combination



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## ABSTRACT

The present study focuses on the assessment of the effects of different activation methods on carbonate-rich clays, to understand the mineralogical differences originated and to exploit such information to industry for traditional and innovative applications, especially as a precursor for alkali activated binders.

Illite carbonate-rich clay samples were subjected to thermal activation in ox/red atmosphere between 400 and 900 °C, mechanical activation (grinding for 5, 10 and 15 min) and to a combination of such treatments. Mineralogical and textural changes in the activated samples were evaluated through X-ray powder diffraction, Fourier transform infrared spectroscopy and thermal techniques.

The activated samples with the highest content of amorphous phase underwent leaching tests in a 3 M NaOH solution by means of inductively coupled plasma-mass spectrometry. The application of the three processing routines, yielded three types of activated clays with different leaching modes of Si, Al, K and Ca: (1) high energy grinding preferentially delaminates clay minerals and reduces the grain size of calcite. K leaching reaches the highest values; (2) thermal heating at 800 °C increases relatively the Si/Al solubility ratio, but the absolute concentrations of these elements are equal or lower than those obtained from ground clays. The relatively higher leaching of Ca is influenced by the formation of non-stoichiometric and poorly crystalline Ca-silicates and -aluminosilicates; (3) high energy grinding combined with heating treatment yields an extended amorphisation, mainly at the expense of clay minerals, with the highest leaching of Si and Al, and the lowest of Ca. New formed K-feldspars inhibit the concentration of K in alkaline solution.

## 1. Introduction

Natural clays are important industrial raw materials used directly or in combination with other materials for the production of structural ceramics and building materials. In the recent years, there has been increasing interest in studying the use of such natural feedstocks for the synthesis of alkali-activated binders, because of their low cost and abundance in most countries. The literature on the subject remains scarce and further efforts could be made to better understand the potential of such complex systems.

Alkali-activated materials are inorganic binders obtained by alkaline or alkaline-earth activation of aluminosilicates and represent nowadays a greener alternative to ordinary Portland cement, owing to their low-CO<sub>2</sub> emission for their production at relatively mild temperature (below 100 °C) and their good thermal (Cheng and Chiu 2003; Kamseu et al. 2010), chemical (Bakharev 2005; Palomo et al. 1999a)

and mechanical (Lee and van Deventer 2002) properties.

A large number of studies have focused on the synthesis of these novel engineering materials from calcined kaolinitic clays (metakaolinite) (e.g. Barbosa et al. 2000; Davidovits, 1991; De Silva et al. 2007; Duxson et al., 2007a, b; Granizo et al. 2000; Palomo et al. 1999a), or from fly ash, blast furnace slag and other industrial by-products too (Buchwald 2006; Duxson et al. 2007a; Palomo et al. 1999b; van Jaarsveld et al. 2002). Recently, the suitability of common clays other than kaolinite for geopolymeric purpose have been also investigated as they represent widely available and relatively cheap raw materials and may show a certain reactivity after the activation processing (Buchwald et al. 2009; Ferone et al. 2013, 2015; Ruiz-Santaquiteria et al. 2013; Seiffarth et al., 2013). The reactivity of clays can be in fact increased by using an appropriate activation treatment, i.e. thermal (He et al. 1995a) or mechanical (MacKenzie et al. 2007a). The thermal treatment, which is the most used activation strategy, transforms clays in a disordered

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metastable state (Fernandez et al. 2011; He et al. 1994, 1995a, b; Tironi et al. 2013) by effect of the dehydroxylation of clay minerals occurring in the temperature range between 500 and 800 °C, which enhances the solubility in alkaline solution of the derived amorphous to low crystalline phases (Buchwald et al. 2009; Essaidi et al. 2013, 2014, Ferone et al. 2013, 2015; Kaps and Hohmann 2010; Ruiz-Santaquiteria et al. 2013; Seiffarth et al., 2013). The reaction mechanisms concerning the thermal activation of natural clay resources are affected by the complex nature of these materials, as well as by the specific operating conditions of the heating treatment (Habert et al. 2009; Snellings et al. 2012). In particular, the presence of secondary minerals and contaminants other than silicoaluminates in the raw materials can affect the properties of the final products and add reaction pathways during alkali activation (Mackenzie and Welter 2014).

The adoption of a mild reducing atmosphere during thermal treatments can represent a more ecological method, although poorly studied, to enhance the clay reactivity at lower temperatures compared to the commonly adopted oxidising regime (Seiffarth et al., 2013). In the case of carbonate-rich clays the reducing regime can also increase the temperature range which separates the achievement of the maximum clay reactivity and the occurrence of crystalline high-temperature phases (Bauluz et al. 2003; Carretero et al. 2002; Cultrone et al. 2001; Duminuco et al. 1998; Gonzalez Garcia et al. 1991; Letsch and Noll 1983; Maggetti et al. 2011; Maritan et al. 2006; Rathossi and Pontikes 2010; Riccardi et al. 1999; Tschegg et al., 2009), less reactive with respect to the alkali activation.

The mechanochemical activation, performed through high energy grinding, can represent another sustainable and time saving alternative to amorphise clays compared to the calcination process, but currently is scarcely considered as activation procedure of clays for the production of alkaline binders (Mackenzie et al., 2007). Several studies demonstrated that the mechanochemical activation can be used to obtain an amorphous material by breaking the clay bonds and the original OH groups to form new particles aggregates of increased porosity, specific surface area, altered cation-exchange capacity and solubility (Baláz 2003; Balek et al. 2007; Gonzalez Garcia et al. 1991; Hamzaoui et al. 2015; MacKenzie et al. 2007; Suraj et al. 1997; Sánchez-Soto and Pérez-Rodríguez, 1989; Sánchez-Soto et al., 1994, 2000).

Grinding also influences the thermal behaviour of clay minerals, enhancing phase transformations during heating (Balek et al. 2007; Sánchez-Soto and Pérez-Rodríguez, 1989; Sánchez-Soto et al., 1994) and can represent a valid method to enhance the reactivity at lower temperatures of heated clays, interested by previous changes in their physico-chemical properties. However, there is a lack of literature dealing with the mechanical activation of three-layer clay minerals as geopolymeric raw materials and in particular, the application of both mechanical and thermal treatments promoting clay activation for the geopolymer production represents a never investigated field.

Despite the literature on inexpensive clays to synthesize novel activated materials is rapidly growing, the use of illite carbonate-rich clays has been scarcely explored (Ferone et al. 2013, 2015) although it may have some advantages (Ferone et al. 2015; Yip et al. 2005, 2008). In particular, it has been proven that the Ca addition, as lime and calcium hydroxide, contributes positively to improve the compressive strength of the resulting geopolymeric products, owing to the formation of a C-S-H/C-A-S-H gel (Temuujin et al. 2009; Khater 2012) which may enhance the precipitation of dissolved monomers acting as nucleation centers (Khater 2012; Temuujin et al. 2009) and may increase the alkalinity of the system, favouring the co-precipitation of the geopolymeric N-A-S-H gel and giving place to an homogeneous and strong structure (Khater 2012). Geopolymerisation is favoured by the formation of the C-S-H gel whose growth is controlled not only by activation parameters (alkalinity of the activator, curing temperature, etc.) (Khater 2012) but also by the nature, crystallinity and particle size of the added Ca-bearing sources (Yip et al. 2008).

Owing to the chemical and mineralogical complexity of such a clay

mixture, several factors are expected to concur and enhance their reactivity for the geopolymeric purpose and, in this connection, the choice of the activation strategy may represent a key point. Different activation methods are expected to exert different effects both on the degree of clay mineral decomposition and on the crystallinity of carbonates, influencing their solubility in the alkaline medium as well as the possibility for calcium compounds to participate to the geopolymerisation as charge balancing cations or to act as fillers (García-Lodeiro et al. 2010, 2011, 2012, 2013; Khater 2012; Yip et al. 2005, 2008).

In this perspective, the present study is focused on the assessment of the effects of different activation strategies on the reactivity of carbonate-rich clays, to gain a deeper insight in the phase transformations occurring in the samples after each treatment and to exploit such information for technological transferability to industry. With this aim, illite carbonate-rich clays from the Apulian region (southern Italy) were subjected to different activation treatments in order to explore their effectiveness in promoting the loss of crystallinity (and thus reactivity) of the clay minerals and at the same time to produce the highest availability of calcium from calcium-bearing minerals. Besides the more explored thermal activation processing, a mechanical activation by vibratory milling, which represents a more ecological pre-treatment methodology, has been used for the first time in this study for the activation of illite carbonate-rich clays, in addition to the combination of both mechanical and thermal treatments, which represents an energy-saving processing favouring clay mineral dehydroxylation reactions. The use of both oxidising and mild reducing conditions during thermal treatments was also tested, in order to evaluate potentially positive effects of the adoption of different burning regimes on clay mineral decomposition reactions. Results of different activation strategies were carefully investigated by using a multianalytical approach and the potential suitability of the resulting treated clays as raw materials for the production of alkali-activated binders was evaluated and discussed on the basis of results of solubility test in a NaOH solution.

## 2. Experimental

The raw materials involved in the present study are Apulian calcareous-rich clay sediments belonging to “Argille subappennine” formation. The sample, labelled as “LCR”, was collected from a clay deposit (Lucera, FG) exploited for structural ceramics.

To increase its reactivity, the investigated clay was subjected to different treatments: mechanical, thermal, combination of mechanical and thermal treatments (Fig. 1). For the mechanical treatment, clay portions of 4 g each were prepared after quartering the whole sample and oven drying at temperature of  $50 \pm 5$  °C. Selected samples were dry ground in a vibratory ball mill for 5, 10, and 15 min at a frequency of 30 Hz ( $1800 \text{ min}^{-1}$ ) using a Retsch MM 400 instrument equipped with two 25 ml tungsten carbide grinding jars with screwable cover and each fitted with 2 tungsten carbide balls of 1.5 mm in diameter. Grinding conditions were evaluated taking into account information from literature (MacKenzie et al., 2007) and on the basis of several preliminary tests. Accordingly, a 5 min milling time (at 30 Hz) resulted to be the minimum time interval for the achievement of an extensive crystallinity loss of clay minerals (detectable by X-ray diffraction); doubling and tripling this time has been chosen in order to verify the effects of the prolongation of grinding on the amorphisation process. Larger times were not considered because they showed significant particle aggregation effects. The thermal treatment was carried out by heating clay samples in a laboratory muffle furnace after placing them in crucibles. A gentle milling in vibratory mill at a frequency of 10 Hz for 120 s was performed to ensure sample homogenisation before heating. Samples were then thermally treated for 1 h at the temperatures of 400, 500, 600, 700, 800 and 900 °C under both oxidising and almost reducing burning conditions, with an average heating rate of about 13 °C/min, and cooled in the oven to room temperature. The

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