



Review on the use of volcanic ashes for engineering applications

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ABSTRACT

Volcanic ashes are pyroclastic materials commonly found in many regions of the world. Many deposits of volcanic ashes are unexploited, despite their potential interest for several engineering applications. The mineralogy and chemical composition of volcanic ashes depend on the type of magma from which they originate. The two common pyroclastic materials of interest for engineering applications are scoria and pumice. These pyroclastic materials are rich natural aluminosilicate geo-resources and their valorization can be of environmental and economic benefit. The current review summarizes the main interesting research outcomes on volcanic ashes in the fields of cements and concretes, geopolymers, ceramics, low grade refractory materials, lunar soil simulants and adsorbents. Factors affecting their suitability for specific applications are screened and possible areas of interest for future research suggested.

1. Introduction

Pyroclastic materials, also called tephra, are formed from cooling magma during explosive volcanic eruptions. They present widely varying physical properties and can range in size from sub-millimetric ash up to boulder size (Brown and Calder, 2005). Pyroclastic materials can have a dense (volcanic tuffs) or a vesicular structure (volcanic scoria and pumice). Scoria and pumice are among the most abundant pyroclastic materials (Alemayehu and Lennartz, 2009; Best, 2002). Creation of a high density of bubbles in a melt produces after solidification, a glassy silicic pumice or mafic scoria in which the proportion of vesicle volume to whole rock is quite high. Corresponding bulk rock densities are low enough (several tenths of grams per cubic centimeter) such that scoria and mainly pumice can float on water (density 1 g/cm³) (Best, 2002; Rocher, 1992). Scoria can contain such a high concentration of minute hematite grains in red-brown scoria that it does not appear glassy in hand sample (Best, 2002). Volcanic ash is a non-generic term which refers to fine fragments of pyroclastic materials. Typical volcanic ashes are pyroclastic debris with size below 2 mm (Dingwell et al., 2012). However, crushed (powdered) volcanic scoria/slags are often referenced as volcanic ashes (Kamseu et al., 2009; Lemougna et al., 2011; Leonelli et al., 2007; Melo and Ndigu, 2004; Tchakouté et al., 2013). Hence, the term volcanic ash will be used in this paper to describe typical volcanic ashes or powdered pyroclastic

debris. Due to common volcanic activities in the world, pyroclastic materials such as volcanic ash, volcanic scoria and pumice are found abundantly in many regions including Europe (Italy, Turkey, Greece and Spain), Central America, China, Southeast Asia, East and Central Africa (Eritrea, Djibouti, Kenya, Ethiopia and Cameroon), Iran and Saudi Arabia (Alemayehu and Lennartz, 2009; Hossain, 2005; Kamseu et al., 2009; Leonelli et al., 2007; Liao et al., 2016; Sabtan and Shehata, 2000; Seyfi et al., 2015; Takeda et al., 2014; Zheng et al., 2009).

The deposits of pyroclastic materials are generally readily accessible and have the advantage that they can be naturally mined with enormous benefits from low cost mining. Such mines have limited negative environmental impact in comparison to traditional open pit (quarrying method) commonly used for clay mining (Demirdag et al., 2008; Lemougna et al., 2011; Leonelli et al., 2007).

Most pyroclastic materials present pozzolanic activity (Rocher, 1992; Siddique, 2011). This refers to materials, which, while not cementitious per se, have constituents that at ambient temperature, can combine with lime in the presence of water to form compounds that behave like hydraulic binders (al-Swaidani et al., 2016).

Pyroclastic materials including pumice, scoria, and ashes, were extensively used in the past (Belfiore et al., 2015; Cabadas-Báez et al., 2017; De Bonis et al., 2016; Jackson et al., 2009). The Romans were the first to use natural aluminosilicate materials to prepare highly durable cements. The ancient Roman builders started to use volcanic aggregate

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to formulate mortars with specific properties from the first century Before Christ (BC). With this knowledge, the Romans, during the imperial age (27 BC–AD 476), created grandiose monuments that still exist today, thus demonstrating the durability of the Roman mortars (Belfiore et al., 2015; Jackson et al., 2009, 2010; Stanislao et al., 2011). Several reports also indicate the use of volcanic ash in the production of ceramic materials since the ancient times (Cabadas-Báez et al., 2017; Morra et al., 2013). For instance, in the Maya area, a volcanic stratigraphic record was associated with a continuous settlement history and ceramic tradition, some of the ceramics lasting from 800–300 B.C (Cabadas-Báez et al., 2017). Nowadays, reported engineering applications of volcanic ashes include cement and concretes, geopolymer materials, ceramic materials, lunar soil stimulants and adsorbents. However, in comparison to their industrial homologues (fly ashes) which have been subjected to extensive researches (Ahmaruzzaman, 2010; Cultrone and Sebastián, 2009; Kumar et al., 2007; Toniolo and Boccaccini, 2017; Xu and Shi, 2018; Zhuang et al., 2016), little is reported on volcanic ashes, despite their potential applications and the presence of many unexploited deposits around the world (Alemayehu and Lennartz, 2009; Al-Fadala et al., 2017; Lemounga et al., 2011; Zheng et al., 2009). Due to their vesicular structure, volcanic scoria and pumice will be easier to process and will be more attractive for engineering applications (Alemayehu and Lennartz, 2009).

The current review summarizes important research outcomes on volcanic ashes for engineering applications, mainly in the last decade, in order to contribute in the valorization of this abundant natural resource. Basic information on their chemistry and mineralogy are provided alongside their potential engineering applications. Factors affecting their suitability for specific applications are screened and discussed and possible areas of future research are suggested, on the basis of their properties and previously reported studies.

2. Properties of volcanic ashes

The chemical and mineralogical composition of volcanic debris deposit depends on the chemistry of the magma from which it originates (Siddique, 2011). Many deposits contain SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , MgO , K_2O and Na_2O as major components (Table 1). Other oxides may also be found in minor percentages. In most cases, SiO_2 is the preponderant oxide, generally between 40 and 52 wt% for basic lava such as scoria and 63–75% for acid lava such as pumice (Demirdag and Gunduz, 2008; Hossain, 2005; Lemounga et al., 2011; Leonelli et al., 2007; Najafi Kani et al., 2012; Ohba and Nakagawa, 2002; Rocher, 1992; Seyfi et al., 2015; Siddique, 2011; Takeda et al., 2014; Tchakouté et al., 2013). The minerals found in these volcanic ashes originate primarily from magma. These minerals crystallize and grow within the magma while below the earth's surface. Hence, the mineralogical composition depends on both the chemistry of the magma and eruption conditions, and can vary from an almost amorphous to a completely crystalline material (Lemounga et al., 2014; Nakagawa and Ohba, 2002; Serra et al., 2015; Siddique, 2011; Zhang et al., 2017).

Rock-forming minerals crystallizing from magma are mainly silicate minerals. Beside silicates, Fe-Ti oxide minerals are also found in most magmas, with Ti-magnetite and ilmenite as the major minerals. Major colored minerals are pyroxenes, amphiboles micas and olivine while major colorless ones are of the quartz and feldspars group (Nakagawa and Ohba, 2002). Pumice and scoria are amongst the most common pyroclastic deposits. Pumice is derived from an acid magma during explosive eruptions. It is a highly micro vesicular pyroclastic with very thin bubble walls. It varies in density according to the thickness of the solid material between the bubbles and many samples can float on water. It is amorphous with mainly quartz, biotite and feldspars as crystalline phases; pumices generally have an acidic (silicic) composition (Alemayehu et al., 2011; Best, 2002; Bryan et al., 2004; Ismail et al., 2013; Nakagawa and Ohba, 2002). Scoria is commonly, but not exclusively basaltic in composition. It differs from pumice in that it is

denser, with larger vesicles and thicker vesicle walls, resulting from the lower viscosity and explosiveness of the magma associated with its formation. With regard to its mineral composition, scoria consists mostly of mafic minerals (pyroxene, olivine and plagioclases). Such mineral composition is typical of basaltic rocks (Alemayehu et al., 2011; Leonelli et al., 2007, 2009; Nakagawa and Ohba, 2002; Sabtan and Shehata, 2000; Zheng et al., 2009). It is noteworthy that rock-forming minerals in the crust and mantle may also be incorporated into volcanic ash by mechanical stripping from conduits or magma chambers (Ohba and Nakagawa, 2002).

Volcanic ashes commonly present pozzolanic activity and their chemical and physical properties can be referenced with ASTM C618, a Standard Specification for 'Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete' (Siddique, 2011). Their bulk density varies with the type of pyroclastic ejection and particle size of the material. For a fraction of crushed particles below 0.075 mm size, Alemayehu and Lennartz, (2009) observed a bulk density of 2.46 g cm^{-3} for volcanic pumice and 2.98 g cm^{-3} for volcanic scoria, both from the Main Rift Valley in Ethiopia. In the same study, they noticed that both volcanic pumice and volcanic scoria possessed almost similar pH, of 7.5 and 7.6 respectively. For individual particles, some authors have found that the density can vary between 700 and 1200 kg/m^3 for pumice, 500 – 1300 kg/m^3 for scoria, 2350 – 2450 kg/m^3 for glass shards and 2700 – 3300 kg/m^3 for crystals (Demirdag and Gunduz, 2008; Siddique, 2011). The typical size of scoria and their compact homologue (volcanic tuff) is 2–64 mm (Schmid, 1981). Fig. 1 shows a sample of volcanic scoria and SEM image of fragmented scoria. The color of scoria debris can vary from black to poorly red while that of pumice can vary from black to white, based on their mineral and chemical composition. Their porous or vesicular structure arises from the release of gases during the cooling of lava (Alemayehu and Lennartz, 2009; Paulick and Franz, 1997).

Due to these vesicles, pumices will have porosity generally in the order of 60 to 70%, as against 30 to 60% for scoria. However, their permeability is very low because of the presence of thin intervesicular vitreous membranes. Pumices can absorb up to 100 – 110% of their weight in water, compared to 10 – 40% for scoria. Given their high silica content, pumice will have a good chemical inertia which makes them inert in most acids (Rocher, 1992). The physico-chemical properties of some commercial pumice are reported in Table 2.

3. Potential engineering applications of volcanic ashes

3.1. Cements and concretes

3.1.1. Some uses of pyroclastic materials

Due to the high energy and CO_2 footprint associated to ordinary Portland cement (OPC) production, there is increasing pressure for the use of supplementary cementitious materials such as fly ash, slag and volcanic ash, to produce more environmentally-sustainable concretes with good structural properties (Al-Fadala et al., 2017; Celik et al., 2014a,b; Jiang et al., 2018; Kaid et al., 2009; Xu and Shi, 2018; Wilson et al., 2017). This section presents the use of pyroclastic materials as Supplementary Cementitious Materials (SCM) or as aggregates for cements and concretes. Actually, due to their pozzolanic properties, volcanic ashes can be used to produce rock masonry elements (ACI committee 232, 2001; al-Swaidani et al., 2016). As stated in the introduction, pyroclastic materials have been extensively used in ancient times to produce materials for building applications and some of these buildings are still operational (Belfiore et al., 2015; Izzo et al., 2016; Jackson et al., 2009). For instance, pumice and other volcanic glasses were added as a natural pozzolanic material for mortars and plasters during the construction of the Villa San Marco in the Roman period (89 B.C. – 79 A.D.), which remain one of the best-preserved *otium villae* of the Bay of Naples in Italy (Izzo et al., 2016). Due to the great interest in the use of volcanic ash in cement as supplementary

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