Czech Technical University in Prague

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Master’s Thesis

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ZADÁNÍ DIPLOMOVÉ PRÁCE

I. OSOBNÍ A STUDIJNÍ ÚDAJE

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Studijní program: Budovy a prostředí
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II. ÚDAJE K DIPLOMOVÉ PRÁCI

Název diplomové práce: Komplexní charakterizace minerálních příměsí pro přípravu cementových a vápenných kompozitů s vysokými užitnými vlastnostmi

Název diplomové práce anglicky: The complex characterization of mineral admixtures for the preparation of cement and lime composites with high performance properties

Pokyny pro vypracování:
Na vzorcích vybraných minerálních příměsí používaných k přípravě cementových a vápenných kompozitů stanovte základní fyzikální, chemické a strukturní parametry včetně pucolánové aktivity. Výsledné vlastnosti testovaných příměsí zhodnoťte z hlediska jejich použití do kompozitních materiálů a porovnejte dosaženou pucolánovou aktivitu.

Seznam doporučené literatury:
Supplementary Cementitious Materials in Concrete, Editors: A.P. Fantilli, D. Jóźwiak-Niedźwiedzka, MDPI, 2021.
Comparison of test methods to assess pozzolanic activity, S. Donatello, M. Tyrer, C.R. Cheesman, Cement and Concrete Composites 32, 2010, 121-127.
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NF P 18-513, 2009. Pozzolanic addition for concrete – metakaolin. Definitions, specifications and conformity criteria. Annex A. Association Francaise de Normalisation.
ČSN EN 196-5, 2011. Methods of testing cement – part 5: pozzolanicity test for pozzolanic cement. Czech Standardization Institute, Prague.

Jméno vedoucího diplomové práce: prof. Ing. Milena Pavlíková, Ph.D.

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Podpis vedoucího práce Podpis vedoucího katedry

III. PŘEVZETÍ ZADÁNÍ

Beru na vědomí, že jsem povinen vypracovat diplomovou práci samostatně, bez cizí pomoci, s výjimkou poskytnutých konzultací. Seznam použité literatury, jiných pramenů a jmen konzultantů je nutné uvést v diplomové práci a při citování postupovat v souladu s metodickou příručkou ČVUT „Jak psát vysokoškolské závěrečné práce“ a metodickým pokynem ČVUT „O dodržování etických principů při přípravě vysokoškolských závěrečných prací“.

Datum převzetí zadání Podpis studenta(ky)

I declare that I worked on this thesis on my own under the professional supervision of prof. Ing. Milena Pavlíková, Ph.D. and that I used only sources mentioned in the References section.

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signature

I would like to express gratitude to my primary supervisor prof. Ing. Milena Pavlíková, PhD., who guided me throughout this process and provided me with all the necessary facilities for the research. I am also grateful to Ing. Martina Záleská, Ph.D. and Ing. Adam Pivák, for their help and valuable advice, together with colleagues from UCT Prague for the provision of XRD measurements and assistance. Finally, I would like to thank my parents and my boyfriend, who have been great support in my studies for many years.

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The complex characterization of mineral admixtures for the preparation of cement and lime composites with high performance properties

Komplexní charakterizace minerálních příměsí pro přípravu cementových a vápenných kompozitů s vysokými užitnými vlastnostmi

Abstract:

This master's thesis deals with the complex characterization of the properties of mineral admixtures, their chemical and physical features with emphasis on the determination of pozzolanic activity. Several materials belonging to different groups, from natural to artificial, were analyzed. The main objective is to evaluate the ability of the materials in question to be used as admixtures for the preparation of cement and lime composites. The theoretical part focuses on the definition of pozzolanic activity and the introduction of the different groups of materials. An important part is devoted to environmental and related issues. The experimental part includes sample analysis, i.e. basic physical properties, XRF and XRD analysis, measurement of pozzolanic activity, determination of particle distribution and electron microscopy. Results are used to compare material groups and determine their suitability as pozzolana active admixtures.

Keywords: *pozzolanic activity, supplementary cementitious materials, lime composites, cement composites, waste recovery*

Anotace:

Tato magisterská práce se zabývá komplexní charakterizací vlastností minerálních příměsí, jejich chemickými a fyzikálními parametry s důrazem na stanovení pucolánové aktivity. Bylo analyzováno několik materiálů patřících do různých skupin, od přírodních až po umělé. Hlavním cílem je zhodnotit schopnost využití daných materiálů jako příměsí pro přípravu cementových a vápenných kompozitů. Teoretická část je zaměřena na definici pucolánové aktivity a představení jednotlivých skupin materiálů. Důležitá část je věnována problematice životního prostředí a souvisejícím otázkám. Experimentální část zahrnuje analýzu vzorků, tj. určení základních fyzikálních vlastností, XRF a XRD analýzu, měření pucolánové aktivity, stanovení distribuce částic a elektronovou mikroskopii. Výsledky jsou použity k porovnání skupin materiálů a určení jejich vhodnosti jako pucolánově aktivních příměsí.

Klíčová slova: *pucolánová aktivita, přídavné cementové materiály, cementové kompozity, vápenné kompozity, využití odpadu*

Contents

List of abbreviations and symbols

MSWI	municipal solid waste incineration
XRF	x-ray fluorescence
XRD	x-ray diffraction
SEM	scanning electron microscopy
FEG	field emission gun
SCM	supplementary cementitious materials
EDTA	disodium ethylenediaminetetraacetic acid dihydrate
HCl	hydrochloric acid
CO_2	carbon dioxide
$Ca(OH)_2$	calcium hydroxide
CaO	calcium oxide
OH^-	hydroxide
Ca^{2+}	calcium ion
Al_2O_3	aluminium oxide
SiO_2	silicon dioxide (silica)
ρ	density
m	weight
V	volume
nm, µm, mm, m	nanometre, micrometre, millimetre, metre
m^3	cubic metre
kPa, MPa	kilopascal, megapascal
kg, g, mg	kilogram, gram, milligram
°C	degree of Celsius
l, ml	litre, millilitre
kV	kilovolt
Mt, Gt	megatonne, gigatonne

1 Introduction

The building industry is still developing rapidly and has the most negative impact on the environment and humanity in general. The production of building materials is a source of greenhouse gases and other hazardous air pollutants, thus harming the climate, nature and our entire planet. However, the production of the materials themselves is not the only problem; the construction industry is also closely linked to the production of excessive amounts of waste, which is not used, but is dumped in landfills, leaching hazardous substances into the ground, which then enter the water we drink or the food we grow, or the waste is burned, creating an additional burden on the air.

Unfortunately, despite a significant increase in investment and progress at a global level in reducing the energy intensity of buildings, the sector's total energy consumption and CO_2 emissions in 2021 are still above pre-pandemic rates. According to the UNEP-hosted Global Alliance for Buildings and Construction (*GlobalABC*) [1], energy demand even increased by around 4% to 135 EJ and CO_2 emissions reached an all-time high of 10 $GtCO_2$ per year. Nor is the construction industry on track to decarbonise in 2022 and 2023. The possibility of reaching the 2050 collective target is receding by the moment. In addition, the expected population growth will increase the demand for fresh raw materials for concrete production and other resources, such as cement [2]. Specifically, according to [3], cement production for 2022 has climbed to 4.1 billion metric tonnes. China was the largest producer, followed by India, together responsible for 2 billion and 370 million metric tons, more than half. It is important to concentrate on prospective ways to promote the decarbonisation of cement production on a global scale as much as possible in the medium to short term.

The reduction in the use of cement does not seem to be compatible with the growth in concrete production, which is expected to continue in the coming years. Thus, there is a drive to produce concrete in a more environmentally friendly direction, the solution to which is the use of various supplementary cementitious materials (SCMs). SCMs have been tested and some have been standardized as mineral admixtures for cements of various types, among the best known SCMs are silica fume, blast-furnace slag, silica and calcium fly ash from coal combustion or calcinated shale [4]. There are many other potentially viable materials waiting to prove their ability to replace Portland cement.

The history of pozzolanic materials dates back to ancient Greece and Rome. The name Pozzolan is derived from Pozzuoli, a town in the Bay of Naples where a highly prized deposit of weathered ash from Vesuvius was found. Naturally occurring pozzolan was widely used in the United States in the 1930s and 1940s in the construction of mass concrete for hydraulic structures. The earliest use, in fact, dates back to the beginning of the 20th century, specifically in Los Angeles and in the construction of the Golden Gate. Local resources of volcanic origin, including diatomite and opaline materials, were used. Calcined clay, used by the aforementioned Romans in their pottery, is now back in construction in the form of metakaolin. Pozzolans are more widely available as by-products of variety of processes. For a number of reasons, not all waste materials are suitable for use in concrete. For example, when power companies use scrubber products to remove sulphur dioxide from stack gases, many fly ashes are mixed with the scrubber products and contain free lime and calcium sulphates or sulphites. It is therefore advisable to source all materials from proven manufacturers to be able to predict suitability for use and its behaviour in concrete [5].

1.1 Aim of the thesis

In this work, the basic physical and chemical properties of the materials across all categories are studied, with emphasis on their pozzolanic activity. Their potential for use as a replacement for conventional Portland cement leads to the environmental benefits already mentioned, but also to potential economic benefits such as reducing initial costs. The main reason for using natural or waste materials is primarily to reduce CO_2 emissions and avoid landfilling of waste materials, connected with the global cement production and associated problems.

The theoretical part focuses mainly on the pozzolanic activity of materials and their classification. Emphasis is placed on the materials that have been tested and how they relate on a global scale, both in terms of waste management and production.

The experimental part deals with individual materials and their analysis. Measurements of basic physical properties, chemical composition, mineralogical composition, pozzolanic activity and particle size distribution were made, together with microscopic images. The main objective is to compare the properties of individual representatives and groups with each other and to evaluate their suitability for use as supplementary cementitious materials.

2 Theoretical part

2.1 Pozzolanic activity

According to ASTM C125 [6] is *pozzolan* defined as *“a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties”*. The use of materials with pozzolanic properties, as mentioned in the introduction, goes back as far as the ancient times. A mixture of lime and brick dust was used by the Phoenicians in 700 BC. The ancient Greeks used lime mixed with soil from the island of Santorini. The ancient Romans were also familiar with volcanic rock. They used the ash from the village of Puzzuoli, near Naples, and this is how the Pozzolans got their name [7].

The term *pozzolanic activity* covers all the reactions that take place between the active components of the pozzolan, lime or calcium hydroxide, and water, and practically defines the maximum amount of lime that the pozzolan can react with and the rate at which it does so. The activity of pozzolans has many variables, all depending on the nature of the pozzolan used, its quality, the amount of active ingredients contained, the ratio in the mixture, the specific surface, the water content, but also the chemical composition, the grain size and of course the ambient conditions of the reaction, specially temperature, humidity and partial pressure [8].

From a chemical point of view, pozzolans are materials containing silica and reactive silicates, aluminates, and aluminosilicates. Silica should be present in amorphous form, so that it reacts with the calcium oxide to form hydrated lime silicates. The hydration reaction is accompanied by a gradual solidification and hardening of the system to form a new microstructure, which guarantees an increase in the mechanical properties of the system, especially strength [9; 10]. The pozzolanic reaction therefore takes place in a water-pozzolan-calcium hydroxide mixture. Calcium hydroxide is strongly alkaline, the pH of the saturated solution at 25 °C is 12.45 and dissociates in water in two phases: dissolution *(1)* and dissociation of the strong base *(2)*.

$$Ca(OH)_2 \rightarrow CaOH^+ + OH^- \text{ (1)}$$

$$Ca(OH)^+ \rightarrow Ca^{2+} + OH^- \text{ (2)}$$

The first step is the attack of the structure of the active components of pozzolans by OH^- ions, resulting in the breaking of the bonds of silicates and aluminosilicates to form simple ions:

$$\equiv Si - O - Si \equiv\ + 8\,OH^- \ \rightarrow 2\,[SiO(OH)_3]^- + \ H_2O \ (3)$$
$$\equiv Si - O - Al \equiv\ + 7\,OH^- \ \rightarrow \ [SiO(OH)_3]^- + \ [Al(OH)_4]^- \ (4)$$

The newly formed silicate and aluminate ions form a series of compounds with Ca^{2+}. Hydrated calcium silicates (C-S-H) in the form of x-ray amorphous phase that coat the surface of pozzolan grains and subsequently formed hexagonal aluminates C_4AH_{13} and other hydration products.

When pozzolan is mixed with Portland cement and water, it reacts with calcium hydroxide $Ca(OH)_2$, which is released by the hydration of calcium silicates, especially alite (C_3S) and belite (β-C_2S). The principle reaction between hydroxide and amorphous silica or reactive alumina is displayed in the following equations:

$$Ca(OH)_2 \ + \ SiO_2 + \ H_2O \ \rightarrow CaO \cdot SiO_2 \cdot H_2O \ (5)$$
$$Ca(OH)_2 \ + Al_2O_3 + \ \ H_2O \ \ \rightarrow CaO \cdot Al_2O_3 \cdot H_2O \ (6)$$

The resulting amount of portlandite is influenced by the consumption of calcium hydroxide in the pozzolanic reaction. The pozzolanic admixture also affects the hydration of some clinker minerals, such as accelerates the hydration of C_3S. It can be simplified to say that the C-S-H phase is preferentially precipitated on the surface of the pozzolan particles, thus reducing the impermeable C-S-H phase on the C_3S grains. The highly siliceous surface of the pozzolanic particles adsorbs Ca^{2+} ions, thereby reducing their concentration in the vicinity of C_3S grains, on which an impermeable highly calcareous surface layer formed during hydration into a more permeable layer. Even more the hydration of C_3S is accelerated by siliceous drift and fumed silica - Aerosil, their large specific surface area and high content of active SiO_2 playing a significant role.

Pozzolans have both significant and negligible effects on the hydration of cement and consequently on the properties of composite materials. The reaction mixture of pozzolan - cement - water is much more complicated than a mixture where lime is used instead of cement, mainly due to the mineralogical and chemical composition of the cement. There may be other sources of OH^- ions that cause the pH to rise above 13. For example, the dissolution of alkali sulphates described by the following equations:

$$K_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2KOH \text{ (7)}$$
$$KOH \rightarrow K^+ + OH^- \text{ (8)}$$

The pozzolanic reaction is favoured by a higher concentration of OH^- ions, but at the same time Ca^{2+} ions, whose concentration is influenced by the "common ion effect", are necessary for the reaction. Under constant conditions, the $Ca(OH)_2$ product ($K_s = [Ca^{2+}] \, . \, [OH^-]_2$) takes on a constant value, so as the concentration of OH^- ions increases, the Ca^{2+} concentration necessarily decreases = the solubility of calcium hydroxide decreases. Pozzolans themselves may be a source of ions affecting the reaction. Due to the variety of materials, it is not possible to summarise the reactions in the pozzolan-cement-water mixture in general terms [8; 11].

2.1.1 Pozzolanic activity determination methods

In recent years, researchers have proposed many methods for evaluation of pozzolan activity. Many countries have also selected different test methods and standardised them to provide the industry with a basis for assessing the activity of pozzolanic materials. The methods used for the determination of pozzolanic activity can be divided into two categories: direct and indirect. Direct methods monitor the presence of calcium hydroxide and its subsequent reduction during the pozzolanic reaction using analytical methods such as X-ray diffraction, thermogravimetric analysis, or classical chemical titration. Indirect methods include the measurement of physical properties such as the determination of the strength characteristics of the test specimens, electrical conductivity, or thermal conduction [12; 13].

2.1.1.1 Physical methods

The physical test methods, including the strength activity index method, electrical conductivity test, isothermal calorimetry test, thermal analysis method and bound water ratio method, indirectly reflect the activity by measuring the conductivity of the solution, the strength of the mortar, heat release or other factors [12]. These methods are defined by standards, specifically ASTM C331 [14], ASTM C1702 [15] and ASTM D8329 [16].

2.1.1.2 Chemical methods

The chemical testing procedure quantitatively identifies the amount of $Ca(OH)_2$ consumed or the content of SiO_2 and Al_2O_3 in the material based on the nature of the pozzolanic reaction to precisely assess the activity, including the Frattini test [17], lime absorption method, Chappell test [18] and acid/alkali dissolution method [12]. The Frattini test and the Chapelle method will be the subject of further discussion in the experimental section.

Other methods include the determination of pozzolanic activity by microstructure analysis (degree of polymerisation) or the kinetic model method [12]. All of these methods have their own advantages and disadvantages and will find their own specific applications. The appropriateness of using methods has been the subject of much research. In summary, chemical methods are more intuitive and precise than physical methods, which are more likely to be interfered with by the external environment.

2.2 Pozzolanic materials

Pozzolanic materials are divided into two main groups: natural and artificial. Natural pozzolans are created either by weathering and sedimentation of soil or by hot magma and rocks from volcanic eruptions. The pozzolans from the eruption can be either volcanic ash or volcanic pumice. Used in their natural form, they usually only need to be milled and sifted. Artificial pozzolans, on the contrary, are industrial by-products that have been processed or heat treated. As a result, their chemical and physical properties are modified [19; 20; 21]. The following chapters deal in detail only with the groups of pozzolans tested in the experimental part.

Fig. 1: Basic classification of pozzolans

2.2.1 Natural pozzolans

2.2.1.1 Diatomaceous earth

With its unique combination of physical and chemical properties, diatomaceous earth (also known as diatomite) is a very important natural material used in industry. It is usually a soft, friable, fine-grained, weakly cemented, porous (up to 80 – 90 % of voids) and lightweight sedimentary siliceous rock. Further properties include low bulk density, low thermal conductivity, inert chemical reactivity with most liquids and gases, and low solubility in water. A wide range of shapes and sizes are available from 0.75 μm to 1500 μm. The structure is amorphous silica with small amounts of alumina and iron oxide, followed by crystalline quartz, muscovite, feldspar, also characterised by a specific surface area of up to 200 m^2 [22].

Diatomaceous earth has a wide range of usage and application such as obtaining moisture control materials, material for filtration, raw material for cement production, production of porous ceramics, etc. Due to its high porosity, dolomite is not only used as a filter material for beverages, but it is also used as a mild abrasive or mechanical pesticide. Typically, diatomaceous earth extracted from geological deposits needs to be purified before use, thermal pre-calcination and HCl washing are commonly used treatments to improve powder quality and to make the biomaterial inactive as a filter support [23; 24]. In order to increase the cementitious material content, to improve the workability of hard cement blends and to achieve high strength without causing high internal temperatures, various types of mineral admixtures are added. When diatomaceous earth is mixed with ordinary Portland cement, it increases the strength or simply acts as a filler while retaining a comparable strength development [25].

The investigation of the addition of diatomaceous earth as a substitute for Portland cement has been the subject of many academic papers. For example, Kastis [26] described the pozzolanic activity of diatomaceous earth, resulting in the formation of higher levels of hydrated products. Also, dos Santos and Cordeiro [27] observed an increase in the pozzolanic activity as a result of grinding. On the contrary, Aydin and Gül [28] showed that the increase in diatomite content in concrete led to a sudden decrease in its compressive strength. Diatomite also requires more water, resulting in inferior concretes. The data that have been reported so far on the use of diatomaceous earth as a pozzolan are often contradictory and point to some negative effects on the performance and properties of diatomite-cement mixtures. Despite all, it is necessary to continue to study this material with a view to its widespread use.

2.2.2 Artificial pozzolans

2.2.2.1 Fired clay – metakaolin

Clay minerals are part of the phyllosilicate family of minerals. Phyllosilicates are characterised by their laminated structures, which consist of polymeric sheets of silica tetrahedra joined by octahedral sheets. Due to their natural abundance, reactivity, low cost, safety in handling, etc., the study of clay minerals has attracted much attention. They are important in various environmental, industrial, and geological areas [29]. There are five main groups of clay minerals - kaolinite, illite, smectite, vermiculite and chlorites [30].

Clay in general is a widely used material around the world. It is cheap and easily accessible, with a wide variety of mineralogical compositions, which is why much of the literature is devoted to analysing the possibility of using clays from specific deposits to produce SCM in the calcination process. Raw clays tend to have a moderate or low level of pozzolanic activity. Clays need to be activated in order to increase it, i.e., the minerals go through a process of dehydroxylation and amorphisation and the associated change in the coordination of the Al ions. Activation can be mechanical or thermal. The temperature needs to be high enough to destroy the structure, but low enough to prevent recrystallisation. The best solution is a combination of both methods. It is also possible to add chemical additives to improve the properties [31].

Metakaolin is a type of calcined clay. It is obtained by calcining kaolin clay at a temperature between 500 °C and 800 °C [32]. The consequence is dehydroxylation, i.e., the release of up to 14 % of hydroxyl water presented in the following equation:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \uparrow \quad (9)$$

The effect of metakaolin on the properties of mortars and concretes has shown a number of benefits, such as an increase in mechanical strength and durability but also a reduction in shrinkage. Its use is therefore relatively wide, e.g., in the production of high performance and lightweight concrete, mortars, stuccos, repair material, precast concrete or glass fiber reinforced concrete [33]. The use of metakaolin is limited by its high price [34].

2.2.2.2 Sewage sludge ash

Throughout the world, large quantities of sewage sludge are produced by municipal wastewater treatment plants. In recent decades, rapid urbanization, and industrialization, especially in developing countries, have led to significant increases in sewage sludge production. In all wastewater treatment processes, sludge is an inevitable byproduct and requires appropriate, efficient, and environmental management [35; 36]. This is due to the presence of pollutants such as heavy metals, persistent organic compounds, bacteria, viruses, pharmaceuticals, hormones, and dioxins. In general, sewage sludge is composed of a suspension of solids and aggregated colloidal substances originally contained in wastewater and produced during its treatment. Aggregated colloidal substances are characterised by a large surface area. This allows them to hold a significant amount of water. The composition is mainly dependent on the quality of the treated wastewater and on the treatment process that is chosen [37].

In recent years, land constraints and stringent regulations have put increasing pressure on traditional disposal methods such as landfill, agricultural application, and incineration. Thermal conversion of sewage sludge appears to be the most promising management alternative in the context of regulatory limits and legislation. Thermal treatments such as combustion, gasification and pyrolysis not only sterilize the sludge, but also result in significant volume reduction and energy recovery from sludge [38].

Combustion produces sewage sludge ash, the main constituents SiO_2, CaO, Al_2O_3, and Fe_2O_3 are also present in ordinary Portland cement [39]. Calcination affects the microstructure of the ash and improves its pozzolanic activity. According to literature, reusing sludge calcined at 700-800°C as a partial cement substitute is technically achievable and contributes to saving natural resources and energy [36]. There is a large amount of published research on the topic of waste sludge utilization, which confirms the great differences between the different ashes studied, according to their characterization and purpose of application [40].

2.2.2.3 Fly ash

Globally, around 600 million tonnes of coal ash are produced annually; of which around 500 million tonnes are fly ash, only 25-30 % is reused. Over the last two decades, many researchers have been working on the effective use of fly ash in different sectors, reducing the environmental impact and increasing the economic benefits [41].

Fly ash is, together with bottom ash (or boiler slag) and flue-gas desulfurization gypsum, coal combustion product [42]. It is obtained by electrostatic or mechanical separation of dust particles from the flue gas when burning black or brown coal and consists of the unburnt mineral portion of the coal, which is formed into a smooth, undefined structure during combustion. It has large volume with extremely wide range of particle sizes. From a morphological point of view, the shape of fly ash particles is mainly spherical, either hollow or solid, and irregularly shaped. The level of iron and unburned carbon affects the visible colour. This can range from white to yellow, orange to deep red, or brown to opaque. Smaller quantities have a greyish colour. Specific surface area and bulk density are the other main physical characteristics of fly ash [41].

The specific characteristics vary according to the type of coal used, the burning conditions and the position of the collectors, to name but a few. The main components are silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) in the form of amorphous alumina-silicate-ferrous spheres. Fly ash also contains many elements that may be harmful to the environment. Heavy metals can also vary depending on the coal used and the burning process used [43].

Over the past few decades, many researchers have been investigating the use of fly ash in a variety of applications, the most common of which is in the construction industry. It has also been used in metal matrix composites, in geopolymer coatings and in the agricultural sector [41]. In addition to the environmental and economic benefits of reusing fly ash, another advantage is that fly ash can contribute to improving the long-term durability properties of mortar or concrete [44]. It acts as a chemically inert filler and pozzolanic binder and thus improves the properties of the structure [45]. The use of fly ash is expected to improve the various industrial requirements due to several processes using recycled fly ash. Unfortunately, most of the published literature on utilisation is still at the laboratory scale, there is a need for more advanced work in the specified fields [41].

2.2.2.4 Biomass ash

Biomass as a renewable energy source has the potential to be a sustainable and reliable source of energy in the long term and could even provide the majority of energy supply by 2050. Interest in using biomass as a fuel source for heating, electricity generation, transport and as an alternative cementitious material in concrete production has grown in recent years [46]. Biomass is derived from organic material such as wood, agricultural and urban waste, plants, and shrubs, etc. Energy from biomass is close to being carbon neutral. It has undeniable environmental advantages including improved combustion efficiency and decreasing emissions, on the other hand disadvantage of generating huge quantities of ash [47]. There are six technologies for the processing of biomass: direct combustion, anaerobic digestion, fermentation, oil exaction, pyrolysis, and gasification. The process may be followed by secondary treatments [48].

Biomass ash is the residue from the combustion of biomass. Most of it is either dumped in landfills or recycled in open agricultural fields with no controls. There is a high risk of groundwater contamination due to leaching of heavy metals from the ash. The properties of ash from biomass can vary and depend mainly on the characteristics of the biomass, the combustion technology, e.g. fixed bed or fluidised bed, and the location where the ash is collected [49]. Biomass ash contains silica, alumina and other minerals that possess pozzolanic properties. This makes it a potential substitute for fly ash in concrete production. The source and combustion process of biomass ash determines its suitability for use in concrete. However, the use of biomass ash as a cementitious component presents a number of challenges. In some cases, ash can cause reduced durability and cracking, while other studies have shown an increase in workability, compressive strength, and durability. It all depends on the quality of the ash, which is related to the processing method already mentioned [46].Therefore, there is a need to further investigate biomass ash, especially its secondary treatment. The recycling of biomass ash, like all other ashes, will have a huge impact on CO_2 emissions and landfill reduction [50].

2.2.2.5 Municipal waste ash

The world generates approximately 2.12 billion tonnes of municipal solid waste each year. This will increase to 3.4 billion as the world's population grows to around 10 billion in 2050. In most countries, solid waste management is typically a local competence, and almost 70 per cent of countries have created institutions responsible for policy development and regulatory oversight in the waste sector. Approximately two-thirds of countries have developed specific laws and regulations for solid waste management. However, enforcement varies widely. It is a common misconception that technology is going to solve unmanaged and growing waste. Technology is no silver bullet and is usually only one factor to be taken into account in managing solid waste [51; 52; 53].

There are several ways to manage waste. Unfortunately, open dumping is the most common, followed by unspecified landfills. Nowadays, there is a great effort to recycle material. Another option is incineration, which undoubtedly has a number of advantages and disadvantages. Incineration produces energy from the heat combustion, which can be further utilised and is considered a better method than conventional landfilling [53; 54]. In general, two main types of ash, bottom ash and fly ash, are produced during the incineration of municipal solid waste. The waste generated by MSWI usually ends up in one of two ways: landfilled or re-used as a secondary raw material. Reuse and application can be limited by high concentrations of heavy metals, salts, chlorides and organic contaminants and the threat of their release causing air pollution. This is one of the reasons why incineration is criticised, along with the fact that it requires high capital costs and trained operators, which leads to moderately high operating costs, and that additional fuels are needed to achieve the high combustion temperatures required. Advantages include a reduction of 85-90 % of the volume of municipal solid waste, also with careful selection of the incinerator location it reduces transport costs and last but not least energy sales can offset operating costs and the heat produced is used [55; 56].

The incineration process has three main components: combustion, energy recovery and air pollution control. Municipal solid waste is continuously fed into the furnace. Burnout is improved by following a few principles. The high temperature should reach at least 850 °C, turbulence should be increased to expose more surface area to the waste, and the holding time for flue gas and MSW should be longer than two seconds. There must be sufficient air supply throughout the process, ensuring complete combustion of the waste and preventing the formation of dioxins and carbon monoxide. For energy recovery, the heat is used to produce steam in the boiler, which drives the turbine to generate electricity. Any excess heat can be used for other purposes as well. Air pollution is one of the major problems associated with incinerating waste. To minimise pollution and ensure compliance with environmental standards, modern incinerators are equipped with an advanced pollution control system. There are a number of technological processes to neutralise acid gases, adsorb heavy metals or organic pollutants or filter and remove fine dust particles [55].

The incineration process produces various residues, including slag, bottom ash and various types of air pollution control residues (e.g. boiler ash and fly ash). Municipal waste ash is a black or grey, amorphous, glasslike material and often contains inorganic and organic hazardous substances such as heavy metals (Hg, Cd, etc.) or dioxins. The ashes are most often landfilled or stored but can be used as a supplementary material in construction work or as neutraliser for acid waste. The nature and quality of the ash is highly dependent on the type of waste, the type of incinerator and the type of air pollution control equipment. Nowadays, research into the use of these ashes as substitute materials is underway in view of advances in the removal of heavy metals from the material [57; 58].

2.2.2.6 Coal mining waste

In many countries, coal is one of the most important sources of energy. World coal production was 8,618 Mt in 2022, an increase of 8.2 % from previous years. China was the largest producer, responsible for 51 % of production. There was also a significant rise in Europe, mainly due to escalating gas prices. Europe was characterised by a decline in coal production in previous years [59]. Approximately 10-15 % of total coal production is coal gangue, a solid waste produced during coal mining and washing. The accumulation of large amounts of coal waste not only takes up a lot of land resources. It also causes serious environmental problems, such as soil and air pollution and geological hazard. Heat accumulates during the coaling process, resulting in spontaneous combustion with oxidation of the coal gangue and release of large amounts of SO_2, NO_x, CO and other harmful gases into the atmosphere. Another risk is leaching into the soil and impacting groundwater, because of heavy metal content such as As, S, Pb, Sn, As, Cr, etc., leading to contamination of ecosystems and bioaccumulation in human systems. Therefore, an important step is to stop these negative environmental impacts, whether by limiting coal mining or properly managing the resulting waste [60].

In view of the many negative environmental impacts caused by coal gangue, various technologies have been developed to investigate its use. The most common uses are power generation, brick production, excavation fill, land levelling, engineering works such as local roads and embankments, and the production of low value-added building materials. In cement production, coal gangue can also be used as an alumina adjuster to replace some or all the clay. However, recycling varies widely from country to country and huge amounts of waste end up in landfills [60; 61].

In recent years, research has been carried out into the use of aluminosilicate minerals as supplementary cementitious materials, as they are the main constituents of coal mining waste. Coal gangue is a residue of abandoned coal. It varies in colour from grey to grey-brown and brown-black. The main mineralogical components are kaolinite, illite and quartz.

Raw coal gangue has low pozzolanic activity and cannot be used directly as a replacement for Portland cement. The most commonly used methods for enhancing pozzolanic activity include thermal, mechanical, microwave and combined activation. The ash residue of coal gangue changes colour to grey-white, yellow-white or red, depending on the iron oxide content, after spontaneous combustion or thermal activation. As the basis of coal gangue activation is primarily the dehydroxylation of clay minerals and particle size reduction, a combination of thermal and mechanical methods is advisable [62; 63].

2.2.2.7 Brick dust

The ceramics industry is well known for generating huge quantities of calcined clay waste per year. Clay brick buildings are widespread throughout the world. Unfortunately, a large proportion of this waste - millions of tonnes every year - is landfilled, which takes up a lot of space and is very expensive. Careful maintenance of building materials is essential to ensure that they are used repeatedly and to their full potential. In order to obtain recyclate, it is necessary to follow the currently known technological procedure, starting with appropriate demolition, followed by sorting the rubble and crushing it, including handling [64; 65].

Ceramics, including brick products, are classified as inorganic, non-metallic, nearly water-insoluble materials containing approximately 30 % by mass of crystalline compounds. It is the partial crystallinity of brick dust that is a disadvantage compared to metakaolin, which is almost amorphous. Brick soil with a predominant clay mineral content is the base raw material, which is shaped and then it is usually fired at a temperature more than 800 °C when the structure of the body is hardened [66].

Nowadays, brick dust is also a by-product of the production of calibrated bricks, which are precisely ground to exact dimensions for bricklaying without the use of mortar. Dust properties vary from plant to plant, but within a plant they are almost constant. It is a very fine dust that can be used in the manufacture of other brick products or become unused waste. Re-use would therefore be an improvement [10].

In the foreseeable future, it will be required to use recycled aggregates in concrete, including brick dust. The use of bricks as a replacement for Portland cement has been investigated for many years. For example, Brito et al. used well-burnt bricks as coarse aggregate in concrete, resulting in high strength between 22 % and 45 %. The improvement in strength was also confirmed by Kae et al. [67] On the other hand, Debieb and Kenai [68], as well as Poon and Chan [69], reported a reduction in strength when crushed bricks were used as fine aggregate. There are other authors who have studied the effects of brick dust as an aggregate and powder in mortar, Mohammed et al. [70] and Neceri and Chikouche [71], and concluded that the strength is improved because of the production of additional x-ray amorphous phase due to the reaction between brick powder and CH, which reduces the pores in the mortar. Turanli et al. [72] found that waste brick powder has pozzolanic activity due to its mineral composition, which helps in its use as a cement substitute.

Most of the studies deal specifically with the use of crushed brick as a substitute for part of the aggregate in concrete; the number has been increasing in recent years, focusing mainly on mechanical properties. Only a few studies deal with moisture properties, salt transport and durability. Thus, the investigation of brick dust is still in process [10].

3 Experimental part

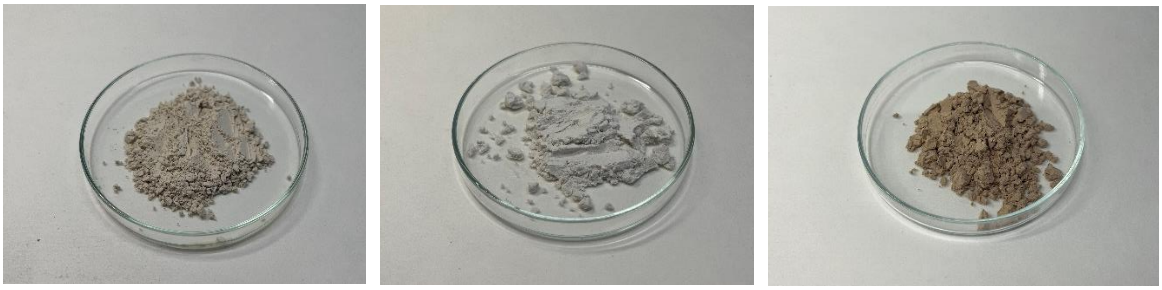
3.1 Characterization of samples

The subject of analysis was twenty-eight samples of natural and technogenic pozzolans originating mainly from Czech Republic, for comparison also from Poland, Greek, Italy or even Argentina. The samples were selected based on their characteristics so that the suitability of each group could be assessed from the analysis.

3.1.1 Natural-based materials

3.1.1.1 Diatomaceous earth

Three types of diatomaceous earth were tested. The first diatomaceous earth **(BOR)** *Fig. 2a* was mined in the Miocene Mydlovary formation in the South Bohemian basins. This is the largest quarry in the Třeboň basin between Ledenice and Borovany. Diatomaceous earth is pale in colour, gray to ochre, earthed or loosely cemented and placed almost horizontally. A spongo-diatomite layer is present in some parts. In the central part, the diatomite layer reaches a thickness of 100 m, while the average thickness is 5.85 m. The Borovany profile was opened in 1909 and in 1961 was discovered new fabric Colofrig there. The other two were from Italy (Dal Cin Gildo S. p. a., Concorezzo, Italy). They were tested for the comparison as a different type of calcinated diatomaceous earth – Enoradall^{TM} 3 *Fig. 2b* **(ENO3)** and Enorandall^{TM} 7 *Fig. 2c* **(ENO7)** [73].



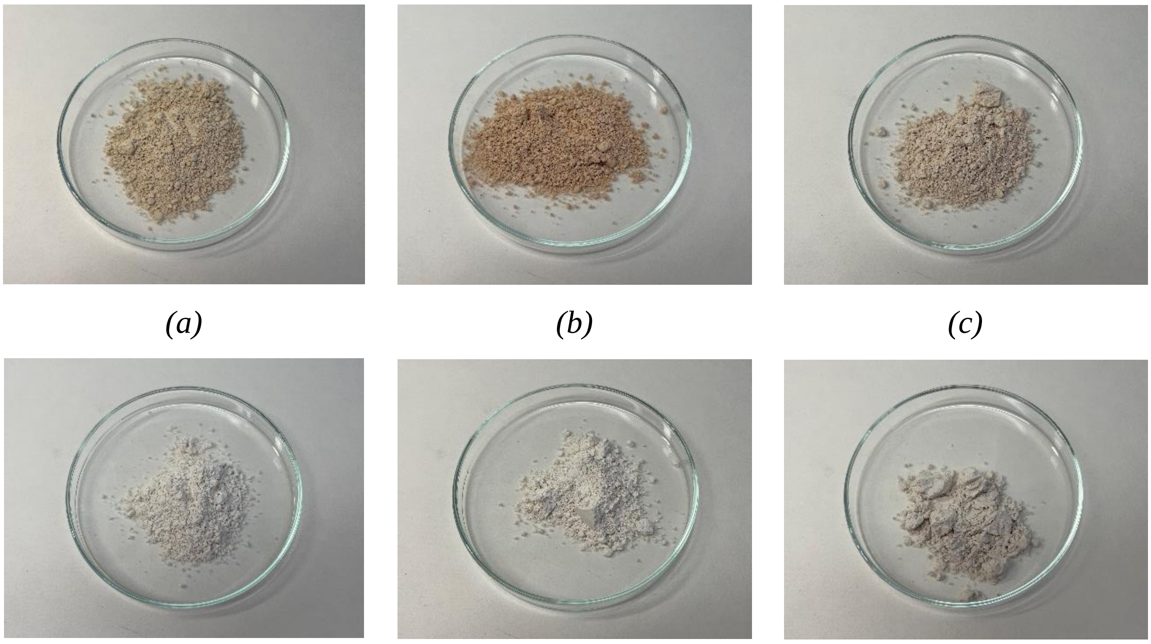
(a) *(b)* *(c)*

Fig. 2: Diatomaceous earth a) BOR; b) ENO3; c) ENO7

3.1.2 Burnt clay rocks

3.1.2.1 Metakaolin

The analysis was performed on six different types of metakaolin: Metaver W *Fig. 3a* – pozzolanic additives, Esolyt, Inc. **(MW)**, Metaver I *Fig. 3b* **(MI)**, Metaver S *Fig. 3c* **(MS)**, Metaver N1 *Fig. 3d* **(MN1)**, Metaver N2 *Fig. 3e* **(MN2)** and Mefisto K_{05} *Fig. 3f* **(MK)**. Metakaolins were obtained by controlled processes of thermal and granulometric treatment of clays and floated kaolins of stable chemical composition. The origin is the Czech Republic, specifically České lupkové závody a.s. founded in 1958 [74].



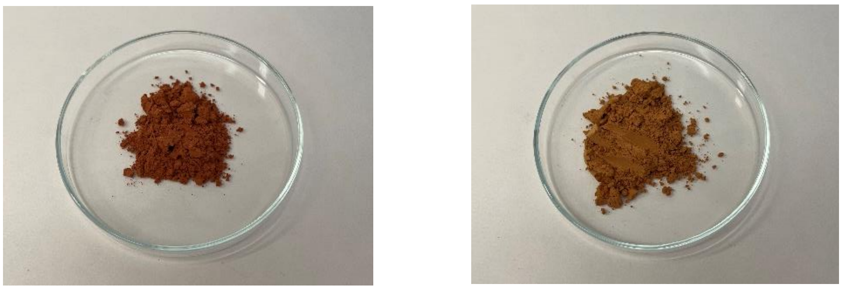
(a) *(b)* *(c)*

(d) *(e)* *(f)*

Fig. 3: Metakaolins a) MW; b) MI; c) MS; d) MN1; e) MN2; f) MK

3.1.2.2 Argentinian clay

Two types of Argentinian illitic clay were analysed: 2886 Illitic *Fig. 4a* **(ACI)** and LUT-HET Illitic *Fig. 4b* **(ACLI)**. The waste ceramics were obtained from the Argentinian city Olvarría. The samples consisted of scrap from the local brick manufacturer at the LOIMAR Tandil plant. In this factory, the bricks are calcined at 950-1050 °C. The waste bricks were crushed and finely ground on a ball mill [75]. Before measurement clays were fired at 700 °C for 2 hours.



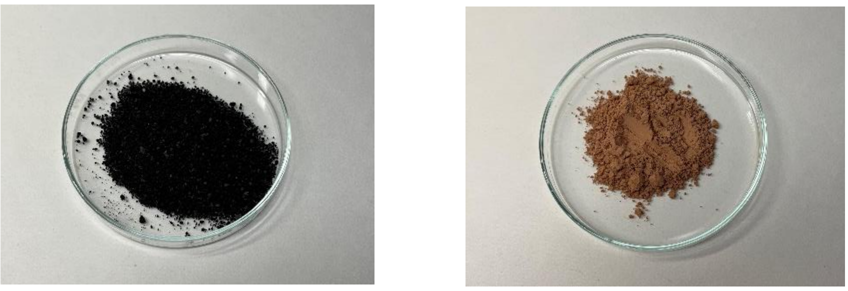
(a) *(b)*

Fig. 4: Argentinian clay a) ACI; b) ACLI

3.1.3 Waste materials

3.1.3.1 Sewage sludge

Two types of sewage sludge were investigated. The first *Fig. 5a* **(GSS)** comes from a wastewater treatment plant in Greece - Patras. It was collected by centrifugation and contained 14 % wt. solids and water. It was dried using sunlight before analysis. After analysis, the dried sludge was fired in a laboratory furnace at 700 °C for 2 hours and additionally ground in a disc mill to achieve cement fineness. The second *Fig. 5b* **(PSS)** was obtained from the Polish Hajdow wastewater treatment plant of the city of Lublin. The sludge was fermented in fermentation chambers and mechanically dewatered. The dewatered sludge was dried. As with Greek sludge, based on measured properties, the sludge was fired at 700 °C for 2 hours and then grind [37].



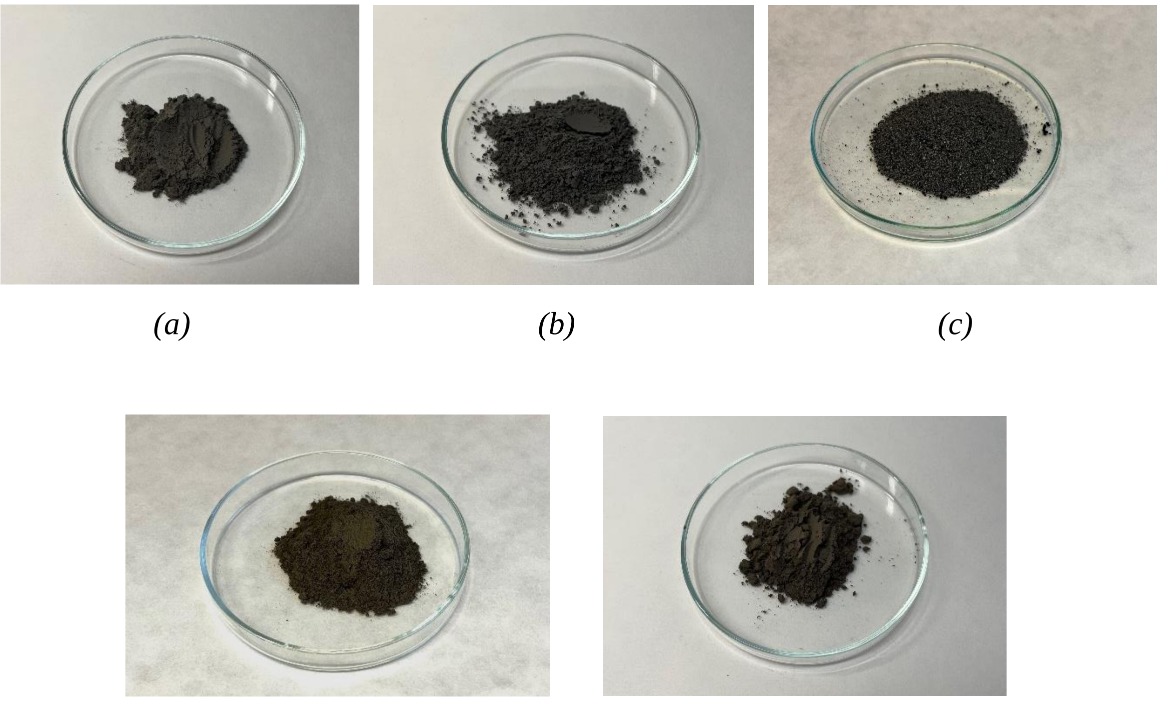
(a) *(b)*

Fig. 5: Sewage sludge ash a) GSS; b) PSS

3.1.3.2 Fly ash

Four types of power plant ashes were analysed. First fly ash was from cogeneration thermal power plant for high-temperature combustion of brown coal in Opatovice. It was a by-product of coal combustion in a pulverized coal boiler. Lignite was coming from the mine

Silesia from Poland Upper Silesian Coal Basin and the mine Profen in Saxony – Anhalt. There was a comparison of the properties of unground fly ash *Fig. 6a* **(FAO)** and fly ash ground for 180 minutes using a ball mill *Fig. 6b* **(FAO180)** [76]. Another two types of ASTM class F brown coal fly ash produced in Czech power plants Počerady *Fig. 6c* **(FAP)** and Chvaletice *Fig. 6d* **(FACH)** using deposits of North Bohemia. The last one brown coal fly ash is from Vřesová power plant *Fig. 6e* **(FAV)**.



(a) *(b)* *(c)*

(d) *(e)*

Fig. 6: Fly ash a) FAO; b) FAO180; c) FAP; d) FACH; e) FAV

3.1.3.3 Biomass ash

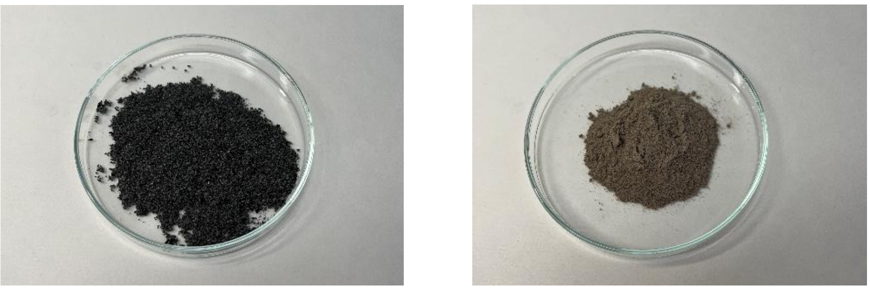
Biomass ashes were obtained from Plzeň and Žlutice heating plants in Czech Republic. Both biomass from wood chip ash *Fig. 7a* **(BAP)** and from wheat straw ash *Fig. 7b* **(BAZ)** were grinded for 15 minutes using a vibratory disc mill and dried in a vacuum oven for 72 hours at 70 °C. The third ash is a sample from the burning of Robinia pseudoacacia also known as black locust *Fig. 7c* **(BAA)**.

(a) *(b)* *(c)*

Fig. 7: Biomass ash a) BAP; b) BAZ; c) BAA

3.1.3.4 Municipal waste ash

Two types of municipal waste ash were analysed. Municipal waste incinerator is located in Malešice, Prague *Fig. 8a* **(MWAM)** in Czech Republic. Fly ash is mixture of ashes collected from boiler and electrostatic precipitator. Second type is collected from incinerator in Białystok, Poland *Fig. 8b* **(MWAP)**.



(a) *(b)*

Fig. 8: Municipal waste ash a) MWAM; b) MWAP

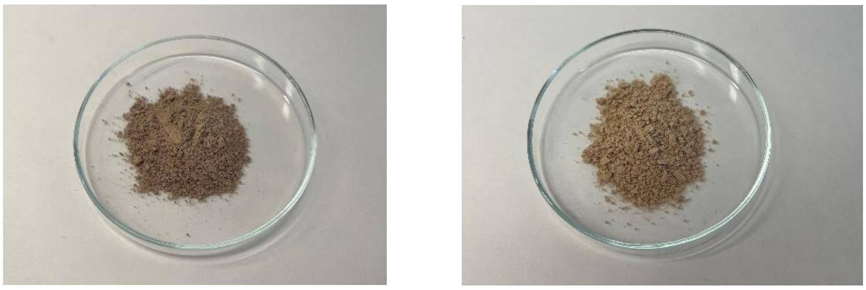
3.1.3.5 Coal mining waste

Activated coal mining waste (ACMW)

Coal gangue *Fig. 9a* was obtained from the Bogdanka mine (Lublin coal basin, Poland). Firstly, an analysis of homogenized and milled raw waste was made. Based on its properties, heat treatment was carried out, namely thermal activation at 600 °C for 2 hours in a muffle furnace. A colour change from gray to orange has occurred, this indicates the presence of iron oxides and successful oxidation [77].

Activated extracted shale (AES)

Extracted shale *Fig. b9* was obtained from coal mining waste from the Bogdanka mine (Lublin coal basin, Poland). Raw extracted shale was analysed and then to reduce additional energy the activation at 600 °C was made. A colour change from gray to light beige proves, as it was for coal mining waste, full carbon burning [4].



(a) (b)

Fig. 9: Coal mining waste a) ACMW; b) AES

3.1.3.6 Waste bricks

Brick dust was obtained from the production of ground bricks by the HELUZ company. HELUZ is a traditional Czech company that was founded in 1876 in Dolní Bukovsko *Fig. 10a* **(WBB)** near České Budějovice. Ceiling constructions, lintels and brick chimneys are produced here. The production of a complete range of bricks is in Hevlín *Fig. 10b* **(WBH)**. The last brick factory, which produces panels is in Libochovice *Fig. 10c* **(WBL)**, near Prague. Bricks are produced in a way where the laying surfaces are ground flat after firing using special equipment. The bricks have the same height ± 1 mm and parallel faces. With this procedure the consumption of masonry mortar is reduced, and labour simplified. At the same time, the thermal insulation properties are improved [10].

(a) (b) (c)

Fig. 10: Waste bricks a) WBB; b) WBH; c) WBL

3.2 Methodology and used instruments

Tab. 1: Methodology

Analysis type	Method	Apparatus
Material parameters	Pycnometry	Pycnomatic ATC – Thermo Scientific
	Permeable method according to Blaine	Blaine air permeability apparatus – UTEST
Chemical composition	X-ray spectrometry	ED-XRF Spectrophotometer ARL QUANT’X – Thermo Scientific
Mineralogical composition	X-ray diffraction	BRUKER desktop diffractometer D2 – PHASER
Granulometry	Laser method	Analysette 22 Micro Tec plus – FRITSCH
Pozzolanic activity	Chapelle test	-
	Frattini test	-
Morphology	Scanning electron microscopy	SEM Tescan Lyra dual channel

3.2.1 Basic physical properties

3.2.1.1 Matrix density

Matrix density ρ_{mat} [kg/m^3] was determined pycnometrically using an automatic Pycnomatic ATC - Thermo Scientific *(Fig. 11a,b)* with fully integrated temperature control with an accuracy ± 0,01 °C. The pressure resolution is 0,001 kPa and reproducibility is 0,01 % when measuring the sample volume at 20 °C.

In general, helium pycnometry is one of the most accurate methods for determining material density. The pycnometer uses helium as the measuring gas, the size of the helium atom is 0.22 nm (for water vapour it is 0.28 nm) and can fill even the smallest pores of the material. Gas pycnometers work on the principle of comparing the volume of the calibrated reference chamber and the chamber containing the sample. The ideal gas equation is the basis. The dried sample is placed in a crucible and then into the measuring chamber. The instrument has three basic calibrated chamber volumes - small, medium, and large. Helium injected into the sample chamber displaces air from the pores during the measurement cycles. Subsequently, both chambers are degassed. The helium is then injected into the reference chamber. The partial pressure is read and converted to a volume corresponding to the volume of the reference chamber. This exact volume is introduced into the measuring chamber and the partial pressure converted to volume is read again. The volumes are compared, and the residual volume is determined. The mass of the sample is determined before the measurement, and this allows us to calculate the density according to equation:

$$\rho_{mat} = \frac{m_d}{V} \left[\frac{kg}{m^3}\right] \quad (10)$$

Where m is weight of the dried sample

V is sample volume without pores and cavities.

Fig. 11: Pycnomatic ATC – Thermo Scientific

3.2.1.2 Specific surface area

Specific surface area was determined according to standard Blaine method specified in ČSN EN 196-6 [78] using an automatic Blaine air permeability apparatus – UTEST *(Fig. 12a,b).* The weight of the tested materials was determined using a digital scale with an accuracy of 0,001 g.

The fineness of grinding the material is expressed as a specific surface, calculated from the time required for the flow of a certain amount of air through a compacted bed of a given size and porosity. The permeable method therefore measures the specific surface area (surface area by weight) compared to the specific surface area of a reference cement sample.

The automatic Blain apparatus performs automatic calibration with the calculation of the K constant according to the standard [78] and performs the test by measuring the liquid drop between the marks of the glass tube. All calculations are displayed on the instrument screen by which the instrument is operated. All results are stored and can be exported to a USB drive.


(a) *(b)*

Fig. 12: a) UTEST – Blaine apparatus; b) equipment

3.2.2 Chemical composition

3.2.2.1 X-Ray fluorescence (XRF)

Chemical composition of materials was determined by means of X-ray fluorescence using ED-XRF Spectrophotometer ARL QUANT'X - Thermo Scientific *(Fig. 13a,b)*. X-ray fluorescence spectroscopy is one of the most versatile methods of inorganic analysis. It can analyse elements of lower concentrations down to tens of percent of elemental content and is non-destructive. Another advantage is the simplicity of sample preparation. Disadvantages could include acquisition costs and inter-elemental interference requiring matrix reference materials for calibration [79].

The device for the measurement itself contains a rhodium X-ray tube and Si(Li) crystal detector. The output signal of the detector is processed by powerful electronics using a multi-channel analyser. The dependence of the pulse frequency on the corresponding energy is represented by XRF spectra and is derived from the detector spectrometer record. The visible peaks describe the element present in the sample. The measurement is computer controlled.

UniQuant software collects and evaluates the obtained data. The output is chemical composition in elemental form or in form of oxides.

(a) *(b)*

Fig. 13: a) ED-XRF Spectrophotometer ARL QUANT'X – Thermo Scientific; b) equipment and samples

3.2.3 Mineralogical composition

3.2.3.1 X-Ray diffraction (XRD)

X-ray diffraction analysis is a fundamental method for the determination of the structure of solids. Any crystalline substance has a unique diffractogram to identify it. The method, based on the interaction of X-rays with the electrons of atoms by elastic scattering, is experimentally simple and rich in information. Due to the regular periodic arrangement of atoms in the crystalline phase, diffraction maxima occur after scattering and subsequent interference of X-rays. The position of the maxima, their intensity and shape depend on the type of atoms and the perfection of the arrangement in 3D geometry [80].

For measurement was used BRUKER desktop diffractometer D2 PHASER *(Fig. 14).* Phase determination was performed using software Profex that serves as a graphical user interface for Rietveld refinement of powder X-ray diffraction.

Fig. 14: Diffractometer D2 PHASER – BRUKER

3.2.4 Particle size distribution

Particle size distribution was performed with Analysette 22 Micro Tec plus – Fritsch *(Fig. 15)* device, which works on the principle of laser diffraction. The device consists of a light source (laser), a flow-through optical cell and a photodetector. The photodetector converts the optical signal into an electrical signal, which is transformed into a computer and used to generate data. So, the diffraction is based on determination of the angle of light scattering by particles, which depends on their size. The angle of diffraction is inversely proportional to the size of the particles and the intensity of scattered beam at a given angle is a measure of the number of particles of a given size. The data were evaluated using Frauenhofer's theory. It is the most widely used method with many advantages, such as easy sample preparation, the possibility of using ultrasound in the actual measurement and highly reproducible results [81].

Fig. 15: Analysette 22 Micro Tec plus – Fritsch

3.2.5 Pozzolanic activity

Determination of pozzolanic activity was performed according to the Frattini test specified in the EN 196-5 Standard [17] and the modified Chapelle method described in the French standard NF P 18-513:2009 [18].

Solution factors were determined according to the EN 196-5 Standard [17] prior to the actual analysis.

<u>Determination of the EDTA solution factor</u>

Into a 250 ml beaker containing 100 ml of water was weighed 1 g of calcium carbonate to the nearest 0,0001 g and 50 ml of dilute hydrochloric acid was added. The beaker was covered with a watch glass. The contents were stirred until the calcium carbonate was completely dissolved. All was added to a 500 ml volumetric flask. From the solution, 50 ml was taken, further diluted with 150 ml of water and the pH was adjusted to 13 using sodium hydroxide. The murexide indicator is then added and the solution is titrated with EDTA solution until the colour changes to purple, see *Fig. 16*.

The factor of the EDTA solution is calculated from its consumption according to the following equation:

$$f_1 = \frac{m_1}{100{,}09} \times \frac{1000}{10 \times 0{,}025 \times V_1} = \frac{m_1}{V_1} \times 39{,}96 \quad (11)$$

Where m_1 is calcium carbonate weight [g],

V_1 is consumption of EDTA during titration [m^3],

100,09 is molecular weight of calcium carbonate [*g/mol*].

Fig. 16: Solution before and after colour change to purple - titration with EDTA

<u>Determination of the solution factor of 0,1 mol/l hydrochloric acid</u>

0.1 g of sodium carbonate was weighed into a 250 ml Erlenmeyer flask and dissolved in 50 ml of water. Methyl orange indicator was added to the solution and titrated with dilute hydrochloric acid until the colour of the solution changed from yellow to orange, see *Fig.17*.

The factor of HCl solution is calculated according to the following equation:

$$f_2 = \frac{2 \times m_2}{105{,}989} \times \frac{1000}{0{,}1 \times V_2} = \frac{m_2}{V_2} \times 188{,}7 \quad (12)$$

Where m_2 is sodium carbonate weight [g],

V_2 is consumption of HCl during titration [m^3]

100,09 is molecular weight of sodium carbonate [*g/mol*].

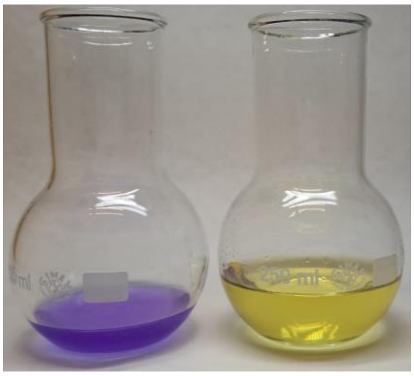


Fig. 17: Solution before and after colour change to orange - titration with HCl

3.2.5.1 Modified Chapelle method

The Chapelle test indirectly expresses the rate of pozzolanic reaction as $Ca(OH)_2$ consumed. Standard limit for pozzolanic activity is 650 [CH] mg/SCM g. This method can be used for large variety of materials – natural or artificial; it is not suitable for iron bearing slag, such as metallurgical slag [12; 82].

The mixture was prepared from 1 g of tested sample, 2 g of calcium oxide and 250 ml of redistilled water. The reaction was carried out at 80 °C for 24 hours in a sealed vessel with constant stirring (shaker IKA KS 4000 ic control). After completion, the sealed vessel was cooled to room temperature. Sucrose was added to the mixture and the solution was stirred for 15 minutes. The samples were filtered through a Büchner funnel and titrated with hydrochloric acid with phenolphthalein indicator from violet colour to discoloration, see *Fig.18a-c*. At the same time, a blank experiment was carried out without the investigated substance.

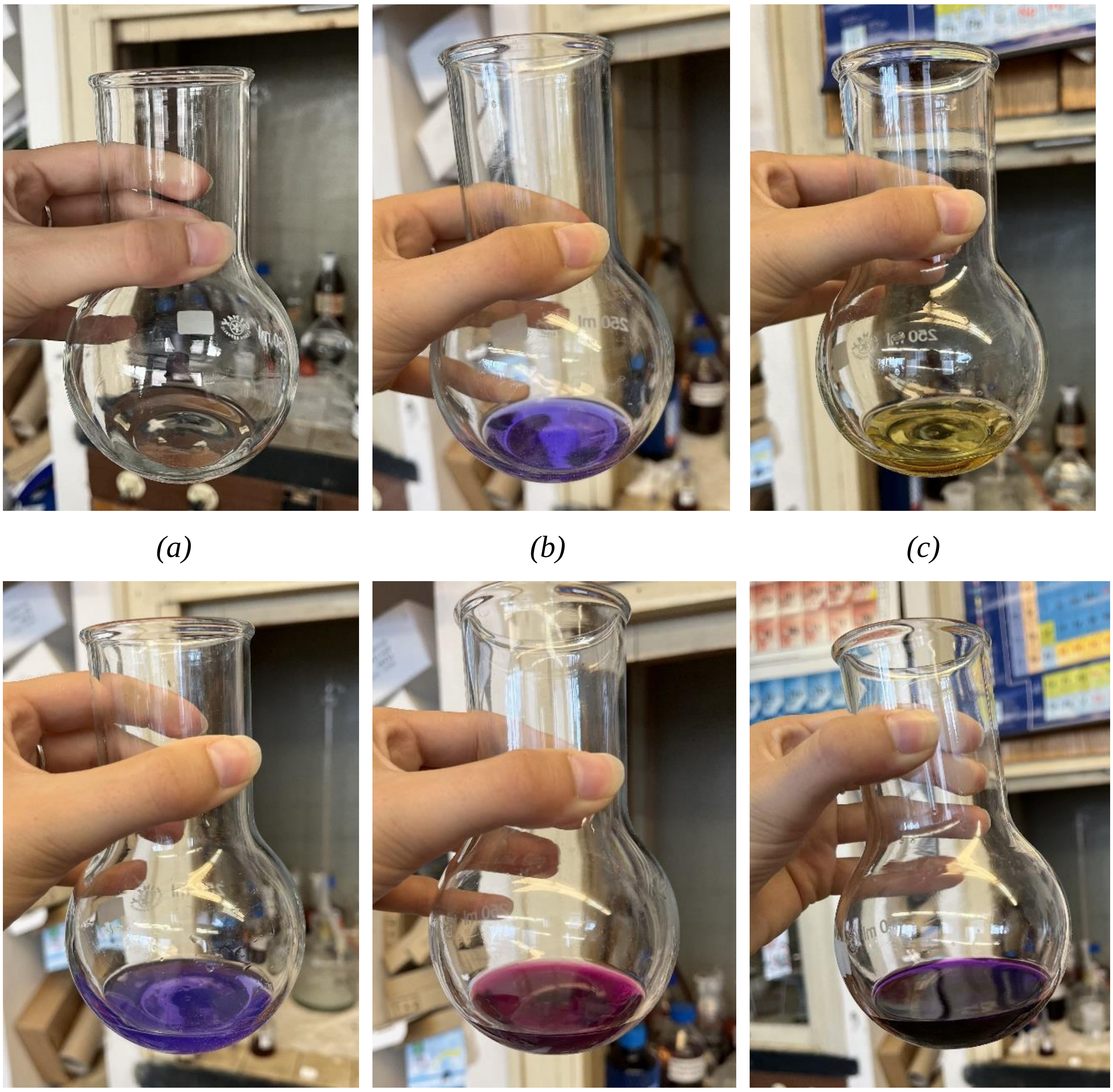
(a) *(b)* *(c)*

Fig. 18: Titration process: a) filtrate; b) phenolphthalein indicator; c) discoloration after HCl titration

3.2.5.2 Frattini test

In simple terms, the Frattini test works on the basis of comparing the amount of $Ca(OH)_2$ in the tested material and the amount of $Ca(OH)_2$ in the material of the same alkalinity. The solubility curve was obtained from the theoretical maximum of the CaO concentration and the corresponding OH^- concentration. The tested sample is evaluated as pozzolanic if the plotted point is below the solubility curve [12].

The mixtures were prepared from the tested samples, which replaced Portland cement CEM I 42.5 R from 5 – 70 % by weight. and 100 ml of distilled water. The sealed containers were placed in a cabinet thermostat (Lovibond) and left for 8 (15) days at 40°C. Then the samples were filtered through a Büchner funnel, and the resulting filtrates were analysed using a titration against hydrochloric acid with the indicator bromophenol blue, to determine the concentration of OH^-. Subsequently, they were adjusted with sodium hydroxide to pH 12.5 and titrated with an EDTA solution (disodium ethylenediaminetetraacetic acid dihydrate) using the indicator murexide to determine the concentration of Ca^{2+} expressed as CaO. The colour changes of the titrated solutions are presented in *Fig. 19a-f*.



(a) *(b)* *(c)*

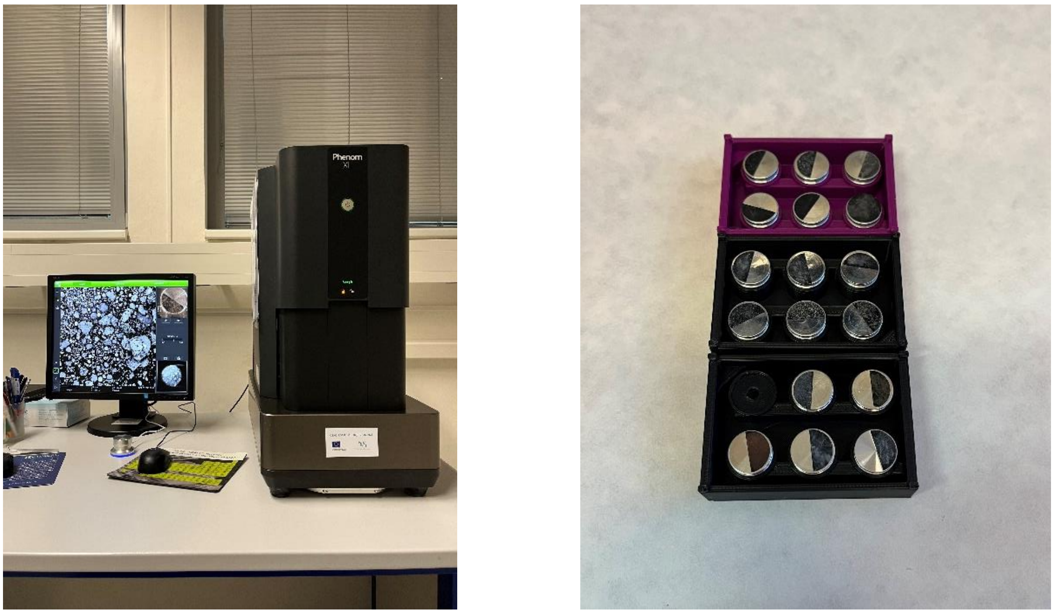
(d) *(e)* *(f)*

Fig. 19: Titration process: a) filtrate; b) bromophenol blue indicator; c) yellow colour after HCl titration; d) NaOH acidity adjustment; e) murexide indicator; f) purple colour after EDTA titration

3.2.6 Microstructure and morphology

The morphology of the materials was investigated by scanning electron microscopy (SEM) with a FEG electron source - Tescan Lyra dual channel microscope, see *Fig. 20a*. For the measurements, the samples were placed on a conductive tape, see *Fig. 20b* and a 5 kV electron beam was used.

In a simplified principle, the effect of the accelerated primary electron beam on the sample influences the shape of the region below the sample surface. There is elastic and inelastic scattering - movement of the primary electrons. Based on the chaotic motion, they generate signals that are detected by the instrument through mathematical treatment, thus providing information about the sample surface [10].



(a) *(b)*

Fig. 20: a) SEM Tesca Lyra dual channel; b) prepared samples

3.3 Evaluation and discussion of results

3.3.1 XRF

Determination of the chemical composition of materials is one of the initial steps in the classification of pozzolanic materials. According to ASTM C [83] and Czech national standard 72 2072-3 [84], the total content of hydraulic oxides, i.e. SiO_2, Al_2O_3 and Fe_2O_3, should be at least 70 % by weight. And at the same time, the active SiO_2 level should be at least 25 % by weight.

3.3.1.1 Natural-based materials

The composition of all the diatomite samples shown in *Tab. 2* meets the requirements of the standards with hydraulic oxide contents of 98, 95 and 96 % by weight.

Tab. 2: Chemical composition (XRF) – Natural-based materials

Substance	Oxides [wt %]		
	Diatomite		
	BOR	*ENO3*	*ENO7*
SiO_2	82.9	89.7	90.9
Al_2O_3	13.2	3.4	3.2
Fe_2O_3	1.5	2.1	3.1
	97.6	95.2	97.2
TiO_2	0.6	0.6	0.6
CaO	0.3	0.6	0.6
MgO	0.2	0.2	0.2
K_2O	0.9	0.3	0.3
Na_2O	0.1	2.7	0.2
P_2O_5	0.1	0.1	0.8
SO_3	0.1	-	-

3.3.1.2 Burnt clay rocks

Also, for all fired clay samples the requirements are met, in the marked row of *Tab. 3* we observe all values over 70% wt. and the corresponding SiO_2 content greater than 25 % wt.

Tab. 3: Chemical composition (XRF) – Burnt clay rocks

Substance	Oxides [wt %]							
	Metakaolin						*Argentinian clay*	
	MW	*MI*	*MS*	*MN1*	*MN2*	*MK*	*ACI*	*ACLI*
SiO_2	54.0	42.0	52.0	52.0	52.0	59.0	60.9	58.1
Al_2O_3	36.0	40.0	41.0	43.0	43.0	38.0	20.0	22.6
Fe_2O_3	1.9	2.0	2.0	1.0	1.0	0.7	8.1	7.6
	91.9	94.0	95.0	96.0	96.0	97.7	88.9	88.3
TiO_2	1.0	1.0	1.0	1.0	1.0	0.5	0.7	0.8
CaO	0.9	0.5	0.5	0.5	0.5	0.2	1.7	0.7
MgO	0.6	0.4	0.4	0.4	0.4	0.4	2.4	3.8
K_2O	2.8	2.0	2.0	1.0	1.0	0.8	6.0	4.6
Na_2O	0.4	0.1	0.1	0.1	-	-	-	1.3
BaO	-	-	-	-	-	-	0.1	0.1
SO_3	-	-	-	-	-	-	0.1	0.1

3.3.1.3 Waste materials

The chemical composition of waste materials varies widely across groups. In *Tab. 4* we observe sufficient values only for fly ashes *(FAO, FAP, FACH, FAV)* together with wheat straw biomass ash (*BAZ)*. *Tab. 5* shows the other samples in the waste material category, with the two coal mining waste samples *(ACMW, AES)* and all three brick dust samples *(WBB, WBH, WBL)* meeting the requirements.

Tab. 4: Chemical composition (XRF) – Waste materials

Substance	Oxides [wt %]									
	Sewage sludge ash		*Fly ash*					*Biomass ash*		
	GSS	*PSS*	*FAO*	*FAO180*	*FAP*	*FACH*	*FAV*	*BAP*	*BAZ*	*BAA*
SiO_2	22.9	30.8	50.3		52.4	52.5	41.1	41.7	64.2	2.8
Al_2O_3	8.9	7.9	35.4		32.4	30.8	32.4	13.9	4.5	3.3
Fe_2O_3	5.9	3.5	6.8		5.6	7.4	12.3	4.6	0.9	0.7
	37.6	42.2	92.5		90.4	90.7	85.8	60.2	69.6	6.8
TiO_2	1.0	1.0	1.5		2.0	2.2	5.8	0.7	-	-
CaO	25.4	19.7	1.8		2.7	1.5	3.0	17.5	7.6	72.5
MgO	5.4	4.1	1.4		1.8	1.7	2.2	3.7	3.3	3.3
K_2O	4.5	2.3	1.7		2.1	2.4	1.4	7.4	14.6	13.3
Na_2O	4.8	0.6	0.1		0.1	-	-	0.4	-	-
P_2O_5	12.5	25.3	-		-	-	0.1	2.3	2.8	1.4
SO_3	6.7	2.7	0.4		0.5	1.0	0.9	4.5	1.2	1.7
ZnO	0.3	-	-		-	-	-	-	-	-
Cl	4.1	0.1	-		-	-	-	1.3	0.1	-
BaO	-	-	-		-	-	0.2	-	-	-

Tab. 5: Chemical composition (XRF) – Waste materials

Substance	Oxides [wt %]						
	Municipal waste ash		*Coal mining waste*		*Brick dust*		
	MWAM	*MWAP*	*ACMW*	*AES*	*WBB*	*WBH*	*WBL*
SiO_2	29.2	10.5	55.9	54.7	63.5	51.3	49.7
Al_2O_3	3.2	7.3	29.3	35.5	20.4	20.0	20.1
Fe_2O_3	1.5	2.2	5.2	3.3	4.8	6.0	4.7
	33.9	19.9	90.4	93.5	88.7	77.3	74.5
TiO_2	0.1	1.8	1.6	1.4	0.8	0.8	0.7
CaO	15.0	33.1	0.7	0.3	4.2	11.5	16.6
MgO	5.7	3.4	1.1	1.0	1.8	4.5	2.7
K_2O	18.2	4.4	2.3	2.6	2.5	3.2	3.2
Na_2O	-	7.4	0.5	0.3	1.1	1.3	0.4
P_2O_5	17.6	2.2	0.6	0.4	-	-	-
SO_3	8.1	18.6	2.2	0.2	0.5	1.0	1.4
ZnO	0.9	1.3	-	-	-	-	-
Cl	-	7.0	-	-	-	-	-
BaO	-	0.2	0.1	-	-	-	-
MnO	0.1	0.2	-	-	-	-	-

3.3.1.4 Discussion

In terms of chemical composition, diatomites, metakaolins, Argentine clays, fly ashes, coal combustion waste and brick dust can be considered as very promising materials, together with a single representative of biomass ash from wheat straw *(BAZ)*. Acacia biomass *(BAA)*, on the other hand, performed very poorly, with a hydraulic oxide content of just under 7 % by weight. Low values are also shown by ashes from sewage sludge (38 %; 42 %) and ashes from municipal waste (34 %; 20%), the last ash from wood chip biomass *(BAP)* reached 60 % wt. of hydraulic oxide content, but the content of SiO_2 alone was almost 42 %. It is important to point out that the reactivity of the material does not depend only on the chemical composition, which is why we monitor other factors such as particle distribution, grain morphology and others.

3.3.2 XRD

The full chemical analysis does not tell us anything about the reactivity of the materials tested in an alkaline environment. This is why knowledge of the content of reactive amorphous phases, which engage in the process of hydration, is essential.

3.3.2.1 Natural-based materials

The differences in the mineral and phase composition of the studied minerals are shown in *Tab. 6*. Amorphous content was highest for ENO7. The raw material processing method is explained by the presence of cristobalite, which anneals at high temperatures. While BOR is manufactured mechanically, the remaining two, ENO3 and ENO7, are calcined. As opal is replaced by quartz in compacted rock, the opal content in sample ENO3 is an indication of the rate of compaction [73].

Tab. 6: Mineralogical composition (XRD) – Natural-based materials

Substance	Content [wt %]		
	Diatomite		
	BOR	*ENO3*	*ENO7*
Amorphous phase	**53.9**	**37.7**	**66.1**
Opal CT	-	22.0	-
Quartz	6.0	-	17.0
Tridymit	-	1.1	-
Cristobalite	-	39.2	16.1
Kaolinite	32.7	-	-
Illite	7.3	-	-

3.3.2.2 Burnt clay rocks

Tab. 7 shows the quantitative analysis of metakaolins. All samples have an amorphous phase over 60 % wt., the highest value being 91 % wt. for MN1 and 90 % wt. for MN2, which shows the effectiveness as a pozzolan. The highest values for crystalline phases are kaolinite, illite and quartz.

Tab. 7: Mineralogical composition (XRD) – Burnt clay rocks

Substance	Content [wt %]					
	Metakaolin					
	MW	*MI*	*MS*	*MN1*	*MN2*	*MK*
Amorphous phase	**60.0**	**69.0**	**72.0**	**91.0**	**90.0**	**60.0**
Quartz	5.0	9.0	7.0	5.0	6.0	7.0
Kaolinite	19.0	15.0	15.0	-	-	15.0
Muscovite	9.0	-	-	-	-	-
Illite	7.0	7.0	6.0	-	-	5.0
Pyrophilitte	-	-	-	3.0	3.0	-
Mulitte	-	-	-	-	-	13.0
Anatase	-	-	-	1.0	1.0	-

3.3.2.3 Waste materials

The mineral composition of the waste material groups was divided into three tables. *Tab. 8* shows the quantitative XRD analysis results for sewage sludge and fly ash. *FAO* has the highest content of amorphous phase, while the other ashes have between 16 % and 33 % wt. less. The content of calcium phosphate in the form of whitlockite for *PSS* probably depends on the composition of the sludge and the temperature and time of its thermal treatment. Fly ashes from brown coal combustion in general have the highest value of the crystalline phase in the form of mullite and quartz.

Tab. 8: Mineralogical composition (XRD) – Waste materials

Substance	Content [wt %]						
	Sewage sludge ash		*Fly ash*				
	GSS	*PSS*	*FAO*	*FAO180*	*FACH*	*FAP*	*FAV*
Amorphous phase	**41.0**	**52.3**	**74.0**		**47.0**	**58.0**	**53.0**
Quartz	11.9	22.4	5.0		12.0	11.0	5.0
Mullite	-	-	19.7		36.0	30.0	42.0
Calcite	5.5	-	-		-	-	-
Anhydrite	4.3	4.7	-		-	-	-
Hematite	4.6	5.2	-		5.0	1.0	-
Halite	2.9	-	-		-	-	-
Albite	1.7	3.2	-		-	-	-
Microcline	5.7	3.8	-		-	-	-
Apatite	1.6	-	-		-	-	-
Biotite	0.9	-	-		-	-	-
Chabazite	1.8	-	-		-	-	-
Bassanite	17.2	-	-		-	-	-
Whitlockite	-	11.6	-		-	-	-
Magnesioferrite	-	-	1.0		-	-	-

In *Tab. 9* we observe the results for biomass ash, municipal waste ash and coal mining waste. The amorphous phase of *BAZ* is 67 % wt., the value of the second biomass ash is half of that, i.e. 34 % wt. The lowest content is shown by *AES* with 18 % wt. The crystalline phase consists of quartz, supplemented by other minerals for all the samples.

Tab. 9: Mineralogical composition (XRD) – Waste materials

Substance	Content [wt %]					
	Biomass ash		*Municipal waste ash*		*Coal mining waste*	
	BAP	*BAZ*	*MWAP*	*MWAM*	*ACMW*	*AES*
Amorphous phase	**34.0**	**67.0**	**53.0**	**40.0**	**60.0**	**18.0**
Quartz	34.0	12.0	22.0	10.0	20.0	32.0
Calcite	11.0	5.0	5.0	-	-	-
Anorthite	17.0	-	-	32.0	-	-
Cristobalite	-	12.0	-	-	-	-
Anhydrite	-	-	18.0	6.0	1.0	-
Ephesite	-	-	-	2.0	-	-
Olivine C25	-	-	-	12.0	-	-
Illite	-	-	-	-	10.0	11.0
Muscovite	-	-	-	-	9.0	39.0
Calcium phosphate hydrate	4.0	4.0	2.0	-	-	-

Last of the waste materials, *Tab. 10* shows three representatives of brick dust. Lowest amorphous phase-content was analysed for *WBB*. The most abundant crystalline phase is again quartz. Its quantity is practically the same for *WBH* and *WBL*, for *WBB* it is almost 45 % wt.

Tab. 10: Mineralogical composition (XRD) – Waste materials

Substance	Content [wt %]		
	Brick dust		
	WBB	*WBH*	*WBL*
Amorphous phase	**28.5**	**46.7**	**55.8**
Quartz	44.8	23.6	23.5
Hematite	3.0	1.4	2.8
Albite	11.9	6.5	2.1
Microcline	7.8	7.2	8.8
Muscovite	4.0	2.6	6.0
Orthoclase	-	2.8	-
Biotite	-	0.9	-
Akermanite	-	4.4	-
Hedenbergite	-	3.8	-
Anhydrite	-	-	1.0

3.3.2.4 Discussion

The aim of the analysis approach is the determination of all crystalline phases present and the differentiation of amorphous contents. Measurement of the amorphous phase of the three samples was not performed after evaluation of the basic XRD analysis, where it was evident that no amorphous component would be detected in the measurement. Namely, these were acacia biomass ash and Argentine clays. With exceptions, most analysed samples contain an amorphous phase greater than 50 % wt. The reactive amorphous phase is the key determinant of the pozzolanic activity of the material. In general, it should be taken into account that the entire amorphous phase measured cannot be considered to be pozzolan active as it contains a large amount of organic matter. The XRD analysis is consistent with the chemical composition determined by XRF and the measured pozzolanic activity, which will be discussed in the following section.

3.3.3 Particle size distribution

The results for the particle distribution of each material are shown in a table for each group, where the calculated values of particle volume fraction 10, 50 and 90 % corresponding to the particle size are visible. The distribution curves of the samples tested are then plotted on a graph and compared. Importantly, the pozzolanic activity depends, among other things, on the size and form of the material particles. According to literature, some materials are known to be pozzolanic only when particles smaller than 45µm are presented [85].

3.3.3.1 Natural-based materials

Of the three representatives of diatomites, we can see in *Tab. 11* that *BOR* is the finest. However, the particle size of *ENO3* and *ENO7* is also sufficient for the intended use of the diatomaceous earth analysed as a partial cement replacement. The particle distribution curves are shown in the *Fig. 21*.

Tab. 11: Particle size distribution – Natural-based materials

Material		Freq d10 [µm]	Freq d50 [µm]	Freq d90 [µm]
Diatomite	*BOR*	9.5	23.0	32.5
	ENO3	22.3	37.5	63.5
	ENO7	19.6	29.0	43.0

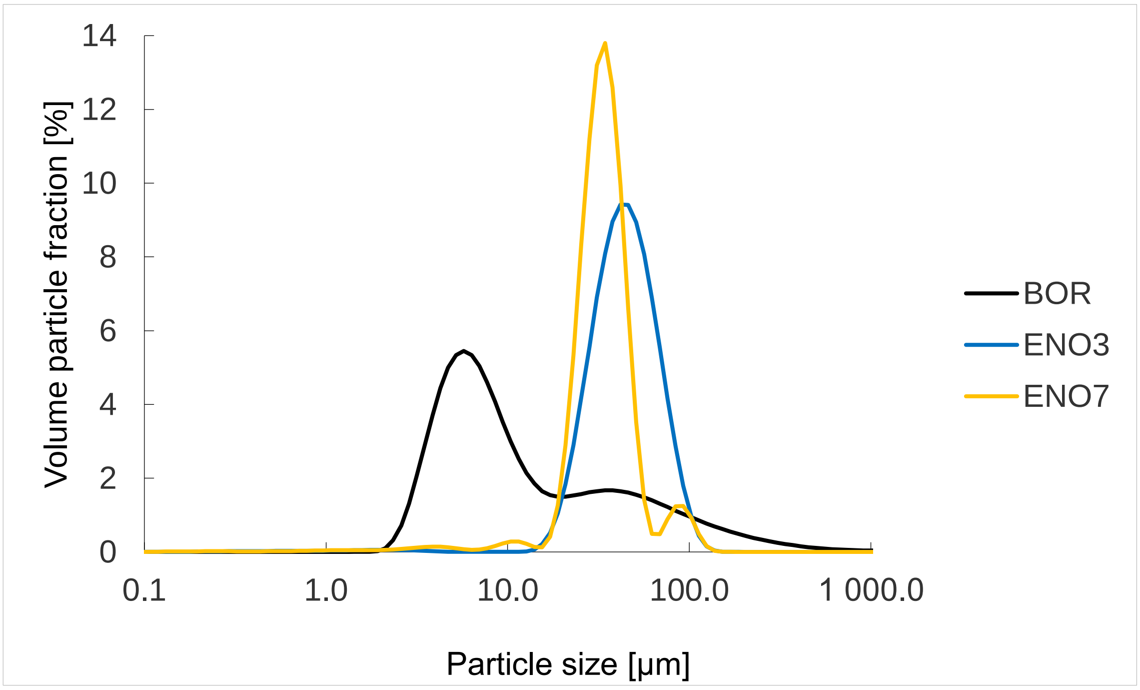


Fig. 21: Particle size distribution – Natural-based materials

3.3.3.2 Burnt clay rocks

In *Tab. 12* we can observe that 90 % particles of *MW*, *MI*, *MS* and *MN2* have size under 48 µm and for *MN1* and *MK* even below 49 µm. The finest is metaver *MK*. Argentinian clays *ACI* and *ACLI* have bigger particle sizes that metakaolins. *Fig. 22* shows the particle size distribution curves of tested materials.

Tab. 12: Particle size distribution – Burnt clay rocks

Material		Freq d10 [µm]	Freq d50 [µm]	Freq d90 [µm]
Metakaolin	*MW*	2.3	21.0	47.6
	MI	1.4	7.4	41.1
	MS	1.6	11.9	47.5
	MN1	1.2	6.6	39.4
	MN2	1.2	11.0	46.8
	MK	1.0	3.8	10.4
Arg. clay	*ACI*	2.1	26.9	54.1
	ACLI	1.3	25.1	64.7

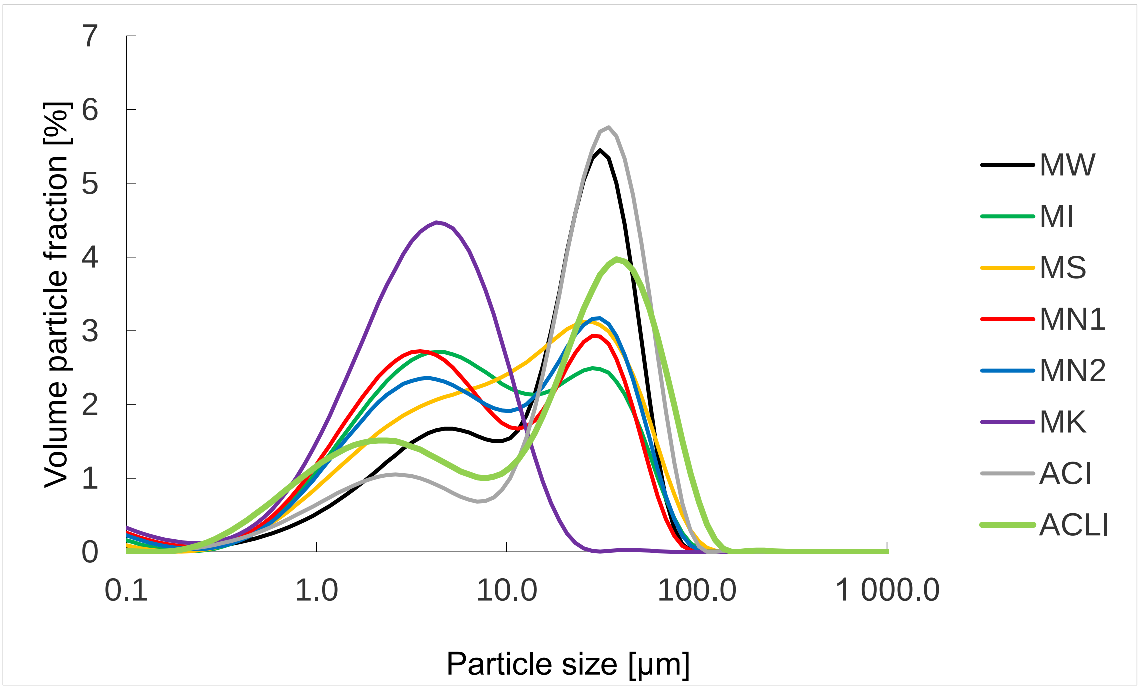


Fig. 22: Particle size distribution – Burnt clay rocks

3.3.3.3 Waste materials

In *Tab. 13* we can observe a comparison of the particle size distribution of all waste materials tested. For fly ashes, in the particle size range 24 – 42 µm, 50 % of particle size occurred. Similarly, for biomass ash, sewage sludge ash, municipal waste ash and brick dust with a dispersion of 29 – 53 µm. *ACMW* coal combustion waste showed the largest size, i.e. 90 % of particles below 233 µm. *FACH*, *FAV*, *BAA*, and *MWAP*, on the other hand, exhibited 90% of particles below approximately 50 µm. For *FAO* fly ash, we see a significant decrease in particle distribution with milling to *FAO180*. In a raw state 90 % particles were lower than 104 µm, while milled for 180 minutes showed 90 % particles below 22 µm. The particle distribution curves are shown in coherent groups in the *Fig. 23-25*.

Tab. 13: Particle size distribution – Waste materials

Material		Freq d10 [µm]	Freq d50 [µm]	Freq d90 [µm]
Sew. sludge	*GSS*	16.2	40.3	143.1
	PSS	6.0	28.5	69.6
Fly ash	*FAO*	7.3	33.1	104.3
	FAO180	0.9	5.4	21.6
	FAP	21.5	41.6	69.6
	FACH	19.7	34.5	51.3
	FAV	4.5	24.3	55.7
Biomass	*BAP*	2.6	28.9	66.1
	BAZ	21.2	52.7	101.4
	BAA	22.1	33.8	46.4
Mun. waste	*MWAM*	32.6	52.7	79.1
	MWAP	24.8	37.2	51.9
Coal mining	*ACMW*	30.1	79.8	233.2
	AES	3.5	38.1	61.5
Brick dust	*WBB*	19.1	36.6	56.2
	WBH	4.9	34.9	62.4
	WBL	5.4	42.7	77.7

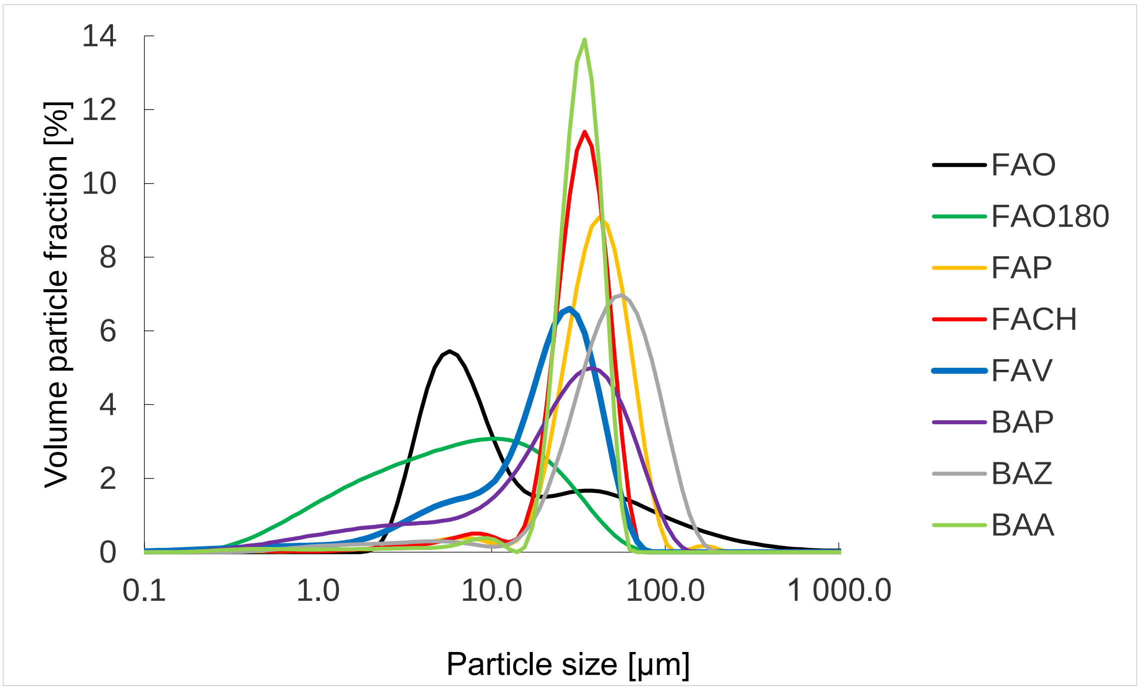


Fig. 23: Particle size distribution – Waste materials

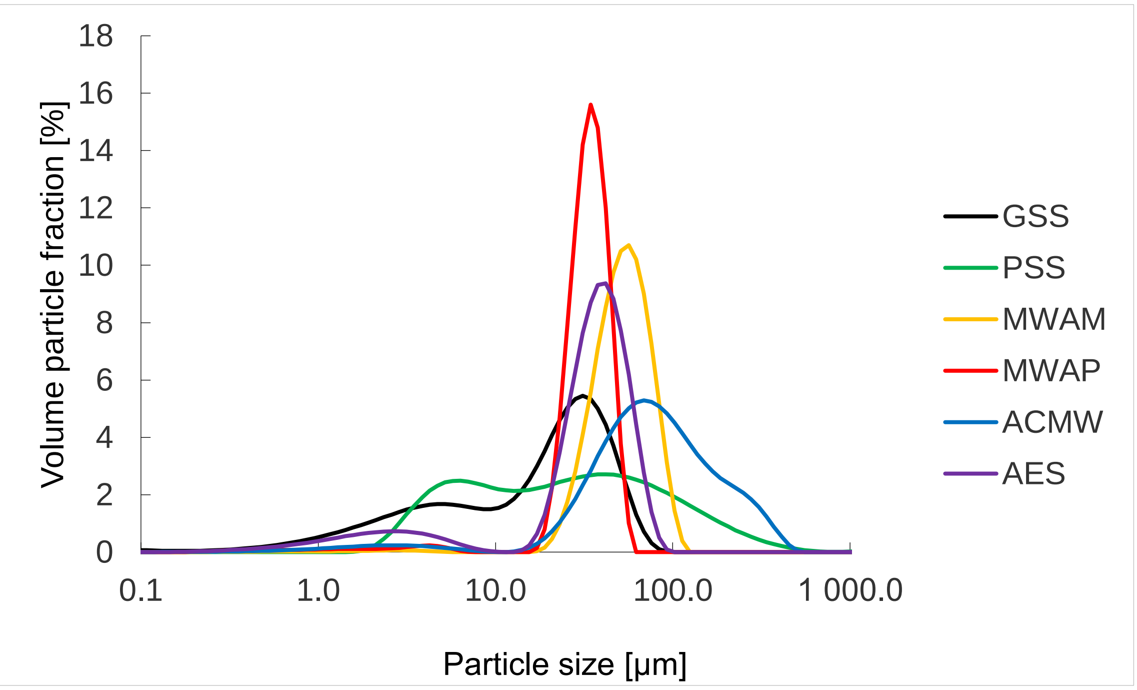


Fig. 24: Particle size distribution – Waste materials

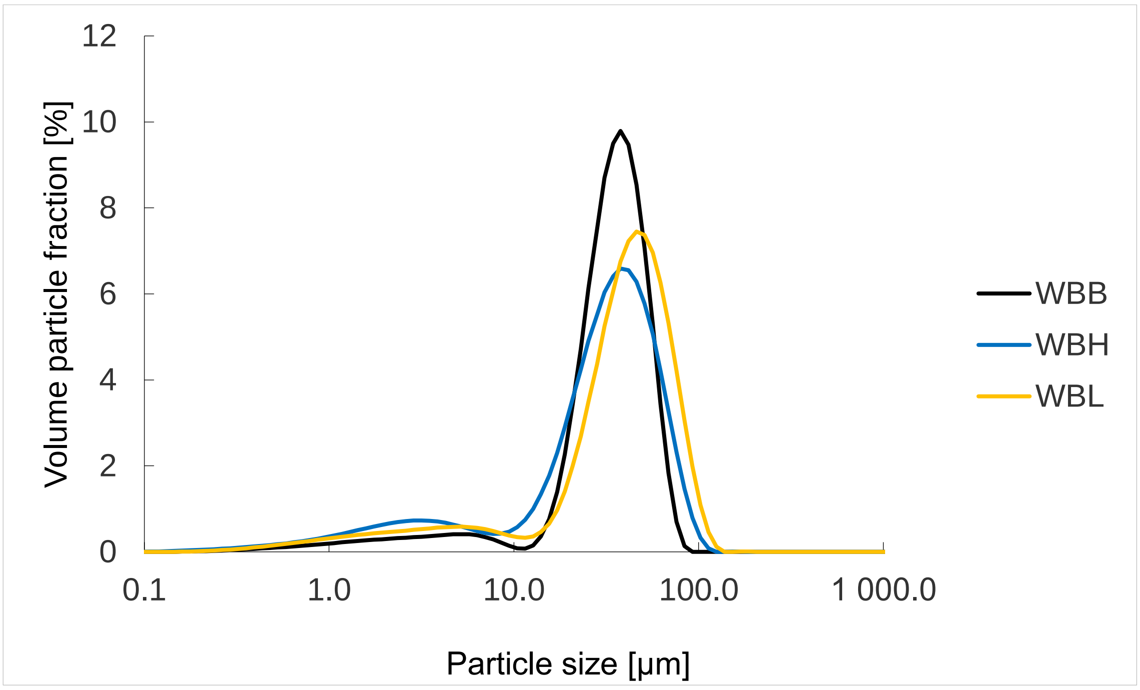


Fig. 25: Particle size distribution – Waste materials

3.3.3.4 Discussion

The results presented in literature [76] show that particle size can affect the pozzolanic activity of the material. This characteristic is therefore rightly considered as one of the major factors together with chemical structure and specific surface. All materials show a good predisposition for reactivity, which can be even increased by milling the material. Whether there is a direct relationship between particle distribution and reactivity for our materials compared across groups will be discussed in the next section. Focusing primarily on *FAO* fly ash, which is the only one measured unground and ground for 180 minutes.

3.3.4 Pozzolanic activity and basic physical properties

The reactivity of pozzolanic materials is correlated to their fineness and specific surface area. This implies that the activity of the mineral can also be increased by increasing the fineness. Therefore, one of the measured basic physical properties is the specific surface according to Blaine, another is the density of the matrix.

For the determination of pozzolanic activity using the Frattini test, the Portland cement was replaced by 40% by weight, unless otherwise stated or commented. The average values calculated from the Frattini measurements represent a point on the pozzolanic diagram. The test result is considered satisfactory if the concentration of dissolved $Ca(OH)_2$ in the suspension is lower than that of the saturated solution. The sample analysed is pozzolanic as the point is below the $Ca(OH)_2$ saturation isotherm.

The results of the Chapelle test are expressed in mg of $Ca(OH)_2$ fixed by 1 g of powder tested and give direct information on the pozzolanic activity of the sample analysed. Raverdy et al. [86] originally proposed that the mineral admixture is considered pozzolanic if 1 g of the tested sample absorbs more than 650 mg $Ca(OH)_2$. The titration reaction is controlled by calculation, which expresses the determination for a blank sample, according to equation:

$$\frac{56}{2} \times V_1 < 1000 \ (13)$$

where V_1 [ml] is volume of 0,1N HCl used in the titration of 25 ml of the solution obtained in the blank.

The amount of $Ca(OH)_2$ in the test itself is calculated according to equation:

$$Ca(OH)_2 = 2 \times \frac{V_1 - V_2}{V_1} \times \frac{74}{56} \times 1000 \ (14)$$

where V_2 [ml] is volume of 0,1N HCl used in the titration of 25 ml of the solution obtained when reacting with the test substance [18].

3.3.4.1 Natural-based materials

In *Tab. 14* we observe a comparison of the density, specific surface area and pozzolanic activity of the diatomites. The highest specific surface area is shown by *BOR* - 2049 m^2/kg, which also has the highest value of fixed calcium hydroxide according to the Chapelle test – 1614 mg $Ca(OH)_2/g$. According to the Frattini test shown in *Fig. 26*, BOR and ENO7 were pozzolanic, which agrees with the results obtained by Chapelle. Possibly the lowest a-SiO_2 content of diatomaceous earth ENO3, based on XRD analysis described in previous chapter, is responsible for its poor pozzolanic activity.

Tab. 14: Comparison of physical properties and pozzolanic activity – Natural-based materials

Material		Matrix density [kg/m^3]	Specific surface area [m^2/kg]	Chapelle test [mg $Ca(OH)_2/g$]	Frattini test
Diatomite	*BOR*	2416	2095	1614	Yes
	ENO3	2334	785	246	No
	ENO7	2399	1865	1349	Yes

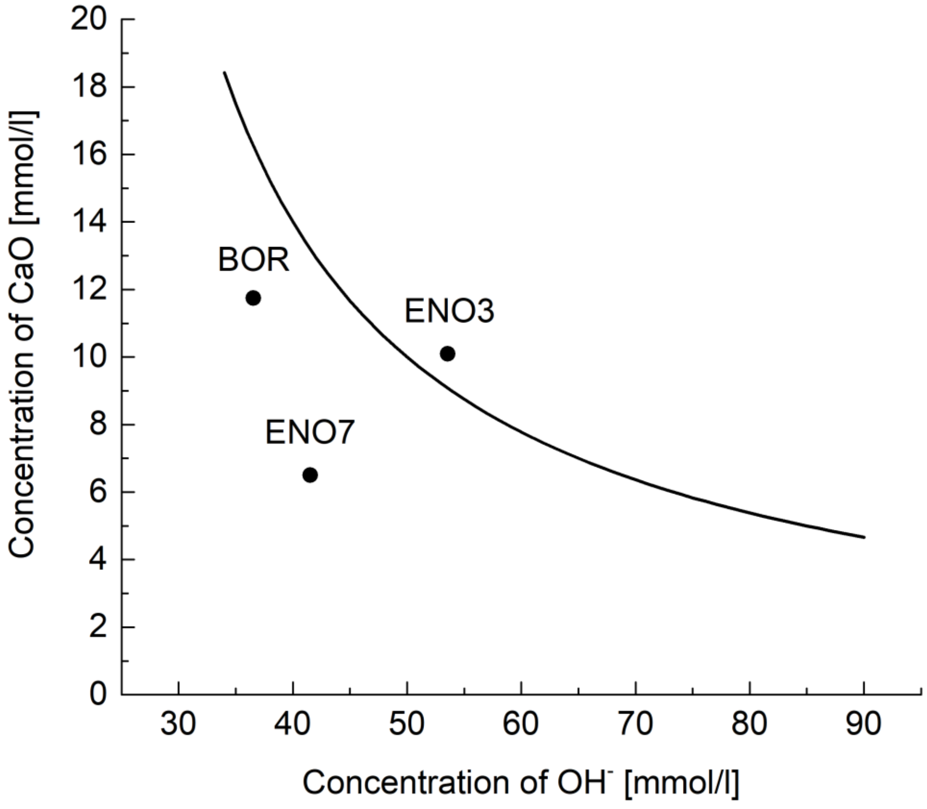


Fig. 26: Frattini test results – Natural-based materials

3.3.4.2 Burnt clay rocks

As can be seen in *Tab. 15*, metakaolins and Argentine clays have different specific surfaces and matrix densities. Matrix densities of metakaolin are around the same values in the range 2612 – 2653 kg/m^3. The highest matrix density displayed Argentine clays. Similarly for the specific surface area, where clays exceed metakaolins by a factor of 5 to 7. All metakaolins meet the minimum of 650 mg $Ca(OH)_2$/g and show high pozzolanic activity according to both Chapelle and Frattini test. Frattini results are displayed on *Fig. 27*, where we can observe that Argentine clays also show pozzolanic activity, because they lie below the solubility isotherm, even though they scored low on the Chapelle test. According to Chapelle's low measurements, the reaction was left to run for 15 days instead of 8. This result proves that the reaction is slower, and activation for some materials can occur later.

Tab. 15: Comparison of physical properties and pozzolanic activity – Burnt clay rocks

Material		Matrix density [kg/m^3]	Specific surface area [m^2/kg]	Chapelle test [mg $Ca(OH)_2$/g]	Frattini test
Metakaolin	*MW*	2653	1048	1905	Yes
	MI	2615	1619	1671	Yes
	MS	2612	1445	1967	Yes
	MN1	2647	1396	2085	Yes
	MN2	2625	1346	1993	Yes
	MK	2622	1608	1967	Yes
Arg. clay	*ACI*	2743	5787	366	Yes
	ACLI	3118	7850	332	Yes

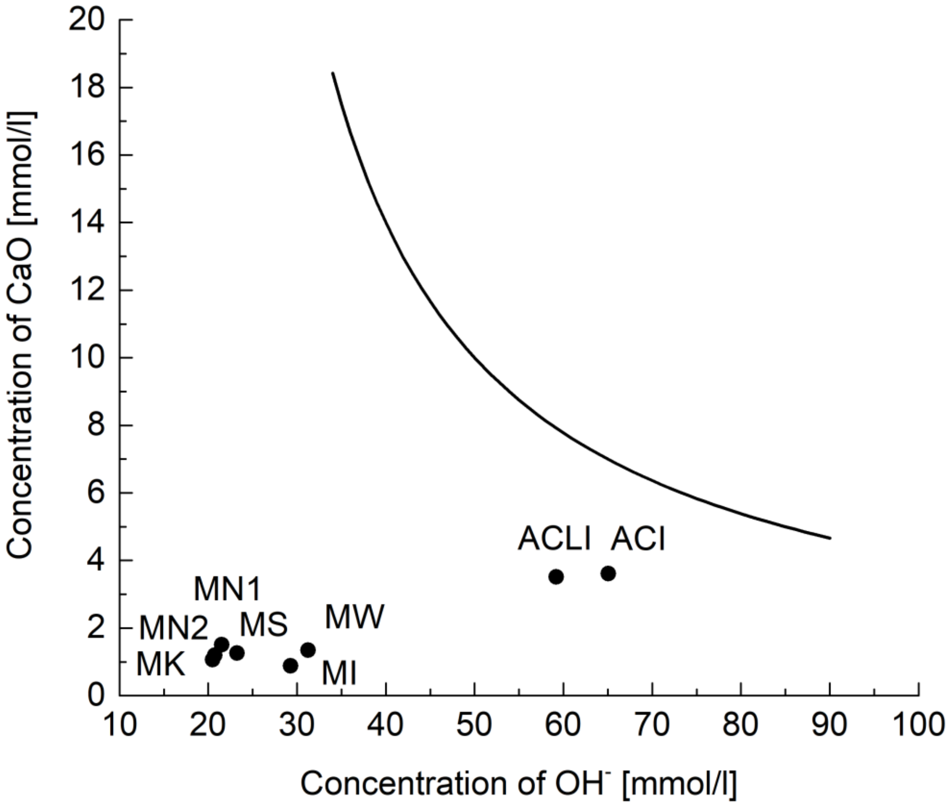


Fig. 27: Frattini test results – Burnt clay rocks

3.3.4.3 Waste materials

In *Tab. 16* we observe density values in the range 2057 – 2810 kg/m^3, on the other hand the specific surface varies greatly. For example, among the fly ashes, the value for *FAV* is up to almost 45 times higher than that for *FACH*. Similar to the burnt clay rocks, based on Chapelle's results, some samples were left to react for the Frattini test for 15 days, specifically *FAV, BAA, MWAM, MWAP, WBL, WBB, WBH, ACMW and AES*. *Fig. 28* shows that FAP and BAA, which are above the curve, did not come out as pozzolanic active. In *Fig. 29* we again see two values above the curve, namely *MWAM* and *MWAP*.

Tab. 16: Comparison of physical properties and pozzolanic activity – Waste materials

Material		Matrix density [kg/m^3]	Specific surface area [m^2/kg]	Chapelle test [mg $Ca(OH)_2$/g]	Frattini test
Sew. sludge	*GSS*	2549	1799	1349	Yes
	PSS	2800	1405	1373	Yes
Fly ash	*FAO*	2057	402	768	Yes
	FAO180	2760	833	2187	Yes
	FAP	2131	277	504	No
	FACH	2164	119	657	Yes
	FAV	2383	5308	744	Yes
Biomass	*BAP*	2557	781	1134	Yes
	BAZ	2447	834	1726	Yes
	BAA	2454	5100	73	No
Mun. waste	*MWAM*	2452	1763	546	No
	MWAP	2763	2150	359	No
Coal mining	*ACMW*	2795	275	732	Yes
	AES	2779	1199	714	Yes
Brick dust	*WBB*	2730	478	60	Yes
	WBH	2810	845	90	Yes
	WBL	2790	935	270	Yes

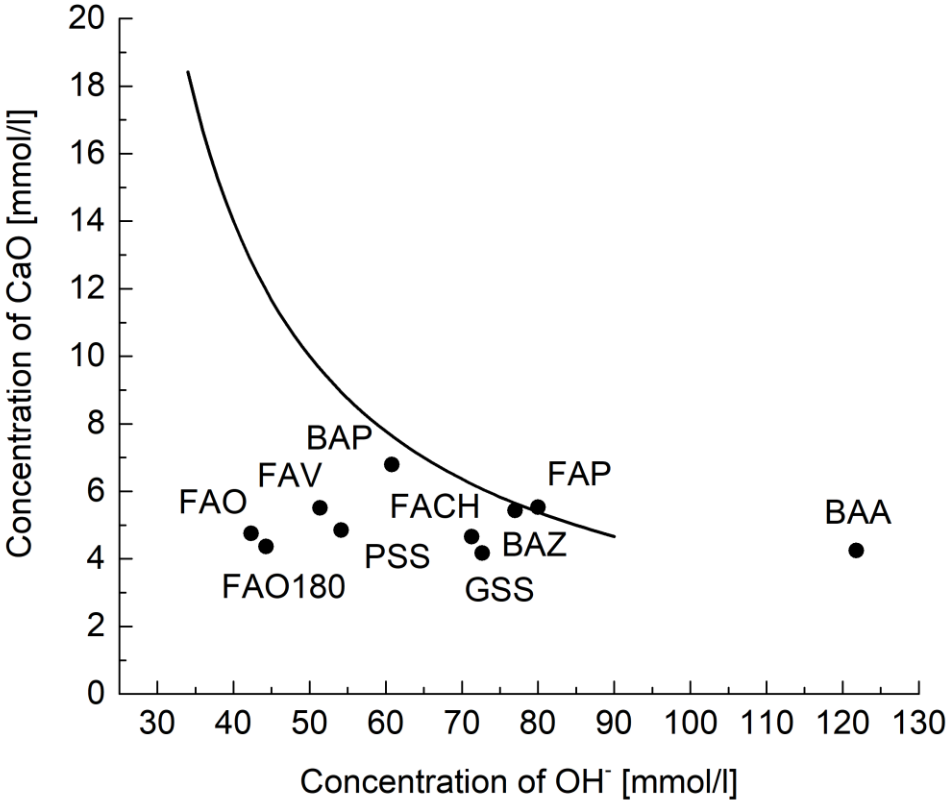


Fig. 28: Frattini test results – Waste materials

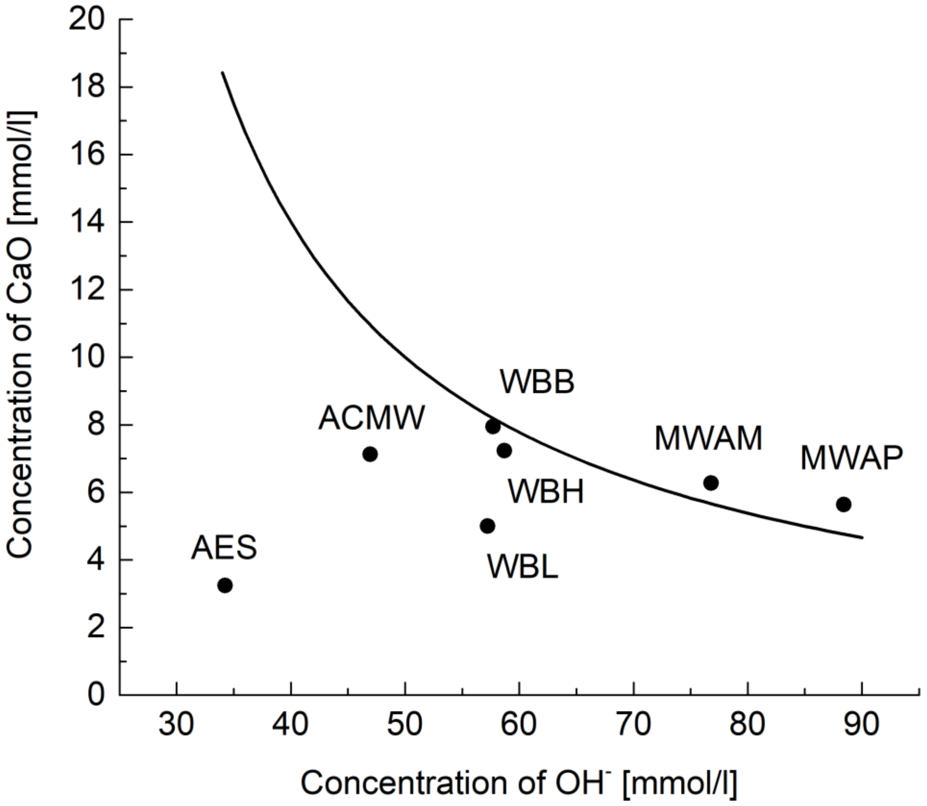


Fig. 29: Frattini test results – Waste materials

3.3.4.4 Discussion

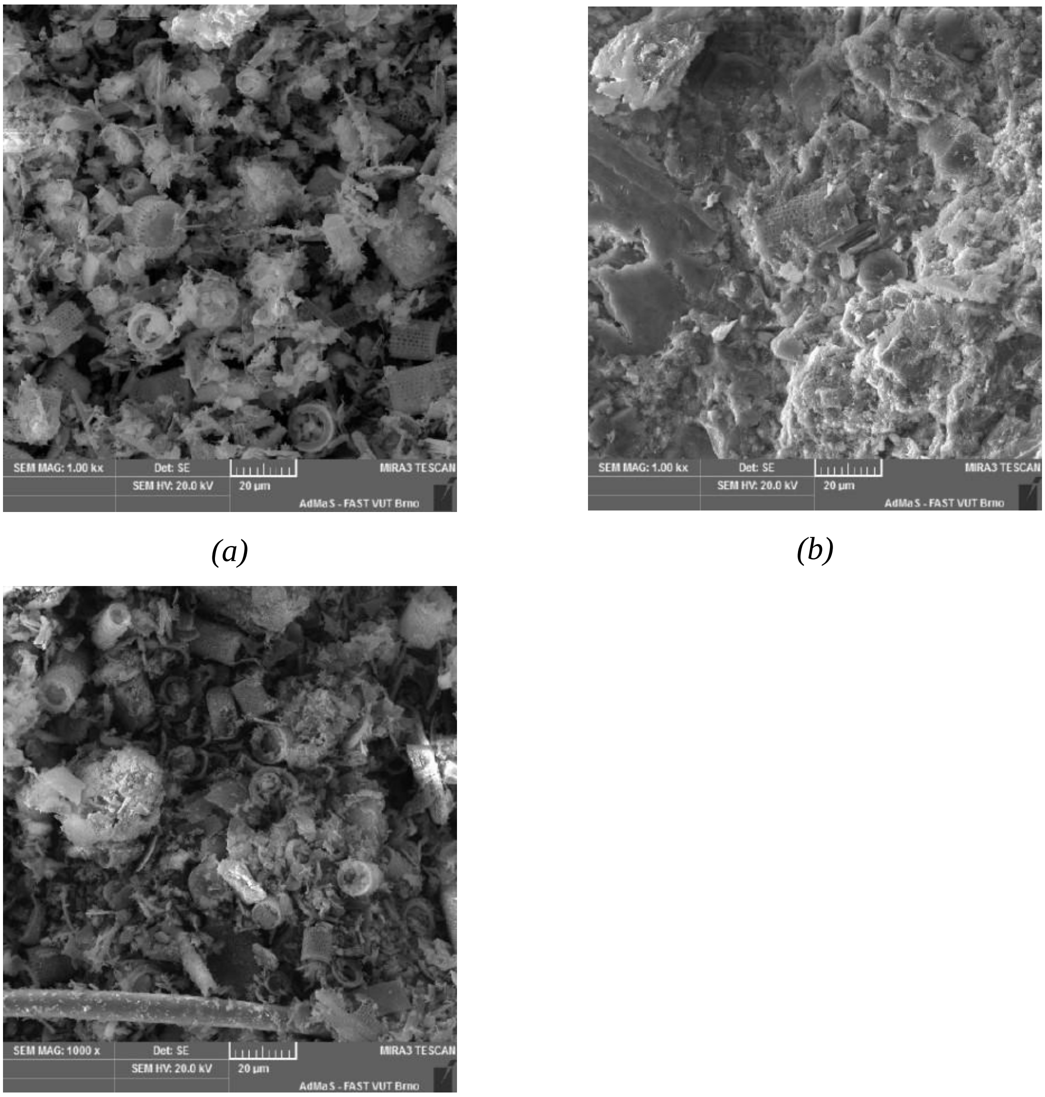
The Frattini test is used to assess the pozzolanic activity of a material as an additive to Portland cement in particular, while the Chapelle method is used to determine pozzolanic activity in general. The chemical reactivity depends mainly on the size of pozzolana particles and the content of active components; it means the amount of amorphous siliceous and aluminous compounds. Across materials, only 5 samples showed no pozzolanic activity, *municipal waste ashes, ENO3, FAP* and *BAA*. For the *FAP* and *ENO3* the reaction was only left for 8 days, the question arises as to whether it would not show activity after a longer period of time, as is the case with brick dust for example, which clearly showed the worst values for the Chapelle test. On the other hand, for acacia biomass *BAA,* that was left to react for 15 days, the result is still inactive, which is consistent with the chemical composition and the measurement of the amorphous component that was not performed.

3.3.5 SEM

Electron microscopic analysis was performed to get a better idea of the morphology of the studied samples. Unless otherwise stated, the images are at 1 kx magnification for comparison with each other.

3.3.5.1 Natural-based materials

The microstructure and morphology of the diatomaceous earth particles can be seen well in the following *Fig. 30a-c* taken over from [73]. You can also see that the sedimentary rock consists of fossil SiO_2-based cells of dead organisms called Diatomacea.



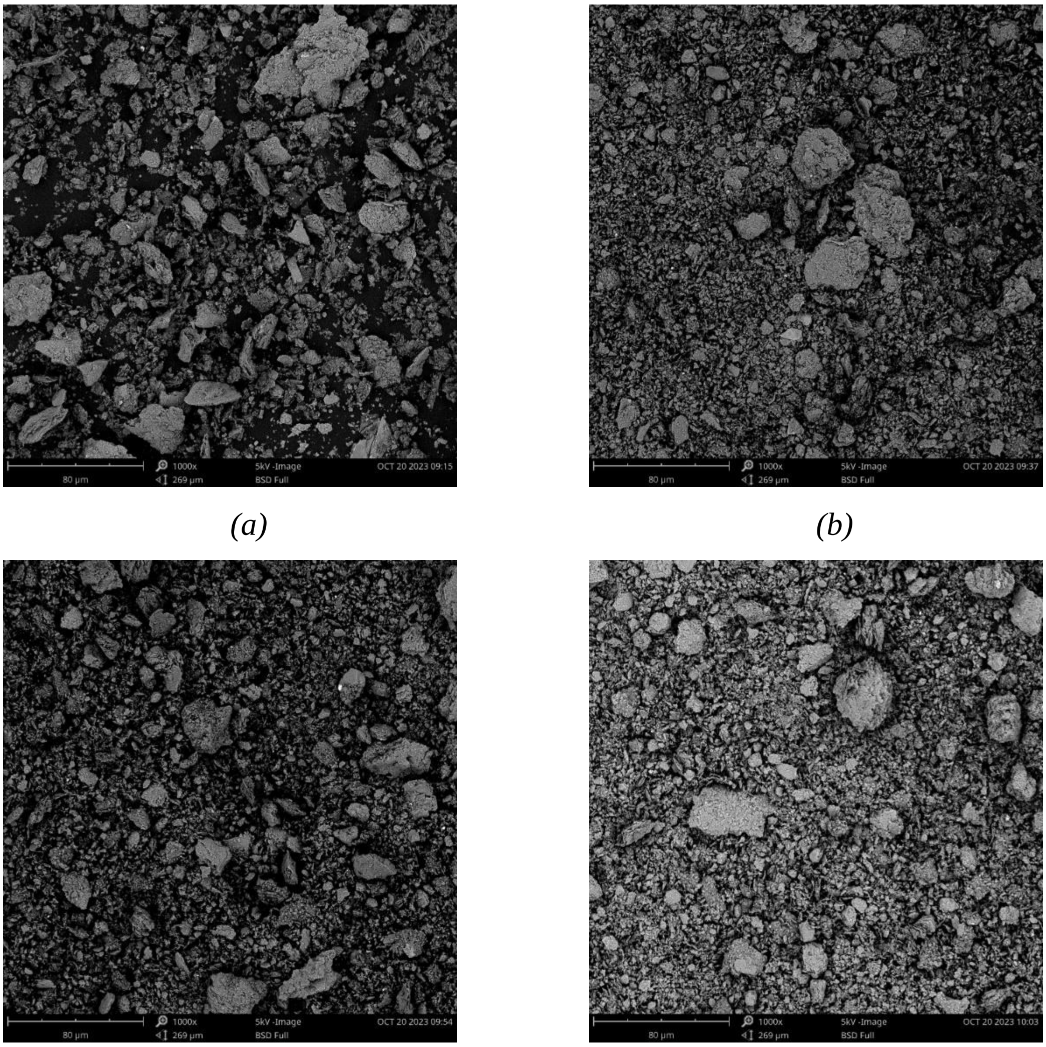
(a) *(b)*

(c)

Fig. 30: SEM micrograph a) BOR, b) ENO3, c) ENO7 [73]

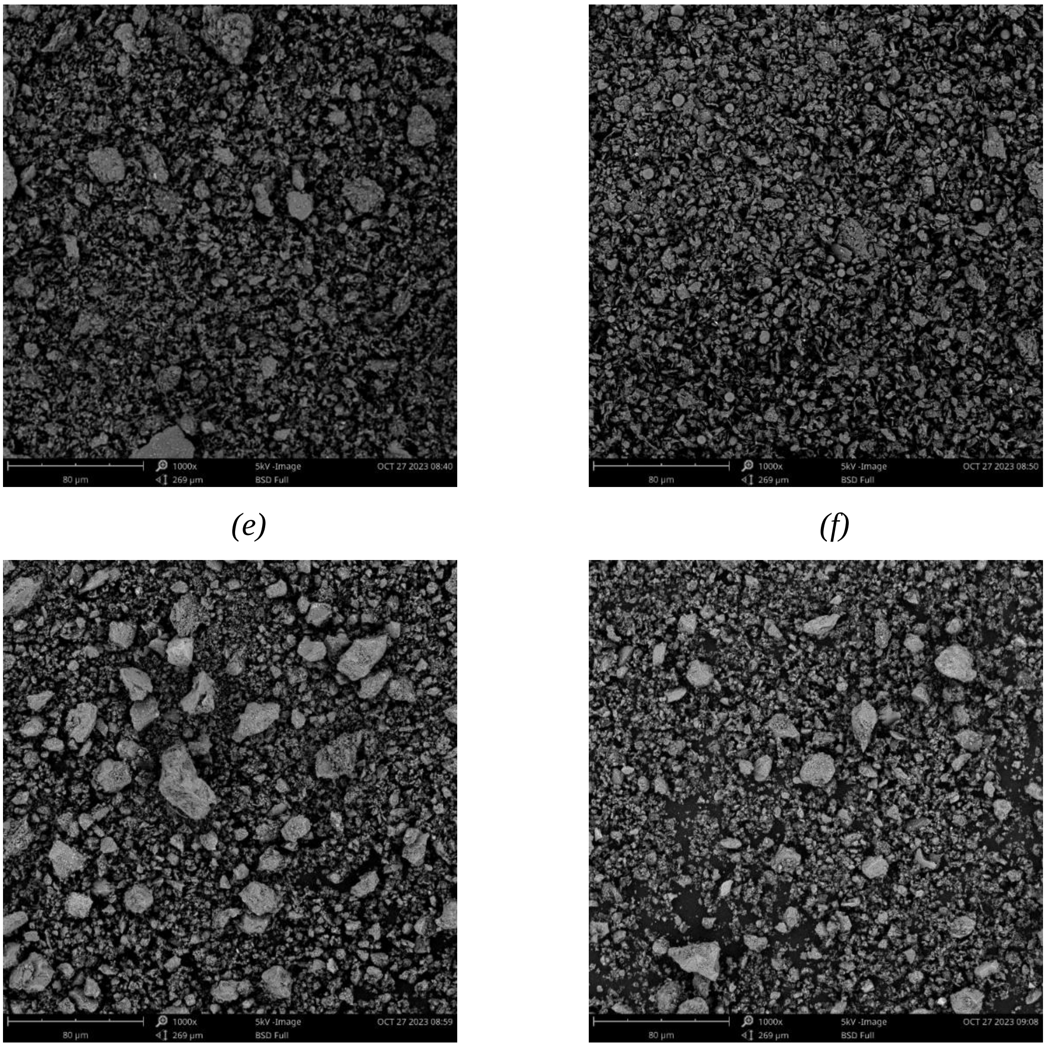
3.3.5.2 Burnt clay rocks

In *Fig. 31a-f* we observe the morphological composition of metakaolins. In all cases, we observe irregular grains of several sizes. The visual similarity of the samples agrees with the same particle size distribution and specific surface. Argentine clays, the other representatives of fired clay materials, show a similar structure on *Fig. 31g-h*. We see fine irregular grains as for the metakaolins.



(a) *(b)*

(c) *(d)*



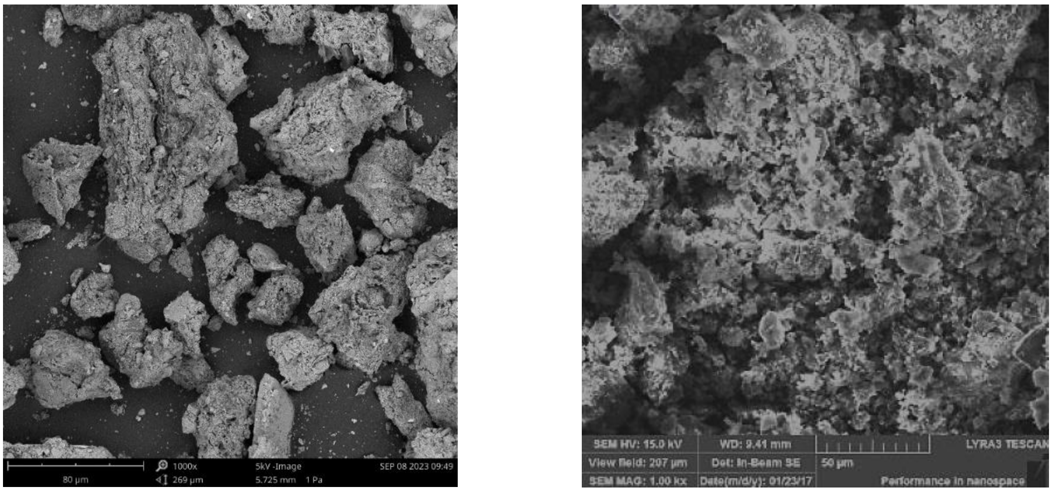
(e) *(f)*

(g) *(h)*

Fig. 31: SEM micrograph a) MW, b) MI, c) MS, d) MN1, e) MN2, f) MK, g) ACI, h) ACLI

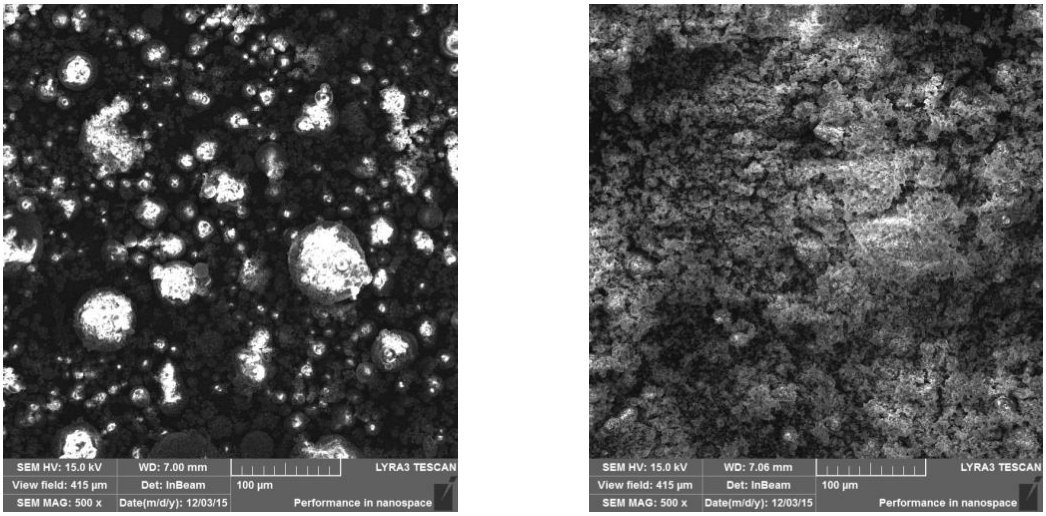
3.3.5.3 Waste materials

Sewage sludge ashes on *Fig. 32a-b* taken over from [37] show irregular particle shape and high porosity. *Fig. 33a-b* taken over from [76] shows the strong influence of grinding time on particle size and shape. It is evident that the longer milling time led to the breakdown of the primary spherical particles into very fine particles of irregular shapes, which was positive in terms of their reactivity, as shown by the results of the Chapelle test. The other fly ashes have typical spherical particles most evident for *FAV* and *FACH* in the *Fig. 33c-d*. We also see irregular and partially angular particles with a complex surface that corresponds to the specific surface area results. *Fig. 33c* shows big irregular particles. Biomass ash particles are also irregular shaped – *Fig. 33f-h*, where we can observe wooden fragments of acacia. Microscopic *Fig. 34a-b* of the municipal waste ash also show irregular grains with a porous structure. *AES* on *Fig. 34d* taken from [4] has a clear pellet shape with a smooth surface and sharp edges. On *Fig. 34c* [77] coal mining waste shows compact mass without distinct crystals. The compact surface confirms the assumption of the amorphous nature of the material. The last waste material is the brick dust shown in *Fig. 35a-c* taken over from [10]. All bricks show a rugged surface the difference between them is small. In general, a rugged surface is typical of ground materials.

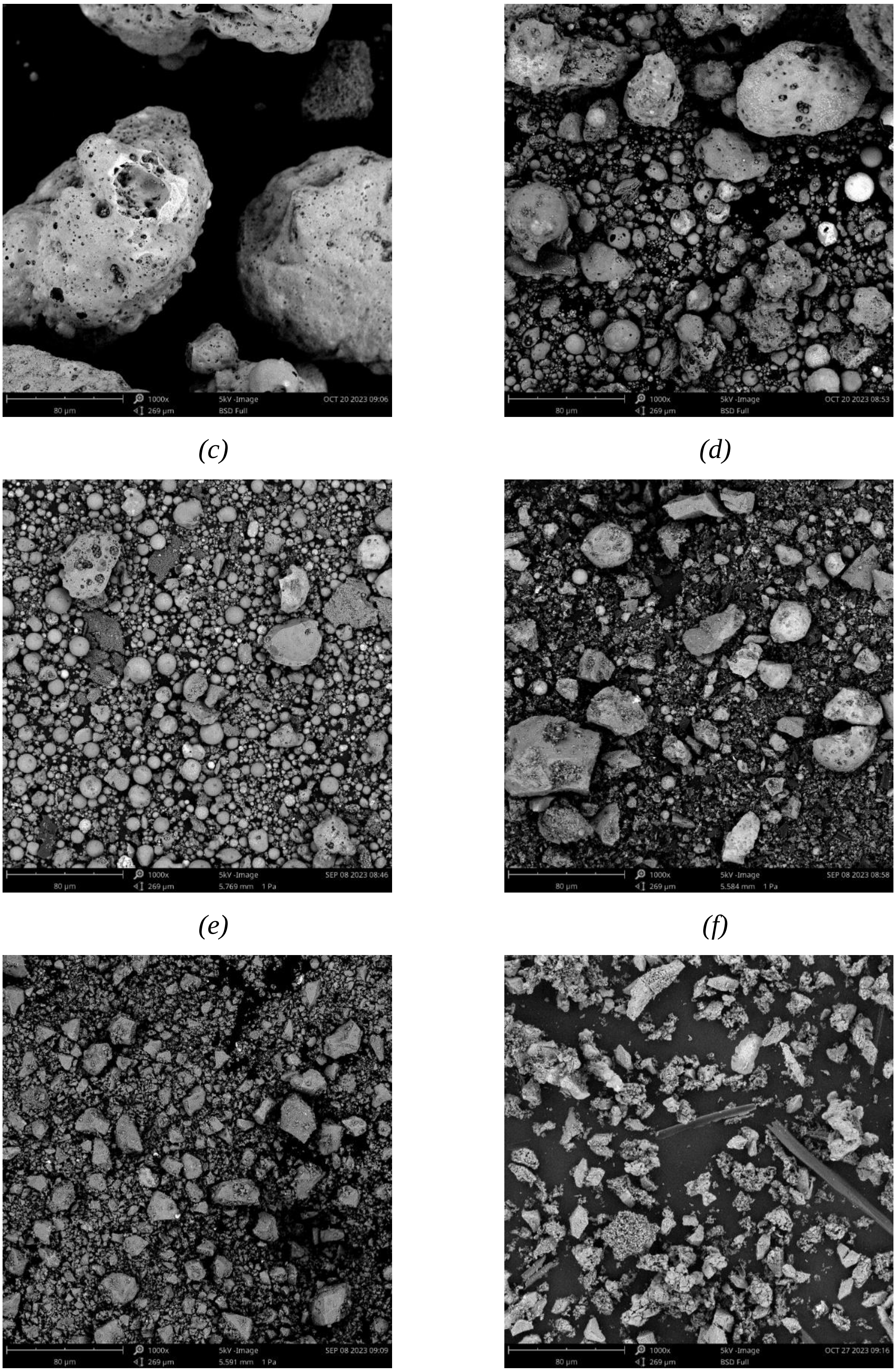


(a) *(b)*

Fig. 32: SEM micrograph a) GSS, b) PSS [37]



(a) *(b)*

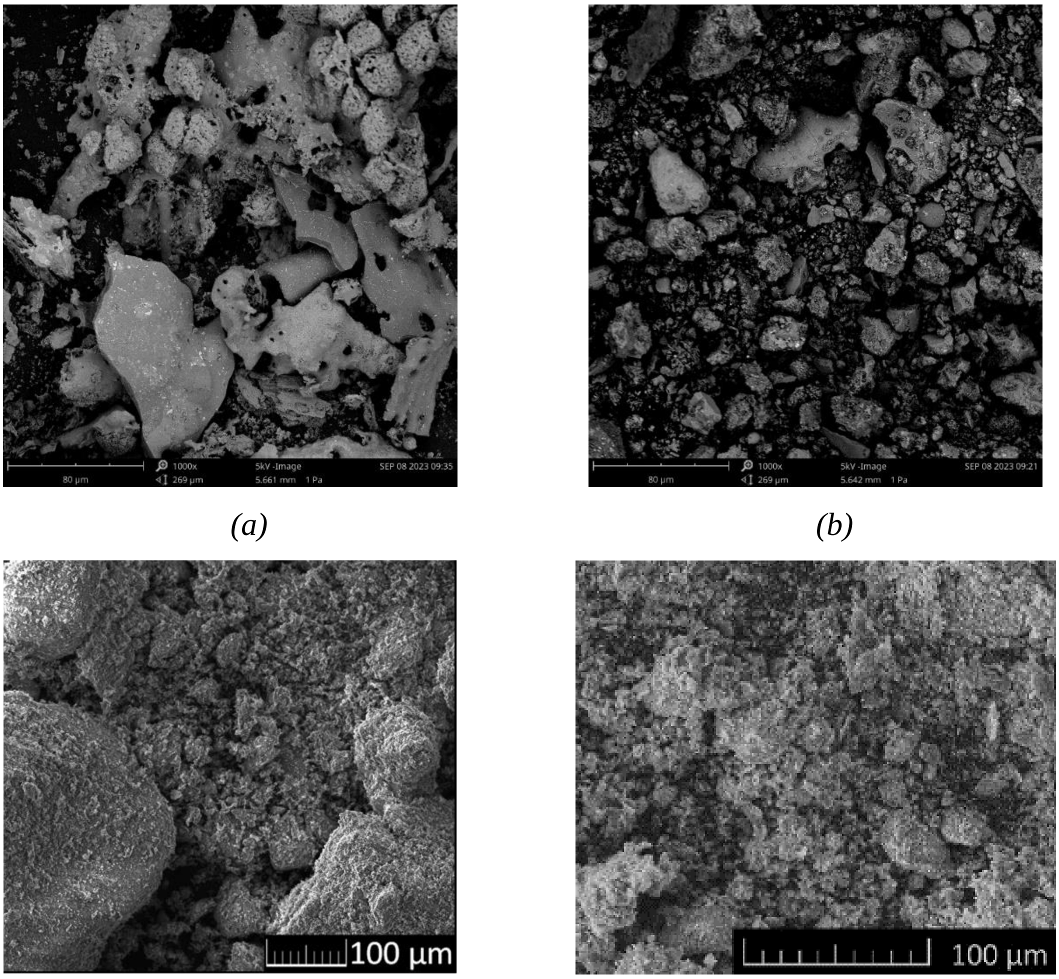


(c) *(d)*

(e) *(f)*

(g) *(h)*

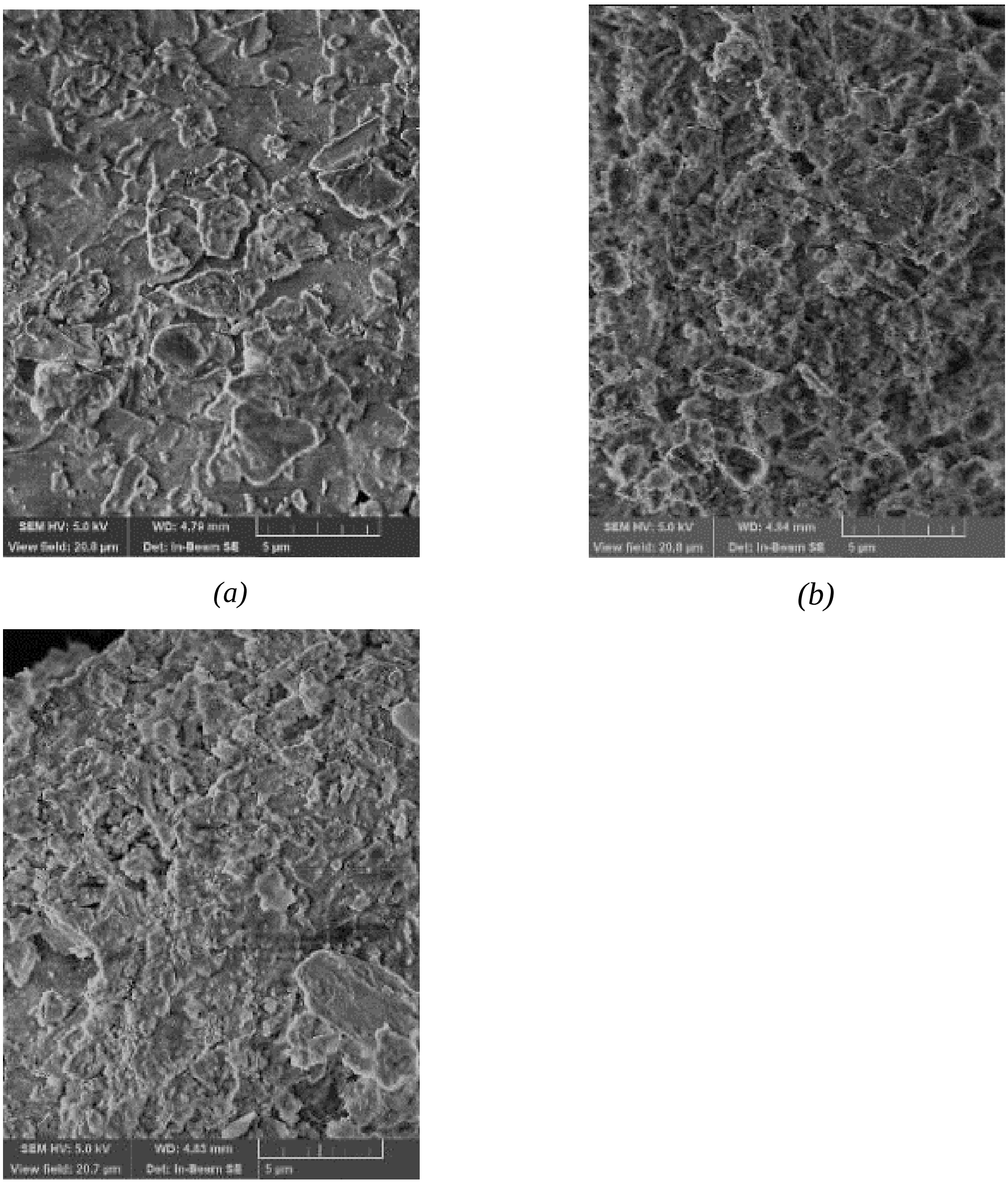
Fig. 33: SEM micrograph a) FAO, b) FAO180) [76], *c) FAP, d) FACH, e) FAV, f) BAP, g) BAZ, h) BAA*



(a) *(b)*

(c) *(d)*

Fig. 34: SEM micrograph a) MWAM, b) MWAP, c) ACMW [77], *d) AES* [4]



(a) *(b)*

(c)

Fig. 35: SEM micrograph a) WBB, b) WBH, c) WBL [10]

4 Conclusion

In many countries, the construction industry is one of the largest energy consumers. A significant amount of CO_2 is released during production, and as the world's population and economy continue to grow, so too does the amount of building material required. This results in a wide range of environmental impacts, such as negative changes in habitat for plants and animals, soil erosion, water and air pollution, the creation of dust that irritates the eyes and respiratory system, traffic congestion and noise pollution. The amount of waste is increasing along with these problems. Protecting the environment should be an absolute priority and it is therefore necessary to look for ways to recycle and recover as much waste as possible, while at the same time thinking environmentally in the production of materials and preventing the accumulation of waste.

Twenty-eight samples of materials on different bases that could potentially be used as admixtures in the production of cement and lime composites were investigated in this work. The main characteristic of these materials was the pozzolanic activity and its dependence on other chemical and physical parameters. All materials were first introduced and characterised in the theoretical part, and their relationship with the environment was assessed in terms of quantity produced and subsequent waste management. Measurements characterised within the methodology were performed in the experimental part. Specifically, density, specific surface area, particle size distribution, pozzolanic activity, XRD and XRF analysis and morphology assessment by electron microscopy were determined. The results of the measurements were used to characterise the materials themselves with respect to the diversity of the groups and to compare them with each other, leading to an assessment of their suitability for use as admixtures in the production of building materials, and to determine the relationship between pozzolanic activity and other properties, i.e. whether the material can be considered pozzolanic on the basis of the results of the other measurements.

The best-rated group are the metakaolins, which, according to the Chapelle test, showed an average dissolved $Ca(OH)_2$ content of 1931 mg/g, while at the same time pozzolanic activity was confirmed in all the Frattini test results after 8 days. The particle size distribution of all metakaolins was in 50 % less than 11.9 μm (or 21 μm for Metaver W). The average proportion of amorphous phase was almost 74 %, with the most common crystalline phases being kaolinite, illite and quartz. The chemical composition was very satisfactory, with hydraulic oxides more than 90 % wt. and a SiO_2 content of at least 52 % wt.

Next are sewage sludge ashes from Poland and Greece, where the dissolved $Ca(OH)_2$ content was measured to be 1030 and 1373 mg/g, they were also found to be pozzolanic active in the Frattini test after 8 days. The particle size distribution for 50 % was 28.5 and 40.3 µm, the proportion of amorphous phase as 52 and 40 %, the most abundant crystalline phase was quartz. However, it is interesting to note that neither sludge appears promising in terms of chemical composition, with the content of hydraulic oxides not approaching 70 % wt. and the Greek sludge having a SiO_2 content of just under 25 % wt.

The following group are the diatomites, two of which show 1614 and 1349 mg of $Ca(OH)_2$ per g, but the last representative, Enorandall 3, showed only 246 mg $Ca(OH)_2$/g according to Chapelle, which was confirmed by the result of the Frattini test, which declared the material inactive. The chemical composition of all three diatomites was promising. The amorphous phase for the pozzolanic active exceeded 50 % for the inactive 37 %, the mineralogical composition varies. The particle size distribution was on average less than 29.8 µm for 50 % of all particles.

For the power plant fly ash group, the amount of $Ca(OH)_2$ ranges from 657 to 768 mg/g. Only the ash from the Počerady power plant is 504 mg/g and the Frattini test after 8 days also showed no pozzolanic activity. We must turn our attention to the comparison of the ash from Opatovice, which was measured unground and ground for 180 minutes. We observe a reduction in particles by a factor of 6 and a corresponding increase in the amount of $Ca(OH)_2$ to almost a factor of 3. Both the chemical composition and the amorphous content were promising for all the ashes.

The biomass ashes from wood chips and wheat straw showed a promising chemical composition and a strong pozzolanic activity, with $Ca(OH)_2$ contents of 1134 respectively 1726 mg/g, on the other hand, the acacia ash obtained only 73 mg/g in the Chapelle test and, even after 15 days of continuous reaction, did not show its activity in the Frattini test in combination with Portland cement, its chemical composition was poor and the proportion of the amorphous component did not even need to be measured, since it was shown to be negligible by the basic XRD determination.

Thermally activated coal mining waste had two representatives, both showing activity with a $Ca(OH)_2$ content above 700 mg/g. However, in the activated extracted shale, the proportion of amorphous phase was only 18%, most of which was the crystalline phase of quartz and illite. For the activated waste, it is interesting to note the particle size distribution where 50% of all particles were almost 80 µm in size, despite this coarseness the material was pozzolanic active.

In both cases, municipal waste ash showed no reactivity, as indicated by its chemical composition, and confirmed by the Chapelle test, with values below 500 mg/g, and the

Frattini test, left to react for 15 days. Compared with the others, this is clearly the least suitable group for use as a partial replacement for Portland cement.

The Argentinian clays had a good chemical composition, but the amorphous content was negligible, the Chapelle test did not show any pozzolanic activity, but on the contrary, according to Frattini, both materials proved to be active for 15 days in partial replacement of 40 % Portland cement.

Similarly, in the case of brick dust, all three representatives showed minimal amounts of $Ca(OH)_2$ mg/g, while the chemical composition and the proportion of amorphous phase were favourable. Thus, the Frattini test after 15 days of partial replacement of cement with pozzolana confirmed the activity. Brick dust and Argentinian clays are prime examples of the importance of activation time in an ongoing reaction. Therefore, it is possible that the Počerady power plant fly ash together with the diatomite - Enorandall 3 would have proved to be pozzolanic active for the partial replacement of Portland cements after 15 days, as all other properties suggested their activity.

The results therefore show that metakaolin best meets all the requirements. The measurement of metakaolin also confirms the main role of the chemical composition, i.e. the content of silicates and aluminosilicates, especially their amorphous phase. This is also the case for the other samples, the chemical composition is the most important indicator, for samples that did not show hydraulic oxide content and 70 % wt. and SiO_2 content alone above 25 % wt., did not show pozzolanic activity neither. There are some exceptions, the Greek and Polish sludges, where the content of all three hydraulic oxides is not 70 % wt., but the SiO_2 content is 30 % wt. in one case and almost 23 % wt. in the other, while the content of the amorphous phase, which is more than 40 % and 52 % respectively, needs to be monitored, as in the case of wood chip biomass ash, where the SiO_2 content is almost 42 % wt. and the hydraulic oxides together are more than 60 % wt.

Unfortunately, therefore, it is not possible to clearly estimate the pozzolanic activity or inactivity of a material based on a single measured parameter. Along with the chemical and mineralogical composition, the degree of fineness is an important factor, together with the specific surface area and morphology. If we focus on the particle size distribution of the Opatovice fly ash, we see a clear example where grinding, and thus refining the material, increases its real value of pozzolanic activity according to Chapelle by almost three times. It is not possible to say with certainty at what particle size the material becomes reactive, because in a cross section of twenty-eight samples we observe very active with large grains and the reverse, but it can be stated that by grinding to smaller particles the reactivity increases.

In general, it can be said that the reactivity and therefore the suitability of using material as an admixture to produce cement and lime composites is influenced by several factors at once, which are interrelated and need to be determined. Methodologically, a pattern can be identified by which reactivity can be estimated, i.e. focusing first on chemical composition, then on mineralogy with emphasis on the amorphous fraction and fineness of the material. These three criteria are essential and the real value of pozzolanic activity corresponds to them. The Frattini test then complements the pozzolanic activity in terms of partial replacement of Portland cement, where the time taken to activate the material greatly influences the result. The next step in material analysis would be to determine the amorphous phase of iron oxide and alumina, for which there is currently no method available.

All the materials studied can be used, some more readily than others, as admixtures for cement or lime composites. Obviously, the most suitable materials are natural materials and fired clay materials, which mostly only need to be ground or heat-treated, but their sources are not infinite, and they do not solve the main problem of waste management in the construction industry. Within the group of waste materials, we observe suitable candidates such as fly ash, sewage sludge ash and biomass ash, together with brick dust, but at the same time the completely unsuitable material of acacia ash, as well as municipal waste ash, also carries several risks. The content of toxic and environmentally hazardous substances in waste materials is another important factor. The next step should be the analysis of composites with admixtures from each group, in particular the investigation of their strength characteristics and the determination of the ideal replacement percentage. From a few studies already carried out, it can be argued that in many cases the use of additives actually improves the properties of the composite, particularly in terms of resistance and durability. All composites produced must be tested over an extended period of time to confirm adequate endurance. The analyses carried out in this thesis are a first essential step.

The use of selected waste materials in the construction industry can be a promising solution for the construction industry, both from an environmental and economic point of view, particularly a significant reduction in production costs. Due to the diversity of materials, both in terms of origin and the variety of individual wastewater treatment plants, municipal waste incinerators or power plants, as well as the method of storage and processing, it is always necessary to analyse the concretes for the preparation of composites and to determine whether their parameters meet the requirements.

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