



Influence of the type of pre-calcined asbestos containing wastes on the properties of sintered ceramics



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HIGHLIGHTS

- New interesting possibility for cement-asbestos wastes utilisation.
- Asbestos containing wastes thermally pre-treatment as an useful secondary raw material for production of sintered ceramics.
- The preparation of dry ceramic masses eliminates the efflorescence formation on the surface of the ceramics.
- Asbestos-cement wastes heat pre-treated at different temperature influence on the ceramic properties.

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ABSTRACT

The paper presents the issue of using asbestos-containing materials as well as one of the possible methods that allows to change the dangerous properties of asbestos in cement-asbestos (“eternit”) to a harmless material that can be used in further applications. The article presents the experimental results in which the possibility of cement-asbestos use as a secondary raw material for the manufacture of sintered ceramics (clinker ceramics) as well as the influence of the pre-calcined cement-asbestos type were studied. Three variants of cement-asbestos waste were used: raw, without any thermal treatment or after previous calcination at selected temperatures (700 and 1200 °C). These materials were added (0–10 wt %) to commercial mixtures (ceramic mass) to produce sintered ceramics. Green compacts were formed from dry ceramic masses (with a limited amount of mixing water) and were then sintered. After the firing cycle, ceramic properties such as linear shrinkage, water absorption, open porosity, apparent density, compressive strength and freeze resistance were determined.

The results of the study show that cement-asbestos material can be used as an interesting secondary raw material to produce sintered ceramics. The obtained ceramics samples were characterised by low water absorption, high compressive strength and full frost resistance. The type of introduced cement-asbestos material had an influence on the ceramic properties.

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1. Introduction

Commonly known ‘asbestos’ includes natural fibrous silicate minerals of the serpentinite and amphibole groups. The six types of asbestos that have been used commercially are actinolite asbestos, amosite (cummingtonite–grunerite asbestos), anthophyllite asbestos, chrysotile, crocidolite (riebeckite asbestos), and tremolite asbestos. Generally, these are hydrated magnesium, calcium, iron and sodium silicates. Asbestos minerals possess unique and useful properties, so they were widely used in the past especially for the

manufacture of building materials. The most popular form of asbestos to be used was in cement-asbestos roofing (the so-called “eternit”), boards and pipes. Approximately 85% of imported asbestos (commercial deposits of asbestos do not exist in Poland) was used to produce this popular and inexpensive material. During a period of several years of application of the product in Poland, ca. 15.5 million ton of asbestos and asbestos-containing materials were accumulated [1].

Nowadays, asbestos belongs to a group of dangerous materials [2]. It is generally known that asbestos possesses carcinogenic properties. The absorption of asbestos fibres takes place through inhalation and may cause various diseases of the human respiratory system.

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Due to these confirmed health hazards, there are limitations and bans on the use of asbestos in several countries, especially in developed countries. In 1991, EU member states were obligated to limit their application of asbestos. The main legal act in Poland that bans asbestos is a bill that was passed on 19 June 1997 [3].

The production and consumption of asbestos has decreased over the years, but there are still places where it is mined and used. According to the US Geological Survey [4], world production of asbestos was about 2 Mt in 2014 and it was delivered by Russia, China, Brazil and Kazakhstan.

According to the Polish national programme [1], the main form of disposal of asbestos-containing materials and wastes is storage in special landfills designated for dangerous wastes. However, such a procedure does not represent the final solution because the hazardous fibrous structure of asbestos is still maintained. Moreover, storage of hazardous wastes causes strong opposition among local communities – in Poland there is still an insufficient number of landfills for these wastes. The problem of utilising and recycling asbestos waste has not been fully solved and thus remains controversial. Due to significant amounts of asbestos wastes (especially cement-asbestos) accumulated in Poland alone, it could be a potentially serious secondary raw material.

Fibrous-structure destruction of asbestos and transforming it into an inert substance can be achieved in several ways. Some literature reports have dealt with the chemical treatment of wastes [5–7], in which asbestos is decomposed in an acidic medium. These methods are available especially for chrysotile treatment due to this asbestos variety's poor resistance to acids; for which strong inorganic or organic acids should be used. Another possibility of asbestos destruction may be mechanochemical treatment, in which a high energy milling process is applied [8–10]. Amorphisation of asbestos wastes is obtained in this method. The widely reported in the literature methods of asbestos disposal and recycling are based on thermal treatment [11–21], where a sufficiently high temperature is used. Such a high temperature ensures the thermal decomposition process of asbestos mineral. Consequently, destruction of the dangerous fibrous structure can be achieved. In turn, the material obtained after thermal treatment may be used as an interesting secondary raw material for many attractive products in the broadly understood construction industry.

We continued studies with regard to our own previously described results of studies in which plastic ceramic masses were used and some minor efflorescence on the obtained clinker ceramics was formed [22]. The assumption of this work was to prepare ceramic masses with a clearly limited quantity of mixing water to be used.

The aim of this study was: (i) to investigate the possibility of using asbestos-cement waste in dry ceramic masses designated for the manufacture of clinker bricks and (ii) to determine and compare the influence of the cement-asbestos waste form on the ceramic properties of the obtained ceramics.

2. Experimental

2.1. Raw materials

A commercial raw mix of ceramic clinker was used for the asbestos wastes recycling studies (CRH Klinkier; Patoka, Poland). This mixture contained 70 wt% of clay minerals and 30 wt% of the non-plastic components which were introduced to reduce shrinkage. The main components of "Patoka" clay are: kaolinite, illite, quartz, hematite and siderite [23,24].

Corrugated asbestos-cement slate that came from Upper Silesia was used for the studies. It was exposed to external weather conditions for about 30–40 years. Because it had been produced a long time ago, no details about the production plant, its age and conditions of conservation were available. A macroscopic examination of this specific asbestos waste showed both yellowish and blue bundles of asbestos fibres and indicated the presence of chrysotile and crocidolite type of asbestos mineral. This asbestos-containing material was used in the study in three

forms: (i) as received, without any thermal treatment; (ii) after initial calcination at 700 °C for 2 h; and (iii) after initial calcination at 1200 °C for 2 h. These temperature values were chosen to thermally deactivate harmful asbestos. They were selected based on the literature and on our own research.

Due to the presence of only chrysotile and crocidolite asbestos in cement-asbestos material, in this case calcination at 700 °C was sufficient for the thermal dehydroxylation process of both asbestos varieties [25,26], and consequently for thermal utilisation of this waste. Moreover, this temperature does not allow for the thermal decomposition of calcite from the cementitious matrix of cement-asbestos material and does not allow to generate a significant amount of reactive calcium oxide. Free CaO is an undesirable component of ceramic masses due to the possibility of its reacting with water to form Ca-hydroxide, after which rheological problems may occur. The second temperature of cement-asbestos thermal pre-treatment was based on data selected from the literature. According to studies in Italy [27–29], calcination at 1200 °C, even for short periods of time, is sufficient for the transformation process of all varieties of asbestos minerals to take place, also including tremolite or amosite asbestos. Moreover, this temperature provides thermal deactivation of free calcium oxide and, consequently, reduces the rheological problem. Shin et al. showed that lime calcined at 1200 °C had a clearly visible lower specific surface area and that reactivity decreased in comparison to lime calcined at lower temperatures [30].

2.2. Ceramic sample preparation

Different amounts of prepared asbestos-cement material (0–10 wt%) were added to the commercial clinker mass used in this study. All raw materials had the same grain size: <0.2 mm, and seven sets of raw materials were prepared (Table 1). All mix components, carefully weighted to the predetermined proportion, were firstly homogenised in a ball mill for 15 min, then a negligible amount of water was added (~6–7 wt%) to obtain dry ceramic masses capable of forming. The dry ceramic masses were then subjected to further homogenisation. They were placed inside closed foil bags to prevent humidity variations and kept in those conditions for 24 h. Before formation the masses were granulated by wiping through a sieve with a mesh aperture of 0.5 mm. Subsequently, the samples were formed as cylinders (30 mm in diameter and about 30 mm in height, uniaxial pressing at 40 MPa with a pressure vent at 20 MPa). Then the green samples were dried in natural conditions at room temperature and in a laboratory dryer at 105 °C. The dried samples were sintered to establish their final properties. This process was conducted in a high-temperature electric furnace at 1100, 1150 and 1200 °C for 1 h upon reaching the maximum temperature by the furnace. Finally, the clinker ceramic samples were naturally cooled until they reached room temperature.

2.3. Methods

The amounts of mixing water and drying shrinkage were determined for the prepared ceramic masses and formed samples. Firing shrinkage as well as total linear shrinkage were measured after thermal treatment. In accordance with standard PN-EN 771 [31] and applicable sections of standard PN-EN 772 [32], water absorption and compressive strength of the obtained ceramics were established. In accordance with the methodology set forth in standard PN-B-12016:1970 [33], resistance was determined of the ceramic samples to low temperatures and to negative impacts of marl grains and soluble salts. Besides the scope of the relevant standards, open porosity and apparent density of the samples were determined by the hydrostatic weighing method. Each parameter was determined at least in three parallel samples.

The qualitative phase composition of raw cement-asbestos material and after calcination at two different temperatures was measured by X-ray diffraction (XRD). The microstructure was observed by scanning electron microscopy (SEM). XRD analysis of the examined asbestos-cement samples was carried out using a

Table 1
Composition of dry ceramic masses used to obtain clinker ceramics.

Sample designation	Content (wt%)				
	Input raw material				
	Plastic		Non-plastic		
"Patoka" clay	Commercial	Asbestos-cement			
			Raw	Calcined at 700 °C	Calcined at 1200 °C
0S	70	30	–	–	–
5BsS	70	25	5	–	–
5Bp7S	70	25	–	5	–
5Bp12S	70	25	–	–	5
10BsS	70	20	10	–	–
10Bp7S	70	20	–	10	–
10Bp12S	70	20	–	–	10

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