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EXPERIMENTAL APPLICATION OF WASTE BLEACHING CLAYS IN THE PRODUCTION OF CONSTRUCTION MATERIALS FOR CIVIL INFRASTRUCTURES

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Contents

List of publications

This doctoral dissertation consists of a summary of the following publications, referred to the research project "Experimental application of Waste Bleaching Clays in the production of construction for Civil Infrastructures". The numeration of the papers follows the order of the activities in the research program.

1. Sangiorgi C., Tataranni P., Mazzotta F., Simone A., Vignali V. and Lantieri C. "Alternative Fillers for the Production of Bituminous Mixtures: A Screening Investigation on Waste Powders". Coatings, 2017, 7, 76.
2. Sangiorgi C., Tataranni P., Simone A., Vignali V., Lantieri C. and Dondi, G. "Assessment of waste bleaching clay as alternative filler for the production of porous asphalts". *Construction and Building Materials*, 2016, 109, 1–7.
3. Tataranni P., Besemer G.M., Bortolotti V. and Sangiorgi C. "Preliminary Research on the Physical and Mechanical Properties of Alternative Lightweight Aggregates Produced by Alkali-Activation of Waste Powders". *Materials*, 2018, 11, 1255.
4. Tataranni P. and Sangiorgi C. "Experimental application of synthetic lightweight aggregate for the production of special asphalt concretes". Accepted paper in *Sustainable Materials, Systems and Structure Conference 2019*, Rovinj, Croatia, 18 – 22 March 2019.

Introduction

The Italian road infrastructures system consists mainly in roads built in the last 30 years, which today are not able to guarantee the functional properties for which they were designed [1-3]. This is due to the increasing traffic volume that was registered in the last years, which is not combined to an adequate improvement of the infrastructures maintenance level. Moreover, due to the recent recession, administrations and road managing operators possess a lower and lower budget for the restoration of the infrastructure system. As results, most of the roads are close to the end of their service life, compromising the level of comfort and safety for users.

The improvement of the road infrastructure system cannot be separated from the reduction of costs related to their construction and maintenance. In the last years, many studies and researches have been conducted on the use of designing solutions and construction technologies able to reduce both these aspects [4-6]. It is necessary to identify alternative solutions, able to increase the profitability of the budgets prepared for the interventions on the roadway system: the recycling of waste materials represents one of these possibilities.

In Italy, as well as in the whole Europe, the production of wastes has progressively increased, as the direct consequence of the economic progress and the increased consumptions. The generated effect has a significant influence on the environment and on the population [7]. The field of civil engineering is not beyond this rapid increasing in consumptions as well. According to the Communication from the European Commission named “Resource Efficiency Opportunities in the Building Sector”, in the EU the building industry is responsible for about half of the extracted raw materials and the energy consumption, as well as about a third of the water consumption. There are also all the indirect effects on the environment generated by the building's life-cycle, including the manufacturing of construction products, building construction, use, renovation and the management of wastes [8-10].

It is obvious that in a modern society, all these direct and indirect impacts on the environment and on the population are no more acceptable. Issues like sustainable development and use of renewable resources are today topical subject. The direct effect is the promotion of policies to encourage the reduction of costs and consumptions related to the construction and maintenance of civil infrastructures [11]. The use of resources is mainly related to the design solutions, including the choice of building materials and working technologies. Furthermore, the construction and maintenance operations of civil infrastructures lead to the production of remarkable quantities of refuses, named Construction and Demolition wastes (C&D) [12-14]. According to the European Union, in this category fall every waste which is included in the NACE code F (construction sector): mainly road by-products, crushed concrete, tiles, ceramic, bricks, glass and wood. It is worth noting that almost 90 % of C&D wastes can be recycled and reused, since they are inert and non-hazardous. The reintroduction of these wastes in the production cycles of new constructions is the challenge for engineers and researchers. According to the Directive 2008/98/EC, the target proposed by EU is to increase the recycling of C&D wastes to 70 % by 2020.

However, the demand for new infrastructures has rapidly grown especially in high-density regions and new developing countries, combined with the simultaneous current deficiency in natural resources to build and maintain them [15]. From this prospective, the reuse and recycling of only C&D wastes as construction materials is just part of the solution for a sustainable development and for the decreasing of the life cycle costs connected to building sector [16]. For this reason, in the last decade it has been registered a growing interest for wastes and industrial-by products, not directly related to civil engineering field, suitable for the production of innovative and sustainable construction materials [17-19]. Today there are many examples of the success of industrial waste recycling in civil engineering applications. Coal fly ash, blast furnace slag and silica fumes are the most widespread wastes used all over the world as construction materials [20]. The technological evolution and the growing interest in recycling have gradually allowed the increasing in the quantities of wastes used as well as the treatment of hazardous trashes for their applications in infrastructures construction [21-23]. The recycling of these waste materials is a mean to improve the efficient and conscious usage of resources and to avoid the negative impacts connected to the use of raw materials and not-renewable resources [24]. The aim is to create an ideal and virtuous life cycle for the infrastructure system, in which the by-products and wastes from one construction should be able to serve as resource for another new construction [25-26].

In the light of the above, the present work shows a laboratory study on the application of a waste digested bleaching clay for the production of materials within the civil infrastructures field. The final aim of the project is to give scientific evidence of the use of this industrial-by product as construction material. Still, to combine the dual effect of reducing the quantities of material disposed to landfill with the definition of a functional intended use for this waste. The possible positive outcomes are also related to the reduction of costs, both environmental and economic, connected to the landfilling of this waste material.

1. Objective and Background

The present research is financed by Unigrà Srl, which is a food company founded in the 1970s in Conselice (Ravenna, Italy). Unigrà is in the business of transforming and selling oils and fats, margarine and semi-processed products to produce food, especially confectionery. Over the years, the company has developed its mission to produce top quality primary ingredients, semi-finished and finished products for all the channels in the sector: industrial, artisanal, retail and Ho.Re.Ca. (Hotellerie-Restaurant-Café).

The objective of the research is the analysis and the evaluation of the possible application of a waste digested bleaching clay as construction material. The project covers the different fields related to civil infrastructures, to find a functional intended use for this waste. It is worth noting that the idea, which is basic for the project, is that the reuse and recycling of this waste material could be effective only through the promotion of its application. Under this point-of-view, the use of the industrial-by product as construction material is not considered a simple alternative to the landfilling, having a specific function in its final application able to confer quality to the waste. The final aim is to give scientific evidence on the use of the waste bleaching clay as construction material through the laboratory validation of its applications in several products related to the civil infrastructures field.

1.1. Bleaching Clay

The bleaching clays are hydrous aluminium silicates containing small parts of Mg, Ca, and Fe. They are similar to traditional clays but more hydrated. The main property of bleaching clays is the capability of absorbing coloured impurities from mineral, vegetable and animal oils, and from other liquids.

Bleaching clays are generally divided into Bentonite clays, which are active only after a chemical treatment, and Floridinic ones, whose activity is due to their natural state [27]. The decolouring power of these silicates is related to the high inner surface and to the porosity of their particles. The most common type of bentonite is the so-called Fuller's Earth, which is widely adopted as absorbents for oil, grease, and animal wastes, as well as a carrier for pesticides and fertilizers. Their applications is generally preceded by the drying, grinding and sieving operations and the absorbing properties are sometimes enhanced by a slight acid treatment. Among the other natural bleaching clays, the magnesium silicate is widely used thanks to its porosity and lightweight. The activated bleaching clays instead are produced from traditional bentonite earth rich in montmorillonite, which are subject to a chemical treatment to modify the clay and to confer a high bleaching activity.

Both natural and activated bleaching clays are especially used in the mineral oil industry, as a bleaching, neutralizing and stabilizing agent, but several applications are known from the food to the pharmaceutic sectors. The most widespread bleaching clay is the bentonite.

The Bentonite is an absorbent aluminium phyllosilicate clay rich in montmorillonite, named by Wilbur C. Knight in 1898 during the study of Benton Shale, a geologic site formed after Cretaceous in Wyoming. In the bentonite, the presence of montmorillonite is generally associated to other clay mineral (kaolinite) or quartz and feldspar. The presence or absence of these minerals can influence the quality of bentonite and makes it more or less suitable for specific applications. The different kinds of bentonite are named based on the respective dominant element, such as potassium, sodium, aluminium and calcium. However, for industrial purposes, sodium or calcium bentonite are used. The main property of this material is to absorb liquid by swelling, but not every bentonite has the same absorbing property [28]. The hydration level and the swelling capability depend on the crystalline lamellae surfaces and on the repulsive osmotic forces, for which the lamellae are forced to detach each other opening according to an "accordion" structure.

Thanks to his specific properties, the fields of application of this material are various and different. Today the following sectors foresee the use of bentonite:

- Foundry: bentonite is widely used as a foundry-sand bond in iron and steel factories. It acts as a binder for the production of high quality casting in iron, steel and non-ferrous foundries.
- Civil engineering: in geotechnical applications, the bentonite is used as drilling fluid to lubricate and cool the cutting tools, to remove excavated materials, and to help prevent blowouts. The bentonite is common in oil drilling, during the excavations operations for water wells and in tunnel and mini-tunnel drilling. The properties of the bentonite make it suitable for self-hardening mixtures used for plastic diaphragms, clogging mortars and soil injections.
- Water treatment: thanks to its ion-exchange capacity, flocculation and sedimentation, bentonite is common in water treatment as an auxiliary of polyelectrolytes and inorganic flocculants.
- Agriculture: given the high ion-exchange capacity, bentonite is traditionally used in soil conditioning. The material is also able to absorb moisture in garden soils as well as to be a vehicle for pesticides and herbicides.
- Ceramic: Bentonite, in small percentages, is used as an ingredient in commercially designed clay bodies and ceramic glazes. Its application improve the working qualities of bodies, with positive outcomes in terms of increase in the mechanical properties of the final product.

- Food industry: thanks to his absorbing properties, bentonite is widely adopted for the decolouring process of vegetable oils and fats. The material has the capability of adsorbing considerably amounts of protein molecules from aqueous solutions. For this reason, the bentonite represents the most widespread system to remove the surplus of protein from wine in the process of winemaking.

1.2. Waste Bleaching Clay

The bleaching clay used in the present research is a waste that comes from two consecutives industrial processes to whom the bentonite clay is subject. The first is related to the decolouring oils process, while the latter is an anaerobic digestion process for the production of biogas. At the end of these two stages, the bleaching clay has a residual oils content up to 2 % on its dried weight and is currently landfilled (CER code n. 020399).

The industrial processes to which the bleaching clay is subject are described below.

Oils decolouring process

The term “refinement” refers to all the industrial processes that lead to the elimination of all the undesired substances from the product, in order to obtain a better oil quality, without changing the composition and the structure of the product. The decolouring process is effectively a refinement treatment.

The purpose of the discoloration is to eliminate substances that cause unwanted colourings of the oils. It can be carried out using both physical and chemical methods: in the oil and fat technology, the physical method is applied with adsorbent materials. These materials are of two types, namely bleaching clay and activated carbon. The first is the material used in the decolouring plant in Unigrà s.r.l. The bleaching clay acts as a filler: the voids between the particles and their porosity allow catching the oil, which is than retained during the process. Regardless of how the discoloration system is made, the process foresees for a vacuum drying of the oil at about 60 °C, the mixing of oil and bleaching clays, a heating period (around 30 minutes at 90-110 °C) and then the filtration with the recovery of the oil retained by the bleaching clay. The separation between oil and bleaching clay is made through discontinuous leaf filters equipped with accessories that allow the cleaning of the panels and the ejecting of the clays by mechanical shaking.

Anaerobic digestion and production of biogas

The anaerobic digestion is a biochemical conversion process that occurs in the absence of oxygen and consists in the demolition of complex organic substances (lipids, proteins, carbohydrates), for the production of biogas. The materials used for the process are traditionally animal dejections, civil wastes, food wastes and the organic fraction of municipal solid wastes. The biogas consists of 50-70 % of methane and the remaining mainly of CO_2, having an average Low Heating Value (LHV) around 23.000 kJ per cubic meter. Generally, the produced biogas is collected, dried, compressed and stored. It can be used as fuel for powering gas boilers, for combined cycle power plants or internal combustion engines.

In the Unigrà s.r.l. factory there is an anaerobic digestion plant with a cogeneration system, consisting of an endothermic engine, able to use biogas as fuel to produce electrical and thermal energy. The digestion system is powered by the remains deriving from the activity of the food industry, still rich in fats, suitably diluted with wastewater coming from the production departments and rich in nutrients, such as phosphorus and nitrogen. The plant is powered automatically by a system that mix the liquid part, accumulated in a special tank, and the solid compound, consisting of the exhausted bleaching clay. The power supply of the digester is of about 11 m^3/h. The tank, which has a volume of 500 m^3, performs the function of mixing, homogenizing and heating the incoming liquids. An automatic pump introduces the compounds into the intermediate layer of the tank, excluding air from outside. The incoming quantities are controlled by an automatic plant management system based on the progress of the fermentation process and the production of biogas.

The proper functioning of the digestion process is ensured by the continuous control of pH and temperature conditions and guaranteeing the correct presence of the necessary nutrients (nitrogen and phosphorus). In these conditions, a bacterial flora develops and, feeding on the organic substrate present, originates a biogas stream. There is a self-regulating dosing apparatus for each additive, which automatically plays in order to keep constant these conditions.

The digestion phase takes place in closed tanks where the material is kept perfectly mixed through an appropriate mechanical stirring system. The process consists of a series of biological reactions carried out by specialized bacteria, which are generated spontaneously according to the present substrate. The plant consists of two twin digesters, operating in parallel, with a volume of 3.500 m^3 each. The outgoing mud is collected and conveyed to the thickening and dehydration section, while the produced biogas is transmitted to a possible gasometer or directly to the gas treatment section. The production of biogas is about 10.000 m^3/day, corresponding to about 3,5 million m^3/year.

Before being used, the biogas undergoes a drying treatment, in order to remove the residual moisture content. Once treated, it is conveyed through stainless steel pipes to the engine group to be used as fuel for the production of electricity. The cogeneration plant consists of an endothermic engine coupled to an alternator, which is capable of delivering an electrical output of 999 kW. The production of electricity at full capacity is equal to 24.000 kWh/day.

The last section of the plant concerns the treatment of the waste mud produced by the digester, the so-called digested bleaching clay. This waste material is sent from the digester to a solid-liquid separation treatment operated by a centrifugal separator. The outgoing liquid is then convoyed to the company's wastewater treatment plant, while the solid fraction resulting from the thickening (centrifugation) is sent as waste to disposal at the internal landfill. The waste digested bleaching clay at this stage has a residual oil content up to 1 % on its dried weight.

A block diagram of the whole plant is represented in Figure 1.1.

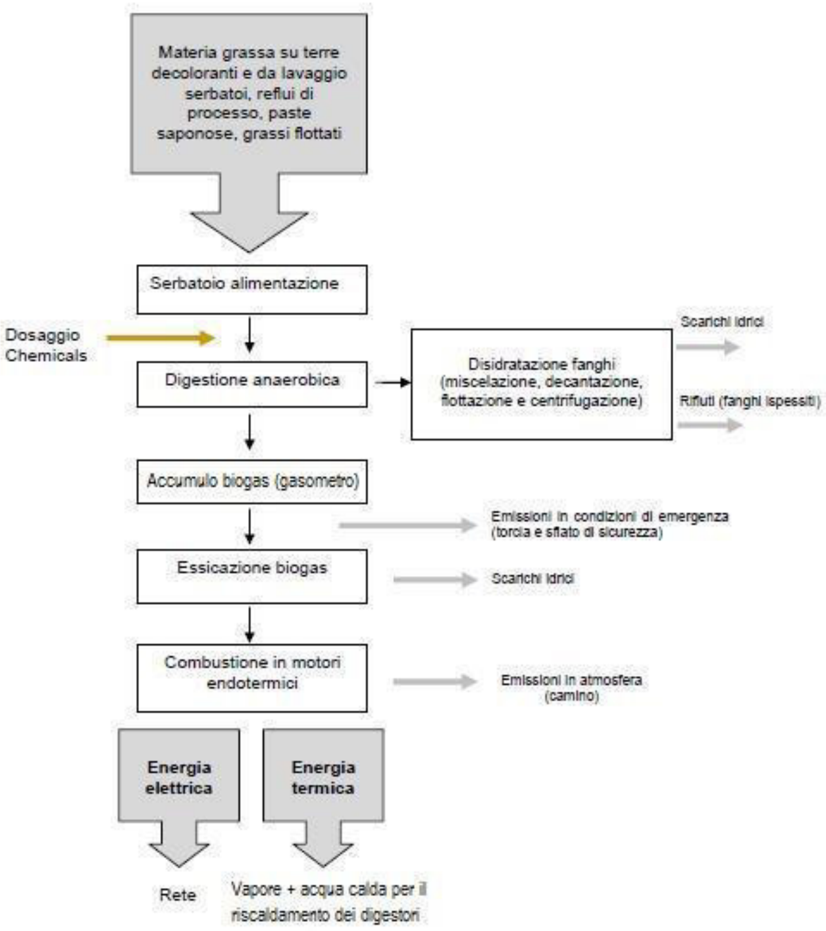

Figure 1.1. Block diagram of the digester plant.

Before being used in the current research, the waste digested bleaching clay was subject to specific heating treatments in relation to its final application with the purpose of eliminating the moisture content.

2. Research Program

The research project was developed in continuity with the preliminary study carried out by the principal investigator in 2014, related to the application of waste bleaching clays within bituminous mixtures. Following the positive preliminary outcomes of the study, the idea that is the basis of the new project is to extend the application of this waste to other applications related to civil infrastructures. Furthermore, the project foresees the use of waste bleaching clays not only in the form of filler for the production of construction materials, but also according to new innovative technologies.

The potential fields of application of this waste in the civil engineering sector can be classified on the basis of its function within the different final products. Figure 2.1 shows the functions that the project has focused on and it foresees the application of waste bleaching clays as filler for mixtures, matrix for synthetic aggregates and precast elements, binder for synthetic mixtures.

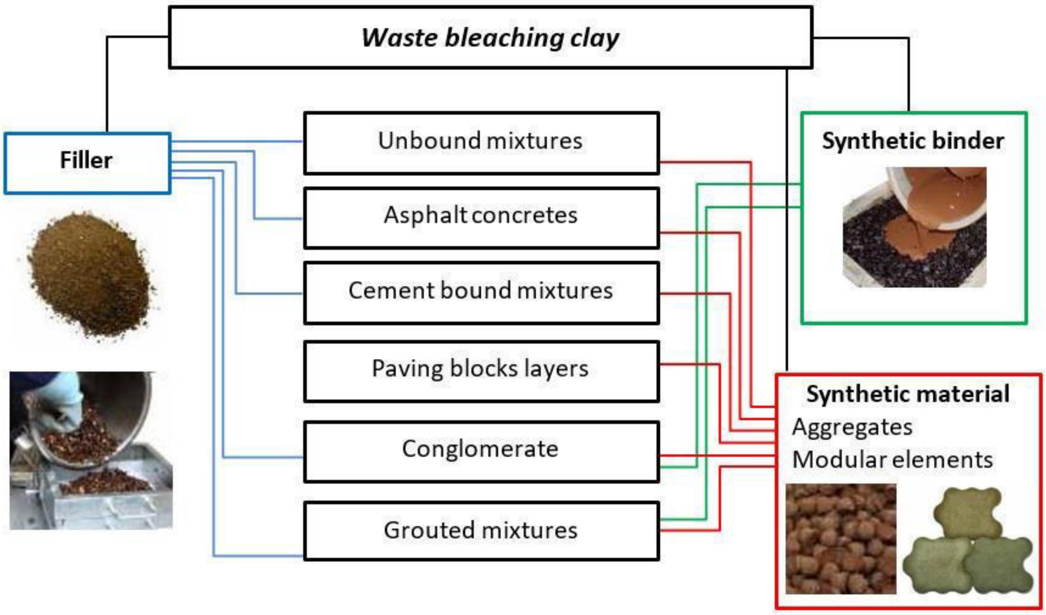

Figure 2.1. Fields of application of waste bleaching clay within the project.

Furthermore, as highlighted in the figure, the project is rich in interconnections and parallel applications. In the light of the above, the research program was divided in macro-activities, each of which is focused in one or more group of applications of the waste bleaching clay. In every activity, the validation of the possible experimental application is given through a full laboratory characterization. Specific tests evaluated the mechanical properties, the durability and, in general, the compliance with the requirements imposed by the most common technical specifications for building materials.

The research program can be divided in the following four activities:

1. Preliminary characterization of the physical, chemical and mechanical properties of the waste digested bleaching clay;
2. Experimental application of waste digested bleaching clay as filler for the production of Asphalt Concretes;
3. Experimental application of waste digested bleaching clay as filler for the production of Cement Bound Mixtures;
4. Experimental application of waste digested bleaching clay for the production of synthetic material for civil infrastructure.

Activity 1: Material characterization.

The knowledge of the basic properties of the waste material is fundamental for the following studies of its possible applications. Taking as a reference the EN 13043 standard that specifies the requirement for fillers suitable for construction material, a complete characterization of the waste material was carried out.

Activity 2: Asphalt concrete.

Once defined the properties of the waste bleaching clay, the first application is related to its use as filler for the production of a porous asphalt concrete. The evaluation of this possible application is given through a laboratory characterization. Taking as a reference some technical specifications for porous asphalt mixtures, the research activity was based on tests in compliance with the EN 12697 standard.

Activity 3: Cement bound mixture

The third application is related to hydraulically bound mixture for the construction of foundations or base layers in a traditional road section. In this case, two type of mixtures were prepared, with or without recycled aggregates. The laboratory evaluation is based on tests required from the most widespread technical specification for this type of mixtures, in compliance with the EN 13286 standard.

Activity 4: Synthetic materials

The last activity is related to the use of the waste bleaching clays for the production of synthetic materials. This represents the most wide and transversal activity, involving several different applications which range in the fields of civil infrastructures. The common factor is the technology used for the production of the materials, which is the alkali-activation.

It is worth noting that a unique and homogenous sampling of waste digested bleaching clay was carried out in order to have constant and comparable results. Before being used in the different applications, the waste was dried to eliminate the high moisture content due to landfilling. The material have been stored in the laboratory during the whole research project.

In the following chapters, each activity will be specified, as a wide summary and an overview of the works shown in the annex related papers.

3. Activity 1: Characterization of the Waste Bleaching Clay

The first activity foresaw a detailed laboratory characterization of the waste bleaching clay. The knowledge of its physical, chemical and mechanical properties is fundamental for the following experimental applications.

The research program is organized according to several tests suggested by the reference European standards and basic for the characterization of construction materials. Moreover, some specific tests were carried out to assess the chemical composition of the waste and its possible leaching properties. The following results here shown are related to the paper "Alternative Fillers for the Production of Bituminous Mixtures: A Screening Investigation on Waste Powders" by C. Sangiorgi, P. Tataranni, F. Mazzotta, A. Simone, V. Vignali and C. Lantieri in Coatings (2017, 7, 76) annex in the present thesis.

3.1. Experimental program

The research program is organised in several tests in compliance with the EN 13043 standard, which specifies the required properties of materials to be classified as aggregates for road constructions. In the case under examination, all the tests are referred to the characterization of the material as filler. It is worth noting that the aforementioned standard indicates some limits for each test, but there are not restrictions for fillers that are not in line with the suggested values. The only obligation refers to filler producers, which are obliged to highlight the uncommon values in the technical sheet of the product during the CE marking process.

The experimental program includes the following tests:

- Size distribution (EN 933-10, ISO 13320);
- Water content (EN 1097-5);
- Particle density (EN 1097-7);
- Voids of dry compacted filler (EN 1097-4);
- Variation in "Ring and Ball" temperature (EN 13179-1);
- Harmful fines (EN 933-9);
- Water solubility (EN 1744-1);
- EDS Chemical composition;
- Leaching test (EN 12457-2) and pH evaluation.

In the following paragraph the tests procedure are described and the related outcome are commented.

3.2. Size distribution analysis (EN 933-10, ISO 13320)

The evaluation of the geometrical properties of aggregates and filler are fundamental to define a correct mix design for the final mixture. The EN 933-1 standard describes the particle size distribution test procedure and, specifically for fillers, it refers to EN 933-10 standard.

The test consists of dividing and separating, by means of a series of sieves, a filler aggregate into several granular classifications of decreasing sizes. The dimension of sizes and the number of sieves are reported in specific tables. The mass of the particles passing each sieve is related to the initial mass of the material.

As general requirement for fillers added within the mixture, the EN 13043 standard specifies that the 100 % of material must pass the 2 mm sieve. Still, the percentage of passing material at 0,125 mm should range between 85 and 100 % and between 70 and 100 % to 0,063 mm sieve. On the basis of the particle size distribution, each filler is classified in a specific category.

Furthermore, considering the presence of 100 % material passing the 0,063 mm sieve, the particle size distribution of the waste bleaching clay was assessed by the means of the laser diffraction method (ISO13320). This is a widespread used technology for the study of materials ranging from hundreds of nanometres up to several millimetres in size. According to this method, the particle size distributions is evaluated by measuring the angular variation in intensity of light scattered as a laser beam passes through the particles of a dispersed sample. The angles of scattered light on particles vary in relation to their dimensions. The angular scattering intensity data is analysed to calculate the size of the particles, which is then represented as a volume equivalent sphere diameter.

3.3. Water content (EN 1097-5)

The EN 1097-5 standard specifies a method to determine the water content of a filler by drying the material into a ventilated oven. The result is a direct indication of the total mass of free water within the filler. Moisture can come from the surface of the particles themselves or from their accessible pores.

According to the test procedure, the water content is determined as the difference between the humid mass and the dried mass, and it is expressed as a percentage on the last one. The standard considers the dried weight as the constant mass of the dried sample, measured after successive weighing. The drying of the test sample is given by placing the material into a ventilated oven (110 °C).

The results should be declared in accordance with the relevant category specified in EN 13043 standard, according to the particular application or end use.

3.4. Particle density (EN 1097-7)

The EN 1097-7 standard specifies a method to determine the particle density of filler according to the pyknometer method. This is a well-known method to calculate the volume of samples with irregular volume. The principle is based on the replacement of a specific amount of liquid of known density with the test sample. A pyknometer with known volume, containing the test sample, is than filled with the liquid. The volume of this liquid is calculated by dividing the mass of the liquid added by the liquid density. The volume of the test portion is then calculated by subtraction of this volume from the pyknometer volume.

In the case under study, the test portion, with a minimum mass of 50 g and complying with EN 932-2, was oven-dried at around 110 °C until reaching a constant mass and then left drying for at least 90 min. This operation means that the filler can be checked for lumps. The dry filler is then sieved through a 0,125 mm mesh and the fraction passing the sieve evaluated. The material is then inserted into the pyknometer that, after being weighted, is filled with liquid and weighed again (Figure 3.1).

Figure 3.1. Pyknometer filled with water (left) and with material (right).

3.5. Voids of dry compacted filler (EN 1097-4)

The voids of dry compacted filler (Rigden Voids) is one of the most important properties of filler suitable for bituminous applications. This porosity is considered as the space in the bulk material that is filled with air, indicated as a percentage of total volume of the filler, after compaction using a specific method indicated by the EN 1097-4 standard. The intergranular porosity directly affect the absorption properties of the filler, hence it is a basic parameter that must be considered for the mix design of an asphalt concrete. The higher the RV value is, the more the filler will absorb the bitumen. Thus, it is considered as an indicator of the stiffening power that the filler exercises on the bituminous mastic. Indeed, it is possible to consider a quota of bitumen “fixed” in the voids between the filler particles and another part of “free” bitumen, which is the binder that remains after the intergranular voids are filled.

The amount of “free” bitumen is an important parameter that helps in the characterization of the rheology behavior of the mixture. It is today well known that a low value of filler porosity corresponds to lower rigidity in the mastic, since the filler particles are no longer in close contact, and every addition of binder acts as lubrication between the particles themselves. On the contrary, a high number of voids determine a greater amount of adsorbed bitumen, strengthening the bitumen-filler link and, in other words, reducing the quantity of excess bitumen.

The EN 1097-4 foresees the use of the Rigden compactor to carry out the test. The apparatus is filled with a specific quantity of material and compacted through 100 blows with a piston. After the compaction, the final height of the compacted filler is registered. Based on the dimensions and weights of the Rigden compactor and the particle density of the material, the RV values are calculated. The results should be declared in accordance with the relevant category specified in the EN 13043 standard, according to the particular application or end use.

3.6. Variation in “Ring and Ball” temperature (EN 13179-1)

Considering the great influence of filler on the rheological and mechanical properties of bituminous mixtures, the EN 13043 standard indicates the variation in “Ring and Ball” temperature, for the evaluation of the interaction bitumen-filler.

Using the test set out in the EN 13179-1 standard, it is possible to assess the level of interaction of these two components on the basis of the variation in the softening point of the binder. A bituminous mastic is formed with 62,5 % of binder and 37,5 % of filler (percentages on the volume of the mastic) (Figure 3.2).

Figure 3.2. Bitumen samples with and without filler (left) and test apparatus (right).

The traditional procedure is applied for the evaluation of the softening point, by placing the bituminous samples on the top of a specific ring and applying a determined steel sphere on it. The Ring and Ball value is measured as the temperature needed to soften the binder, allowing the sphere to touch a metal plate placed underneath at a distance of 25 (±0.4) mm. The difference between the normal softening point and the one measured for the bitumen mixed with filler is the Ring and Ball delta.

3.7. Harmful fines (EN 933-9)

The harmful fines test is needed to evaluate the quantity of swelling clay within the filler through the Methylene Blue test, in compliance with the EN 933-9. The presence of clay trace could have a detrimental effect on the mechanical properties of the filler since it affects its behaviour in the presence of water.

The test described in the EN 933-9 standard consists of adding drops of methylene blue at a concentration of 10 g/l at regular intervals to a suspension of filler in water. The purpose of the test is to examine whether there are fine particles within the filler. Fine fraction, composed mainly of hydrated aluminosilicate clay minerals, absorbs the methylene blue solution (a cationic dye) in an aqueous solution, because of the superficial loads involved and its cation-exchange capacity. The quantity of methylene blue absorbed by the filler that is observed during the test increases proportionally to the quantity of fine particles present in the sample.

Every time that the drops are added, the suspension is checked for any free, non-absorbed blue colouring. Its relative amount is quantified by observing the stain and halo produced on the filter paper. On the basis of the volume of blue liquid absorbed by the test fraction and its weight, the Methylene Blue Value (MBV) is calculated.

In Figure 3.3 the mixing and detection operation are shown.

Figure 3.3. Methylene Blue is added to the test portion (left) and results detection (right).

According to the MBV, the filler is classified in a specific category. If the value of liquid absorbed exceeds 25 g/kg, the MBV must be declared in the technical sheet of the filler.

3.8. Water solubility (EN 1744-1)

The water solubility test represents one of the most important test for the evaluation of the chemical properties of the filler. Water solubility is a measure of the amount of chemical substance that can dissolve in water at a specific temperature. The level of water solubility of a filler has relevant influence on its application as construction material.

According the EN 1744-1 the water solubility of the test portion of material is determined by extracting the previously dried and weighed filler with a quota of water equal to around fifty times the mass of the filler itself. If the examined filler contain calcium hydroxide trace, its content must be evaluated in compliance with the EN 459-2. The waste digested bleaching clay is devoid of this inorganic compound, as shown forward in the chemical analysis paragraph. Hence, in compliance with the EN 1744-1, the water solubility is determined using the standard procedure.

According to this process, two glass bottles are filled with a fixed amount of dried material and a mass of distilled water equal to fifty times the mass of filler contained in the bottle. A glass rod is placed in the bottles, which are then sealed (Figure 3.4). They are placed in a mechanical shaking device with rollers for at least 24 hours, so the mixing is continuous and the filler cannot form sediment. After mixing, as much liquid as possible is filtered, using a funnel and some filter papers of suitable porosity and known mass. The bottles and the filter paper, with their respective contents, are placed in an oven until the solid residue, once dried, reaches a constant mass. The ratio between the mass of the filler before and after the extraction is the water solubility value.

Figure 3.4. Bottles sealed with liquid, material and glass rods.

The filler is classified in specific class according to the results. The EN 13043 suggests a value of solubility in water up to 10%. If the obtained values exceed the reference threshold, the actual solubility in water should be declared in the technical sheet of the filler.

3.9. EDS Chemical composition

The chemical characterization of a filler has a relevant role in the analysis of the material since it could affect the final properties of the mixture, especially the interaction between filler and bitumen. In the case under examination the study of the chemical composition is needed, being the material tested a waste.

The chemical analysis of the waste digested bleaching clay was given by a Scanning Electron Microscope (SEM), which is an electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons (Figure 3.5). This microscope is used for the X-ray microanalysis according to an analytical technique used for the chemical characterization that is called Energy-dispersive X-ray Spectroscopy (EDS).

Figure 3.5. Scanning Electron Microscope used for chemical analysis.

It relies on the interaction of a source of X-ray excitation and a sample. The fundamental principle of EDS is that each element has its own atomic structure, which generates a unique set of peaks on its electromagnetic emission spectrum. The X-ray spectrum is emitted by a specimen bombarded with a specific beam of electrons. The level of energy of the X-rays emitted is measured by a spectrometer, which allows the identification of the elements that compose the material.

3.10. Leaching test (EN 12457-2) and pH evaluation.

The chemical composition is not the only information needed to evaluate the possible use of a waste or by-product for new applications. Considering the currently landfilling of the waste bleaching clay, its reuse and recycling cannot be contemplated without a specific study of its leaching properties, to assess if harmful substances may then enter the environment.

Leaching tests were carried out in order to have information about the constituent concentration and constituent release from the waste material under specific conditions. According to these tests, soluble constituents of material are removed by liquid passing through. Leaching tests can be classified into two categories on the basis of whether the leachant is renewed: extraction tests and dynamic tests. The former does not consider a leachant renewal, the latter do.

In the case under examination, the leaching tests were carried out in compliance with the EN 12457-2 standard, according to a procedure which is defined "one stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm". It is considered as a basic characterization test, used to obtain information on the short and long-term leaching behaviour and on the characteristic properties of the waste. In these tests the liquid-solid ratios, the composition of the leaching agent, the factors controlling the leaching, such as pH, redox potential, complexing capacity and physical parameters are treated.

3.11. Analysis of Results.

The results of the chemical, physical and mechanical characterization are presented in Table 3.1, while the laser grain size distribution is shown in Figure 3.6.

Test	Unit	Value
Size distribution (EN 933-10)	%	100 P63
Water content (EN 1097-5)	g	4,65
Particle density (EN 1097-7)	Mg/m^3	1,86
Voids of dry compacted filler (EN 1097-4)	%	53,9
Variation in "Ring and Ball" temperature (EN 13179-1)	°C	32,0
Harmful fines (EN 933-9)	g MB/kg Filler	33,3
Water solubility (EN 1744-1)	%	14,84

Table 3.1. Waste digested bleaching clay properties.

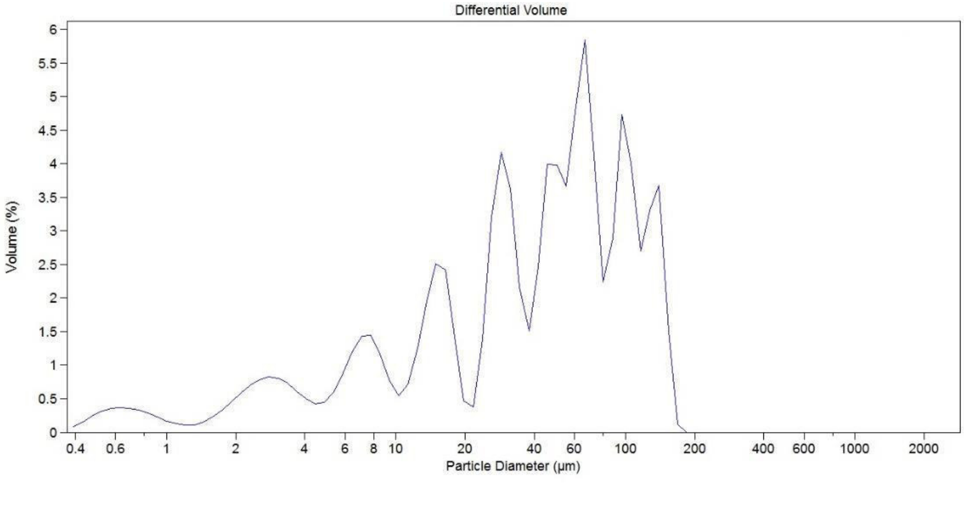

Figure 3.6. Laser particle size distribution analysis.

In terms of particle size distribution, the waste bleaching clay is 100 % passing the 0,063 mm sieve, and according to the EN 13043 standard, the material could be classified as filler by its geometrical properties. Moreover, according to the laser method, the 100 % of material is below 200 μm and around 40 % is below 50 μm. In terms of water content, the value exceed the 1 % suggested by the standard for fillers. The limestone filler, which is the most widespread filler for bituminous mixture has a water content up to 0,8 %. This result is mainly due to the high specific area of the waste digested bleaching clay particles. The particle density of the material is due to its chemical and mineralogical composition, for this reason there are not suggested values for fillers within the EN 13043 standard. In wider terms, the waste digested bleaching clay can be classified as “low density” material if compared to other fillers used for construction materials (2,70 Mg/m^3 for limestone, 2,72 Mg/m^3 for hydraulic lime, 3,29 Mg/m^3 for Portland cement and 2,87 Mg/m^3 for basaltic filler). As for the Rigden voids, the waste digested bleaching clay has a high content of intergranular porosity. According to the EN 13043 standard, it can be classified in the V44/55 class, which is the highest class in terms of Rigden Voids. Values over this limit must be highlighted in the technical sheet of the product and, above all, could have a detrimental effect on the bituminous mixture. The variation in the softening point of the binder is significantly high if compared to reference values for limestone filler (8,0 °C) and this is mainly due to the rich intergranular porosity. Both the harmful fines and the water solubility values are a direct consequence of the chemical composition of the waste material. Being the bentonite an aluminium phyllosilicate consisting mostly of montmorillonite, some trace of clay remain despite the undergone treatments until the landfilling.

The chemical composition in terms of un-normalized concentration in weight percent of the element (unn. C), normalized concentration (norm. C) and atomic concentration in atomic weight percentage (atom. C) of the waste bleaching clay are presented in Table 3.2.

Element	unn. C. (wt %)	norm. C. (wt %)	atom. C. (at %)
O	34,41	48,01	63,06
Na	0,87	1,21	1,11
Mg	3,42	4,77	4,13
Al	5,13	7,16	5,57
Si	20,51	28,61	21,41
P	0,29	0,4	0,27
S	0,58	0,81	0,53
K	0,67	0,94	0,51
Ca	1,56	2,17	1,14
Ti	0,45	0,62	0,27
Fe	3,79	5,29	1,99

Table 3.2. Chemical composition of waste digested bleaching clay by EDS method.

Table 3.3 shows instead the results of the leaching test.

Element	Unit	Value
Nitrate	mg/l	0,906
Fluoride	mg/l	3,247
Sulphate	mg/l	81,832
Chloride	mg/l	18,405
Cyanide	μg/l	< 20
Barium	mg/l	0,056
Copper	mg/l	0,021
Zinc	mg/l	0,005
Beryllium	μg/l	0,1
Cobalt	μg/l	6,15
Nickel	μg/l	144,2
Vanadium	μg/l	30,95
Arsenic	μg/l	40,28
Cadmium	μg/l	< 0,1
Chromo	μg/l	2,94
Plumb	μg/l	0,18
Selenium	μg/l	0,4
Mercury	μg/l	0,7
pH	unit pH	7,5

Table 3.3. Leaching test results and pH value.

From the chemical composition of the waste, it is evident that the material is rich in Silicon and Oxygen. Furthermore, from the analysis in terms of percentage in weight of their oxides presented in the annex paper, it can be observed that silicon dioxide (SiO_2) is the main component of the recycled filler (43,8 %).

From the analysis of the leaching properties, there are no relevant values in terms of environmentally harmful concentrations. However, being different the possible intended uses for this waste, the compliance with limits imposed by standards and laws for environmental protection must be verified for each possible application.

3.12. Conclusions

In terms of geometrical properties, the material is characterized by a very fine size distribution of grains and, as verified in different researches, it can affect the mechanical properties of the bituminous mastics. Furthermore, the effect of the high specific area of the particles, if compared to traditional fillers, must be related to the mechanical properties of the waste. The results of the Rigden Voids test show indeed a high number of intergranular voids for the waste digested bleaching clay. This value, as well as the specific area, are significant in determining the physical and mechanical properties of the bituminous mixture, since it affects the filler's ability to fix the bitumen. This phenomenon could be related to the rise in the softening point of the mastic formed by bitumen and waste bleaching clay (delta Ring and Ball temperature test).

The chemical properties of the waste bleaching clay are clearly influenced by its initial chemical composition, being the bentonite made mostly of montmorillonite. Some traces of clay are detected with the methylene blue test and the water solubility test, both with values that exceed the limit suggested by the EN 13043 standard. However, EDS results highlighted the presence of oxide calcium (CaO) compounds which, according to several studies, could have a positive effect increasing the filler-bitumen interaction. As for the leaching properties, no alarming value has been detected. However, the possible use of this waste must be verified in compliance with the legislation related to its final application.

The chemical, mechanical and physical characterization of the waste digested bleaching clay highlighted that this material can be considered as a filler for construction materials. However, some properties of this waste are not in line with the traditional values given by the EN 13043 standard. In the light of the above, the application of this waste as filler for bituminous mixtures could need a specific mix design and above all a detailed characterization of the final bituminous mastic and mixture.

4. Activity 2: Experimental application of Waste Bleaching Clay as filler for the production of Asphalt Concretes

The second activity is related to the experimental application of the waste material as filler for the production of bituminous mixtures. The adopted asphalt concrete is a porous asphalt mixture. This activity follows the outcomes obtained from a 2014 research, in which the author experienced the substitution of limestone filler with the waste bleaching clay within an asphalt concrete for binder layers. The following results here shown are related to the paper "Assessment of waste bleaching clay as alternative filler for the production of porous asphalts" by C. Sangiorgi, P. Tataranni, A. Simone, V. Vignali, C. Lantieri and G. Dondi in Construction and Building Materials (2016, 109, 1-7) annex to the present thesis.

4.1. The filler within Asphalt Concretes

Traditionally, Asphalt Concretes (ACs) contain two main components: aggregates and bituminous binders. While the aggregates act as a lithic skeleton for the material, bitumen acts as a binder for all the elements in the mixture [31, 32]. In more detail, the fraction of aggregates passing through a 63 µm sieve, together with the mineral filler, which is added to the mixture during ACs production, are combined with the binder to form a bituminous mastic. The resulting mastic is capable of affecting the physical and mechanical properties of the mixture to a considerable degree [33].

It follows that the presence of fillers plays a fundamental role in the production of bituminous mixtures, both in terms of mix design and for the physical-mechanical characteristics of the mixture. However, despite its very wide use in the production of ACs, a classification of all the functions performed by the filler within the mixture is difficult to profile [34, 35]. In all the reference standards and technical specifications, the lack of specific requirements for this material is evident. At the same time, the difficulty of the operators is clear in indicate precisely the link between filler and the performance of the mixtures in use [36]. Following the direction drawn by the most recent scientific experiences, it should be possible to determine a relationship between the quality of the filler, verified by laboratory tests, and the performance of the AC [37].

Several studies and experimental applications have shown that, in addition to completing the aggregate particle size, reducing the voids in the mixture, the filler is able to perform important functions within the bituminous mixture [38]. It affects the thermal susceptibility of the AC and regulates the thickness and mechanical properties of the mastic film covering the aggregates [39-41]. The filler must possess physical and chemical properties able to favour and strengthen the adhesion between aggregates and bitumen, and ensure an optimal rheological behaviour of the mastic at different temperatures of use [42].

In general, the reasons for adding the filler within a bituminous mixtures are:

- Complete the particle size distribution of the aggregates, reducing the voids in the final compacted mixture;
- Favour the adhesion properties between aggregates and bitumen;
- Increase the stiffness of the mixture and improving the development of mechanical properties;
- Favour the curing of the AC when the material is laid down and compacted;
- Reduce the thermal sensitivity of the final bituminous mixtures.

These properties are generally owned by some fillers traditionally used as: hydrated lime, Portland cement and above all limestone filler. Generally, these fillers are added to the bituminous mixture during the production in the asphalt plant. However, during in-plant production, another filler, called "recovery filler" is added to the mixture. The recovery filler is made of fine grain wastes passing the 63 μm sieve, which is generated in hot-mix asphalt plants. This powder comes from the rotating drum together with the combustion gases and water vapour and is retained by baghouse filters to prevent its dispersal into the environment. Generally, it is partially stored in silos to be used as recovery filler in the production of new ACs, mixed with the traditional filler [43].

Today, topics such as saving energy and resources have concentrated attention on the potential re-use of various kinds of industrial by-products in road construction. In several well-known cases, researchers have successfully experimented the use as filler of wastes like glass powder, silicon carbide, coal ash, solid urban waste, polyvalent powder from fire extinguishers and even biomass powder [44]. These are just a part of the wide applications of waste fillers within ACs, whose target is to reduce the use of virgin raw materials and find an intended use for material landfilled. Of course, the proposed applications should not have a detrimental effect on the performance of the final bituminous mixture.

Following this prospective, in the present research the waste bleaching clay is proposed as filler in total substitution of traditional limestone filler for the production of a porous ACs.

4.2. Porous asphalt concrete

Over the years, engineers and researchers have designed road layers and materials able to satisfy the increasing demand in safety and comfort for the road users. Under this point-of-view, porous asphalt (PA) is an environmentally friendly road material rich in air voids content, up to 25 % [45]. Today, this material represents a valid alternative to the traditional asphalt or concrete pavements suitable for regions with a high level of precipitation. This particular mixture is widely used in motorways, due to the combined properties of reducing the traffic noise and increasing the safety of users in wet conditions [46].

The reduction in traffic noise is due to the particular surface texture that is able to damp the noise emissions of the tyre-pavement contact. In terms of safety, the porous structure of the layer enables the surface water flowing, preventing the aquaplaning effect and spraying on the road surface (Figure 4.1.). Furthermore, it improves the visibility by eliminating the light reflected from the road surface.

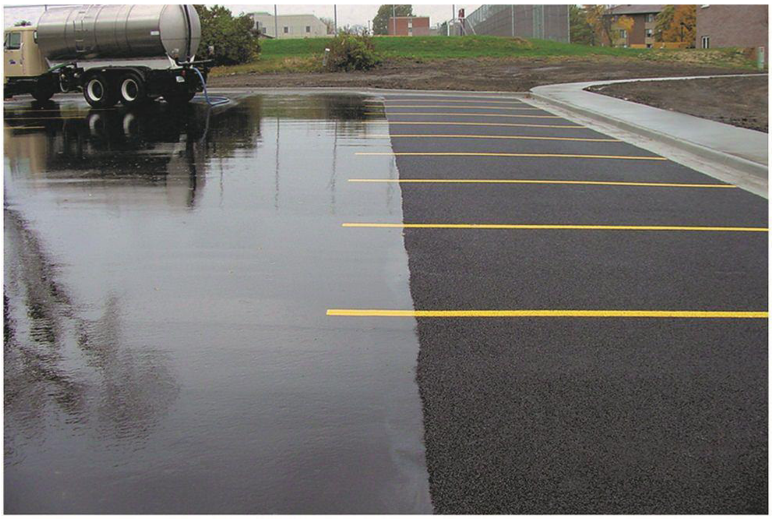

Figure 4.1. Porous asphalt trial field: comparison between traditional AC (on the left) and PA (on the right).

However, as a direct consequence of its porous structure, PAs are characterized by lower mechanical properties if compared to traditional dense bituminous mixtures [47]. Many studies confirmed that due to the high air voids content, the contact areas between aggregates through the asphalt mastic are very small, and this involves low performance for the mixture.

In addition, another weak point of this material is the high cost related to its production and maintenance [48-50]. The mix design needs of high quality aggregates and PmB binders in order to have an adequate level of performance. Furthermore, the necessity of keeping the air voids accessible let PA not suitable for its use in urban areas, involving high maintenance costs for its cleaning form dust or particles.

4.3. Research program

The possible use of the waste bleaching clay in total substitution of limestone filler within PAs, was evaluated and assessed through a detailed laboratory characterization. A traditional PA was taken as a reference, and results were compared also with the limits imposed by some technical specifications for this type of bituminous mixtures. Every test was carried out in compliance with the reference EN standards.

The experimental program was divided in five many phases:

- Mix design and production of samples (EN 933-1, ASTM D6925, EN 12697-30);
- Physical characterization (EN 12697-8);
- Static and dynamic mechanical characterization (EN 12697-23, EN 12697-26);
- Water sensitivity and durability evaluation (EN 12697-12, 12697-17, 12697-25);
- Permeability test (EN 12697-19).

In the following paragraphs the tests procedure are described and the related outcome are commented.

4.4. Mix design and production of samples

The mix design of the asphalt mixture and the reference values for each test were taken from an Italian technical specification for porous asphalt.

However, considering the different properties of the waste bleaching clay in comparison to the limestone filler, the mix design for the experimental mixture was optimized. As verified in Activity 1, two main waste bleaching clay properties could influence the final performance of the asphalt mixture: the internal porosity of the compacted filler (Rigden voids) and the very fine particles dimension. Both these properties could affect the workability and mechanical performances of the mixture if a specific mix design is not considered. In the light of the above, considering the very different particles densities and specific area, the substitution of limestone filler with the experimental material was done in volume and not in weight. This led to a modification of the original particle size distribution (Figure 4.2) but the amount of binder was keep constant. The reference mixture was labelled Pa F, while the experimental one was labelled PA Ud.

A 45/80 pen grade Polymer modified Bitumen was used as a binder (Table 4.1); its dosage was set to 5,1 % on the weight of aggregates.

Test	Unit	Value	Standard
Penetration @ 25°C	dmm	45 – 80	EN 1426
Soft. Point	°C	70	EN 1427
Dynamic Visc. @ 160°C	Pa·s	0.4	EN 12596
Force Ductility Test @ 10°C	J/cm^2	3	EN 13589 EN 13703

Table 4.1. Properties of PmB 45/80 binder.

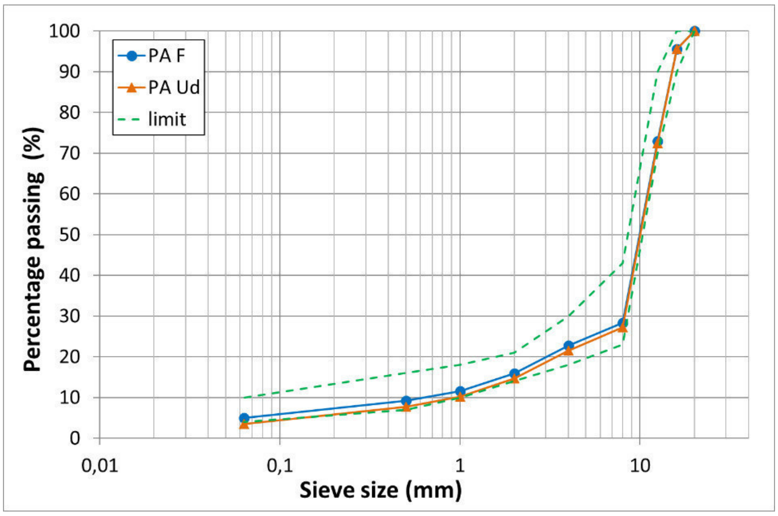

Figure 4.2. Particle size distribution for the reference (PA F) and experimental (PA Ud) mixtures.

For the whole research, thirteen specimens were prepared for each mixture: ten with gyratory compaction (ASTM D6925, 600 kPa, external angle of 1.25° and 80 revolutions) and three with Marshall compaction (EN 12697-30, 75 blows) (Figure 4.3). All samples were compacted at a processing temperature of 180 °C, needed to let the mix workable considering the use of a hard-modified bitumen.

Figure 4.3. Gyratory compactor (left) and PA samples (right).

All samples was stored at ambient temperature for one day before being tested, to ensure the complete curing of the material after compaction.

4.5. Physical characterization

The physical analysis was based on the evaluation of the workability and compactability of the mixtures in terms of compaction curves, obtained from the gyratory compactor, and air voids content (EN 12697-8) within the samples.

From the compaction curves for each mixture, it was possible to calculate a trend line of compactability properties, using the following equation:

$$\%\rho_m = a \cdot ln(x) + b \qquad (1)$$

Where:

%ρm is the percentage of maximum densification,

a is the slope of the compaction curve,

x is the number of revolutions,

b is the intercept of the regression curve.

Thanks to the analysis of the compaction curves, for each gyration is it possible to calculate the three parameters which are traditionally used for the evaluation of the volumetric properties of a bituminous mixtures: VFA, VMA and Va.

VFA are the Voids Filled with Asphalt, and it is the percentage of voids in the compacted aggregate mass that are filled with bitumen. According to scientific literature, VFA is a parameter for the evaluation of the quality of the mix design, representing the volume of the effective asphalt content. VMA are the Voids in the Mineral Aggregate. This value represents the volume of intergranular void space between the aggregate particles of a compacted mixture that includes the air voids and the effective asphalt content, expressed as a percent of the total volume of the specimen. Generally, mixtures with a low VMA are more sensitive to small changes in asphalt binder content; on the other hand, an excessive VMA could have a detrimental effect on the mixture stability. Va is an indication of the air voids content, which are small airspace that occur between the coated aggregates in the final mix. This parameter is fundamental to ensure an adequate structure to the ACs and it depends on the mix design.

For the evaluation of the air voids content, following the indication of the EN 12697-6 standard, the bulk density of the specimens was calculated through the geometrical procedure, which is indicated as suitable for porous asphalts.

4.6. Static and dynamic characterization

The evaluation of the quality of the mix design and the compliance with the technical requirements for PAs, was assessed through the mechanical characterization of the mixtures, with static and dynamic tests.

The static analysis encompassed the Indirect Tensile Strength (ITS) test at 25 °C. In line with the EN 12693-23 standard, a constant velocity of 50 mm/min was applied to the specimen until failure (Figure 4.4). In literature the ITS test is often used to evaluate the level of tenacity reached by the aggregates-filler-bitumen bond.

Figure 4.4. ITS test at 25 °C on PA sample.

It is also an indicator of the quality of the mix design, giving information about the dosage of binder within the mixture.

The dynamic mechanical characterization was based on the evaluation of the Stiffness Modulus in compliance with the EN 12697-26 (Annex C) standard. This parameter describes the behaviour of the asphalt mixture under dynamic loads able to generate a prefixed elastic deformation within the sample. The stiffness modulus is important as it is used as design parameter for the calculations and verification of road sections in software for pavements design.

According to the standard, the Modulus was determined through a pulse loading with a 124 ms rise-time, to generate a predefined horizontal deformation of 7±2 μm in the core of the sample (Figure 4.5).

Figure 4.5. ITSM test on PA sample.

The effect of the waste filler within the PA was assessed also with the analysis of the thermal sensitivity of the mixture. The specimens were conditioned for six hours and then tested at three reference temperatures: 5, 20 and 35 °C.

4.7. Water sensitivity and durability evaluation (EN 12697-12, 12697-17, 12697-25);

The fourth phase of the experimental program was based on the evaluation of the water sensitivity and durability of the mixtures. The presence of water is considered one of the main causes of asphalt mixture degradation. The evaluation of water sensitivity is of particular interest for porous asphalt, considering that the run-off water system for this type of mixtures foresees the water flowing through the bituminous layer thickness. Different tests have been designed during the years for research purpose. In compliance with the reference technical specification, the water sensitivity is evaluated through the reduction in ITS (ITSR) values after saturation in water of samples (EN 12697-12). According to the standard, the specimens were kept in a water bath at 40 °C for 72 hours prior testing.

The mechanical characterization is than completed trough the evaluation of the durability of the mixtures, taking into account that the porous structure involves a reduction in the performances if compared to a dense asphalt concrete. The durability is evaluated through the resistance to permanent deformations (Repeated Load Axial Test, RLAT) and to abrasion (Cantabro test).

The resistance to permanent deformations was evaluated in a direct uniaxial compression test configuration. The test was carried out according to EN 12697-25, with a uniaxial load of 100 kPa, repeated for 3600 cycles at 40 °C (Figure 4.6). The tests was performed both on samples cured at room temperature and on samples kept in a water bath at 25 °C for 72 hours before testing.

Figure 4.6. Repeated Load Axial Test performed at 40 °C on PA sample.

According to scientific literature, the total accumulated strain and the average strain obtained from this test can be effective in evaluating the potential permanent deformations. In particular, the strain rate (με/cycle) relates to the linear phase of the material’s deforming response, calculated as a linear regression between 1800 and 3600 load cycles. Many authors consider this parameter to be the most reliable in determining the resistance to permanent deformations, as it is independent from the initial deformation resulting from the first few load cycles.

The Cantabro test (EN 12697-17) is a common test for PAs. This test was invented in Spain, and represent a method to address the characterization of porous asphalt by mechanical tests. The procedure developed allows the evaluation of the resistance of the mixture to its disintegration by impact and abrasion. According to the standard, the test is performed on Marshall samples, conditioned at 25 °C for six hours, which are placed inside the Los Angeles drum and subject to 300 revolutions, at around 30 revolutions/min. The mass loss at the end of the test gives a measure of the resistance to ravelling of the mixture (Figure 4.7). This type of test is particularly adopted for porous mixtures, considering their inner structure, poor in contact areas between particles.

Figure 4.7. PA sample before (left) and after (right) the Cantabro test.

This test can be considered as a measure of the abrasiveness of porous asphalt as well as an assessment of the cohesion and the bond between aggregates and bituminous mastic.

4.8. Permeability test (EN 12697-19)

In the fifth and final phase of the experimental program, the vertical permeability of the two PA mixtures was analysed (EN 12697-19). This standard specifies a method for determining the vertical and horizontal permeability of cylindrical specimens of bituminous mixtures with interconnecting voids. The test procedure is suitable both for cores taken from the pavement or for samples prepared in the laboratory.

It allows the evaluation of probably the most important property of a porous asphalt, which is its ability to allow the run-off of surface water through its thickness. The water flowing capability is related to the level of porosity within the mixture, as well as to the interconnection of voids. According to the test procedure, a column of water with a constant height of 30 cm was applied to a cylindrical specimen and was allowed to permeate through it for a given lapse of time. The resultant flow rate is a conventional measure of the material permeability in terms of the vertical flow of water through the specimen (Qv) and vertical permeability (Kv) according to Darcy's theory. In Figure 4.8 the apparatus and the test procedure are shown. In this case results were compared to ranges suggested by the EN standard for porous asphalt and with limits imposed by the Italian technical specification taken as a reference.

Figure 4.8. Vertical permeability apparatus (left) and on-going test (right).

4.9. Analysis of results

Table 4.2 summarizes the average results for each test and the comparison between the values obtained for both the tested mixtures. It is worth noting that every tests were carried out on a specific number of samples, as imposed by the aforementioned standards.

Test	Unit	PA F	PA Ud
Va content @ 80 gyrations (EN 12697-8)	%	15,4	14,5
VFA content @ 80 gyrations	%	23,5	22,9
VMA content @ 80 gyrations	%	34,4	36,5
ITS @ 25 °C (EN 12697-23)	MPa	0,92	0,98
ITSM @ 5 °C (EN 12697-26)	MPa	7669	11949
ITSM @ 20 °C (EN 12697-26)	MPa	3390	5554
ITSM @ 35 °C (EN 12697-26)	MPa	821	2091
ITSR (EN 12697-12)	%	88	83
RLAT @ 40 °C (dry samples) (EN 12697-25)	Acc. Strain (%)	0,43	0,27
RLAT @ 40 °C (wet samples) (EN 12697-25)	Acc. Strain (%)	0,43	0,25
Cantabro Test (EN 12697-17)	Particle loss (%)	7,6	15,1
Vertical permeability (EN 12697-19)	Kv (10^{-3}m/s)	1,46	1,31

Table 4.2. Average results for PA F and PA Ud.

In terms of porosity, both mixtures show a comparable air voids content, which is in line with the lower range generally imposed for this type of bituminous mixtures. The porosity is a direct consequence of the adopted grading distribution, which is close to the lower limit indicated by the Italian technical specification taken as a reference. The difference between the experimental PA and the reference one is related to the volumetric substitution of limestone filler with the waste digested bleaching clay. If the compaction curves are taken into account (Figure 4.9) the PAs reach a final level of densification equal to 85 %.

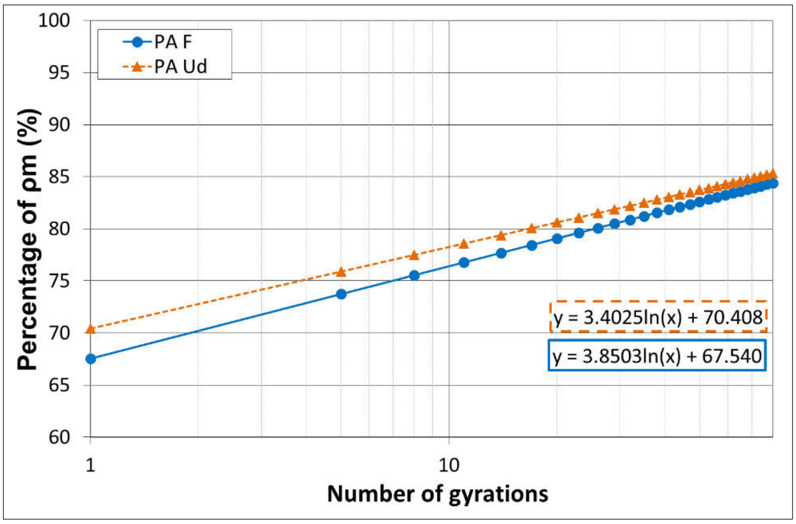

Figure 4.9. Comparison between compaction plot trends.

However, the slope of the compaction plot trends indicate that the PA F has a higher level of compaction, denoting better workability properties if compared to the experimental mixture.

In terms of Indirect Tensile Strength, there is no relevant difference between the reference and the experimental PA. According to the scientific literature, the ITS test is generally adopted for the evaluation of the level of tenacity reached by the aggregates-filler-bitumen bond. In the case under examination, the bond between aggregate and bituminous mastics seems to be higher when the waste bleaching clay is added to the mixture. These results could be related to the higher absorption power of the waste filler, due to its significant intergranular porosity and the high specific surface of particles. In wider terms, if the reference values are considered, the Italian technical specifications suggest a lower limit for ITS equal to 0,60 MPa. Both mixtures exceed this threshold limit.

The mechanical characterization is supported by the evaluation of ITSM and of the thermal sensitivity of the mixtures. Results are in line with ITS values, confirming the high mechanical performance for the experimental mixture. In this case, the difference in the stiffness between the two PAs is relevant. It is registered an average increase in ITSM values by the 80 %. The reference technical specifications do not impose any limit, however in absolute terms the ITSM values for PA Ud can be compared to a traditional dense asphalt concrete. The thermal sensitivity is affected by the substitution of limestone filler with the waste bleaching clay. The ITSM trend for the experimental mixture shows a rise in values for each temperature, but the highest one is verified at low temperatures. However, the most interesting results is verified at 35 °C, where the ITSM value is even higher if compared to a traditional dense graded mixture. This could be significant in terms of durability because at high temperature are generally verified problems related to rutting.

The results of ITS tests in wet conditions show that the experimental mixtures reach a high failure resistance, considering the type of asphalt concrete. Even after being subject to saturation in water at 40 °C for 72 hours, both mixtures have ITS resistance exceeding the lower limit imposed for specimens cured ad room temperature (0,80 MPa for the PA F and PA Ud). The ratio between ITS on normal samples and the ones submerged in water gives information on the water susceptibility of the mixture. According to the reference technical specification, this ratio must be higher than 75 %. In the case under study, PA Ud shows a lower value of ITSR (83 %) if compared to the reference mixture (88 %). Even if lower, the experimental mixture provides for enough mechanical resistance, and do not seem to be negatively affected by the saturation in water.

As for the durability evaluation, according to scientific literature the RLAT test can be effectively used to assess the rutting resistance, in its direct uniaxial compression test configuration. Furthermore, in order to better investigate the behaviour of mixtures after saturation in water, the tests were repeated in traditional configuration and on samples placed in a water bath at 25 °C for 72 hours. In both cases, the test temperature was kept equal to 40 °C. The results are represented in Figure 4.10 in terms of accumulated strains.

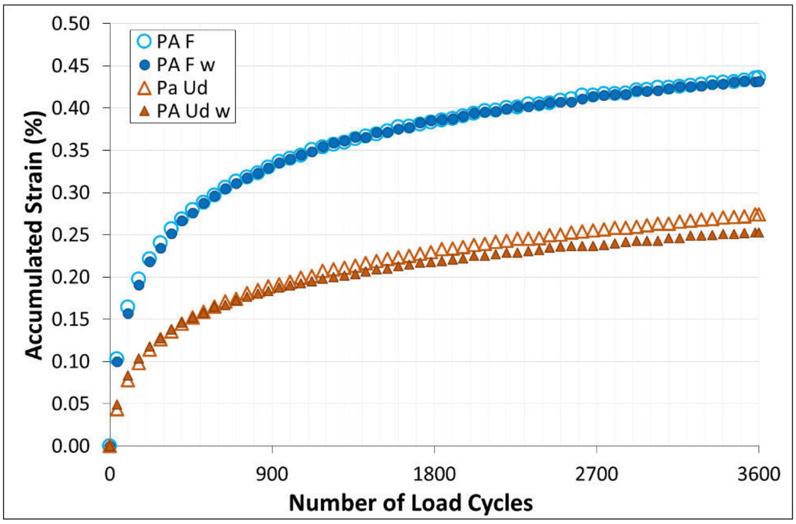

Figure 4.10. Accumulated strains from RLAT test for PA samples in dry and wet conditions.

The results clearly show the different behaviour of the two materials under cyclic load applications. These results are in line with what verified during the whole mechanical characterization. The substitution of limestone filler with waste digested bleaching clay promotes the increasing in the stiffness and resistance of the PA mixture. The average reduction in the accumulated strain registered is 37 %. In this case, there are no suggested or imposed values for RLAT test from the technical specification used as reference. If the trend of the permanent deformation is considered, both PAs registered a significant increase in the accumulated strains in the first 500 cycles. There are no relevant differences in the behaviour of the mixtures for samples cured in wet conditions, which reach the same level of permanent deformations registered in normal conditions.

The results of the Cantabro test can be related to the stiffening power conferred to the bituminous mastic by the addition of the waste digested bleaching clay. The increasing in the embrittlement of the mastic is also verified for the ITS test, in which the experimental mixture registered a significant reduction in the vertical displacement, if compared to the traditional PA (3,19 mm for PA F vs. 2,39 mm for PA Ud). The PA Ud registered a loss in particles double if compared to the reference mixture. However, the percentage of mass loss is significantly lower than the limits imposed by some Italian technical specifications for PA mixtures (25 %).

The vertical permeability for the mixtures exceed the lower limit indicated by the EN 12697-19 standard, which suggests a vertical permeability between 0,5 and $3{,}5 \cdot 10^{-3}$m/s, in relation to the particle size distribution and the internal porosity. The vertical permeability of the two mixtures can be considered comparable and falls in the aforementioned range. The slight difference is related to the higher air voids content of the traditional PA.

4.10. Conclusions

Considering the presented results, it is clear the effect conferred by the substitution of limestone filler with waste digested bleaching clay within PA mixtures. As a general result, the stiffening power of the waste filler on the bituminous mastic is confirmed, as already verified by Sangiorgi and Mazzotta [29, 30].

The mix design of the PA is influenced by the geometrical and physical properties of the waste filler, which involved a substitution by volume of limestone filler with the experimental one. As a result, the variation in the particle size distribution was not significant for the internal porosity of the mixture. To have comparable results, the amount of bitumen was kept fixed and equal to 5,1 % by the weight of aggregates for both the mixtures. However, considering the high absorption power and the stiffening effect of the waste bleaching clay, the amount of bitumen might be increased for the experimental PA.

As a result, even if both mixtures reach a comparable final density, the analysis of the gyratory compaction curves shows that the reference PA has better workability properties. This could represent an evidence of the slight low amount of binder for PA Ud caused by the high absorption properties of the waste digested bleaching clay.

In terms of mechanical properties, this phenomenon is verifiable by the substantial ITS, ITSM and RLAT values. In this case, the significant Rigden Voids value of the waste filler are responsible for the mechanical properties of the mixture. As suggested by well-established scientific literature, a high intergranular porosity of filler involves an increment in the stiffness of the bituminous mastic, due to the increase of the quantity of fixed bitumen. It is worth noting that traditional limestone filler has a RV content lower by the 25 % if compared to the waste bleaching clay.

The increase in stiffness is evident for every testing temperature and this might be effective at high temperatures, conferring an improvement in the durability of the mixture in terms of rutting resistance. This is verified for the RLAT test carried out at 40 °C, in which the level of accumulated strain is almost halved if compared to the reference PA. On the other hand, the stiffening effect of the filler has a detrimental effect for the embrittlement of the bituminous mastic as confirmed by the high particles loss after Cantabro test. However, Cantabro results are in line with values suggested for PAs.

If the water susceptibility is taken into account, the presence of the waste filler does not modify the properties of the traditional mixture, as evaluated through ITSR and RLAT test in wet conditions. The same conclusion can be drawn for the vertical permeability, which is proportional to the porosity of the two PA mixtures.

Based on the experimental results here presented, the substitution of traditional limestone filler with digested waste bleaching clay seems to be possible for PA layers. The physical and mechanical properties of the experimental PA are in line with values and ranges suggested by the current standard and the most common technical specification for this type of bituminous mixture. The presence of waste digested bleaching clay improves the mechanical properties of the PA. This represents a positive outcome, since the mechanical performances are a weak point for this type of mixture. On the other hand, an excessive presence of waste filler could involve an unwanted brittle behaviour of the material. In the light of the above, the traditional recipes for bituminous mixtures could not be adopted for materials produced with waste bleaching clays in substitution of limestone filler. Hence, the mix design of the mixture need to be optimized taking into account the specific properties of the recycled filler.

5. Activity 3: Experimental application of Waste Bleaching Clay as filler for the production of Cement Bound Mixtures

The third experimental activity is related to the application of the waste material within Cement Bound Mixtures (CBM). In the case under examination, the waste digested bleaching clay is applied in total substitution of the limestone filler, which is traditionally used for this type of mixtures.

5.1. Cement Bound Mixtures

A Hydraulically Bound Mixture is a mixture of aggregates, water and a hydraulic binder, which is traditionally used for the production of base or foundation layers in a typical road section for heavy traffic infrastructures. Its common function within the road section is to improve the bearing properties of the structural layers and to optimize the traffic loads propagation to the subgrade [51].

According to the specific road section, it can be used as foundation for flexible road sections, as sub-base layer for semi-rigid road sections and as base layer under the concrete slab for rigid pavements (Figure 5.1).

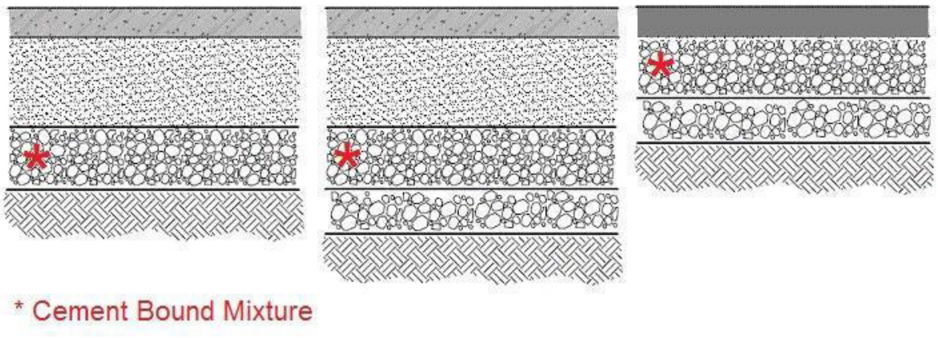

Figure 5.1. CBM within flexible (left), semi-rigid (centre) and rigid pavements (right).

The development of this mixture is due to several factors:

- Improvement of the structural performance of the road section;
- Flexibility of its use according to several applications;
- Facility of production and operation processes (laying and compaction);
- Low environmental impacts;
- Low costs.

The CBM layer improves the structural performance of the pavement by the combined effect of a specific particle size distribution and the bonding and stiffening power conferred by the hydraulic binder [52]. In terms of design, the CMB is generally preferred to unbound or stabilized mixture, allowing the increase in the bearing properties of the road structure often reducing the thickness of the layers [53].

It can be produced either in situ or in plants. In the latter case, a traditional cement concrete plant is not modified for the production of CBMs (Figure 5.2). The in-plant production ensures a high control for the final product and allows the production of relevant quantities of mixture. The newest plants are equipped with an automatic system that permits the instant detection of the aggregates moisture, allowing the correction of the water content for the final mixture, if needed.

Figure 5.2. Plant for the production of CBMs.

On the other hand, the need of carrying the final mixture in a short time to the yard as well as the transportation costs are the weak point related to in-plant production. In the last years, mobile CBM plants have been developed to overcome these limitations. Once the mixture is produced, the material is laid down with the traditional paver machine used for bituminous mixtures and compacted by means of rollers.

From an environmental point-of-view, the CBM in situ production is considered as a green technology for the production of sustainable construction materials [54]. This is related to the combined possibility of reducing the environmental costs, if compared to the in-plant production, allowing the recycling of existing materials. This technique is suitable either for the construction of new roads or for the deep rehabilitation of existing ones [55, 56]. The in situ CBM production is permitted by mobile plant or special machines, which allow the milling of the existing pavement and the mixing of the recycled material with virgin aggregates, if needed, and cement (Figure 5.3). Once the material is mixed, the surface is levelled with a grader and the layer is compacted with rollers until. In this case, the environmental benefits are enhanced considering the significant energy savings associated with the possibility of re-use waste materials, reducing the demand for primary resources. Still, the decrease in lorry delivery from CBMs plants allow a significant reduction in CO_2 emissions connected to the production of the mixture.

Figure 5.3. CBM in situ production.

On the other hand, the possibility of recycling waste materials is limited in relation to the final performance of the mixture. Furthermore, a weak point of this technology is related to a more limited control of the final material, if compared to in-plant production. To overcome these limits, the in situ production of CBM needs a specific mix design and laboratory characterization of the mixture in order to maximize the use of recycled materials without decrease the mechanical properties of the final product. Different studies and direct applications showed the possibility of producing 100 % recycled CBMs with performances comparable to traditional mixtures made of virgin aggregates.

In the last years, the low environmental impacts and costs connected to this mixture gained interest, concerning the possibility of use waste and second-hand materials, even not connected to the construction field, in substitution of virgin aggregates or hydraulic binder. Today, the use of Construction & Demolition wastes, including the Reclaimed Asphalt Pavement (RAP), within the mixture is a well-established practice [57]. The technological evolution and the growing interest of researchers in recycling have gradually allowed to increase the quantities of waste materials combined within recycled mixtures, without detrimental effects on the mechanical properties of the mixture [58]. The replacement of raw materials with wastes is not only limited to the aggregates, but also to the total or partial substitution of the hydraulic binder. Some researchers investigated the feasibility of recycling high contents of fly ash and ladle furnace slag as binders, as well as fly ashes from coal combustion wastes. Other applications are also known about the use of glass or cement concrete powder and many other are still under study. All these experiences have highlighted the importance of the laboratory characterization as a crucial step for the validation of the experimental mixture.

5.2. Research program

Following the last trend of research on the application of recycled material for the production of CBM, in the present work two experimental mixtures were prepared, both of them with waste digested bleaching clay in total substitution of limestone filler. The difference between the two experimental CBMs was the constituent aggregates: one mixture (labelled CBMV Ud) was made of virgin aggregates, the second one (labelled CBMR Ud) was prepared with Reclaimed Asphalt Pavement (RAP) by the 50 % on the weight of aggregates. The latter mixture combines indeed the presence of recycled aggregates with the application of an industrial-by product as filler.

Two reference mixtures were prepared: a traditional CBM with limestone filler (CBM L) and a mixture with the same filler and RAP by the 50 % on the weight of aggregates (CBMR L). In order to have comparable results, two grading distributions were fixed: one for the two CBMs with raw materials and one for the recycled ones.

The experimental program was divided in four different phases:

- Mix design and definition of the optimum water content (EN 933-1, EN 13286-2);
- Preparation of samples and evaluation of the physical properties (EN 13286-2, EN 13286-50);
- Mechanical characterization (EN 13286-41, EN 13286-42);
- Evaluation of the durability after freeze and thaw cycles (EN 13286-52).

The evaluation of the results is based on the comparison between the experimental and the traditional mixtures as well as on the compliance with ranges and limits imposed by the most widespread Italian technical specifications for CBMs.

In the following paragraph the tests procedure are described and the related outcomes are commented.

5.3. Mix design and definition of the optimum water content

The mix design of the mixtures was based on the compliance with some grading distribution limits taken from an Italian technical specification. The grading curve of both recycled and virgin mixtures are shown in Figure 5.4.

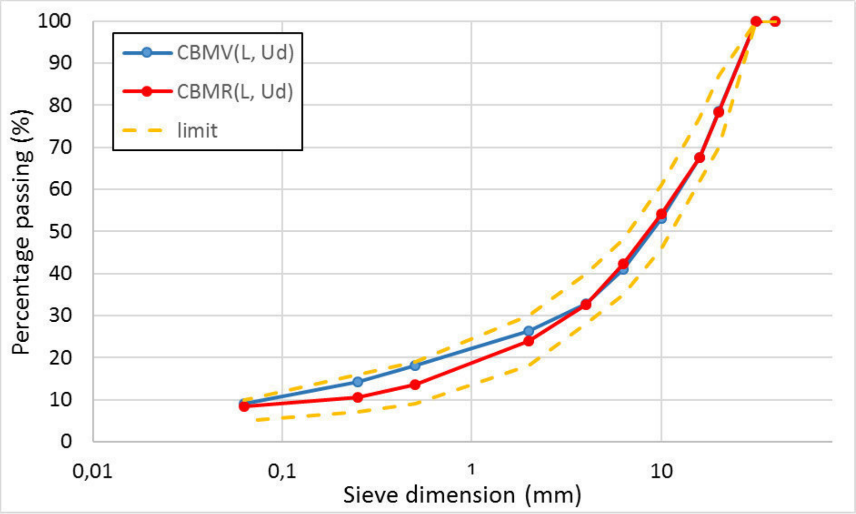

Figure 5.4. Grading distributions for virgin and recycled CBMs.

As clearly in Figure 5.4 shows, both the grading distributions are in compliance with the gradation limits imposed by the Italian technical specification. In the case under examination, the particle size distribution is indicated for foundation layers. As aforementioned, the CBMV mixtures were produced with 100 % virgin aggregates while the CBMR ones with 50 % of RAP. The amount of filler either limestone or waste digested bleaching clay was keep constant and equal to 5 % on the weight of aggregates.

Once defined the grading distributions of the mixture, the following step was the evaluation of the optimum water content. This parameter is fundamental for CBM since it affects its workability and compactability properties. It allows an estimate of the mixture density that can be achieved on construction sites and provides a reference parameter for assessing the density of the compacted layer of the mixture. The study of the optimum moisture is traditionally performed by Proctor compaction method, as indicated by the EN 13286-2 standard. On the basis of the maximum dimension of the aggregates a specific test procedure is suggested. According to the standard, the compaction of the sample is given by a specific hammer. The number of blows, the layers that form the sample, the falling height and the type of hammer, depend on the particles size distribution of the material. Different samples are compacted with increasing amount of water added to the mixture and their dry densities are then calculated. The maximum dry density corresponds to the optimum water content of the mixture.

Two different Proctor studies were carried out for the virgin and recycled mixtures. For both, three different amount of water content were defined: 4, 6 and 8 % on the weight of aggregates. Figure 5.5 and 5.6 present the results of the Proctor study.

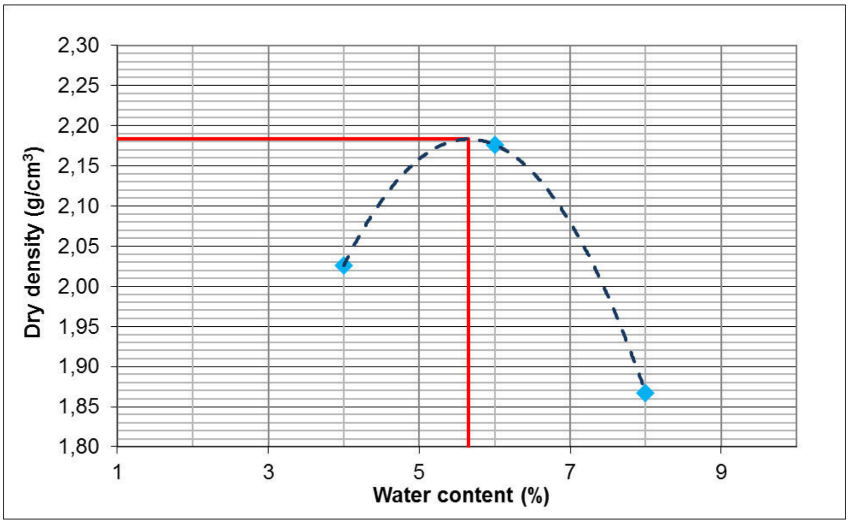

Figure 5.5. Proctor study for CBMV.

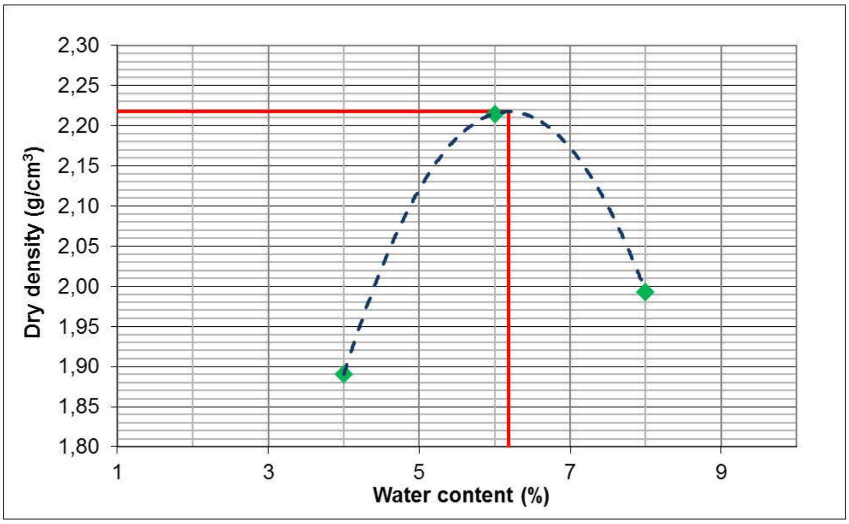

Figure 5.6. Proctor study for CBMR.

For the virgin mixture, the optimum water content is equal to 5,8 % on the weight of aggregates. The maximum dry density registered for the CBM is 2,183 g/cm^3. As for the recycled mixture, the optimum water content is higher and equal to 6,2 % on the weight of aggregates. The increased amount of water needed to achieve the maximum dry density is due to the presence of RAP, which has relevant water absorption properties. With the aforementioned humidity, the mixture registered a density equal to 2,217 g/cm^3.

It is worth noting that the optimum humidity content is evaluated on mixtures devoid of hydraulic binder. The water content is adjusted in relation to the amount of cement added to the mixture. However, considering the type of aggregates and the amount of cement used, equal to 3,5 % on the weight of aggregates, the optimum water content was not modified.

5.4. Preparation of samples and evaluation of the physical properties

Once fixed the particle size distribution and the optimum humidity content, six samples were prepared for each mixture following the Proctor compaction. The cement amount was fixed equal to the 3,5 % on the weight of aggregate for each CBM. As aforementioned, the optimization of the water content was not needed. Figure 5.7 shows some steps of the Proctor compaction.

Figure 5.7. Proctor compaction and prepared samples.

During and after the compaction operations, some material was collected from the mixture to verify the water content and the samples were than weighted to calculate the real density of the compacted CBMs. Average results are presented in Table 5.1.

Mixture	Dry Density (g/cm^3)	Water content (%)
CBMV L	2,191	5,8
CBMV Ud	2,185	5,8
CBMR L	2,256	6,1
CBMR Ud	2,234	6,1

Table 5.1. Average volumetric results and water content for the CBMs.

Table 5.1 shows that the dry densities as well as the water contents are unvaried compared to values registered during the Proctor study. This means that the hydraulic binder added to the mixture does not affect the water absorption properties of the materials. The fixed humidity is suitable to achieve a proper final density. There is no relevant difference between the CBMs even if lower values are registered in terms of dry density for the experimental mixtures. This is probably due to the hygroscopic properties of the recycled filler. However, the addition of additional water was no needed, considering the reached final densities. Hence, the presence of waste digested bleaching clay does not have a detrimental effect on the compactability and volumetric properties of the final material.

5.5. Mechanical characterization

According to the reference Italian technical specification, the evaluation of the mechanical performances of CBMs is based on static tests carried out on samples cured for 7 days in a constant moisture ambient.

Some technical specifications required the gyratory compaction for the production of samples. However, based on several studies and researches, the gyratory compaction was seen to lead to higher levels of compaction if compared to the Proctor method. For safety reasons, the CBM samples were prepared by means of Proctor compaction.

The mechanical characterization was based on the evaluation of the compressive strength (EN 13286-41) and indirect tensile strength (EN 13286-42). For each mixture, six specimens were prepared with Proctor compaction (EN 13286-50) according to the mix design fixed in the previous step of the experimental program (Figure 5.8).

Figure 5.8. CBM samples after Proctor compaction.

The samples were kept for 7 days at constant moisture condition and then tested: three specimens for the evaluation of the compressive strength and three for the ITS test.

According to the EN 13286-41 standard, a load shall be applied in a continuous and uniform manner without shock so that breaking occurs within 30 to 60 seconds of commencement of loading. The load is then registered and the compressive strength is calculated as the ratio between the load and the surface area of the specimen. The sample is not confined during the test (Figure 5.9). The type of failure of the specimen shall be noted using some figures reported in the standard, and if satisfactory, the test shall be recorded. Generally, unsatisfactory failures are caused by mistakes happened during the mixing and compactions processes, de-moulding and testing specimens.

Figure 5.9. CBM before (left) and after (right) compressive strength test.

Table 5.2 and Figure 5.10 show the compressive strength result for the four mixtures.

Mixture	Compressive strength (MPa)	Avg. Compressive strength (MPa)
CBMV L 1	4,46	4,45
CBMV L 2	3,96	
CBMV L 3	4,93	
CBMV Ud 1	2,78	3,83
CBMV Ud 2	4,10	
CBMV Ud 3	3,56	
CBMR L 1	3,05	3,06
CBMR L 2	3,13	
CBMR L 3	3,00	
CBMR Ud 1	3,46	3,72
CBMR Ud 2	3,86	
CBMR Ud 3	3,83	

Table 5.2. Compressive strength results.

As overall result, all mixtures show adequate compressive strength to be suitable for road applications. The most widespread Italian technical specifications generally require a compressive strength within 2,5 to 4,5 MPa. Every tested samples fall in this range.

Between the virgin mixtures, the reference one shows the highest mechanical performance while the substitution of limestone filler with waste material leads to a reduction in compressive strength. As for the recycled CBMs, it is worth noting that even if the mixtures are made by 50 % of RAP, the mechanical properties are in line with the values registered for the virgin CBM. This is a further confirmation of the quality of the mix design.

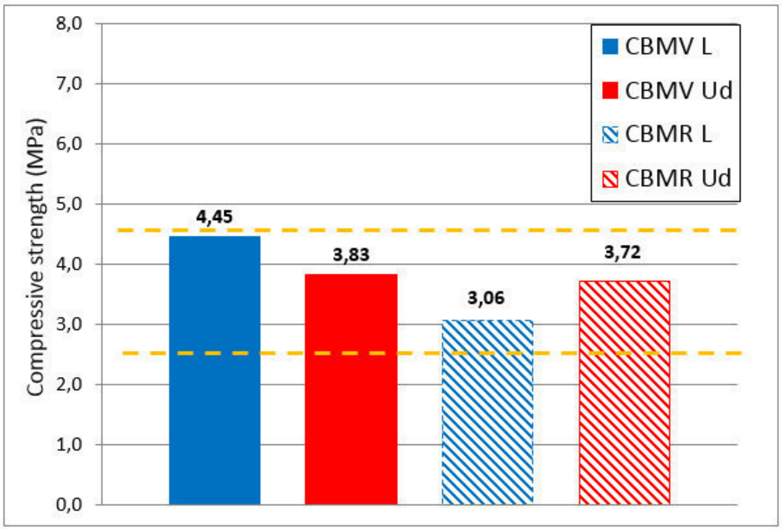

Figure 5.10. Average compressive strength results.

If the CBMR L and CBMR Ud are considered, the presence of waste digested bleaching clay does not negatively affect the compressive strength, which is enhanced instead.

The static mechanical characterization was then completed with the evaluation of the Indirect Tensile Strength (EN 13286-42). According to the standard, a Proctor specimen of hydraulically bound mixtures is subjected to a compression force applied along the two opposite generatrix until breaking. The load is then applied in a continuous and uniform manner without shock to obtain a uniform increase in stress not greater than 0,2 MPa per second. The maximum load is registered and the indirect tensile strength is calculated. The test setting is shown in Figure 5.11, while results are presented in Table 5.3 and Figure 5.12.

Figure 5.12. CBM before (left) and after (right) the indirect tensile strength test.

Mixture	Compressive strength (MPa)	Avg. Compressive strength (MPa)
CBMV L 1	0,65	0,68
CBMV L 2	0,64	
CBMV L 3	0,76	
CBMV Ud 1	0,63	0,67
CBMV Ud 2	0,71	
CBMV Ud 3	0,59	
CBMR L 1	0,40	0,40
CBMR L 2	0,44	
CBMR L 3	0,37	
CBMR Ud 1	0,66	0,60
CBMR Ud 2	0,53	
CBMR Ud 3	0,62	

Table 5.3. Indirect tensile strength results.

The results confirm the quality of the mix design and its constituent materials. Every tested CBM exceeds the minimum requested value of indirect tensile strength which ranges between 0,25 and 0,32 MPa according to the most common technical specification for this type of mixture.

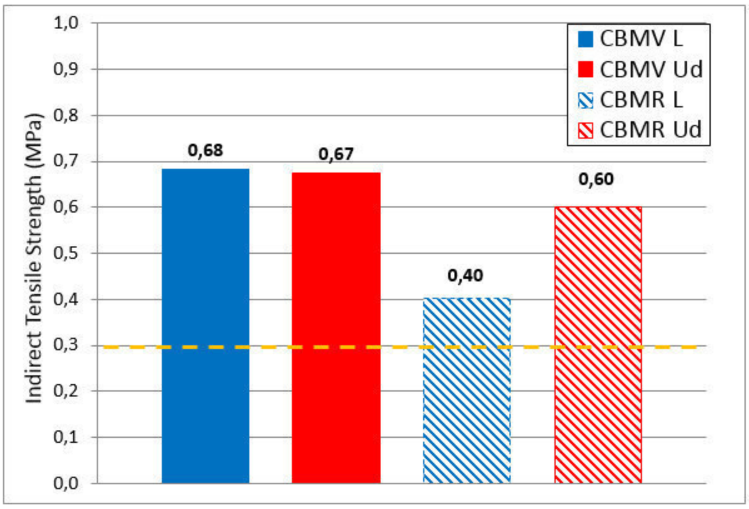

Figure 5.11. Average indirect tensile strength results.

If the virgin CBMs are considered, there is no difference between the mixtures when the limestone filler is substituted with the waste digested bleaching clay. Both the CBMVs show ITS values that double the limit imposed by the Italian technical specifications.

As for the recycled mixture, a significant reduction in ITS value is registered for CBMV L. However, the indirect tensile strength exceeds the aforementioned limit. All in all, the adoption of waste bleaching clay as filler for recycled hydraulically bound mixture, does not affect its mechanical properties in terms of ITS value.

These data are in line with the mechanical behaviour of the material verified during the compressive strength tests.

5.6. Durability evaluation

The last phase of the experimental program was related to the evaluation of the durability of CBMs. Taking into account the type of material and its application as foundation layer, the study on its durability was related to the reduction of its mechanical properties after freeze and thaw cycles.

In compliance with the EN 13286-54 standard, the CBM samples were subject to thermal stress cycles, able to accelerate the deterioration of their mechanical properties. After the thermal treatment, the samples were tested to evaluate the reduction in compressive strength. Three samples for each mixture were prepared with Proctor compaction, based on the fixed mix designs. Once cured for 7 days at constant moisture, the samples were placed in a water bath for 48 hours. The specimens saturated in water were then wrapped in a plastic film and subject to 10 thermal cycles of 24 hours each, whit temperatures ranging from – 20 to +20 °C (Figure 5.12).

Figure 5.12. CBM samples in the water bath (left) and plastic wrapping (right).

After the thermal shocking, the compressive strength of the samples was evaluated. The assessment of the damage caused by thermal treatment is represented by the ratio between the compressive strength calculated in the mechanical characterization step and the values registered on samples after freeze and thaw cycles (Compressive Strength Reduction, CSR).

Average results are presented in Table 5.4 and Figure 5.13.

Mixture	C.S. (MPa)	C.S. f/t (MPa)	C.S.R. (%)
CBMV L	4,45	4,00	90
CBMV Ud	3,83	3,40	89
CBMR L	3,06	2,84	93
CBMR Ud	3,72	3,25	87

Table 5.4. Average reduction in compressive strength after freeze and thaw cycles.

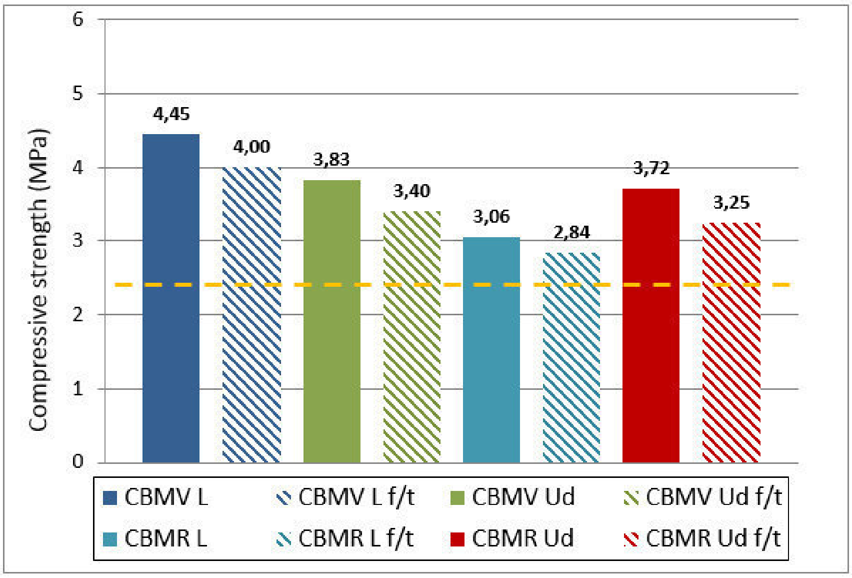

Figure 5.12. Compressive strength before and after freeze and thaw cycles.

From the analysis of results, the first relevant data is related to the compliance of every tested samples to the compressive strength required for CBMs suitable for the construction of roads. Even after the thermal shocking treatment, both traditional and experimental mixtures ensure adequate mechanical properties.

In terms of reduction of compressive strength, there is no relevant difference between the mixtures prepared with virgin aggregates and CBMs formed by recycled material by their 50 %. The same consideration can be drawn if the type of filler in taken into account. The substitution of limestone filler with waste digested bleaching clay does not affect the durability of the mixture in terms of reduction of mechanical properties after the thermal treatment.

From the comparison of mixtures before and after the freeze and thaw cycles, the maximum reduction is registered for CBMR Ud (87 %) while the minimum one is related to CBMR L (93 %). The lowest compressive strength is verified for CBM L after thermal treatment, but the value exceeds the lowest limit imposed for this type of mixture, tested after normal curing. The slight reduction in compressive strength for every mixture is probably due to the high final density achieved after the Proctor compaction. The volumetric properties of the compacted CBMs do not allow additional water absorption, preventing the detrimental effect of water susceptibility. Moreover, this data is a further confirmation of the quality of the mix design for both the virgin and the recycled CBMs.

5.7. Conclusions

In the present research, the experimental application of a waste digested bleaching clay as filler within hydraulically bound mixtures was evaluated. For this purpose, two different mixtures were designed, in which the traditional limestone filler was substituted by the waste material. One of them, following the last trends of research, was prepared with RAP up to 50 % on the weight of aggregates.

Results showed that the addition of the recycled filler to the mixes does not modify the compactability and workability properties of the final products. In terms of dry densities, no relevant differences were detected between the CBMs compacted with limestone filler and the experimental ones. The optimum water contents assessed for the traditional CBMs were kept constant and both CBMV Ud and CBMR Ud achieved a suitable final density without additional water. These results are relevant, considering the hygroscopic properties of the waste bleaching clay. Probably, the chemical composition of the recycled filler does not allow a good interaction of the material with water, involving a hydrophobic behaviour of the material and limiting its absorption properties.

In terms of mechanical properties, the compressive strength and indirect tensile strength results are in agreement and follow the same trend. This is a strong indication of the consistency of data. However, there is no clear relation between the mechanical properties of the mixtures and the adoption of waste digested bleaching clay as filler. If the virgin CBMs are taken into account, the substitution of limestone filler with the waste materials seems to have a detrimental effect in terms of compressive strength and indirect tensile strength. On the contrary, if the CBMRs are considered, results indicate an opposite trend: the use of recycled filler allows an increase in both the mechanical parameters. Based on results, the whether or not of RAP is probably the main factor that influence the behaviour of the CBMs. As already verified and well known from bibliography review and in situ applications, the presence of recycled materials in substitution of virgin aggregates generally leads to a reduction of the mixture performance. However, as overall result, every tested mixture was in compliance with the requirement of the most common Italian technical specification for hydraulically bound mixtures for foundation layers. These data are relevant for the recycled CBMs above all, considering that the limits refers to mixture entirely made of virgin aggregates.

The assessment of the durability was based on the reduction of CBMs mechanical properties after a thermal shocking treatment. Once again, the results are in line whit the limits given by the mechanical characterization. The compressive strength after freeze and thaw cycles follows the same trend verified on samples cured in normal conditions. Furthermore, the presence of waste bleaching clay induces a reduction in the mechanical performance for virgin CBMs while for recycled mixtures the results follow an opposite trend. The presence of RAP in the mixture seems to be the real distinctive parameter for its final performances. However, it is worth noting that even after the significant thermal shocking, each tested CBM shows a mechanical resistance higher than the requirements imposed for hydraulically bound mixtures entirely made of virgin aggregates and cured in normal conditions. This is a further indication of the quality of the mix design.

In the light of the above, the application of waste digested bleaching clay in total substitution of limestone filler seems to be suitable for the production of cement bound mixtures. Still, despite the different physical and chemical properties of the two materials, in the case under examination the replacement of the traditional filler with the recycled one did not require an optimization of the mix design. Finally, in an environmental sustainability point-of-view, the use of the waste filler seems to be relevant especially within recycled hydraulically bound mixtures.

6. Activity 4: Experimental application of waste digested bleaching clay for the production of synthetic material for civil infrastructures.

The last activity of the project is related to the use of the waste bleaching clay for the production of synthetic materials. This represents the most wide and transversal activity of the whole research project, involving several different applications which range in the field of construction materials. The common factor for the different applications is the technology used for the production of the material that is the alkali-activation.

The production of synthetic materials can be considered as the most innovative technology presented in the project, since there are no references in scientific literature about the alkali-activation of waste digested bleaching clay. Furthermore, the synthetic process fully embraces the philosophy that is basic for the entire project, about the production of innovative and sustainable construction materials. The final products represent a real example of green materials, involving the reduction in energy and CO_2 emissions for their production and allowing the recycling of wastes.

In the following paragraphs, starting from the description of the synthetic processes, the production of several materials related to the construction field will be presented. Concerning the intended use of the alkali-activated materials, the following applications (Figure 6.1) were tested:

- Synthetic binder;
- Modular elements;
- Synthetic aggregates;
- Lightweight synthetic aggregates;
- Special asphalt concretes.

Figura 6.1. Examples of syntehtic paving block (left), lightweight aggregate (centre) and high friction asphal concrete (right).

6.1. Introduction to Alkali-activated materials

Environmental issues such as wastes production and reuse, and the need for the reduction of the energy demand to produce construction materials, pushed the boundaries of the modern research. According this point of view, the key reason why alkali-activated materials are gaining increasing recognition, after more than 100 years of sporadic utilization, is related to the reduction of CO_2 emissions when they are used in place of the traditional construction materials [59]. Furthermore, this technology allows the recycling and reuse of industrial by-products, which are generally not related to the constructions field [60].

Portland cement can be considered as the most widespread binder material in the manufacture of concrete. However, over the last decades its applications has been extensively questioned due to the environmental impact of clinker production. According to the last statistics, the cement production involved a total contribution of around 9 % of the global anthropogenic CO_2 emissions. Moreover, the rapidly increasing demand for civil infrastructures in the new developing countries from the East of the world is expected to expand the cement and concrete industries significantly [61]. If the emissions given from the concrete production are coupled with the environmental and economic costs related to the transport of the materials, it is clear that innovative and eco-friendly solutions are needed for a sustainable development of the constructions sector [62].

Alkali-activated materials (AAM) are alternative cementitious materials, which can be synthesized by combining resources rich in silica and alumina (called precursors) with strong alkali solutions (called activators) [63]. The result is the formation of a strong amorphous binder, with similar or even better performances than those achieved by cement concrete. The potential of alkali-activated binders to replace the traditional Portland cement is supported by the abundance in industrial by-products potentially suitable to be used as precursors (i.e. fly ashes, blast furnace slags and calcinated clays) [64]. The opportunity for an effective reuse of these wastes could reduce the environmental and economic cost connected to their landfilling [65].

A wide number of studies have examined the emissions of concrete and cement, making comparisons largely based on their production steps [66]. If compared to the alkali-activated process, by avoiding the high direct emissions of CO_2 from cement production and by reducing the process energy, the synthetic materials could efficiently reduce emissions [67]. Greenhouse gas production would be up to 5 or 6 times lower than those for cement. The calculations of different studies estimated a CO_2 emission reduction ranging between 35 and 80 % given by the use of alkali-activated binders instead of Portland cement. This wide range is related to local conditions such as availability of resources and transport distances as well as electricity generation and the choice of mix design. According to the life cycle analysis published by McLellan [68], who evaluated the possible production costs for a typical Australian AAM, the improvement in greenhouse gas over Portland cement is estimated between 44 and 64 %.

History and background

Alkali-activated materials, including the so-called “geopolymers”, have attracted much interest in the academic and commercial sector in the last twenty years. These materials are produced through the reaction of an aluminosilicate, generally supplied in powder form as an industrial by-product or recycled material, within a strong alkaline environment, which is usually a concentrated aqueous solution of alkali hydroxide, silicate, carbonate or sulphate.

The first studies on AAMs were given by Davidovits in the 1970s, who synthesised a solid material by the reaction of an aluminosilicate powder in an alkaline solution [69]. This ratified the beginning of the scientific research on “geopolymer” material, as called by Davidovits. However, the technology of alkali-activation predates this terminology by more than 60 years, with a patent awarded to Kühl in 1908, who investigated the behaviour of mixtures of slag powder synthetized in a potassium hydroxide solution. Later, some applications were registered by Purdon (1930s–1950s) and Glukhovsky (1950s) who get relevant results about the alkali-activation of blast furnace slags. Finally, investigations in this field had a significant increase after the results of Davidovits, who developed and patented binders obtained from the alkali-activation of metakaolin. The main difference between Glukhovsky’s synthetic material and Davidovits’ inorganic polymer relies in the final structure of the material. Still, while the first one has crystalline organisation of its structure, the Davidovids’ compound can be considered as amorphous material. This is due to the quick reactions that occur during geopolymerisation, which do not permit the growth of a well-crystallised structure [70].

From the first studies on this material until today, many terms have been developed referring to geopolymer as “low-temperature aluminosilicate glass”, “alkali-activated cement”, “geocement”, “alkali-bonded ceramic”, “inorganic polymer concrete” and “hydroceramic”. A long debate took place about the difference of geopolymer from alkali-activated material. According to the most respected school of thought, the main difference between the materials relies in the stability of the compound obtained from the activation of aluminosilicate materials by alkalis [71]. According to Davidovids the AAM is just the first step in the production of a geopolymer, in which the addition of metakaolin leads to the development of a stable and well defined crystalline structure.

Despite this variety of nomenclature, these terms define materials synthesized utilizing the same chemistry process, which can be described as a complex system of coupled alkali mediated dissolution and precipitation reactions in an aqueous reaction substrate [72].

From an environmental perspective, one of the most relevant advantages of AAMs over traditional cements is the lower CO_2 emission rate in the production process. This is mainly due to the absence of the high-temperature calcination step in the alkali synthesis, which is instead fundamental for the cement clinker, involving moreover considerable amount of energy consumption. On the other hand, the use of alkaline solutions rather than water for cement hydration, does reintroduce some emission costs, but the energetic and environmental balance is on the side of alkali-activation [73]. Furthermore, the environmental benefits are also related to possibility of using wastes and industrial-by products as precursors if characterized by a proper chemical composition (Figure 6.2).

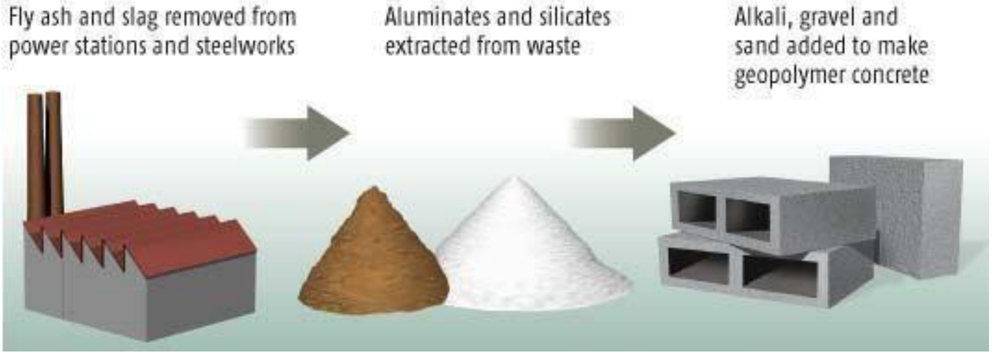

Figure 6.2. Recycling and production of AAMs from industrial-by products.

In the light of the above, there is a growing interest on these innovative materials. Moreover, the technologic progresses as well as the development of specific studies on AAMs mix-designs and final properties, led to the achievement of following well-established physical, chemical and mechanical properties:

- High compressive strength;
- Good abrasion resistance;
- Rapid controllable setting and hardening;
- High thermal resistance (up to 1000 °C) and no emission of toxic fumes when heated;
- High level of resistance to acids and salt solutions;
- Low shrinkage and low thermal conductivity;
- Adhesion to fresh and old concrete substrates, steel, glass, ceramics;
- High surface definition that replicates mould patterns.

The versatility of AAMs allows the optimization of mix-designs and formulations to achieve specific requirements at a minimum cost. With a detailed knowledge of raw materials reactivity and chemistry, it is possible to tailor the material to attain combinations of the above properties to optimize both, cost and technical performances.

These variable properties allow the application of AAMs in several fields, including fire resistant and insulating panels, ceramic tiles and refractory items. As for the constructions sector, the most widespread uses to these materials refer to reinforced concrete, plain concrete, precast concrete components (including lightweight elements), mortars and grouts as well as matrices for the immobilization of toxic and nuclear wastes (Figure 6.3)

Figure 6.3. Alkali-activated precast concrete for structural applications.

On the other hand, the weak point and the potential challenge in commercializing on a large scale the alkali-activated technology is the inconsistency in properties and performance shown by various precursors. It is well known that the performance of AAMs is significantly governed by the properties of the source material in terms of chemical composition and physical properties. Even considering the same material, differences among the chemical compositions may be found between products originated from different locations. This represented a significant problem when transferring the AAMs knowledge to the industrial field. The establishment of standard specifications and testing methods and procedures, designed specifically for AAMs, might be one of the steps in developing the AA technology as a suitable alternative to the cement concretes. Furthermore, a complete clarification and modelling of the alkali-activation reaction and chemistry, based on different well-defined source materials, will be necessary to serve as a general guideline for researchers in identifying the crucial parameters and factors to be considered during the mix design and production stage.

Alkali-activation process

In the alkali-activation process, the chemical reactions takes place between the alkaline activating solution and the solid aluminosilicate precursors, defining the nature and the structure of the formed product. Despite the main macroscopic properties of AAMs prepared from different aluminosilicate sources could appear similar, their microstructure and physical, chemical and mechanical properties vary largely depending on the raw materials from which they are derived.

Glukhovsky [74] proposed a conceptual model for the alkali-activation of Si and Al containing materials in the 1950s. This model splits the process into three stages:

1. Destruction and Coagulation;
2. Coagulation and Condensation;
3. Condensation and Crystallization phases.

Figure 6.4 shows the principal processes occurring during the transformation of a solid aluminosilicate compound into a synthetic alkali-aluminosilicate.

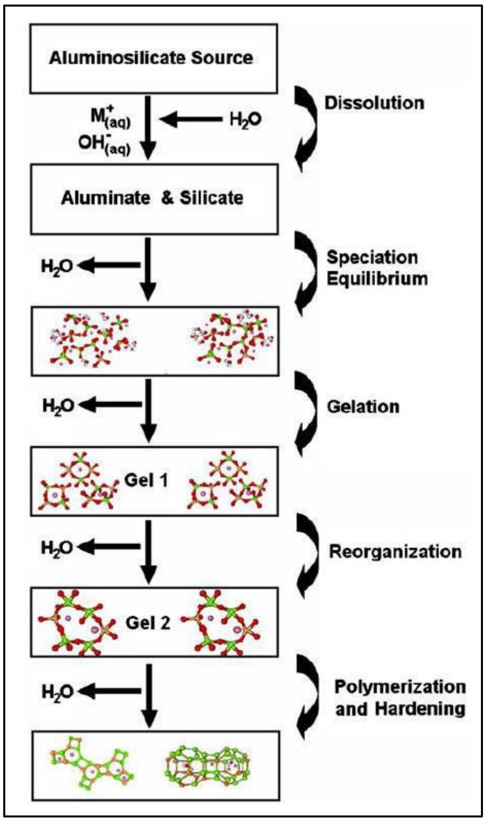

Figure 6.4. Glukhovsky conceptual model for the alkali-activation process.

In the first steps, the dissolution of the solid aluminosilicate source occurs by alkaline hydrolysis As a result, Al and Si hydroxyl species are produced. When in solution, Al and Si are absorbed in the aqueous phase that, according to the activating solution, might already hold silicate. In the following step, an accumulation of the products of the dissolution occurs by the interaction of the particles, forming large networks by condensation. This leads to formation of a coagulated structure, often defined as a gel. This process releases the water that was nominally consumed during the dissolution. After gelation, the system continues to re-arrange and re-organize, as the connectivity of the gel network increases, resulting in the generation of a condensed structure (i.e. the three-dimensional aluminosilicate network commonly attributed to geopolymers).

To deeply understand and clarify the described process, the following citation from Provis [75] is reported: "*The principal means of synthesising geopolymers is to combine an alkaline solution with a reactive aluminosilicate powder (in particular metakaolin or fly ash). This results in the formation of a disordered aluminosilicate gel phase, known as the geopolymeric gel binder phase. Embedded within this phase are unreacted solid precursor particles, and the pore network of the gel contains the water that was used in mixing the precursors (usually supplied via the alkaline activating solution). Unlike in a calcium silicate hydrate (C-S-H) gel, the water does not form an integral part of the chemical structure of a geopolymer binder [...]. The fundamental framework of the gel is a highly connected, 3D network of alumina and silicate tetrahedra, with the negative charge due to* Al_3^+ *in four-fold coordination, localised on the bridging oxygens in each aluminate tetrahedron, balanced by the alkali metal cations provided by the activating solution*".

Still, a detailed explanation was further given by Wang et al. [76]. According to the researcher, the initial formation of an AAM involves the dissolution of the precursor, during which the breakdown of the covalent bonds Si-O-Si and Al-O-Al occurs, and ions (Si and Al) pass into the solution. This step provides the necessary components required for the synthesis, whereas the Si ions liberated from the precursor are only a part of the Si needed. The remaining part comes from the Si ions contained in the activating solution (in the case of sodium silicate Na_2SiO_3 as activator). Simultaneously to the dissolution, also the hydrolysis reaction occurs between the dissolved Al_3^+ and Si_4^+ ions and water. These reactions suggest that during the dissolution phase H_2O molecules and OH^- ions are consumed (this leads to a decreasing alkalinity with digestion time). In the meantime, the aluminosilicate condensation mechanism starts and the $Al(OH)_4^-$ and $[SiO(OH)_3]^-$ species get linked by the attraction through the OH group, resulting in an intermediate complex (coagulation). Next, the OH groups condense forming an aluminosilicate species by releasing a water molecule.

The condensation between $Al(OH)_4^-$ and $[SiO(OH)_3]^-$ species occurs favourably, and a further condensation between the reaction products and $[SiO(OH)_3]^-$ can occur, resulting in large oligomers (stable products). This reaction goes on until all aluminium hydroxyl groups are consumed. Consequently, the polymeric aluminosilicate network begins to build up.

The concentration of the alumina and silica hydroxyls is the crucial factor for the condensation to occur. Therefore, as the Al and Si concentration depends on the alkalinity of the liquid phase (which causes the dissolution), during alkali-activation the alkalinity degree has an important influence on the final products. What Weng et al. clearly observed was the relation between the dissolution rate and the alkalinity of the activator. For a low alkalinity range (1 to 5 M), dissolution was slow and the condensation step hardly occurred. On the other hand, a too high alkalinity led to an unstable condensation. The author concluded that a favourable alkalinity of the activator should range between 5 and 10 M for a stable condensation of the compound.

However, the chemical properties of the activators can control just a part of the synthetic process. The physical characteristics of the AA binders are strongly dependent on the chemical composition of the reaction mixture. Therefore, precursor's chemistry controls the phase evolution and the microstructural development of the AAMs [77].

6.2. Alkali-activated binders

The developing of the alkali-activated binder is the first and basic step for the production of synthetic materials. The type of precursors and activators are not the only variables for the reaction processes and the subsequent development of the AAM structure. The following parameters must be taken into account:

- Precursors chemical and physical properties;
- Activators chemical properties;
- Ratio between precursors and activators (P/A);
- Curing conditions.

Furthermore, it is worth noting that generally precursors and activators are a blend of different materials. As a consequence, the right mix of the materials is another important parameter for the final properties of the AAM. By optimizing the aforementioned variables, very different materials can be produced in terms of chemical and mechanical properties. The versatility of the alkali-activation process allows the tailoring of the material's properties in relation to its final application. On the contrary, the first initial characterization is a crucial step for the evaluation of these properties and it could take long time to define a proper mix design.

In the following sections, the one-year research that led to the characterization of a well-defined recipe for the production of AA binder from waste digested bleaching clay has been summarized.

Precursors

In terms of source materials, the waste digested bleaching clay was used as main precursor. At the beginning of the research, the adoption of this waste was maximized according to several mix designs. However, considering its chemical properties, after several trials its application as only precursor was considered unable to develop a proper alkali reaction with the activators. Furthermore, when a reaction occurred, the final properties of the AAM were sometimes unsatisfactory from the mechanical point of view.

The first expedient was the calcination of the waste digested bleaching clay. The material was kept in a muffle for 6 hours at 600 °C (Figure 6.5). The process was able to remove the 1 % of residual oil content within the particles, which probably limited the alkali-activation synthesis.

Figure 6.5. Waste digested bleaching clay before (left) and after calcination (right).

After the calcination process, the material was able to develop a minimum AA reaction with activator, but the final structure of the material was considered weak for its final application as construction materials.

According to bibliographic review, generally every material that contains reasonable amounts of alumina and silica could be suitable for alkali-activation. Among these, calcinated clays, in particular metakaolin, have been widely used in AA synthesis.

The metakaolin is the anhydrous calcined form of the clay mineral kaolinite, which is traditionally used in the manufacture of porcelains or for cement concrete applications. Metakaolin is formed when mineral kaolin is heated to temperatures between 450° and 650°C. During this dihydroxylation process, the clay mineral goes through a series of transitional phases until it is characterized by a complex amorphous structure with pozzolanic properties. Metakaolin consists of silica and alumina in active form, which reacts with hydroxides at room temperature.

The metakaolin used in the present work is a commercial powder with very fine particle distribution (95% of the particles are smaller than 80 μm) and high purity, with a specific density equal to 2,400 g/cm^3.

The chemical composition of the metakaolin is specified in Table 6.1, while Figure 6.6 shows the material.

Oxide	Percentage (%)
Na_2O	0,40
MgO	0,15
Al_2O_3	40,00
SiO_2	55,00
K_2O	0,40
CaO	0,15
TiO_2	1,50
Fe_2O_3	1,40

Table 6.1. Metakaolin chemical composition by its oxides.

Figure 6.6. Metakaolin in powder form.

Generally, inorganic polymer binders synthesised from the alkali-activation of metakaolin require large volumes of liquid to create workable pastes. Despite their water demand, metakaolin based binders can exhibit comparable or superior mechanical properties to Portland cement. Several researches highlighted the stiffening power conferred by metakaolin, when used as precursor, to the final AAMs.

Activators

To activate the silica and alumina present in the blend of waste digested bleaching clay and metakaolin used as precursors, a strong alkaline medium is required. For the synthesis, two kinds of activator are generally used in AAMs: a straight alkaline hydroxide solution or a liquid mix of alkaline silicate solutions with alkaline hydroxide. The alkali hydroxides most commonly used as activators are sodium and/or potassium hydroxide (NaOH, KOH) used alone or in combination with sodium silicate or potassium silicate (SiO_2Na_2O, SiO_2K_2O).

In the present research, after a preliminary application of different alkaline silicate solutions and blends, a specific mix of Sodium Hydroxide and Sodium Silicate was used as activator.

Sodium Hydroxide (SH) is the most commonly used hydroxide activator in inorganic polymer synthesis, being the cheapest and the most widely available alkali hydroxide on the market. However, the highly corrosive nature of concentrated NaOH, requires a specialised processing equipment to produce large volumes of hydroxide-activated AAMS. The dissolution of Si and Al species during the synthesis of geopolymer is very much dependent on the concentration of NaOH, where the amount of Si and Al leaching is mostly governed by the NaOH concentration. According to several studies, a solution with high concentration provides better dissolving ability and produces reactive bonds for the monomers, increasing the structural strength of the AAM. On the other hand, a too high Na concentration leads to the formation of zeolite crystallization, with a detrimental effect on strength development. Furthermore, high concentrations of Na involve the formation of efflorescence, due to the reaction of the excessive alkali with the atmospheric CO_2. It is today verified that a good sodium hydroxide concentration should range between 8 and 12 M. Following these indications, a 10 M sodium hydroxide was used in the present research.

Sodium Silicate (SS) in the other liquid blended to sodium hydroxide in order to improve the alkali reaction for a better AA final product. The SS employed in this research is a commercial product, with a SiO_2/Na_2O ratio of 1,99 and a viscosity ranging from 150 to 250 MPa·s at 20 °C.

Experimental program for AA binder

The evaluation and validation of the AA binder is a basic step for the development of the research activity related to the use of AAMs suitable for construction materials.

Starting from the choice of precursors and activators, the assessment of the quality of AA binders is given by the visual analysis and mechanical characterization of samples. In this case, the samples were 4 x 4 cm cubic specimens, entirely prepared with the AAM paste: no aggregates of structural reinforcements were added to the mixture.

The research program can be divided in the following activities:

- Mix design and preparation of samples;
- Visual analysis of samples after curing;
- Mechanical characterization (EN 1015-11).

It is worth noting that being the alkali-activation a relatively new technology, there are not standardised procedures for the evaluation of the quality of the final product. Furthermore, being the AAMs extremely variable in relations to their compositions, there is not a specific testing procedure or reference values for the evaluation their mechanical properties. Taking this into account, in the present work the assessment of the mechanical properties of the AA mixtures was based on the compressive strength analysis, following the indication of the EN 10511-11 standard

(Determination of flexural and compressive strength of hardened mortar for masonry).

Mix design and preparation of samples

The mix design step is the most important step in the production of an AAM. The variables that must be taken into account refer to:

- Source materials blend used for precursor;
- Liquid mix for activators;
- Precursor – activator ratio;
- Mixing procedure.

On the basis of these parameters, the final properties of the AAM are determined. The following results represent a summary of the different mixture produced in over one year of trials to identify a mix design suitable for the final application of the AAM.

In terms of precursors, as aforementioned a blend of calcined waste digested bleaching clay and metakaolin was used. Of course, for environmental and economic reasons, the first trials had the target to maximize the use of waste material. Starting from mixtures prepared with 100 % waste digested bleaching clay, the amount of metakaolin was gradually increased, considering its fundamental role in conferring stiffness and strength to the AAM structure.

As for activators, sodium silicate and sodium hydroxide were chosen as alkali solution. Despite several tests with potassium silicate, a blend of the two solutions was evaluated as adequate in terms of workability and quality of the synthetic process. Different mixtures were prepared according to two SS-SH ratio, equal to 4 and 3.

The precursor-activator ratio was adjusted step by step, considering the gradually increase in the metakaolin within the different mixtures. The P-A ratio is indeed mainly governed by the absorption power of the powders used as precursors as well as by the desired workability of the mixture. The waste digested bleaching clay is characterized by high absorption properties, due to its intergranular porosity and particles specific area. By increasing the amount of metakaolin, the hygroscopic properties of the blend of the two powders gradually decreased. As a result, different mixture were produce with a P-A ratio ranging from 0,6 to 1.

The mixing procedures were established and fixed after several trials, being this step fundamental for the final properties of the AAMs. The mixing time for the preparation of precursors and activators was defined as well as the procedure needed to achieve the desired workability of the AAM. Once prepared, the material was poured in 4 x 4 cm cubic mould to be cured. Figure 6.7 shows the procedure and the moulding of samples.

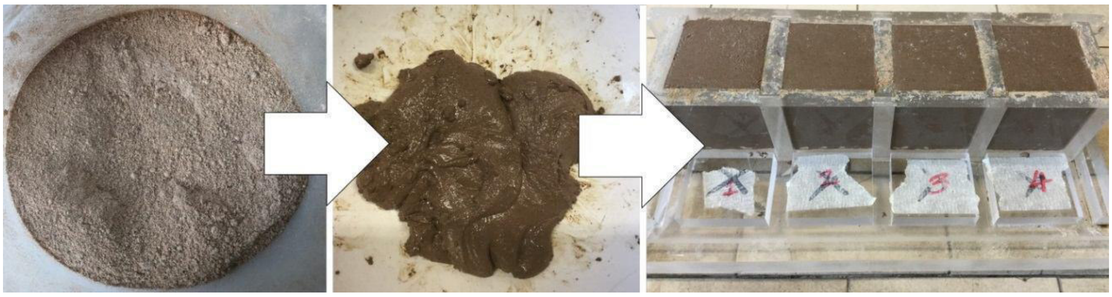

Figure 6.7. Dry precursors mix (left), AAM after mixing (centre) and making of samples (right).

Different curing conditions were fixed, as reported in the following section.

Visual analysis of samples after curing

The evaluation of the quality of the AAM was given by the visual analysis of the samples after curing. The curing regime has a very significant impact on the physical and chemical properties of final material. According to bibliographic review, the heat treatment leads to the dissolution and alkali-activation of the aluminosilicate gel, which results in high early strength gain. It also provides for the acceleration of the dissolution of Si and Al species and the subsequent polycondensation process. However, the heat treatment must be appropriate in order to provide the ideal conditions for the synthetic process. The perfect curing conditions are a direct consequence of the type of AAMs and of the final application of the material. If the heat treatment is pushed at high temperature (up to 130 °C), a rapid increase in the mechanical properties is generally obtained. On the other hand, the AAMs cured at room temperature are characterized by a better quality in terms of lower porosity and higher strength. Nevertheless, according to the most accredited studies, a heat treatment between 30 to 110 °C has a significant contribution to the alkali-activating reaction.

As for the curing time, the increase in strength for heating periods beyond 48 hours is not significant. On the contrary, longer periods of heating lead to the decrease in the compressive strength. The prolonged exposure to high temperature breaks indeed the granular structure of the material, causing dehydration and shrinkage.

All the different mixtures prepared were cured according to several conditions, varying the covering method, the temperature and the time into the oven or/and at ambient condition. The visual analysis of the samples once cured was used as method to verify the ideal curing conditions. Of course, the final evaluation of the quality of the mix was supported by the following mechanical characterization. The visual analysis of samples cured according to several procedures is represented in Figure 6.8.

Figure 6.8. Visual analysis of the samples after curing and demoulding.

After the visual analysis of the external and inner (once tested) surfaces of the samples, the covering method and the temperature into the oven were detected as the main variables that condition the quality of the curing.

When the temperature inside the oven exceeds 60 °C, some cracking occur on the external surface of the samples. Still, if the samples are not perfectly covered during the curing period, a non-uniform drying happens on the external surface (Figure 6.9).

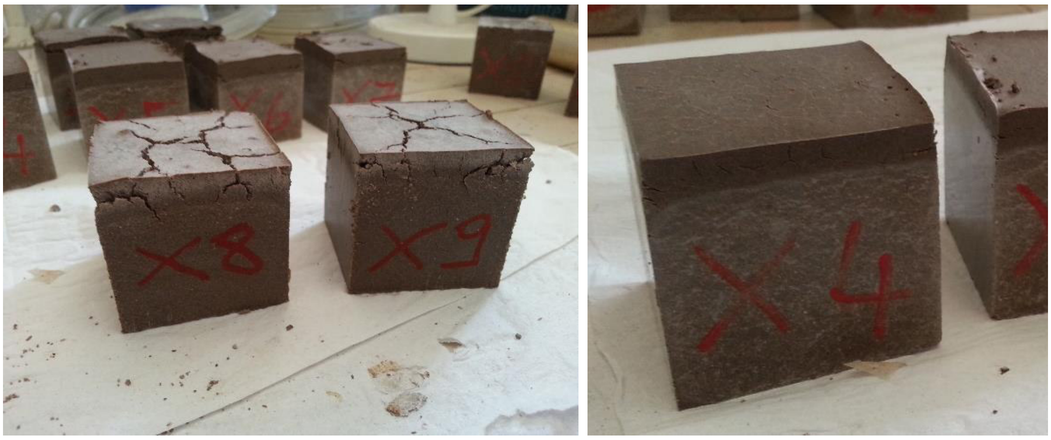

Figure 6.9. External cracking due to high temperatures (left) and non-uniform drying (right).

Furthermore, after the thermal treatment into the oven, some moisture was detected on samples surfaces, below the plastic film covering. To ensure an adequate drying the samples were kept at room temperature for 24 before demoulding.

As a result, the optimal curing method foresaw the hermetic covering of the samples with a plastic film and their conditioning in the oven at 60 °C for 48 hours, followed by the drying at ambient temperature for 24 hours before demoulding.

As aforementioned, the definition of a fixed curing method was validated by the visual detection of the inner structure of samples after the mechanical characterization presented in the following section.

Mechanical characterization

The mechanical characterization of samples was based on the evaluation of the compressive strength of samples. Considering the absence of specific test procedures for the mechanical analysis of AAMs, the EN 1015-11 standard was taken as a reference. According to the standard, the compressive strength of hardened mortar is evaluated applying a load without shock and increasing it continuously at a rate within the range 50 N/s to 500 N/s so that failure occurs within a period of 30 to 90 second (Figure 6.10). The maximum load in registered and the compressive strength is calculated.

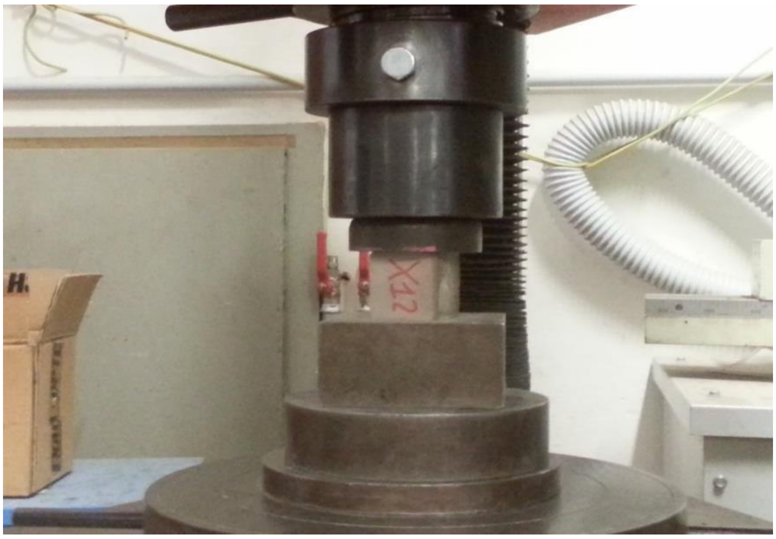

Figure 6.10. Compressive strength test.

For a detailed evaluation of the compressive strength and for the analysis of the development of the mechanical properties, tests were repeated on samples cured for 3, 7, 14 and 28 days. After being tested, the samples were visually analysed to evaluate the possible presence of residual internal moisture or undesired porosity due to an imperfect mixing or curing.

Considering the wide amount of mixtures and the different curing conditions used, Figure 6.11 shows the results only for the best AAM in terms of mechanical properties and curing conditions.

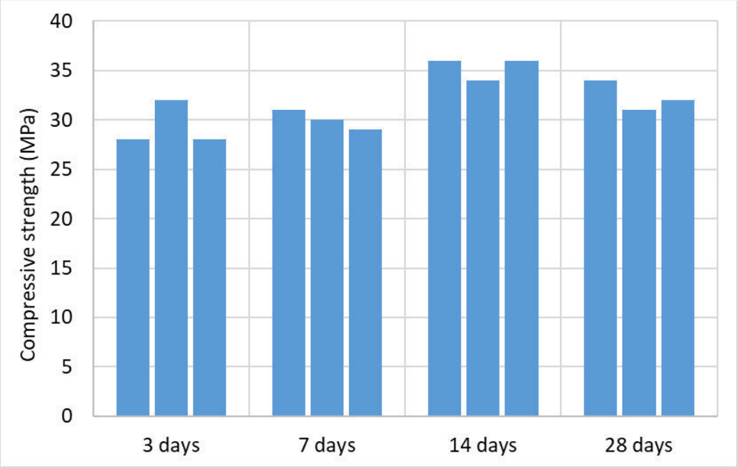

Figure 6.11. Development of compressive strength for AAM.

As overall result, the AAM reaches just after 3 days of curing a compressive strength comparable to a traditional cement concrete fully cured after 28 days. Even if there are no limitations or suggested values for AAMs in the technical specifications related to the construction sector, the mechanical properties verified could presume their application as construction materials.

From the analysis of results, the AA mixture achieves a considerable compressive strength after 3 days and a slight increase in values is registered in the following period, until 14 days of curing, when the material reaches the highest mechanical performance. After 28 days, a minimum decrease in the compressive strength is registered. However, values were always over 30 MPa. Further tests on samples cured after 2 months, verified the maintenance of the mechanical properties calculated after 28 days.

The visual analysis of the tested samples (Figure 6.12) established the absence of residual internal moisture or undesired porosity, validating as optimal the curing method consisting in 48 hours in oven at 60 °C and 24 hours at room temperature before demoulding.

Figure 6.12. Visual analysis of the inner structure of a tested sample.

Conclusions

The last activity of the project is related to the use of the waste bleaching clays for the production of synthetic materials. This represent a wide activity, involving several applications which have for common factor the alkali-activation of the waste material. The first and basic part of the whole activity is related to the mix design and characterization of an AA mixture, needed for the production of materials suitable for each different final application.

The AA synthesis is ruled by several variables, being the mix design and characterization part fundamental for the definition of the final properties of the material. In the case under examination, the calcined waste digested bleaching clay was used as precursor, together with metakaolin, able to confer adequate mechanical and workability properties to the mixture. However, high amount of metakaolin could be inconvenient from an environmental and economic perspective. The activators needed for the alkali synthesis was a blend of sodium silicate and sodium hydroxide.

Several mixtures were produced varying the mix of precursors and activators, as well as the ratio between these two compounds. Furthermore, being the curing of these materials basic for the development of an adequate inner structure, different curing methods were tested. The evaluation of the quality of the AAMs was based on the mechanical characterization of 4 x 4 cm cubic samples (EN 1015-11) and on the visual analysis of samples before and after testing.

From the analysis of results, the following recipe was defined as the optimum mix design:

- Precursors: 50 % calcined digested bleaching clay, 50 % metakaolin;
- Activators: SS/SH equal to 3;
- Activator/Precursor: 1;
- Curing method: 48 hours at 60 °C and 24 hours at room temperature before demoulding. The mixture must be hermetically wrapped into a plastic film for the curing into the oven.

The following mechanical characterization showed the achievement just after 3 days of curing of suitable compressive strength (29 MPa) to assume the application of the AAM as construction material. The maximum mechanical properties are reached after 14 days of curing (35 MPa). If a traditional cement concrete is taken as a reference, the AAM allows the achievement of comparable mechanical properties in a shorter period. Furthermore, it is worth noting the environmental benefits (waste recycling and reduction in CO_2 emissions) related to this new technology for the production of innovative and alternative construction materials.

6.3. Alkali-activated material for modular elements

Once evaluated the mix design and the basic mechanical properties of the AA mixture, the aim of the research project was to define different applications for this innovative material into the constructions sector. Thus, the mix design was optimized to achieve suitable properties in relation to its intended use. It is worth noting that there are no specific test methods or procedures for the AAMs. Therefore, the evaluation of the materials properties was based on the comparison with limits, values and requirements indicated by technical specifications and standards for traditional construction materials.

In the case under examination, the first application in the civil engineering field is related to the use of AAM for the production of modular elements. Considering the application of this material in the infrastructures sector, new innovative AA paving blocks were designed and tested.

The most widespread paving blocks are manufactured by concrete casting and vibro-compression in special moulds and can have various geometric shapes. Generally, these products have shaped side faces to facilitate their installation and to improve the interlocking between adjacent elements. This effect of self-locking favours the lateral transmission of the horizontal components of the loads. In general, the paving blocks have thicknesses between 4 and 8 cm in the presence of light traffic or only pedestrian. As for their installation, usually they are laid on a 5 cm layer of sand placed on properly compacted soil. In the presence of heavy loads, it might be necessary to use blocks up to 10 cm of thickness.

Durability, low costs, eco-compatibility and customization are some of the advantages of these products. Their high level of resistance makes them ideal for outdoor paving, such as:

- Large surfaces: paving in self-locking blocks are commonly used in parking areas for motor vehicles and heavy vehicles, storage areas for industrial activities, container terminals. In these interventions, the use of paving blocks showed a suitable durability, allowing the reduction of the environmental impact thanks to the permeability properties of the layer.
- Urban areas: in local paving roads or in context characterized by aesthetic value, especially in urban areas, this solution retains longer life and less need for maintenance. Moreover, the possibility of choosing different constituent materials with several colorations, limits the visual impact of the paving area on the surrounding. The wide possibilities of aesthetic variations allow the design of pavements that are able to integrate with the historical and cultural building heritage. In this case, the economic factor makes them particularly competitive (Figure 6.13).

Figure 6.13. Exempe of pavements built with modular elements.

The main defects of these pavements fall into the need to pay particular attention to both the design and the installation phase. Furthermore, the presence of joints between the blocks makes the pavement noisy for heavy traffic roads.

Experimental program

The evaluation of the quality and the assessment of the properties of the AA paving blocks were given through a laboratory characterization. The EN 1338 standard specifies materials, properties, requirements and test methods for unreinforced cement bound concrete paving blocks and complementary fittings. It is applicable to precast concrete paving blocks and complementary fittings for pedestrian use, vehicular use and roof coverings, e.g. footpaths, precincts, cycle tracks, car parks, roads, highways, industrial areas, aircraft pavements, bus stations and petrol filling stations. It is worth noting that the standard is a collection of requirements for the characterization of paving blocks, however not every reported test is needed to validate the application of the product. Thus, the required tests are specified according to the final intended use of the paving blocks.

The experimental program was divided in several activities:

- Mix design and characterization of the AAM;
- Production of AA paving blocks;
- Characterization of the material (EN 1338).

In the following sections the materials, test procedure and results are analysed.

Mix design and characterization of the AAM

Starting from the original recipe for the AA binder, the mix design was modified and optimized considering the presence of aggregates within the mixture.

The adoption of adequate aggregates contributes to the achievement of specific properties in the final product. In particular, it improves the mechanical strength and the final performance of the product, with respect to the mixture without aggregates. Each material requires a specific analysis related to the aggregates to be used and it is not possible to have a standard grading distribution for any type of product. The manufacturers of paving blocks use customized grain sizes distribution to create their own commercial products, having certain properties (Figure 6.14).

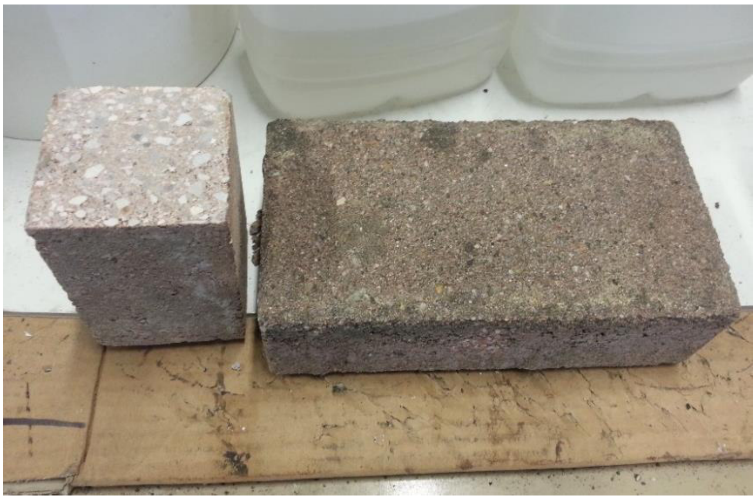

Figure 6.14. Section and example of commercial paving block.

Using basaltic aggregates and sand, the particles size distribution of the experimental paving blocks was designed, as shown in Figure 6.15.

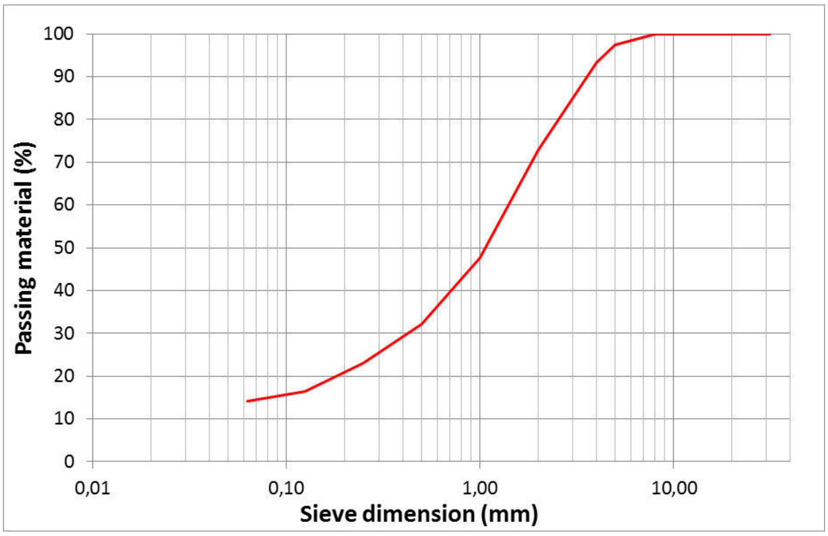

Figure 6.15. Particle size distribution for aggregates within the experimental paving block.

The original mix design of the AAM was optimized in terms of precursors and activators dosages to achieve a good workability of the mixture with aggregates and suitable mechanical properties. The final mix design here presented is the result of several trials occurred during this phase of research:

- Precursors: 50 % calcined digested bleaching clay, 50 % metakaolin;
- Activators: SS/SH equal to 3;

- Activator/Precursor: 1;
- AA paste/Aggregates: 0,9:
- Curing method: 48 hours at 60 °C and 24 hours at room temperature before demoulding.

The mechanical properties of the mixture were evaluated through the compressive strength assessment. The study of the development of the mechanical properties was carried out by test repetitions after 7, 14 and 28 days of curing. Results are presented in Table 6.2.

Curing time (days)	**Compressive strength (MPa)**			**AVG C.S. (MPa)**
7	35	47	45	42
14	40	37	41	39
28	38	37	37	37

Table 6.2. Compressive strength results for AAMs.

The results presented in Table 6.2 shown a slight reduction of resistance from day 7 to day 28. However, values are considerably high if compared to the traditional cement concrete mixtures used for the production of common paving blocks. Furthermore, the presence of aggregates within the mixture led to an average increasing in the compressive strength around 22 % in relation to the AA paste. It is worth noting that the compressive strength is strictly dependant on the mix composition and commercial products have extremely varying mechanical properties in relation to the final application of the materials. However, the minimum compressive strength value requested for blocks for pedestrian sidewalks is 15 MPa. The value registered for the studied AAM is considerably higher.

The visual analysis of the inner and outer surfaces of the samples validated the curing method used (Figure 6.16).

Figure 6.16. Visual detection of the external and inner surfaces of the samples.

Production of AA paving blocks

The following step in the research program was the production of experimental paving blocks. For this purpose a plastic rectangular mould, specific for the production of paving blocks was used (Figure 6.17).

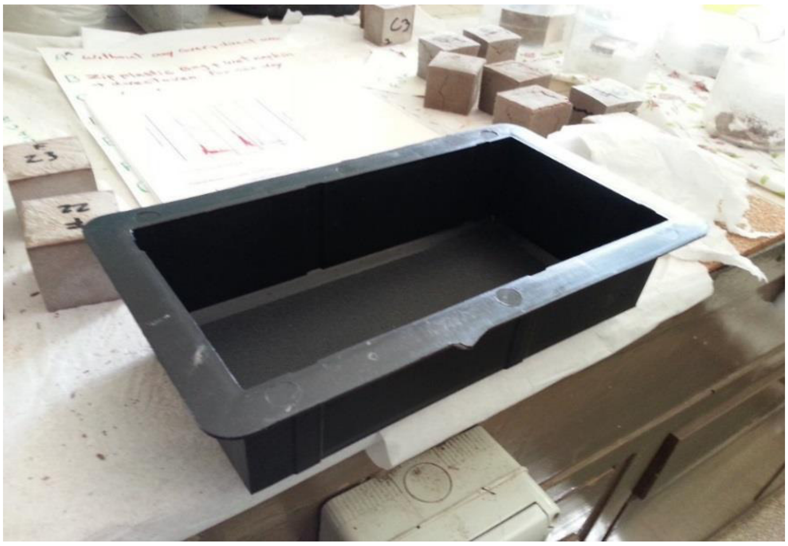

Figure 6.17. Plastic mould for the production of paving blocks.

Six samples were produced and cured according to the procedures defined in the previous step of the research program. Figure 6.18 shows a section of a sample and its outer shape.

Figure 6.18. Cross section and outer shape of an AA paving blocks.

Once cured the paving blocks did not show external cracking on the surfaces and the inner porosity was considered satisfactory. This was a further validation of the mixing, producing and curing procedures as well as of the quality of the mix design.

Characterization of the material (EN 1338)

The EN 1338 standard collects every requirement and technical specification for unreinforced cement bound concrete paving blocks. According to the present research program, the following tests were carried out on the experimental paving blocks:

- Shape and dimensions;
- Slip/skid resistance;
- Water absorption.

According to EN 1338 standard, the shape and dimension of blocks were checked. Size and dimensions of samples were measured precisely. The standard specifies tolerance ranges for deviations of length, width, thickness, flatness and bow. The experimental paving blocks are 201 mm long, 100 mm wide and 60 mm thick. Based on the standard, the AA paving blocks fulfilled the deviations of length, width, thickness, flatness and bow.

The skid resistance is important for the safety of pedestrians' walkways, both in roadside and in recreational areas. The skid resistance test was used to determine the quality of the paving blocks and to determine whether the particular surface finish was appropriate for the application. In the case under examination, the surface texture was giving by moulding, able to stamp a particular texture on the upper surface of the paving brick. To perform the test, the test surface is wetted, and a portable British pendulum is able to evaluate the friction as the resistance offered by the surface to a rubber shoe that is allowed to slide on it (Figure 6.19). Friction resistance is read on a specific scale on the machine as the British Pendulum Number, which is then adjusted according to the surface temperature.

Figure 6.19. Skid resistance test on a AA paving block.

The obtained values are reported in Table 6.3.

Sample	British Pendulum Number (BPN)					AVG (BPN)
AA PB 1	50	48	47	48	51	49
AA PB 2	54	54	54	53	52	53
AA PB 3	49	50	49	48	48	49
AA PB 4	50	47	48	47	47	48
AA PB 5	46	44	44	43	44	44

Table 6.3. BPN results for AA paving blocks.

In terms of results, the AA paving blocks show suitable skid resistance properties. Of course, the BPN values can be improved modifying the internal texture of the mould or by the means of superficial roughening operations. According to the EN 1338 standard, the minimum required BPN for paving blocks for pedestrian use is equal to 45. The average value calculated for the experimental paving blocks is 48. Therefore, the AA paving blocks ensure suitable skid resistance properties.

Water absorption test is very important for pedestrian paving materials considering their exposure to weather conditions. Furthermore, this is an indirect evaluation of the porosity of the material. If the porosity is above a certain limit, the water absorption is generally considerable. Moreover, this phenomenon could have a detrimental effect for the properties of the material during winter condition. With the decrease in temperature, the excess water could freeze the external surface, causing slipping, or could expand its volume, resulting in the development of cracking within the material. To evaluate the water absorption, in compliance with the standard the specimens are immersed in portable water at a temperature of (20±5) °C until a constant mass is reached (Figure 6.20). The water absorption is calculated as the ratio between its weight before and after saturation.

Figure 6.20. Samples placed in a water bath for 72 hours.

The results indicate an average water absorption equal to 15,9 %. This value is considerably higher the water absorption up to 6,0 % suggested for concrete paving blocks. This data is mainly related to the porosity of the AA paving blocks, due to the mixing and casting operations, which can be improved in order to limit the development of air voids content of the mixture.

Conclusions

The production of paving blocks was the first tested application for AAM produced with the calcined waste digested bleaching clay. Considering the absence of specific testing protocols and suggested limits for AAMs, the EN 1338 standard was taken as a reference. The aforementioned standard specifies the testing methods for the characterization of paving blocks prepared with cement concrete. It is worth noting that the limits suggested by the standard are related to the different final application of the paving blocks. The products suitable for road applications have generally higher performance if compared to paving blocks for sidewalks.

To improve the mechanical performances of the final material and to confer a suitable structure to the product, a mix of basaltic aggregates were added to the AAM previously characterized. Of course, the mix design was optimized in order to make the material workable and facilitate the casting operations into a specific mould for paving blocks. The conditioning method tested for the AAMs was verified as suitable for the achievement of proper curing conditions for the experimental paving blocks.

The optimized AAM was firstly tested to verify its mechanical properties. The evaluation of the compressive strength highlighted the achievement of adequate performance. The presence of aggregates within the alkali-activated paste allowed the improve in the compressive strength by the 22 % after only 7 days of curing. The achieved values were considerably higher if compared to the minimum compressive strength requirement for blocks for sidewalks (15 MPa).

The following characterization step was based of the evaluation of the dimensions, skid resistance and water absorption. Despite the compliance with values suggested by the standard for the first two tests, the water absorption was verified as unsatisfactory. The considerable amount of absorbed water is related to the high porosity of the samples, due to mixing and casting properties of the AAMs. These materials are characterized by a relevant thixotropy. This is a time-dependent shear thinning property. The AAMs are indeed thick under static conditions while decrease their viscosity over time when shaken, agitated, sheared or otherwise stressed. Then they take a fixed time to return to a more viscous state. By adding aggregates to the mixture, the viscosity of the material was increased, lowering its workability and casting properties in laboratory conditions. As a result, some air remained trapped within the materials, making its structure porous.

However, despite the air voids content, the mechanical properties of the AA paving blocks were not negatively affected. Of course, even if this preliminary characterization partially validates the application of AAM for the production of paving blocks, further test are clearly needed. To limit the thixotropy of the AAMs, some additives could be added to the mixture to improve its flowing properties. Furthermore, the use of vibrating tables to cast the mould could limit the air voids content of the material after curing.

6.4. Alkali-activated lightweight aggregates

The application of AAMs as construction material, foresaw the production of artificial aggregates. However, considering the current wide use of recycled materials and industrial-by products for the production of sustainable aggregates, the research focused on a specific product: the lightweight aggregates. The following results are related to the paper "Preliminary Research on the Physical and Mechanical Properties of Alternative Lightweight Aggregates Produced by Alkali-Activation of Waste Powders" by P. Tataranni, G.M. Besemer, V. Bortolotti and C. Sangiorgi in Materials (2018, 11, 1255), which is annex to the present work.

Introduction to lightweight aggregates

According to the EN 10355-1, a lightweight aggregate (LWA) is a granular material with a bulk density lower than 1,2 Mg/m^3 and a particle density lower than 2 Mg/m^3. The use of LWA in the construction sector offers functional and economic advantages. The voids and pores in these aggregates improve the thermal and the acoustical insulation of the final product. Moreover, being low-density products, they are capable to reduce the self-weight of the final application. Some LWAs are formed naturally; others are manufactured from natural materials or from industrial by-products [78].

Generally, the natural raw materials suitable for the production of LWA are mineral like pumice, perlite, vermiculite, clay and slate. Except for pumice, these raw materials have to undergo different thermal treatments to be transformed in LWAs [79]. The thermal treatment allows the production of gas inside the material resulting in the expansion and a consequent development of a porous structure [80]. The mentioned materials can be separated into two categories according to their composition, which influence the expansion processes. On the one hand, there are perlite and vermiculite, which are of glass-like composite. These materials contain water, which under heating treatment puffs up and leads to the formation of porous roundish granules. On the other hand, there are clays and slates, which are of clay-like composite. Contrarily to the first category, when these materials undergo high temperatures (1000 – 1200°C), organic carbons and iron hydroxides are formed, which are the blowing agents that cause the expansion of the aggregates [81].

Considering their limited availability, natural LWAs are not extensively used. Furthermore, the physical and microstructural properties of the artificial products can be perfectly controlled, since they are produced applying specific treatments. The most widely used artificial LWAs are the expanded clay, expanded glass, perlite, expanded vermiculite and sintered ash. Among these, the production of Lightweight Expanded Clay Aggregates (LECA) is the most popular because of the abundance in which the raw clay is available all over the world. LECA is an aggregate with a cellular structure enclosed within a hard, strong ceramic "clinkered" outer shell, which optimises the weight-to-strength relationship.

Expanded clay is produced by thermal treatment, which consists in firing a natural, pre-treated and dried clay, which swells at 1000 – 1200°C due to the action of the gases generated inside the mass. The heating process is applied by putting the raw material into a rotary kiln: this is a pyro-processing device made of a cylindrical vessel, slightly inclined to the horizontal, which is rotated slowly around its axis. The clay is introduced into the upper end of the cylinder and undergoes stirring and mixing. Hot gases are produced from the burning fossil fuels, which pass along the kiln and gradually heat up the material up to temperatures of approximately 1200°C (Figure 6.21). This process expands the clay up to five times the original size of the raw material. The resulting particles have a hard and resistant exterior skin and a cellular interior.

Figure 6.21. Section of a rotatory kiln (left) and the produced LECA (right).

As LECA is produced in various particle sizes, a proper grain size distribution is determined in function of the specific final application.

In recent years, much effort has been invested into finding alternative solutions for the production of LWAs using waste materials [82-84]. The main objectives are the reduction of costs and second the possibility of recycling wastes instead of their landfilling, reducing an additional pressure on the environment. Various kinds of waste materials, such as organic waste, sewage sludge, ash, waste glass, polishing residue and glazing waste have already proved their applicability for the LWAs production. These materials are successfully processed with the addition of foaming agents (usually chosen from sulphides, carbonates, water-glass, Fe_2O_3, MnO_2, and SiC), which cause the expansion of the material increasing the porosity of the final product. In general, the granules are prepared by mixing the finely ground wastes together with the foaming agents, and subsequently by treating the raw masses at high temperature. Firing temperatures range between 1000° and 1200°C, when the foaming agents degas, and the resulting gasses remain trapped in the glassy melted structure. Beside these materials, other unconventional wastes (municipal solid wastes, sediments from water reservoirs and harbour dredging, residues from coal power plants) have been tested as partial or total replacement of conventional raw materials for LWAs production.

Furthermore, to better fulfil the ecological needs, the production costs in terms of economic and environmental impact must be limited. A technology for the production of LWAs that does not require high temperature is the cold-bonding palletisation process.

Alkali-activated lightweight aggregates

An interesting option to bypass the expansion process given by thermal treatment is the alkali-activation synthesis. As known, this material has proven to have excellent properties if compared to the traditional Portland cement. Hence, starting from the study of AA concrete, some researchers have investigated the possibility of producing lightweight AA concrete.

Foaming to reduce the density of AAMs is reported in the scientific literature [85]. The challenge for the researchers is to find a suitable balance between the final density of the material and its mechanical properties. The most used method for the production of lightweight AAMs is the addition of chemical foaming agent to the mixture [86]. The most widespread blowing agents are hydrogen peroxide and aluminium powder, while other additives like surfactants and silicon carbide are growing interest in the last years.

The addition of metal powders, such as zinc or aluminium, to the AA paste generates hydrogen gas [87]. On the other hand, hydrogen peroxide and organic peroxides react to evolve oxygen bubbles that remain trapped within the paste, expand and increase its volume. However, a too high amount of foaming agent can lead to the coalescence of the pores or cause pore collapse [88]. This phenomenon is mainly due to the low viscosity of the material prior to hardening and to the long setting time needed for the alkali-activation process.

In the present research, starting from the original AA mix-design defined in the previous step of the experimental program, an AA LWA prepared with waste digested bleaching clay was produced and tested.

Experimental program

Taking as a reference the EN 13055-1 standard, which refers to LWAs suitable as construction materials, the experimental program was divided in the following steps:

- Mix design and production of AA LWAs;
- Evaluation of LWAs geometrical properties;

- Evaluation of LWAs physical properties;
- LWAs mechanical characterization.

The test procedures and the reference limits were taken from the EN 13055-1 standard, but the evaluation of the experimental LWA performance was also based on the comparison with values verified for the LECA. Furthermore, a further AA LWA produced with basalt powder was taken in comparison.

Mix design and production of AA LWAs

Two different mixtures were studied using the waste materials as precursors, combined with metakaolin according to specific proportions in order to achieve suitable mechanical properties. The mix design of the AA LWAs produced with waste digested bleaching clay (labelled LWA_Ud) foresaw the addition of a foaming agent to the already defined compound.

Hydrogen peroxide was used to chemically enable the foaming process of the AA mortar. This material is available on the market as a water solution at various concentrations. The hydrogen peroxide used for the experimentation has a concentration equal to 110 vol.

The other experimental LWA (labelled LWA_B) was prepared through the alkali-activation of a mixture prepared with basalt powder and metakaolin as precursors, and a blend of sodium silicate and sodium hydroxide as activators. Once again, the mix design and the following validation was based on the evaluation of the mechanical properties in terms compressive strength. The chemical composition of the basalt is optimal for alkali-activation. As a consequence, just a small quantity of metakaolin was added to the mixture to increase the mechanical performance of the AAM. The tests carried out of 40 x 40 mm cubic samples highlighted the achievement of a compressive strength equal to 47 MPa after only 3 days of curing. Furthermore, the evolution of the mechanical properties registered an increasing in the compressive strength up to 68 MPa after 28 days of curing.

The addition of hydrogen peroxide to both the mixtures was calibrated in order to balance the volumetric and the mechanical properties. The desired expansion should lower the density of the material without excessively weaken its structure. After some trials, the right dosage of the expanding agent was detected. The final recipes of both the experimental mixtures are reported in Table 6.4 (materials dosages in percentage on the weight of the mixture).

Mixture	Waste DBC	Basalt	Metakaolin	SS/SH	A/P	H. Peroxide
LWA_Ud	50 %	/	50 %	3	1	5 %
LWA_B	/	70 %	30 %	4	0,45	7 %

Table 6.4. LWA_Ud and LWA_B final mix designs.

In terms of mix design, the chemical and physical properties of the two wastes are crucial to define the proper dosage of material. Being the basalt powder much more suitable for the alkali-activation if compared to the waste bleaching clay, the addition of metakaolin to obtain adequate mechanical properties can be limited. At the same time, the sodium silicate-sodium hydroxide ratio is lower for the LWA_Ud, in order to enhance the alkali-activation synthesis. As for the hydrogen peroxide content, its excessive amount results in a weak structure for the LWA_Ud mixture.

The LWAs were produced using a 60 ml plastic syringe, filled with the AAM. The aggregate samples were crafted by extruding the mass from the syringe and by rolling the material to form little balls. The samples were placed onto fine meshed sieves, which are afterwards transferred to the ventilated oven, where the use sieves permitted the airflow around the samples and enable an even curing process (Figure 6.22).

Figure 6.22. Extrusion of material from the syringe (left) and curing into the oven (right).

The curing method foresaw the heat treatment in the oven for 12 hours at 60 °C. Before being tested, the materials were kept at room temperature for 24 hours in order to complete the curing.

During the following physical and mechanical characterization, the properties of the experimental LWAs were always compared with those related to a commercial LECA for structural applications.

Evaluation of LWAs geometrical properties

The evaluation of LWAs geometrical properties was given by the particles size distribution analysis (EN 933-1). The test consists of dividing and separating the material into several particle size classifications of decreasing sizes by means of a series of sieves.

The grading distribution curves of the three LWAs are presented in Figure 6.23.

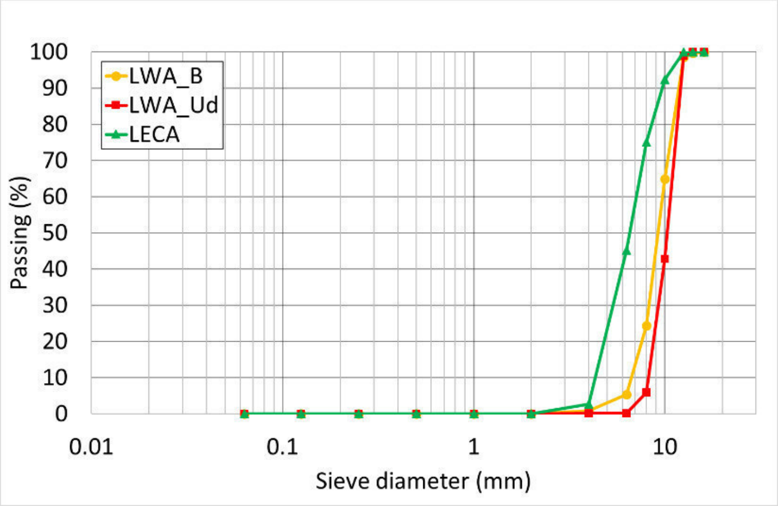

Figure 6.23. LWAs size distributions.

The particle sizes of the experimental LWAs are similar and fall in the 4/12.5 mm designation class. The LECA grading distribution, is characterized by the presence of finer particles and it can be classified as 4/10 mm. The difference in terms of particles shape is presented in Figure 6.24.

Figure 6.24. LWA_B (left), LWA_Ud (center) and LECA (right).

It is worth noting that the different dimension of the experimental aggregates are only related to handcrafted production: every desired dimension could be produced.

Evaluation of LWAs physical properties

The physical properties can be considered as the most important parameters for a LWA. The EN 13055-1 standard suggests a volumetric characterization according to the following tests:

- Loose bulk density and air voids (EN 1097-3) ;
- Water content (EN 1097-5);
- Particle density and Water absorption (EN 1097-6).

Furthermore, a more detailed and in-depth physical analysis was carried out with Nuclear Magnetic Resonance (NMR) and Mercury Intrusion Porosimetry (MIP) tests. The porosity analysis was also supported by the visual detection of the inner structure of the samples given by the optical microscope.

The loose bulk density is the quotient obtained when the mass of dry aggregate filling a specified container without compaction is divided by the capacity of that container. The EN 1097-3 standard specifies the test method. The apparatus needed for the testing is a cylindrical container, internally smooth and with a ratio of the container's internal diameter to its internal depth between 0,5 and 0,8. The minimum capacity of the container depends on aggregate size, in particular on the upper sieve size. According to the testing procedure, using a scoop the container was filled to overflow with dried material, avoiding segregation. Any surplus aggregate was removed from above the top rim, ensuring an even surface by levelling the aggregates (Figure 6.25).

Figure 6.25. Empty container (left) and container filled with LWAs (right).

On the basis of the container volume and the weight of LWAs, the loose bulk density and the percentage of voids were calculated.

The water content was determined in accordance with EN 1097-5 (annex A) by drying the aggregates in a ventilated oven. This method provides a measure of the total free water existing in a test portion of the aggregate particles. The presence of water is related to the absorption properties of the surface of the aggregate as well as to its accessible pores. The water content was determined as the difference in mass between the wet and dry mass of samples and it is expressed as a percentage of the dry mass of the test portion.

The EN 1097-6 standard specifies the reference methods used for the determination of the particle density and water absorption. For lightweight aggregates, the test method is specified in Annex C. According to the standard, a pyknometer method is used for particles ranging between 31,5 and 4 mm (maximum diameter of particles). The density is calculated from the ratio of mass to volume. The mass is determined by weighing the test portion in the saturated, saturated and surface-dried and in the oven-dried condition. The volume is determined from the mass of water displaced in the pyknometer by the aggregate sample (Figure 6.26).

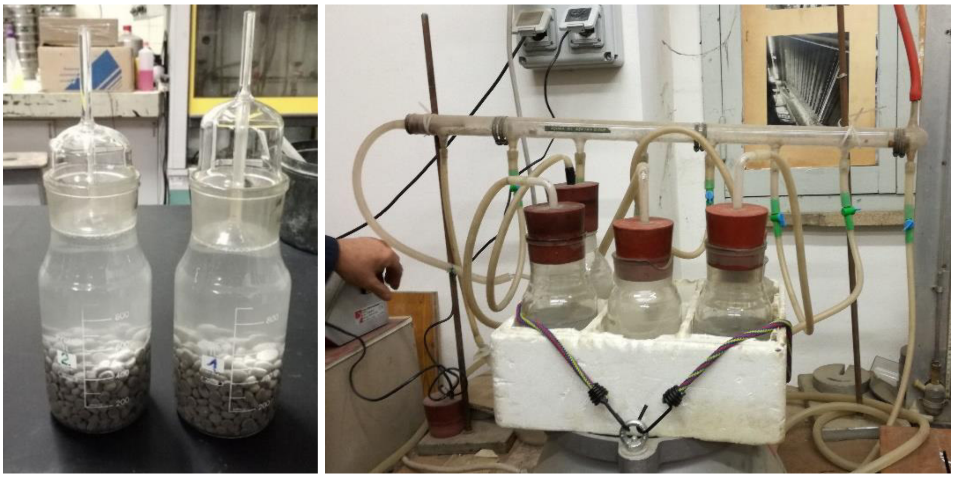

Figure 6.26. Pyknometers filled with LWAs and deareation of water.

Table 6.5 summarizes the average results for each test.

Test	Unit	LWA_Ud	LWA_B	LECA
Loose bulk density	Mg/m^3	0,475	0,702	0,422
Air content	%	36,0	44,3	43,5
Water content	%	4,27	1,27	0,18
Apparent particles density	Mg/m^3	1,18	1,69	0,87
Oven-dried particles density	Mg/m^3	0,74	1,26	0,75
SSD particles density	Mg/m^3	1,11	1,52	0,85
Water absorption after 24 h	%	50	20	17

Table 6.5. Physical properties of LWAs.

The physical properties of the material are extremely dependant on their chemical and mineralogical composition as well as on the expansion process. The particle density is indeed higher for the LECA, whose structure is rich in voids. As overall result, both the experimental LWAs falls in the classification as lightweight aggregates having a particle density lower than 2 Mg/m^3 and a loose bulk density lower than 1,2 Mg/m^3.

Furthermore, LWAs materials were also studied with the Time Domain (TD) Nuclear Magnetic Resonance (NMR) Relaxometry of protons (1H TD-MRR). There is no references in the scientific literature about the evaluation of LWAs Porosimetry according to these methods. This technique is an important non-destructive and non-invasive tool for analysing the structure of porous media. It allows the determination of characteristics such as the porosity and pore size distribution, as well as the permeability. The method is based on the excitation of nuclear states for hydrogen-containing molecules by means of a magnetic field. Since a permeable porous medium is made of a network of interconnected pores of different shapes and sizes, when the test is performed on porous media fully saturated with water, the relaxation times will be influenced by the presence of the pore walls. A molecule of the saturating water continuously moves in the pore network hitting the pore walls, and so the NMR magnetization intensity relaxes back to the equilibrium over a region that is larger than a single pore. If the molecular diffusion is fast enough to maintain the magnetization uniform within the diffusion cell, then the longitudinal and transversal relaxation time (T1 and T2) could be related to the distribution of pore sizes (PSD).

In order to obtain the PSD of a sample via TD-NMR, the surface relaxivity of the sample should be known. Many different techniques are known to obtain it. In the case under examination, the classical Mercury Intrusion Porosimetry (MIP) technique was used. The MIP is an indirect technique for the characterization of the distribution of pore sizes, based on the premise that a non-wetting liquid will only intrude capillaries under pressure. Mercury is therefore used and forced inside the material using pressure. According to several and well-known studies, in the most of the case T1 or T2 relaxation time distribution curves could be very similar to the pore size distribution curves obtained by MIP.

Figure 6.27 shows the distribution of pore size achieved by coupling the TD-NMR results and the information obtained with the MIP analysis.

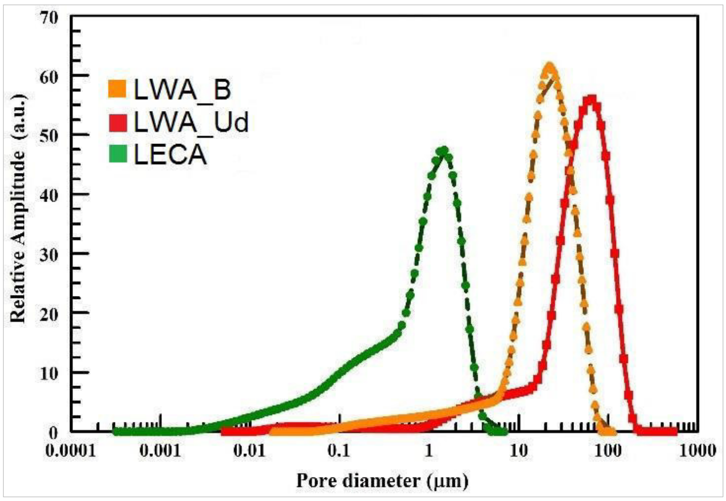

Figure 6.27. PDS from TD-NMR for LWAs.

From the analysis of results, both the experimental materials show a similar pore size distribution. While LECA is characterized by less uniform and smaller pores, both the AA LWAs show more homogeneous and bigger voids. This is a direct result of the different expansion process able to generate the porous structure. These data are in compliance with the visual analysis carried out with the optical microscope on samples (Figure 6.28). The chemical expansion processes confer an inner structure rich in bigger voids for the LWA_Ud, while the reference LECA has a higher porosity formed by smaller voids.

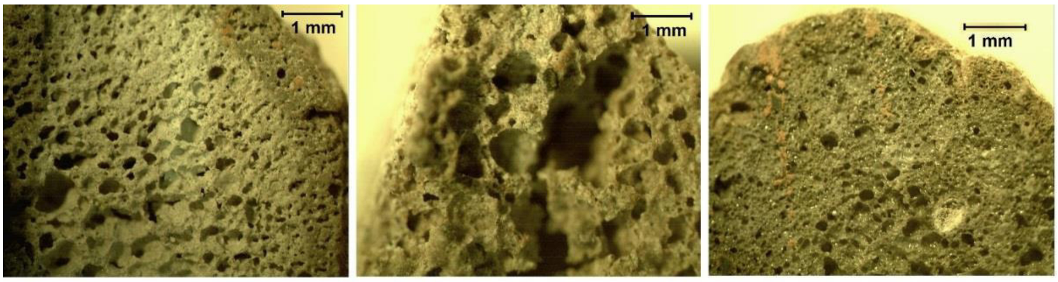

Figure 6.28. Optical microscope pictures for LWA_B (left), LWA_Ud (centre) and LECA (right).

LWAs mechanical characterization

The mechanical characterization of the LWAs is based on the evaluation of the crushing resistance. This is a relevant property for this type of aggregates because it defines the possibility of using the LWA for structural applications.

The test is carried out on a prepared aggregate test specimen, placed in a specified steel cylinder and compacted by vibration. Resistance to crushing is an expression of the force required to compress the test sample, reaching a specific distance in a defined time range. The standard specifies two different procedures depending on the bulk density of the lightweight aggregates. Three test specimens were prepared by filling the steel cylinder with aggregate whilst being vibrated on the vibrating table. When compacted, the aggregate surface was levelled to the top rim of the container and it is placed in test position, under a piston able to reach a compression of 20 mm in approximately 100 seconds (Figure 6.29). The crushing resistance in than calculated taking into account the force exerted by the piston, the compression force and its area.

Figure 6.29. Cylinder filled with material (left) and test procedure (right).

The average results in terms of crushing resistance are reported in Table 6.6.

Results	Unit	LWA_Ud	LWA_B	LECA
Compression force	N	12.150	51.100	38.050
Crushing resistance	N/mm^2	1,07	4,44	3,31

Table 6.6. Crushing resistance average results for LWAs.

As overall result, both the experimental materials show adequate mechanical properties. The basalt LWAs reached the highest crushing resistance, even higher if compared to the LECA traditionally used for structural applications. It is worth noting that the EN 13055-1 standard does not specifies any limitation for the mechanical performance of LWAs. However, the most widespread technical specifications for LWAs generally require a crushing resistance over 1 N/mm^2 to be used for structural applications. In the light of the above, both the AA LWAs are suitable for the production construction materials.

Conclusions

The second possible application of the alkali-activated waste digested bleaching clay was related to the production of synthetic LWAs. The future in the construction sector relies on the use of new-generation techniques and resources, based on sustainable and eco-friendly technologies. Considering the processing and environmental costs related to the production of LECA, the aim of this research was the development of alternative LWAs suitable as construction materials. For this purpose, following the indication of the EN 13055-1 standard, which specifies the testing protocols and the requirement for LWAs suitable for applications in the civil infrastructure field, two experimental LWAs were tested.

In the case under examination, the expansion process needed for the development of the porous and lightweight structure was given by the addition of hydrogen peroxide to the well-defined AA mix design presented in the previous paragraph. Of course, the recipe was optimized to achieve the right balance between internal porosity and structural properties. At the same time, a new mix design was studied and characterized for the production of AA LWAs using basalt powder as main precursor. The evaluation of the mechanical and physical properties was carried out according to a specific research program, and a commercial LECA was used as reference material. Furthermore, the volumetric analysis was supported by specific tests, not usually required for LWAs, being the porosity one of the main characterising properties of these materials. The pores size distribution was studied indeed by the means of TD-NMR and MIP techniques.

After the physical characterization of the LWAs, both the experimental materials showed appropriate properties to be classified as lightweight aggregates according to the EN 13055-1 standard. Both LWA_B and LWA_Ud have densities lower than 2,00 Mg/m^3 and a loose bulk density not exceeding 1,20 Mg/m^3. The voids of the LWAs materials were analysed through the TD-NMR technique coupled with MIP test. The first relevant data is the fitting between the results obtained with the two different methods. There are no reference in the scientific literature about the application of both the technique for the assessment of the porosity of LWAs. Furthermore, the obtained pore distribution data comply with the analysis of the inner porosity given by the optical microscope. The LECA is characterized by smaller voids while the LWA_Ud has a structure rich in bigger pores. The difference in the inner structure of the materials is probably due to the different expansion processes applied.

These data could be related to the mechanical characterization of the LWAs. Even if both the experimental AA LWAs exceed the minimum crushing resistance required by the most common technical specification for construction materials, the LWA_B shows the best mechanical performance. These results are in line with the values recorded during the preliminary mechanical characterization of the alkali-activated paste materials and are mainly dependent on the chemical composition of the wastes used as precursors. However, the basalt aggregates are also characterized by the higher particle density. Furthermore, the lowest result registered for the LWA_Ud is also probably related to its inner structure. As confirmed by the pore size distribution and the optical microscope analysis, the material is rich in large pores and this might have a detrimental effect on its structural properties.

In light of the above, the expansion of these AA waste materials seems to be a suitable eco-friendly solution for the production of sustainable LWAs. According to these preliminary results, both the AA LWAs can effectively be used for the production of construction materials. However, the optimization of their mix design could led to the achievement of better performances. For the LWA_Ud the reduction in its expansion could improve the strength of the structure by reducing the pores size. On the contrary, a slight increase in the LWA_B expansion could reduce the density of the material, without affects its mechanical properties.

6.5. Alkali-activated lightweight aggregates for the production of special asphalt concretes

The final activity of the research project on AAMs is related to the possible application of AA LWAs for the production of special asphalt concretes. The evaluation of its feasibility was verified through a detailed laboratory characterization, as shown in the following sections. The results are related to the paper "Experimental application of synthetic lightweight aggregate for the production of special asphalt concretes" by P. Tataranni and C. Sangiorgi, accepted in the "Sustainable Materials, Systems and Structure Conference 2019" (Rovinj, Croatia, 18 – 22 March 2019), which is annex to the present thesis.

Lightweight aggregates within special road pavements

In the last years, the use of LWAs within the civil engineering field is growing interest due to their thermal and acoustical insulation characteristics as well as for their mechanical properties, combined with the possibility of reducing the self-weight of the final products. Among the LWAs, LECA is the most common product, having great versatility in a wide number of applications through a variety of industries. It can either be used as lightening element within a structural foundation or in an infrastructure on weak and unstable grounds, for insulation under and within floor constructions and for sound proofing buildings. Other uses include the filtering of water or air, the removing of smells from the sewerage, farming applications, to provide aeration and moisture to tree and plant roots, for landscaping or even to decorate plant pots.

Recently many efforts have been made regarding the optimization of pavements, in particular for safety and acoustic matters. LWAs are also used for the construction of road pavements, thanks to their properties and moderately low costs (Figure 6.30).

Figure 6.30. Laying of an asphalt mixture with LWAs (left) and sample's section (right).

The repeated stresses coming from the traffic determine a reduction of the surface properties of aggregates that become polished. Therefore, this process can lead to the loss of adhesion in the contact patch between the road surface and the tires. To solve this problem, high-friction aggregates are inserted in the bituminous mixtures in order to increase the macro-texture of the surface pavement. Lightweight aggregates and LECA, above all, offer a good adhesion contact between the pavement and the tires. Several studies highlighted that common bituminous pavements starts to lose their adhesion properties quickly as time passes by, whereas pavements with LECA can guarantee elevated frictions for a longer time.

Pavements made with LECA have a high skid resistance immediately after paving, due to the rough surface texture of the aggregates. Road surfaces made with traditional natural aggregates (i.e. limestone, dolomite, basalt or porfir) will polish under the action of traffic and lose a large percentage of the in initial skid resistance. On the contrary, even after the stripping effect of the traffic, LECA does not polish completely, having sharp ceramic-like edges that continue to show a high skid resistance.

Furthermore, different studies made in the Nordic countries highlighted the positive outcomes achieved by pavement made with LECA in terms of reduction of frost damaging. Every year the freeze and thaw phenomenon that occurs in the period between winter and spring causes the reduction of the bearing capacity of road pavements. This leads to a relevant increase in a cost for their maintenance. The natural aggregates used in road pavements have low insulation properties due to their mineralogical composition. This allow the penetration and propagation of frost through the whole road structure to the soil. Laboratory analysis verified a reduction in asphalt conductivity up to 42 % when prepared with LWAs. The specific heat capacity of asphalt mixtures with LWAs was found increased by 38 % if compared to common hot mix asphalt. The reduction in conductivity is mainly related to the lower bulk density of these special asphalt mixtures.

Following these indications, in the present research the use of AA LWAs within special asphalt mixtures with high-friction properties was evaluated.

Research program

The assessment of the properties of the Asphalt Concretes (AC) prepared with the AA LWAs is based on a laboratory characterization. Taking as a reference the indications of an Italian technical specification for special asphalt concretes made with LECA, two ACs where produced with the synthetic LWA designed and tested in the previous experimental application. The research program was divided according to the following phases:

- Mix design and production of samples;
- Volumetric analysis (EN 12697-31, EN 12697-8);
- Static mechanical characterization (EN 12697-23);
- Dynamic mechanical characterization and thermal sensitivity evaluation (EN 12697-26);
- Durability and water susceptibility evaluation (EN 12697-17, EN 12697-12);
- Skid resistance analysis (EN 13036-4).

A specific number of samples was produced for each test in compliance with the reference standard. The results obtained for the experimental mixtures were always compared to those obtained from the traditional AC produced with LECA.

Mix design and production of samples

The mix design of the experimental ACs was made in compliance with the gradation limits suggested by the Italian technical specification. The two synthetic LWAs, whose properties are presented in Paragraph 6.4, were used for the production of two experimental mixture, labelled WBC_AC and B_AC. The reference mixture was prepared with LECA (labelled LECA_AC).

To have comparable results, the grading distribution was kept constant for the experimental mixtures and for the reference one. It is worth noting that the aforementioned technical specifications suggest a substitution of natural aggregates with LWAs up to 12 % by the weight of the mixture. Following this indication the maximum rate of raw materials was replaced with LWAs for each mixture. A traditional 50/70 penetration grade bitumen was used as a binder, which dosage (6 % on the weight of aggregates) was kept constant for each AC.

Figure 6.31 shows the chosen grading curve and the limits suggested by the technical specifications.

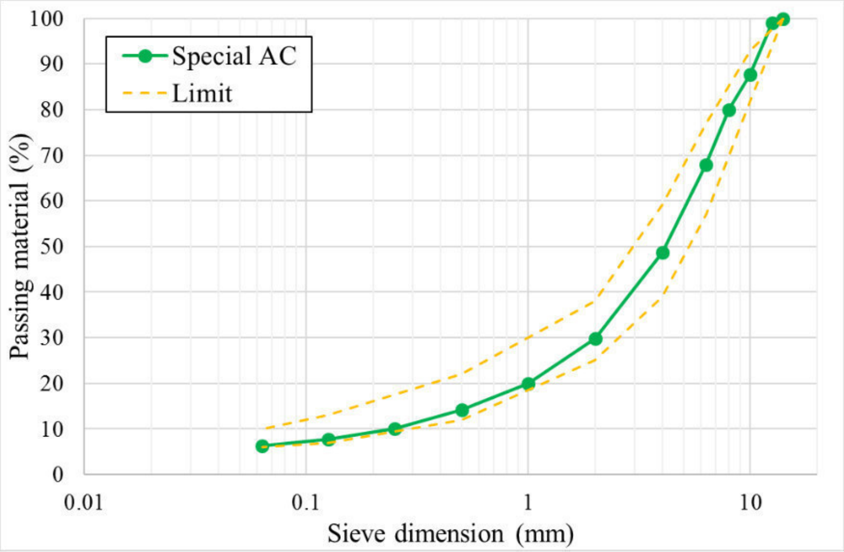

Figure 6.31. ACs particles size distribution.

Considering the experimental program, three samples for each mixture were prepared with gyratory compaction (EN 12697-31, compaction pressure of 600 kPa and 120 revolutions) for the volumetric characterization. Hence, other six SGC samples (80 revolutions) were prepared for the mechanical analysis and four Marshall samples were compacted (EN 12697-30, 50 blows per side) for the Cantabro test (Figure 6.32).

Figure 6.32. SGC (left) and Marshall samples (right).

Volumetric analysis

The volumetric analysis was based on the evaluation of the workability and compactability properties of the mixtures. These parameters are fundamental for an asphalt concrete since they affect the final performances of the material.

The air voids analysis (EN 12697-8) was made on samples compacted with 120 revolutions. The evaluation of the workability properties is based on the calculation of voids at three different compaction energies, corresponding to 10, 80 and 120 gyrations. In order to calculate the air voids content, the bulk density and the maximum density of the mixture were determined according to EN 12697-6 (Procedure D) and EN 12697-5 standards.

Table 6.7 summarizes the average results of three samples for each mixture.

Air voids content (EN 12697-8)	**WBC_AC**	**B_AC**	**LECA_AC**
@ 10 gyrations (%)	22,6	21,4	20,1
@ 80 gyrations (%)	17,1	14,8	13,9
@ 120 gyrations (%)	16,1	13,7	12,7

Table 6.7. Average air voids content for the ACs.

As general result, all mixtures have an high air voids content. According to scientific literature and in situ applications, the porosity of AC containing LWAs is generally higher if compared to traditional bituminous mixtures. Moreover, this porosity is partially responsible for the high-friction surface texture. The differences in the air voids contents are mainly due to a slight variation in LWAs particle size distributions, as specified in Paragraph 6.3. Furthermore, considering the higher absorption properties of the experimental LWAs, the final porosity of the mixtures could be an evidence of their reduced workability due to a non-optimized binder content.

Static mechanical characterization

The static mechanical characterization was based of the calculation of the Indirect Tensile Strength, as specified in the EN 12697-23 standard. Three SGC samples were tested for each mixture, previously conditioned at 25 °C for four hours. Each specimen is placed and aligned in the loading frame between the loading strips (Figure 6.33), and then it is loaded diametrically along the direction of the cylinder axis at a constant deformation rate of 50 mm/min. The calculation of ITS is given by the recorded peak load and the dimension of the specimen.

Figure 6.33. ITS test configuration (left) and samples after failure (right).

According to scientific literature, the test results are generally influenced by specimen cohesion and the adhesion of the bitumen on the aggregates. Considering that the only variable between the ACs is the type of LWA, the analysis of results could be effective in evaluating the interaction between synthetic aggregates and bitumen.

Table 6.8 shows the results.

Mixture	ITS (MPa)	AVG ITS (MPa)
WBC_AC 1	0,94	0,88
WBC_AC 2	0,75	
WBC_AC 3	0,96	
B_AC 1	0,76	0,77
B_AC 2	0,82	
B_AC 3	0,72	
LECA_AC 1	0,67	0,70
LECA_AC 2	0,77	
LECA AC_3	0,67	

Table 6.8. ITS results for the special ACs.

The calculated ITS values for the experimental mixtures are higher if compared to the reference AC, despite the higher content of air voids. This phenomenon could be attributed to the different absorption properties of the synthetic LWAs. As shown in previous applications of waste bleaching clay in bituminous mixtures, the waste material is characterized by a high absorption due to its intergranular voids and remarkable specific area. It is worth highlighting that the Italian technical specifications suggest an ITS value ranging between 0,70 and 1,20 MPa for this kind of mixtures. Both the ACs prepared with the AA LWAs have suitable mechanical properties, exceeding the lower limit suggested for this type of bituminous mixtures.

Dynamic mechanical characterization and thermal sensitivity evaluation

According to the EN 12697-26 standard, the test was performed using the indirect tensile configuration. The Indirect Tensile Stiffness Modulus (ITSM) test is the most widespread testing method for the evaluation of the stiffness of bituminous mixtures. The ITSM was determined through a pulse loading with a 124 ms rise-time, to generate a predefined horizontal deformation of 7±2 μm in the sample.

Before proceeding with the test, the specimens were conditioned in a thermostatic chamber for at least four hours at the desired temperature. In order to verify the thermal sensitivity of the mixtures, different tests were carried out at 10, 20 and 30 °C. The evaluation of the behaviour of material in relation to the temperature is fundamental for asphalt concretes, being the bitumen a thermosensitive material. Hence, the ITSM values must be verified especially at low and high temperatures. In the first case, the AC should not be too stiff, in order to avoid the development of cracking due to its embrittlement. On the other hand, the material should be enough stiff to elude the possibility of accumulating permanent deformations at high temperatures.

The test configuration is presented in Figure 6.34 while Table 6.9 and Figure 6.35 summarize the results.

Figure 6.34. ITSM test configuration in Indirect Tensile mode.

Mixture	ITSM (MPA) at 10 °C	ITSM (MPA) at 20 °C	ITSM (MPA) at 30 °C
WBC_AC	7981	4952	2328
B_AC	7942	5213	2291
LECA_AC	6222	3761	1508

Table 6.9. Average ITSM results for the special ACs.

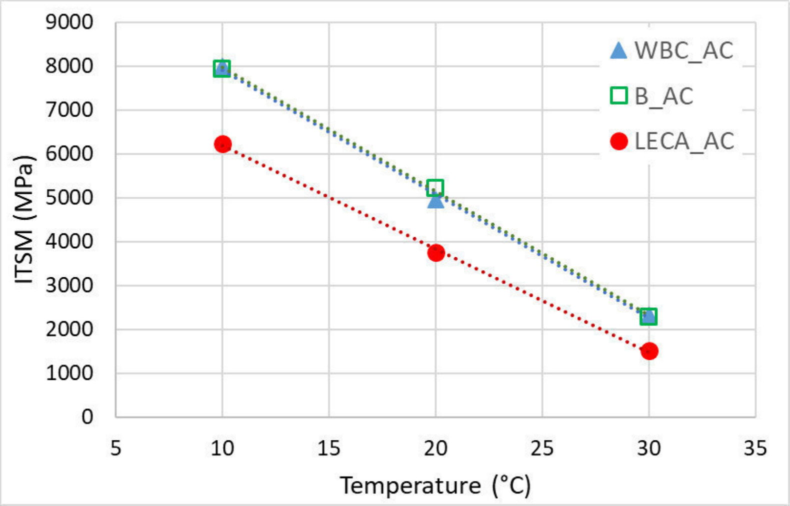

Figure 6.35. Average ITSM results and thermal sensitivity.

As overall result, all the ACs show adequate stiffness at each testing temperature. Generally, bituminous mixture with ITSM values exceeding 3500 MPa at 20 °C can be considered suitable for road applications according to the most widespread Italian technical specifications. Hence, a traditional 50-70 pen bitumen was used as binder. In compliance with ITS results, the experimental mixtures exhibit better mechanical properties if compared to the reference one, despite the remarkable air voids content in the samples. The increase in stiffness for the ACs produced with synthetic LWAs is evident for every testing temperature. In terms of thermal sensitivity, there is no relevant difference between the experimental mixtures, which show the same trend lines. On the contrary, a small variation is verified if the AC produced with LECA is taken as a reference.

Durability and water susceptibility evaluation

The analysis of ACs durability was based on the evaluation of the ravelling resistance according to the Cantabro test, as specified in the EN 12697-17 standard. The Cantabro loss test is used to simulate the effect of vehicles on the road surface, since the estimation of the abrasion resistance gives information about the durability of the road pavements. The particles loss weight is traditionally one of the different method adopted to estimate the durability of ACs. The test is particularly indicated for bituminous mixture rich in air voids, being the contact area between particles limited if compared to dense graded ACs.

The apparatus required for the test is the Los Angeles abrasion machine, which has a steel cylinder with an internal diameter of (711 ± 5) mm and internal length (508 ± 5) mm. According to the standard, four Marshall samples (50 blows) were prepared and kept at 20 °C for 4 hours before testing. The specimens are than inserted into the Los Angeles machine, setting 300 revolutions at a speed ranging between 30 to 33 revolutions/min. After the test, the specimen displays rounded edges and the loss of particles is registered (Figure 6.36).

Figure 6.36. Marshall samples before (left) and after (right) the Cantabro test.

The results are shown in Table 6.10.

Mixture	PL (%) 1	PL (%) 2	PL (%) 3	PL (%) 4	AVG PL (%)
WBC_AC	7,1	5,1	5,8	3,9	5,4
B_AC	6,6	5,5	8,4	4,6	6,3
LECA_AC	9,4	6,1	6,2	8,2	8,2

Table 6.10. Particle Loss (PL) for the special ACs.

The results are in line with the ITS values: the experimental mixtures show the best results if compared to the reference AC. The high porosity of the synthetic ACs does not affect the behaviour of the bituminous mixtures, despite the limited contact area between particles. Those results might indicate a significant cohesion between particles, probably related to the high surface roughness of LWAs.

The durability of a bituminous conglomerate is often related to its water susceptibility, being this a common damaging factor for the bituminous materials. The water susceptibility is generally evaluated through the reduction in ITS value. The test procedure, as indicated in the EN 12697-12 (Method A) standard, foresees for the conditioning of samples in a water bath at 40 °C for 72 hours before testing (Figure 6.37).

Figure 6.37. Samples conditioned in water (left) and specimen after testing (right).

The Indirect Tensile Strength Ratio (ITSR) is than calculated as the ratio between the ITS values verified on samples cured in normal and wet conditions.

Average results are presented in Table 6.11.

Mixture	ITS $_{dry}$ (MPa)	ITS $_{wet}$ (MPa)	AVG ITSR (%)
WBC_AC 1	0,94	0,61	69
WBC_AC 2	0,75	0,69	
WBC_AC 3	0,96	0,53	
B_AC 1	0,76	0,59	90
B_AC 2	0,82	0,64	
B_AC 3	0,72	0,86	
LECA_AC 1	0,67	0,59	98
LECA_AC 2	0,77	0,64	
LECA AC_3	0,67	0,86	

Table 6.11. ITS in dry and wet conditions and average ITSR for the special ACs.

From the analysis of results, there is a relevant difference between the two experimental mixtures. The WBC_AC registered a reduction in ITS values after water imbibition, which is significantly higher if compared to B_AC as well as to the reference mixture. These data are probably influenced by the remarkable air voids content, which makes the mixture more sensitive to the damaging effect of water.

Skid resistance analysis

The EN 13036-4 standard describes the procedure to determine the skid resistance, which is a property of the pavement surface that limits the relative movement between the contact patch of a vehicle type and the surface. The skid resistance is an important parameter for the safety of the users, especially in wet conditions.

This parameter is generally dependent on the following factors:

- Micro and macro-texture of the pavement surface. While the former is related to the contact between the tire rubber and the pavement surface, the latter is determinant when dealing with the wash-off of superficial water;
- Exposure time. Several studies highlighted that during the first two years from the construction of a road pavement, the skid resistance tends to increase since the aggregates are gradually stripped from their bituminous mastic coating. However, the prolonged exposition of pavement to traffic, cause the polishing of aggregates, reducing the skid resistance;
- Weather conditions and season. Skid resistance is generally lower during hot and warmer periods and higher in fall and winter.

The evaluation of the skid resistance is given by the British Portable tester, through a slider mounted at the end of the pendulum arm. From a horizontal position, the pendulum is released and slips onto the pavement surface previously wetted. On the basis of the rising height, which is determined by the pavement-slider friction, the PTV (Pendulum Test Value) is recorded. This procedure was performed five times for each test specimen (Figure 6.38). The PTV value is than adjusted in relation to the surface temperature.

Figure 6.38. PTV test on a bituminous sample.

Results are presented in Table 6.12

Mixture	PTV	AVG PTV
WBC_AC 1	73	73
WBC_AC 2	72	
WBC_AC 3	73	
B_AC 1	70	70
B_AC 2	70	
B_AC 3	70	
LECA_AC 1	66	69
LECA_AC 2	69	
LECA AC_3	73	

Table 6.12. Skid resistance results in terms of PTV for the special ACs.

As overall result, each tested AC shows a significant skid resistance, being this parameter the characterizing property for bituminous mixtures containing LWAs. The substitution of traditional LWAs with synthetic aggregates does not negatively affect the friction properties of the bituminous surface, which are actually improved. Between the experimental mixtures, the AA LWAs from waste digested bleaching clay confer the best results in terms of skid resistance. This data could be also related to the different surface texture of the experimental ACs, being WBC_AC much richer in air voids content.

Conclusions

The purpose of this final activity in the research project was the production of ACs with synthetic LWAs. The application of LWAs in these particular bituminous mixtures allows the achievement of specific features, mainly high skid resistance, reduction of self-weight and drainability properties.

The most widespread LWA is certainly the LECA, which has some environmental and production costs that could be reduced by the AA of waste materials. In the present experimentation, a waste digested bleaching clay and a basalt powder were used as main precursors for the production of AA LWAs. Using these materials, two experimental mixtures were prepared and compared to a traditional AC produced with LECA. The mix design of the mixture was fixed in terms of amount of LWAs, particle size distribution and amount of bituminous binder.

Taking as a reference an Italian technical specification for ACs produced with LWA, the evaluation of the properties of the two experimental mixtures was carried out through a laboratory characterization.

In terms of workability and compactability properties, each mixture is characterized by a high air voids content. These special ACs are characterized by a higher porosity if compared to dense graded mixtures, in order to ensure a specific surface texture. However, the air voids content for the experimental mixture is significant, and this could affect the mechanical properties of the ACs especially in terms of water susceptibility. The WBC_AC shows the higher porosity and this is probably due to the absorption of the synthetic LWAs. In fact, it is worth highlighting that the amount of bitumen was kept constant for every mixture in order to have comparable results. However, the absorption properties of the LWAs are not similar, as verified in the previous experimental activities. The aggregates prepared with waste bleaching clay has an absorption power, which is double if compared to the LWAs containing basalt, while LECA registered the lowest values. The results in terms of air voids content follow the same trend, being the WBC_AC the richest in porosity. The amount of binder should be improved in order to allow a proper compactability to the experimental mixture and reduce the final air voids content.

The volumetric properties as well as the binder absorption influence the mechanical properties as verified in the static and dynamic mechanical characterization. In terms of ITS, the air voids content does not have a detrimental effect on the properties of the mixtures. In this case, the binder absorption is much more important in affecting the mechanical properties of the mixture, conferring stiffness to the mixture. As a consequence, both experimental mixtures show higher ITS results if compared to the reference AC prepared with LECA. However, the Italian technical specifications suggest an ITS value ranging between 0,70 and 1,20 MPa for this type of bituminous mixtures. The ACs prepared with the AA LWAs exceed the suggested lower limit.

The stiffening effect due to binder absorption is detected even after the dynamic mechanical characterization. The experimental mixtures registered an average increase in ITSM values around 35 % at every testing temperature, if compared to the reference AC. Despite the increase in stiffness, the general thermal sensitivity of the mixture is not modified. In absolute terms, even if no limitations are suggested for this type of bituminous mixture by the Italian technical specifications, an ITSM values exceeding 3500 MPa at 20 °C can be considered suitable for AC for roads construction. Thus, both experimental mixtures show adequate stiffness.

Despite the limited contact between particles due to the high air voids content, the Cantabro test registered the best performances for the experimental mixtures. This results can be attributed to the mutual stiffening effect of the binder absorption and the adhesion properties, conferred by the surface roughness of the AA LWAs. On the contrary, the relevant air voids content in the two experimental ACs has a negative effect on the mixture properties if the water susceptibility is taken into account. The presence of water reduce the cohesion between particles and bituminous mastic, which is already limited within the experimental ACs due to the porous structure of the material.

The skid resistance is probably the main significant property for this type of ACs. The addition of LWAs to the mixture in substitution of natural aggregates has the specific intent to enhance the friction properties of the road surface. The use of synthetic LWAs in replacement of LECA allows the achievement of a better skid resistance. This result might be also related to the surface texture of the experimental mixtures, which is characterized by a higher roughness. In absolute terms, it is worth noting that some Italian technical specification suggest a minimum PTV equal to 55 immediately after laying. The experimental mixtures fully exceed this limit.

In the light of the above results, the substitution of traditional LWAs with synthetic materials seems to be a suitable solution for the production of innovative and eco-friendly ACs with high-friction properties. However, the mix design of the mixture must be optimized in order to reduce the layer porosity, which could negatively affect the final performances of the material.

Conclusions

The respect for the environment and the saving of natural resources are current problem, which affect all the sectors within a modern society. In the field of civil engineering, the main action to overcome these issues is related to the research on innovative solutions, able to combine environmental benefits with the reduction of costs. As a consequence, the recycling and reuse of wastes and industrial-by products for the production of new materials represent the new frontier in the constructions sector.

Following this trend, the present research project pursued the possible application of a waste digested bleaching clay for the production of construction materials in the field of civil infrastructures. The waste material is an industrial by-product from Unigrà Srl, and is the output of two consecutive processes for the decolouring of vegetable oils and the subsequent production of biogas. Today this waste is landfilled, representing an environmental and economic cost. The main aim of the research is to evaluate the possible use of this by-product as a construction material.

The research project was divided into four macro-activities, each of them focused on a specific sector of the civil infrastructures. In every activity, the validation of the possible experimental application was given through a full laboratory characterization and by the comparison of results with the requirements imposed by the most common technical specifications for paving materials.

The physical, chemical and mechanical characterization of the waste bleaching clay highlighted those properties that could influence its application as construction material. Being the original material mostly made of montmorillonite, a large part of its properties are different from the limestone powder, which is the most common material used as filler for the production of asphalt and cement concretes. The very fine particles size distribution, as well as the high specific area of particles and the Rigden Voids, have a significant influence when this waste material is used as filler.

The application of waste bleaching clay as filler within bituminous mixtures highlighted the relevant absorption power of the material. The experimental mixture showed lower compactability properties if compared to ACs prepared with limestone filler and the same dosage of bitumen. The absence of a mastic rich in binder, in certain limits, has a stiffening effect on the material behaviour, as verified in the mechanical characterization. However, the embrittlement of the bituminous mastic could have a detrimental effect on the AC performances, if its durability is evaluated. Hence, the optimization of recipes traditionally used for the production of bituminous mixtures is needed. Nevertheless, the economic benefits related to the use of a waste in substitution of raw materials could be reduced by increasing the amount of bituminous binder.

The waste digested bleaching clay's properties are not so significant when it is used within hydraulically bound mixture as replacement of limestone filler. In this case, the absorption properties of the waste material do not affect the amount of water needed for the hydration of cement. This phenomenon is probably due to the chemical composition of the waste bleaching clays, which limits the interaction with water. As a result, the addition of the recycled filler to the mixtures does not modify the compactability and workability properties of the final cement bound mixtures, either prepared with virgin or recycled aggregates. From a mechanical point-of-view, every tested mixture was in compliance with the requirement imposed by the most common Italian technical specifications for hydraulically bound mixtures for foundation layers. Therefore, the application of waste digested bleaching clay in total substitution of limestone filler seems to be suitable for the production of these mixtures. Furthermore, the addition of this waste material does not require a specific optimization of the recipes traditionally used for their production.

The last activity of the project was related to the use of the waste bleaching clays for the production of synthetic materials. This represents the most wide and transversal activity of the whole research project, involving several different applications which fall in the fields of civil infrastructures. The production of synthetic materials can be considered as the most innovative technology presented in the project and fully pursues the design of innovative and sustainable construction materials, which is basic for the entire research. The final studied products represent a real example of green materials, involving the reduction in energy and CO_2 emissions for their production and allowing the recycling of wastes. The chemical composition of the waste material is adequate to ensure its alkali-activation. However, the addition of metakaolin is needed to achieve suitable mechanical performances, comparable to those obtained for a traditional cement concrete. Additional tests are needed to validate the application of the AAM as main constituent for the production of paving blocks, despite the presented preliminary results are in line with the requirement of the most common technical specifications for this type of construction materials. The definition of a fixed recipe and specific mixing and curing methods are needed, being these parameters fundamental for the definition of the final properties of the synthetic material. However, this variability allows tailoring the material to attain specific properties in relation to its final application.

The alkali-activation and following expansion of the waste bleaching clay seems to be a suitable solution for the production of synthetic lightweight aggregates. The obtained material complies with the physical and mechanical requirements for this type of aggregates. Still, further optimizations of the AA LWAs mix design could led to the production of products with a specific balance between lightweight and mechanical properties in relation to their intended use. Nevertheless, the defined mix design was effective for the production of synthetic LWAs suitable for replacing the LECA in asphalt concrete with high-friction properties. The innovative AC complies with the requirement imposed by the technical specifications for these type of mixtures. Still, the optimization of the mix design is needed to improve the physical properties of the material in terms of air voids content.

As general remark, the alkali-activation of the waste bleaching clay can effectively be a suitable alternative for the production of innovative construction material. Nevertheless, specific recipes for materials containing synthetic compounds must be designed, in order to have final products with well-defined and constant properties. This represented a significant issue for transferring the AAMs knowledge to the industrial field. Furthermore, additional researches will have to focus on the Life Cycle Analysis of the proposed solution in order to justify their development for industrial scale.

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List of Annexes

1. Sangiorgi C., Tataranni P., Mazzotta F., Simone A., Vignali V. and Lantieri C. "Alternative Fillers for the Production of Bituminous Mixtures: A Screening Investigation on Waste Powders". Coatings, 2017, 7, 76.

2. Sangiorgi C., Tataranni P., Simone A., Vignali V., Lantieri C. and Dondi, G. "Assessment of waste bleaching clay as alternative filler for the production of porous asphalts". *Construction and Building Materials*, 2016, 109, 1–7.

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Article

Alternative Fillers for the Production of Bituminous Mixtures: A Screening Investigation on Waste Powders

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Abstract: There has been a significant increase in the demand for using recycled materials in construction because of the lack and limitation of available natural resources. A number of industrial and domestic waste products are being used in the replacement of traditional materials for road construction, and many studies have been carried out in recent years on the use of different recycled materials in substitution of conventional fillers in Asphalt Concretes (AC). The aim of this laboratory research is to analyze the physical characteristics of three different recycled fillers and compare them with those of a traditional limestone filler. The alternative fillers presented in this paper are: a waste bleaching clay that comes from two consecutive stages in the industrial process for decolouring vegetable oils and producing biogas (Ud filler), a dried mud waste from a tungsten mine (MW filler) and a recycled glass powder (Gl filler). Results show significant differences between the fillers, and, in particular, Rigden Voids (RV) seem to have the largest potential influence on the rheology of ACs.

Keywords: asphalt concretes; alternative fillers; waste bleaching clays; mud waste; recycled glass powder; Rigden voids

1. Introduction

In asphalt concretes (ACs), as in cement concretes, fillers are the finest particles among the aggregates. Fillers are powdery materials of various types, most of them pass the 0.063 mm sieve (EN 13043) [1], and their inclusion in bituminous and non-bituminous binders and in aggregate mixtures confers special characteristics to these mixtures. Fillers play a major role in the production of asphalt, in terms of the composition of the mixtures and their physical and mechanical properties [2–4]. Despite being widely utilized in the production of asphalt, it is still difficult to propose a general classification describing all the functions carried out by fillers used in mixtures [5–7]. Fillers are the finest part in asphalt concrete mixtures, completing the granulometry, thereby helping to reduce the voids in the mixture. Various studies and experimental applications have shown that fillers can also perform other important functions, diminishing the asphalt concretes' thermal susceptibility and regulating the thickness and mechanical properties of the film of mastic covering the stone-based aggregates [8,9]. Fillers must have certain physical and chemical properties that encourage and strengthen binding between aggregates and bituminous mastic, while also ensuring that the rheological behavior of the latter is optimal at the various operating temperatures [10]. These are generally properties of commonly used fillers, such as slaked lime, Portland cement and calcium carbonate powder [11–13].

Within the current new awareness about ensuring better use of natural resources and recycling waste materials, a number of new experimentations have been carried out, over the past 20 years, to look at the possibility of replacing some of the natural components in the materials used in road construction with industrial by-products and waste materials from recycling processes [14–19].

Most recycled fillers currently used come from Construction and Demolition (C & D) products, which form the largest volume of waste products from the building sector [20,21]. Given the need to manage this vast volume of waste products, in recent years, there have been many studies concerning their reuse in civil engineering [22,23]. As of today, a number of studies and tests have used the most diverse materials, and not all of them of civil engineering provenance. In several well-known cases, researchers have experimented with glass powder, silicon carbide, coal ash, solid urban waste, polyvalent powder from fire extinguishers and even biomass powder [24–26]. These are only some of the many studies with a positive outcome, underlining the growing scientific interest in using alternative, used and waste materials.

This work presents the results of several laboratory tests carried out to determine some of the physical and chemical properties of three different waste materials for their application as filler in ACs. The first (Ud filler) is a digested spent bentonite clay derived from successive industrial processes and currently sent to landfill. Following the positive results of a previous study on the use of spent bentonite clays as filler in ACs [27], it emerged that further, more detailed work was required to analyze the physical and chemical characteristics of this filler. A dried mud waste (MW filler), which is produced during the tungsten extraction in Panasqueira mine (Portugal), was also studied. The third filler (Gl filler) is a powder from ground waste glass disposed to landfill. It has been produced by milling waste bottles, without any restriction given by glass color. The testing must be framed in the context of protecting the environment and sustainable development, since it proposes a functional use for wastes otherwise sent to landfill, while at the same time limiting the use of natural raw materials. All the tests undertaken are defined within the EN 13043 standard, which specifies the properties of aggregates being used in bituminous mixtures.

2. Materials and Test Methods

2.1. Materials

The fillers used in this test are three different waste materials and one traditional limestone filler (Figure 1).

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

Figure 1. Digested dried spent bleaching clay (**a**), mud waste (**b**), ground glass powder (**c**).

The first labelled Ud filler is a waste digested bleaching clay from the food industry. Bleaching clays are aluminium hydrosilicates containing small amounts of Mg, Ca and Fe. They are similar to normal clays, but more hydrated, and have the capacity of removing colored impurities from mineral, vegetable and animal oils, and from other fluids [28]. These materials are divided into Floridinic clays, which are active in the natural state, and bentonite clays, active only after chemical treatment. The main component of bentonite is montmorillonite, which is a clayey mineral belonging to the class of phyllosilicates called smectites. The special properties found in bentonite clays, especially their adsorption and binding capacities, make them particularly suitable for use in sectors such as the ceramic industry, the food industry, the foundry and smelting sector, water treatment [29] and, indeed, many others. In the case under examination, the bentonite clay is a waste from the bleaching oil process and a consecutive anaerobic digestion for the biogas production. This phase of biochemical conversion determines a reduction of the content of residual oils to below 1% by the weight of particle.

The second recycled filler is a dried mud waste (labelled MW filler), which is produced as a result of extraction operations in the tungsten Panasqueira mine (Portugal). This is one of the oldest and richest tungsten mines in the world. The treatment of ore for the production of wolframite, casserite and chalcopyrite involves the production of mud and slags that today form a massive tailings pile and two mud dams [30].

Glass recycling is a specific sector of waste recycling and consists of processing the waste glass into usable products. Glass is a widely recycled material thanks to its capability to be recycled infinitely without significantly losing its chemical and physical properties. However, a wide amount of glass cannot be recycled due to color mixing, or high recycling costs needed to remove impurities, metals, paper and chemical residues. Thus, part of waste glass is disposed to landfill, with high environmental and management costs. In recent years, many studies and researches have been carried out on the use of waste glass as an alternative to traditional construction materials [31,32]. In this study, a powder from ground waste glass (labelled Gl filler) was analyzed. This powder comes from milled bottles, without any diversification and limitation given by the glass color.

The comparison filler was a limestone filler ($CaCO_3$), traditionally used in Italy to produce asphalt concretes. The tests on bituminous mastic composed of binder and filler were carried out using non-modified 50/70 pen bitumen, commonly utilized in Italy in traditional bituminous mixtures (Table 1).

Table 1. Properties of the 50/70 pen binder.

Test	Unit	Characteristic Value	Standard
Penetration @ 25 °C	dmm	50–70	EN 1426 [33]
Soft. Point	°C	50	EN 1427 [34]
Dynamic Visc. @ 60 °C	Pa·s	$\geq$145	EN 12596 [35]
Fraass	°C	–8	EN 12593 [36]

2.2. Test Methods

An experimental program complying with the international standard for asphalt (EN 13043) was set up to investigate the chemical and physical properties of the fillers, and encompassed the following laboratory tests:

- Size distribution (EN 10343);
- Water content (EN 1097-5) [37];
- Particle density (EN 1097-7) [38];
- Voids of dry compacted filler (EN 1097-4) [39];
- Variation in "Ring and Ball" temperature (EN 13179-1) [40];
- Harmful fines (EN 933-9) [41];
- Water solubility (EN 1744-1) [42].

These tests are only some of those traditionally used to evaluate the properties of fillers used in bituminous mixtures. In the literature, they are described as needed to specify the qualitative properties of materials [43,44].

Furthermore, Energy-dispersive X-ray Spectroscopy (EDS) was performed to know the chemical composition of the recycled fillers.

3. Results

3.1. Geometrical and Physical Characteristics

3.1.1. Size Distribution

In practical applications, fillers are generally defined as material with a granulometry of less than 75 µm [45]. The granulometry of the four different fillers in this test was established through sieving, using the limits set in EN13043 for the sieved material 63 µm (P63). The results are given in Table 2.

Table 2. Size distribution (EN 13043).

EN 13043	P63 (%)
Limestone Filler	98.2
Ud Filler	100.0
MW Filler	100.0
Gl Filler	95.0

According to the standard, 70% of particles must pass through a 63 µm sieve. Every tested filler complies with the requirement.

3.1.2. Water Content (EN 1097-5)

The ventilated oven method drying tests moisture content, that is, the total mass of free water within a filler test portion. Moisture can come from the surface of the particles themselves or from the accessible pores.

Water content is determined as the difference between the humid mass and the dried mass, and it is expressed as a percentage of the dried mass. This, in turn, coincides with the constant mass of the test portion after being oven-dried, obtained through successive weighing. The results here presented (Table 3) are average values of six repetitions for each filler.

Table 3. Water content (EN 1097-5).

EN 1097-5	Initial Mass (g)	Dried Mass (g)	Water Content (%)
Limestone Filler	53.83	53.72	0.20
Ud Filler	52.42	50.09	4.65
MW Filler	53.20	53.10	0.18
Gl Filler	55.48	51.11	7.87

The water content of both Ud and Gl fillers are above the 1% limit suggested in the EN 13043 standard, being 4.65% and 7.78%, respectively. On the other hand, the MW filler shows a water content value strictly comparable to limestone filler. Other studies have recorded water content values generally lower than 1.5% (e.g., 0.79% for hydraulic lime, 1.36% for hydrated lime, 0.21% for Portland cement and 0.04% for basaltic filler) [46].

3.1.3. Particle Density (EN 1097-7)

Filler density was calculated using a pycnometer. The test portion, with a minimum mass of 50 g and complying with EN 932-2, was oven-dried at around 110 °C until reaching a constant mass and then left to dry for at least 90 min. This operation means that the filler can be checked for lumps. The dry filler is sieved through a 0.125 mm mesh and the fraction passing the sieve evaluated. The test was carried out on three samples for each types of filler. The values obtained are given in Table 4.

Table 4. Particle density (EN 1097-7).

EN 1097-7	Particle Density (Mg/m^3)
Limestone Filler	2.70
Ud Filler	1.86
MW Filler	2.89
Gl Filler	2.47

These results give the density of the three recycled fillers, showing that the values range between 1.86 and 2.89 Mg/m^3. The difference is mainly due to the different physical and chemical composition of the three fillers. Traditional limestone filler is 100% calcium carbonate and, therefore, has the same density, 2.70 Mg/m^3. The particle density of mud waste is the highest due to its mineralogical composition. If other traditional fillers are taken as a reference, particle density is equal to 2.72 Mg/m^3 for hydraulic lime, 2.32 Mg/m^3 for hydrated lime, 3.29 Mg/m^3 for Portland cement and 2.87 Mg/m^3 for basaltic filler [47,48].

3.1.4. Voids of Dry Compacted Filler (EN 1097-4)

Intergranular porosity (Rigden Voids) is the space in the bulk material that is filled with air, expressed as a percentage of total volume of the filler, after compaction using the normalized method. The test can be applied to both natural and artificial fillers.

The percentage of Rigden Voids can be determined from the initial weight of the sample to be compacted, the density and the weight of the sample compacted with a defined number of strokes. The results of the test are given in Table 5.

Table 5. Voids of dry compacted filler (EN 1097-4).

EN 1097-4	Limestone Filler	Ud Filler	MW Filler	Gl Filler
Weight of compacted filler (g)	9.95	9.82	10.00	9.91
Mass of filler (Mg/m^3)	2.70	1.86	2.89	2.47
Height of compacted filler (mm)	12.37	22.00	9.50	11.10
Rigden Voids (%)	41.00	53.90	28.12	28.67

Intergranular voids in the filler are determined through mechanical compaction using the Rigden device. The process provides information about the potential amount of bitumen that the filler can adsorb and, as a consequence, is an indicator of the stiffening power that the filler exercises on the bituminous mastic [49]. Indeed, it is possible to consider a quota of bitumen "fixed" in the voids between the filler particles and another part of "free" bitumen.

The volume of the "free" bitumen that remains after the pores between the filler particles are filled with binder is an important parameter that helps in the characterization of the rheology behavior of the mixture. From many studies, it has emerged that a low value of filler porosity corresponds to lower rigidity in the mastic, since the filler particles are no longer in close contact, one on the other, and every addition of binder acts as lubrication between the particles themselves. On the contrary, a high number of voids determine a greater amount of adsorbed bitumen, strengthening the bitumen-filler link, in other words, reducing the quantity of excess bitumen.

According to the EN 13043 standard, the values of the Rigden Voids are restricted to the interval 28%–55%. Taking this standard as reference, every tested filler respects the defined limits. In particular, the Ud filler has a significantly high value of Rigden Voids. This property of the filler acts on the final rigidity of the asphalt, as verified by Sangiorgi and Mazzotta [50,51] in three different experimental applications on the use of Ud filler within bituminous mixtures. On the other hand, MW and Gl fillers show an RV value in line with the lower limit stated by the reference standard. However, it would be desirable to verify how this could affect the workability and the durability properties when used in asphalt mixtures.

3.1.5. Variation in Temperature Using the "Ring and Ball" Method (EN 13179-1)

Using the test set out in the EN 13179-1 standard, it is possible to evaluate how the filler interacts with the bitumen, with the variation in temperature of the bitumen being calculated using the "Ring and Ball" method after it has been mixed with fillers, where the proportions, in volume, of bitumen and filler are 62.5% and 37.5%, respectively. This test can be applied to filler particles of less than 125 µm, and involved calculating the average of the temperatures at which the two samples of bitumen and bitumen with filler soften to the point where a steel sphere, initially placed on top of the samples, can touch a metal plate placed underneath at a distance of 25 (±0.4) mm. The difference between the two average temperatures is the Ring and Ball delta.

As shown by Taylor [52], the variation in temperature using the Ring and Ball method does not seem to be connected either to the properties of the filler or its rheological characteristics. It seems, rather, to be highly influenced by the filler's chemical composition. It is known that fillers have the effect of hardening bituminous mastic. However, the various types of filler can interact in different ways with the bituminous binder, so there can be different grades of rigidity in the AC.

The test results given in Table 6 show that a greater proportion of fine particles in the Ud filler (as shown later in Section 3.2.1) causes the mixture's softening point temperature to increase by several degrees Celsius.

Table 6. Variation in Ring and Ball softening point temperature (EN 13179-1).

EN 13179-1	Limestone Filler	Ud Filler	MW Filler	Gl Filler
Softening temperature bitumen (°C)	47.5	47.5	46.3	46.3
Softening temperature bitumen + filler (°C)	59.5	79.3	54.4	56.5
Variation in Ring and Ball temperature (°C)	8.0	32.0	8.1	10.2

Some studies assess that the bituminous mixture performaces are enhanced with R & B delta values between 12 and 16 °C [49]. However, the Ring and Ball delta, as set out in EN 13043 for traditional fillers, ranges between 8 and 16 °C. For example, researchers assessed a variation in R & B temperature equal to 6.8 °C for basaltic filler, 7.8 °C for Portland cement and 14 °C for hydrated lime [46,53]. The mud waste filler and the glass powder filler comply with these values. The addition of Ud filler, given its high specific surface area, sensibly increases the softening temperature of the mastic, with a Ring and Ball delta of 32 °C.

3.2. Chemical Characteristics

3.2.1. Harmful Fine Particles (Methylene Blue Test) (EN 933-9)

The test described in the EN 933-9 standard consists of adding drops of methylene blue at a concentration of 10 g/L at regular intervals to a suspension of filler in water. Every time the drops are added, the suspension is checked for any free, non-absorbed blue coloring, and its relative amount, by observing the stain and halo produced on the filter paper.

The purpose of this test is to examine whether there are fine particles within the filler. Fine fraction, composed mainly of hydrated aluminosilicate clay minerals, absorbs the methylene blue solution (a cationic dye) in an aqueous solution, because of the superficial loads involved and its cation-exchange capacity.

The quantity of methylene blue absorbed by the filler that is observed during the test increases proportionally to the quantity of fine particles present in the sample. The results are given in Table 7.

Table 7. Methylene blue test (EN 933-9).

EN 933-9	Limestone Filler	Ud Filler	MW Filler	Gl Filler
Mass of the sample (g)	30	30	30	30
Quantity of Methylene blue added (mL)	20	100	10	15
Methylene blue value (g MB/kg Filler)	6.7	33.3	3.3	5.0

These methylene blue (MB) values are similar for MW and Gl fillers and higher for the digested bentonite filler (33.3 g/kg). These data indicate a remarkable presence of fine particles for Ud filler, while values for MW and Gl are in line with those registered for limestone filler. If other fillers used for the production of ACs are considered, MB values are equal to 1.7 g/kg for hyrdated lime and Portlan cement and 5.0 for basaltic filler.

3.2.2. Water Solubility (EN 1744-1)

Water solubility of the test portion of filler is determined by extracting the previously dried and weighed filler with a quota of water equal to around fifty times the mass of the filler itself. None of the different types of filler being examined contains added calcium hydroxide; therefore, according to EN 1744-1, water solubility is determined using the standard procedure.

According to these process, two glass bottles are used for each type of filler to be tested. Each bottle is filled with the fixed amount of dried material and a mass of distilled water equal to fifty times the mass of filler contained in the bottle. A glass rod is placed in the bottles, which are then sealed. They are placed in a mechanical shaking device with rollers for at least 24 h, so the mixing is continuous and the filler cannot form sediment.

After mixing, as much liquid as possible is filtered, using a funnel and filter paper of suitable porosity and known mass. The bottles and the filter paper, with their respective contents, are placed in an oven until the solid residue, once dried, reaches a constant mass.

EN 13043 suggests that the limit value of solubility in water is 10%. The results are given in Table 8.

Table 8. Water solubility (EN 1744-1).

EN 1744-1	Limestone Filler	Ud Filler	MW Filler	Gl Filler
Mass of the filler before extraction (g)	5.02	5.02	6.00	8.90
Mass of the filler after extraction (g)	5.00	4.28	4.10	4.90
Water solubility (%)	0.50	14.84	19.61	2.00

The water solubility for the glass powder filler is close to the value registered for the limestone one; Ud and MW fillers show higher values, even when compared to the limit suggested by the standard.

3.2.3. Chemical Composition

The chemical composition of each recycled filler was evaluated by means of Energy-dispersive X-ray Spectroscopy (EDS). This method is based on the use of the X-ray spectrum emitted by a specimen bombarded with a specific beam of electrons. The level of energy of the X-rays emitted is measured by a spectrometer that can identify the elemental composition of a material. Table 9 shows the chemical composition of each recycled filler in terms of un-normalized concentration in weight percent of the element (unn. C), normalized concentration (norm. C) and atomic concentration in atomic weight percentage (atom. C).

Table 9. Chemical composition by EDS test.

Element	Ud Filler			MW Filler			Gl Filler		
	Unn. C. (wt %)	Norm. C. (wt %)	Atom. C. (at %)	Unn.C. (wt %)	Norm. C. (wt %)	Atom. C. (at %)	Unn. C. (wt %)	Norm. C. (wt %)	Atom. C. (at %)
C	0.00	0.00	0.00	0.00	0.00	0.00	3.49	5.63	10.64
O	34.41	48.01	63.06	43.52	46.27	64.05	22.78	36.73	52.17
Na	0.87	1.21	1.11	0.00	0.00	0.00	0.00	0.00	0.00
Mg	3.42	4.77	4.13	0.00	0.00	0.00	0.00	0.00	0.00
Al	5.13	7.16	5.57	9.74	10.35	8.50	4.14	6.67	5.62
Si	20.51	28.61	21.41	20.96	22.28	17.57	11.98	19.32	15.63
P	0.29	0.4	0.27	0.00	0.00	0.00	0.00	0.00	0.00
S	0.58	0.81	0.53	4.38	4.66	3.22	3.09	4.99	3.53
K	0.67	0.94	0.51	3.01	3.20	1.81	7.15	11.53	6.70
Ca	1.56	2.17	1.14	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.45	0.62	0.27	0.00	0.00	0.00	0.19	0.31	0.15
Fe	3.79	5.29	1.99	8.29	8.81	3.49	5.95	9.60	3.90
As	0.00	0.00	0.00	3.15	3.35	0.99	2.44	3.93	1.19
Zn	0.00	0.00	0.00	1.03	1.09	0.37	0.65	1.05	0.37
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.26	0.09

As expected, the fillers are rich in Oxygen and Silicon, which are the main components of silicon dioxide (SiO_2). For this type of material, the silicon dioxide (SiO_2) and the oxide calcium (CaO) compounds are considered relevant in terms of chemical composition of fillers for the filler–bitumen interaction [54].

Figure 2 shows the chemical composition of the three different fillers in terms of percentage in weight of their oxides.

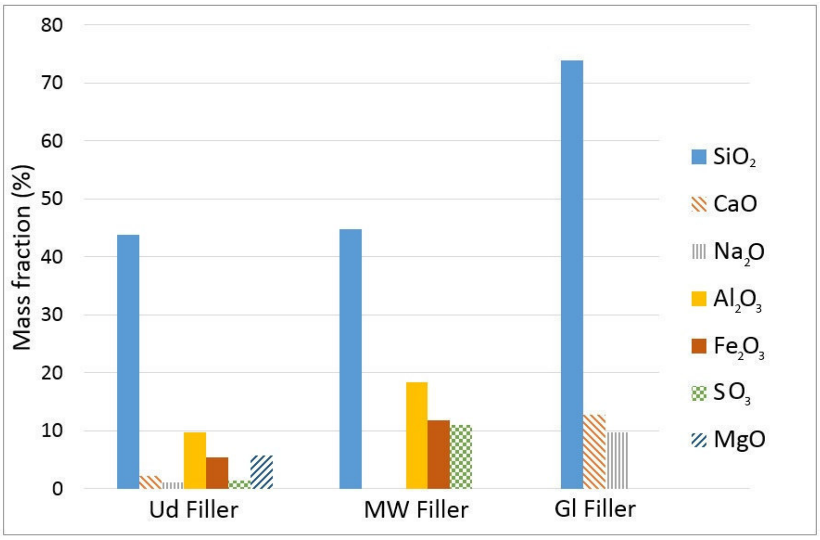

Figure 2. Principal chemical composition of recycled filler.

It can be observed that silicon dioxide (SiO_2) is the main component of the recycled fillers (43.8% for Ud filler, 44.8% for MW filler and 73.9% for Gl filler). Other components are always below 20% of the total mass of each filler.

4. Discussion

The results of the tests specified in EN 13043 for studying the physical and chemical characteristics of the examined recycled fillers are commented on in this paragraph.

It is worth noting that the standard identifies the characteristics of traditional fillers to be used in bitumen mixtures, but does not specify any restriction for fillers with different characteristics than those classified in the standard. The only binding condition is that any characteristic not in line with the standard must be specified in the technical sheet of product during the CE marking process.

Of course, being in line with the requirements concerning the use of fillers in bituminous mixtures specified in the standard does not mean that they can be effectively used. Depending on the mix design, type of binder and, above all, utilized filler, there must be a specific characterization of the mixture and its bituminous mastic. This will assess how the filler interacts with the other components and whether the final material conforms to the performance requirements specified in the most common technical specifications.

In general, on the basis of the presented results, several conclusions can be drawn:

- Every analyzed filler has geometric characteristics in line with the range set out in EN 13043 for the maximum number of particles greater than 63 µm. As verified in different studies, particle size and its shape affect the mechanical properties of the bituminous mastics [55]. In this case, there are no significant differences in particle size between the experimental materials and every filler is in compliance with the standard. However, a particle shape analysis with SEM might be useful to evaluate the real influence of filler particles on the final performance of the mixture.
- While the water content for MW filler is comparable to the traditional limestone one, both bentonite and glass powder fillers are above the values listed in EN 13043. These water content may depend on a prolonged exposure to a humid environment during storage or transport. It is worth noting that for Ud filler, the high water content might be due to the hygroscopic characteristics of its particles, that is, the tendency of bentonite to absorb water. For asphalt production in plants, it is recommended that humidity should be controlled in order to ensure that the process is correct.
- The results of the Rigden Voids test show that there is a high number of intergranular voids for Ud bentonite filler. This value is significant in determining the physical and mechanical properties of the bituminous mixture, since it affects the filler's ability to fix the bitumen. MW and Gl fillers have similar RV values, in line with the lower limit of the EN 13043 standard. However, even if Ud has the highest RV value, previous studies and research have highlighted high values for fillers often used for the production of asphalt concretes (e.g., RV = 71% for hydrated lime, 51% for hydraulic lime or 45% for Portland cement) [46].
- Some relationships could exist between the Ring and Ball temperature and the percentage of Rigden Voids. The higher the porosity, the harder the mastic, with a high softening temperature, as it is shown for the Ud filler. Where this can have a negative effect on the workability of the mixture, the problem can be overcome by using binders containing waxes. On the other hand, MW and Gl filler show a variation in Ring and Ball temperature comparable to the reference filler. Further tests with different binders are needed to back this conclusion as suggested by Antunes [46], showing that there is not a clear linear trend for R&B delta–RV relationship.
- From the methylene blue test, it appears that only the Ud filler contains a proportion of fine particles belonging to the 0/0.125 mm fraction, which is much greater than in the other tested fillers. Kandhal [56] assessed that there could be a relationship between MB value for aggregates and the stripping phenomenon of ACs. Previous research from the authors on the the use of Ud filler for AC production did not verify any relevant negative effects, probably due to the low amount of filler within the mixture gradation. Nevertheless, it would be desirable to verify the detrimental effect of fine particles in inducing stripping on asphalt mixtures with specific tests.

- Apart from the glass powder, for every recycled filler, the water solubility is above the limit suggested in EN 13043. This result is certainly linked to their chemical composition stated by EDS analysis. However, even if water solubility is rarely required by international standards, further investigations are needed to verify if these values can be a limitation for the use of these recycled fillers for the production of ACs.
- EDS tests verified the presence of high quantities of silicon dioxide (SiO_2) in the chemical composition of all the tested fillers. According to past scientific literature, the presence of calcium (Ca) is favorable, due to its good interaction with bitumen [57]. At the same time, its excessive amount might extremely stiffen the bituminous mastic and make it fragile [58]. However, even if the EDS analysis assessed the lack of Ca for the MW and Gl fillers, this does not seem to negatively influence the interaction with bitumen, in relation to the adopted filler–binder proportions. This is confirmed by the variation in Ring and Ball temperature, which is close to that registered for the limestone filler.

5. Conclusions

The test results have highlighted that the particles of the digested Ud filler are in general very fine and this has a substantial influence on the tests results. However, the physical and mechanical properties of MW and Gl fillers are comparable to those registered for the reference filler.

The present preliminary study suggests that all of the tested fillers may be considered as a valid alternative to natural filler in bituminous mixtures. Some results, however, do not meet the standard requirements suggested for traditional fillers. Nevertheless, future developments will determine which filler characteristics directly affect the performance of the final mixture. The subsequent phases of this research project will concentrate on the rheological characterization of the bituminous mastics and mixtures containing the recycled fillers here presented.

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Assessment of waste bleaching clay as alternative filler for the production of porous asphalts

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HIGHLIGHTS

- Substitution of limestone filler with digested spent bleaching clay from food industry.
- The substitution does not worsen the workability and compactability of porous asphalt mixtures.
- Digested spent bleaching clay increases PA stiffness characteristics in a range of temperatures.
- Digested spent bleaching clay improves the permanent deformations resistance of PA.
- The presence of digested spent bleaching clay does not worsen the vertical permeability of PA.

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ABSTRACT

Mineral fillers have a key role in controlling the mechanical characteristics of asphalt concretes (AC). The cohesion properties of bituminous mastics depend upon the fillers used, and, therefore, so do the effective strength of asphalt concretes and the durability of the pavement layers. Recent research has studied the using of waste bleaching clays from the food industry as a substitute of common limestone filler traditionally used in the production of ACs for binder layers. In this paper, a waste bleaching clay is proposed as alternative filler for the production of a porous asphalt (PA) mixture. The waste filler (Ud) comes from two consecutive stages in the industrial process for decolouring vegetable oils and producing biogas from bleaching clays. The aim of this research was to assess the performance of the PA, in terms of physical and mechanical characteristics, when compared to traditional PA. Thus, two porous asphalt mixtures with the same dosages of binder and aggregates gradation were studied in the laboratory: one with traditional limestone filler and one with waste bleaching clay. Tests results are promising in terms of increasing of Indirect Tensile Strength, stiffness, and resistance to permanent deformations.

1. Introduction

For the modern road infrastructure engineer the concept of sustainability often requires to focus on various main design aspects: economic, environmental and architectural. Environmental sustainable development on a global level requires durable road infrastructures that consume a minimum of raw materials and energy during construction and allow reducing traffic induced atmospheric and acoustic pollution during service life [1]. With the increase of demand and limited aggregate and binder supply, along with strict environmental regulations, recycling and use of waste materials had become a priority goal for both administrations and producers [2,3]; [4]. Recent research aimed at developing recycling processes of porous asphalts (PA) containing up to 90% of Reclaimed Asphalt Pavement [5,6].

Nowadays, a porous surface layer is an environmentally conscious alternative to a traditional asphalt or concrete pavement [7]. In many countries PA mixtures are extensively used as motorway surface layer due to their benefits in reducing traffic noise and improving safety in wet conditions (enhanced skid resistance and reduced spray and splash) [8]. The high air voids content involves these advantages but, at the same time, it implies a reduction of the mechanical characteristics of the mixture if compared to dense asphalt concretes. This mechanical deficiency is related to the particular structure of the mixture. In PA, in fact, the contact between aggregate particles through asphalt mastic occurs in a very small area due to the high porosity of the material [9].

It is well know that the bituminous mastic is formed by the combination of the fraction of aggregates passing a 63 μm sieve [10],

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together with the mineral filler, which is generally added to the lithic mixture, and the bituminous binder. This resulting mastic is capable of affecting the physical and mechanical properties of the mixture to a considerable degree [11]. Over the years, various materials have been both studied and used as fillers in asphalt concretes (ACs): from “natural” material (i.e. rock dust) to “imported” ones (i.e. Portland cement, lime, ash and waste) [12]. In several well-known cases, researchers have experimented the use of glass powder, silicon carbide, coal ash, solid urban waste, polyvalent powder from fire extinguishers and even biomass ashes [13–15]. Following the positive results of a previous study on the use of spent bentonite clays as filler in ACs for binder layer [16], in the study here presented, a spent bentonite bleaching clay is used in total substitution of traditional limestone filler for the production of PA mixtures.

2. Materials and test methods

The experimental phase required the mix design of two different PA mixtures. For the one (labelled PA Ud) containing the digested spent bentonite filler (Ud) a 100% filler substitution was considered, while a traditional limestone filler was used in the production of the reference mixture (labelled PA F).

2.1. Alternative filler

Bleaching clays are aluminium hydrosilicates containing small amounts of Mg, Ca and Fe, which are similar to normal clays, but more hydrated and have the peculiarity of being able to remove coloured impurities from mineral, vegetable and animal oils, and from other liquids [17]. In this work, the bentonite clay is a food industry waste, derived from two different and consecutive procedures: vegetable oils bleaching and anaerobic digestion of spent bentonite within a reactor producing biogas. The final material is digested spent bentonite (labelled Ud) which is today dumped. Its re-use has a two-fold environmental benefit, since it saves raw materials such as limestone fillers, and reduces the volume of disposed materials.

Two different fillers were used (Fig. 1): limestone filler and digested spent bleaching clay. The first one is a limestone filler ($CaCO_3$), traditionally used in Italy to produce ACs. The second one is the result of the anaerobic digestion of the waste material resulting from the bleaching phase. This process of biochemical conversion determines a reduction of the content of residual oils and organic substances, to below 1%.

The chemical and physical properties are traditionally analysed to evaluate the compliance of fillers for bituminous mixtures [18]. The Ud filler was analysed to verify the compliance to the requirements recommended by the international standard for asphalt [10]. The results are shown in Table 1.

Table 1
Chemical and physical characterisation of fillers.

	Standard	Limestone filler	Ud filler
Size distribution (P63 %)	EN 13043	98.2	100.0
Water content (%)	EN 1097-5	0.20	4.65
Particle density (Mg/m^3)	EN 1097-7	2.70	1.86
Rigden Voids (%)	EN 1097-4	41.00	53.90
Variation in ring and ball temperature (°C)	EN 13179-1	8	32
Methylene blue value (g_{MB}/kg_{Filler})	EN 933-3	6.7	33.3
Water solubility (%)	EN 1744-1	0.50	14.84

Comparing the volumetric characteristics, a clear difference emerges, in terms of density, between the digested spent bentonite clay and the limestone filler. This difference will affect the mix design refinement of the two PA mixtures, as shown forward. When comparing the Rigden Voids (RV), the Ud filler value is significantly higher than the limestone one, meaning that higher bitumen absorption in expected. This RV value is extremely important in determining the physical and mechanical properties of the asphalt mixture, since it affects the stiffness of the bitumen mastic [19].

2.2. Aggregates and bitumen

The aggregates gradation, filler and binder percentages for PA F mixture were defined according to a recipe commonly used in Italy for the production of porous asphalt layers. The content of bitumen was fixed at 5.1% on the aggregates weight, while the percentage of limestone filler was fixed at 5% on the aggregates weight. Crushed limestone aggregates were used as the aggregates. Sangiorgi [16] have shown that a negative effect on the workability of the mixture, depending on the design mix and the type of binder, can be attributed to the high RV value, as well as the greater adsorption typical of bleaching clays.

For this reason, considering the different particle density of the two fillers, the total substitution of limestone with Ud filler was done in volume and not in weight. This gives a slightly different gradation between the two mixtures, while the bitumen dosage can be kept unvaried (Fig. 2 and Table 2).

A 45/80 pen grade Polymer modified Bitumen was used as a binder; its rheological properties are given in Table 3.

2.3. Test methods and experimental program

Thirteen specimens were prepared for each of the mixture: ten with gyratory compaction (ASTM D6925) and three with Marshall compaction (EN 12697-30). Each specimen from gyratory compaction had a dry mass of 4500 g and a diameter of 150 mm, made with a constant compaction pressure of 600 kPa, external angle of 1.25° and 80 revolutions. The Marshall specimens compaction were compacted with 75 blows on each side. All samples were compacted at a processing temperature of 180 °C.

The experimental program was divided into four phases.

The workability and volumetric characteristics of the mixtures were defined in the initial prequalifying phase, by analysing the compaction curves obtained from the gyratory compactor. In this step, the volumetric analysis was supported by the determination of the air voids content of specimens (EN 12697-8). The objective of this phase was to assess the influence of Ud filler, in terms of workability and compactability of the mixture.

The second phase was as a static and dynamic mechanical characterisation on gyratory specimens. The static analysis encompassed the Indirect Tensile Strength (ITS) test at 25 °C. In line with the EN 12693-23 standard, a constant velocity of 50 mm/min was applied to the specimen until failure. In literature the ITS is often used to evaluate the level of tenacity reached by the aggregates-filler-bitumen bond. The dynamic mechanical characterisation was centred on the study of the Stiffness Modulus as set out in the EN 12697-26 (Annex C) standard. According to the standard, the Modulus was determined through a pulse loading with a 124 ms rise-time, to generate a predefined horizontal deformation of 7 ± 2 µm in the core of the sample. The effect of the waste filler was assessed, looking at the stiffness and at the AC thermal sensitivity. The specimens were conditioned for six hours and then tested at three reference temperatures, 5, 20 and 35 °C.

Fig. 1. Limestone filler (left) and digested spent bleaching clay (right) in the dry state.

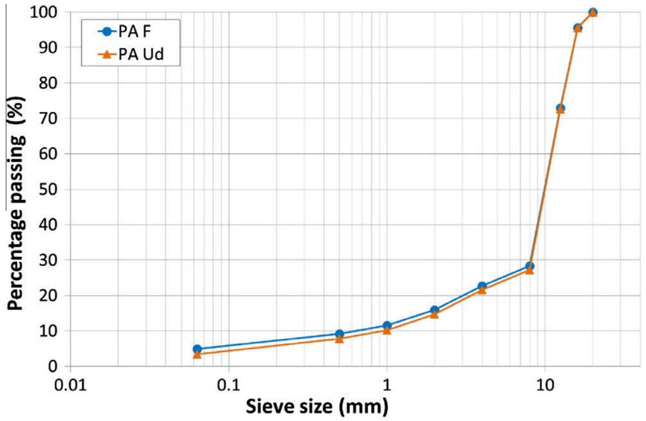

Fig. 2. Comparison aggregates gradation for PA F and PA Ud mixtures.

Table 2
Percentage passing and gradation limit.

Sieve size (mm)	PA F Percentage passing (%)	PA Ud Percentage passing (%)
20	100.0	100.0
16	95.6	95.5
12.5	72.9	72.5
8	28.4	27.3
4	22.8	21.6
2	16.0	14.7
1	11.6	10.2
0.5	9.2	7.8
0.063	5.0	3.9

Table 3
Properties of PmB 45/80 binder.

	Unit	Value	Standard
Penetration @ 25 °C	dmm	45–80	EN 1426
Soft. Point	°C	70	EN 1427
Dynamic Visc. @ 160 °C	Pa·s	0.4	EN 12596
Force Ductility Test @ 10 °C	J/cm^2	3	EN 13589 EN 13703

The third phase was based on the evaluation of the water sensitivity and durability of the mixtures. The first was assessed by the loss in ITS performing indirect tensile tests both in wet and dry condition, according to EN 12697-12 standard. The second was evaluated with two different methods: Repeated Load Axial Test (RLAT) for permanent deformation resistance (EN 12697-25) and Cantabro test for resistance to abrasion (EN 12697-17). While ITS test and RLAT test were carried out on gyratory specimens, for Catabro test Marshall samples were used. In RLAT, specimens are loaded with a frequency of 0.5 Hz and a pressure of 100 ± 2 kPa. The specimen's accumulated axial deformation was measured after 3600 loading cycles at test temperature of 40 °C. The tests were carried out in dry and wet conditions. Cantabro tests were performed subjecting Marshall samples, after conditioning at 25 °C for six hours, to 300 revolutions, at 30 revolutions/min, inside the Los Angeles drum, without metal balls. The mass loss at the end of the test gives a measure of the resistance to ravelling of the mixture.

In the fourth and final phase of the research program, the vertical permeability of the two PA mixtures was analysed (EN 12697-19). A column of water with a constant height of 30 cm was applied to a cylindrical specimen and was allowed to permeate through it for a given lapse of time. The resultant flow rate is a conventional measure of the material permeability.

3. Prequalification results analysis: volumetric properties and evaluation of workability

In this step, the effects of the digested spent bentonite clay on the mixture's workability and compactability were evaluated, comparing the volumetric properties of the PA mixtures.

Table 4
Compaction plots and trend curve coefficients.

Compaction plots and coefficients					
Material	*a*	*b*	Material	*a*	*b*
PA F1	3.8634	67.591	PA Ud1	3.3584	70.626
PA F2	3.7647	67.946	PA Ud2	3.4763	70.199
PA F3	3.9229	67.084	PA Ud3	3.3730	70.401
Model PA F	3.8503	67.540	Model PA Ud	3.4025	70.408

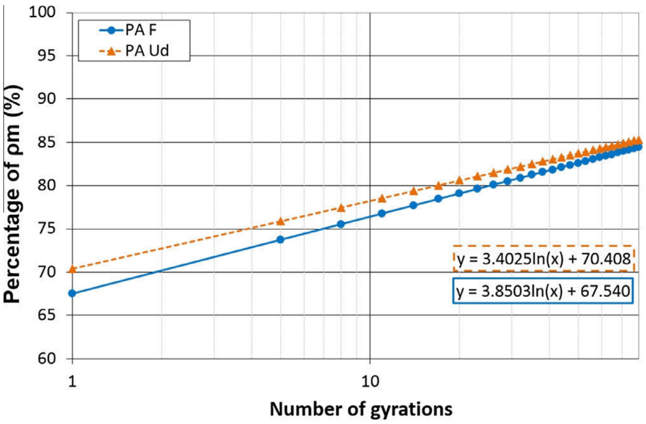

Fig. 3. Comparison between compaction plot trends.

Table 5
Air voids analysis.

Air voids content EN 12697-8							
Material	VMA (%)	Va (%)	VFA (%)	Material	VMA (%)	Va (%)	VFA (%)
PA F1	23.4	15.3	34.6	PA Ud1	22.8	14.5	36.5
PA F2	23.5	15.4	34.4	PA Ud2	22.8	14.4	36.6
PA F3	23.6	15.5	34.3	PA Ud3	23.0	14.6	36.3
Av. PA F	23.5	15.4	34.4	Av. PA Ud	22.9	14.5	36.5

Table 4, Fig. 3 show the trend curves of the average compaction plots for each mixture, represented by means of the following equation:

$$\%\rho_m = a \cdot \ln(x) + b \qquad (1)$$

where $\%\rho_m$ is the percentage of maximum densification,
a is the slope of the compaction curve,
x is the number of revolutions,
b is the intercept of the regression curve.

The analysis of voids, according to EN 12697-8 standard is given in Table 5.

Comparing the compaction curves, it can be seen that both Pas attain final densities close to 85%ρ_m. As for the air voids content, the difference between the two mixtures is less than 1%, and the air voids for PA Ud mixtures are among those typically recommended for porous asphalt layers.

On the basis of these results, Ud seems not to negatively affect the compactability and workability of the mixture. Although the greater binder adsorption of the waste bleaching clay and its high RV value, PA Ud shows higher ranges of density during the compaction process, if compared to the control mixture. This difference is mostly perceivable in the first 10 revolutions. Data confirm the sound mix design of PA Ud and the correct dosage of Ud filler within the mixture.

4. Static and dynamic mechanical characterisation

4.1. Analysis of Indirect Tensile Strength test results

Three specimens prepared with the same compaction energy were tested with the Indirect Tensile Strength test at 25 °C according to EN 12697-23. Results are represented in Fig. 4.

As shown by the histogram, not a significant difference in recorded between the two porous asphalts. In particular, the substitution of limestone filler with digested spent bleaching clay determines an increase of ITS less than 7% if compared to the reference mixture. ITS is generally related to level of tenacity reached by the aggregates-filler-bitumen bond [20]; for this reason the results are directly linked to the volumetric characteristics of the filler. A high value of RV involves to a greater stiffness of the bituminous mastics [21,22] and this event is particularly significant for bituminous mastics containing waste bleaching clays [23]. This could be responsible for the greater ITS value of the PA Ud mixture.

4.2. Analysis of Indirect Tensile Stiffness Modulus test results

In this phase, the dynamic characterisation of the two PA mixtures was carried out by determining their Stiffness Modulus according to EN 12697-26 in indirect tensile configuration. Four specimens were tested at three temperatures (5, 20 and 35 °C) to evaluate the effects of the waste bleaching clay on the thermal sensitivity of the mixture. Results are represented in Table 6 and Fig. 5. Dependence on temperature is described through the following equation:

$$\log S = -\alpha \cdot T + \beta \tag{2}$$

where S is the Stiffness Modulus at temperature T; α and β are experimental parameters depending on the material. Temperature sensitivity is represented by α: high values are typical for materials that are very sensitive to temperature variations.

From the analysis of the Stiffness Moduli, it can be deduced that the use of Ud increases stiffness at every test temperature. Compared to the mixture containing traditional limestone filler, the Ud increases the Stiffness Modulus by 55.8% at 5 °C, 63.8% at 20 °C and 154.6% at 35 °C. This trend validates the deductions made during the static mechanical characterisation phase for the Indirect Tensile Strength test. The increasing stiffness is very positive considering the porous structure of the asphalt concrete and it can lead to improvements of durability and resistance to permanent deformations especially at high temperatures.

Table 6
Indirect Tensile Stiffness Modulus at 5, 20 and 35 °C.

Indirect Tensile Stiffness Modulus (MPa) EN 12697-26							
PA F				PA Ud			
Samples	5 °C	20 °C	35 °C	Samples	5 °C	20 °C	35 °C
PA F 1	7669	2627	558	PA Ud 1	14819	5444	1932
PA F 2	5202	2532	489	PA Ud 2	16070	6886	2546
PA F 3	9326	4390	1129	PA Ud 3	10194	4693	1861
PA F 4	8478	4008	1107	PA Ud 4	11186	5193	2028
Av. PA F	7669	3390	821	Av. PA Ud	11949	5554	2091

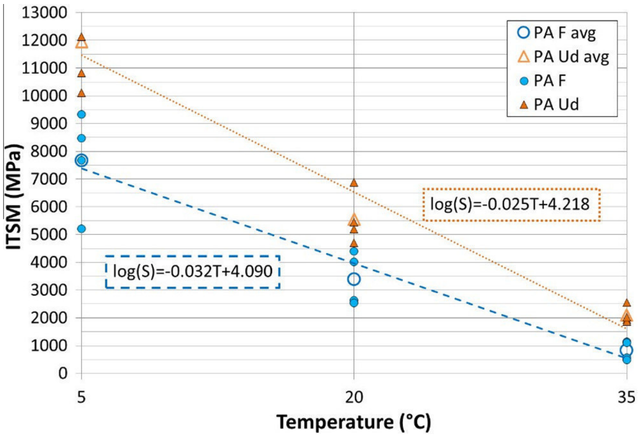

Fig. 5. Indirect Tensile Stiffness Modulus vs. testing temperature.

5. Water damage and durability

5.1. Analysis of Indirect Tensile Strength ratio (ITSR)

According to several study, the in situ water exposure plays an important role in the deterioration of mechanical properties of porous asphalt concrete [24]. The ratio of Indirect Tensile Strength tests in dry and wet conditions can be used to evaluate the water damage, according to the following equation:

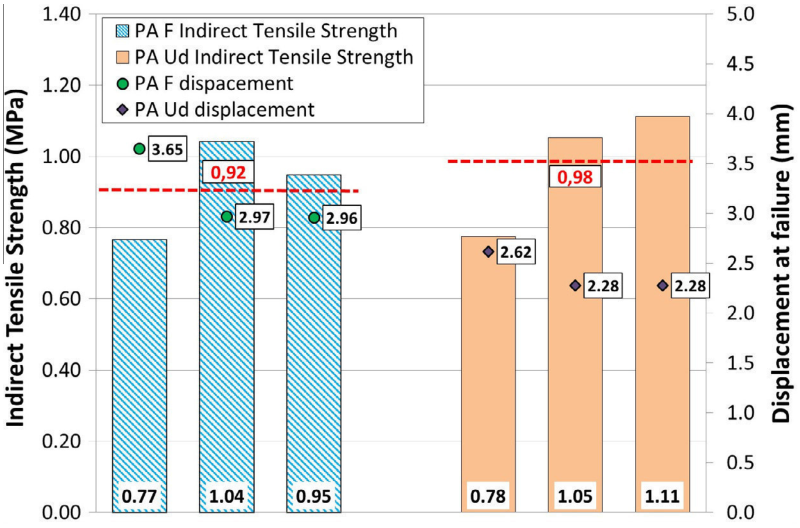

Fig. 4. Indirect Tensile Strength (ITS) at 25 °C: maximum stress at failure vs. displacement for each specimen.

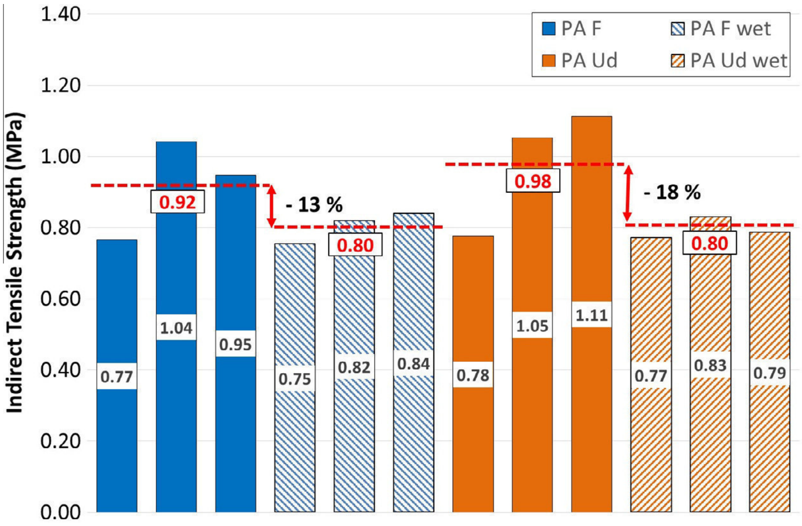

Fig. 6. Indirect Tensile Strength (ITS) in dry and wet conditions: maximum stress at failure for each specimen.

$$ITSR = \frac{ITS_{Dry}}{ITS_{Wet}} \cdot 100 \qquad (3)$$

For ITS test in wet condition, three samples for each mixture were placed in a water bath at 40 °C for 72 h and then tested (EN 12697-12). Results are given in Fig. 6.

The results of the ITS test in wet condition show that both the mixtures reach a high failure resistance, considering the type of asphalt concrete. There is not a significant difference in the reduction of ITS in wet condition between the two mixtures, even if PA Ud shows a lower value of ITSR (83%) if compared to the reference mixture (88%). Both values are higher than ITSR limit imposed by some Italian technical specification for PA mixtures (ITSR $\geqslant$ 75%). Taking as reference these results, the substitution of limestone filler with Ud filler seems not to affect the water susceptibility of PA mixture.

5.2. Analysis of Repeated Load Axial Test results

Three specimens for each mixture were tested according to EN 12697-25 standard. In order to assess the water susceptibility of the mixtures, tests were performed in wet conditions too: a second set of three specimens for each mixture was placed in a water bath at 25 °C for 72 h and then tested. Testing was carried out with a uniaxial load of 100 kPa, repeated for 3600 cycles at 40 °C. According Airey [25] the Repeated Load Axial Test (RLAT) can be effectively used to evaluate resistance to permanent deformations, in a direct uniaxial compression test configuration. The average accumulated deformation curves for each PA mixture in dry and wet conditions are given in Fig. 7 and Table 7.

From the analysis of results, it is evident the different resistance to permanent deformations of the two mixtures: the Ud filler leads to a substantial decrease of the accumulated strain, up to 37.2%. The higher resistance of PA Ud is in accordance with data from the static and dynamic characterisation concerning the increasing stiffness given by the use of digested spent bleaching clay, due to its physical properties. This confirms the studies by Read and Whiteoak [26], according to which the resistance to permanent deformations can vary according to the amount and type of filler used in the bituminous mixtures.

In this case, the results do not show a significant reduction of resistance to permanent deformations in wet condition.

5.3. Analysis of Cantabro test results

The resistance to the degradation of PA mixtures in generally based on results achieved with the Cantabro test. Three Marshall specimens for both mixtures were fist conditioned at 25 °C and

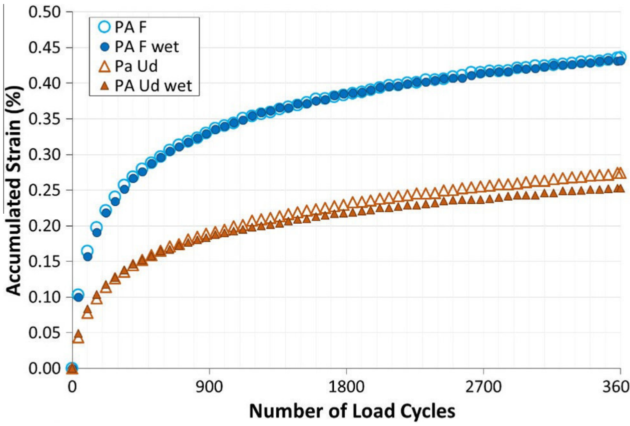

Fig. 7. RLAT: average accumulated strain vs. number of load cycles, dry and wet conditions.

Table 7
Asphalt mixture accumulated strain for dry and wet conditions.

Mixture	Accumulated strain (%)
PA F1 dry	0.37
PA F2 dry	0.49
PA F3 dry	0.44
Average PA F dry	0.43
PA F1 wet	0.39
PA F2 wet	0.47
PA F3 wet	0.44
Average PA F wet	0.43
PA Ud1 dry	0.26
PA Ud2 dry	0.19
PA Ud3 dry	0.35
Average PA Ud dry	0.27
PA Ud1 wet	0.19
PA Ud2 wet	0.27
PA Ud3 wet	0.22
Average PA Ud wet	0.25

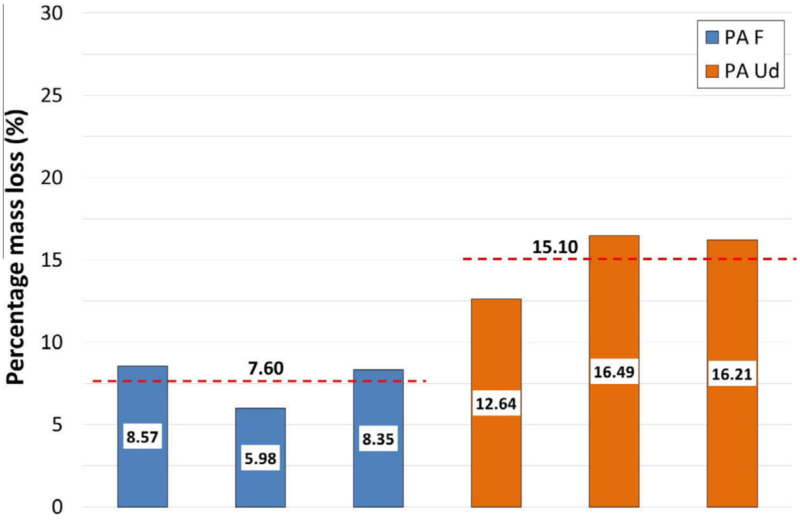

Fig. 8. Cantabro test: percentage of mass loss for PA F and PA Ud.

then tested in compliance with EN 12697-17 standard. Results are given in Fig. 8.

From the analysis of the histogram, it is evident that for PA Ud the percentage of mass loss at the end of the test is twice that for the reference mixture. However, the percentage of mass loss is significantly lower than the limits imposed by some Italian technical specification for PA mixtures (25–30%).

The difference in mass loss is more likely due to the different degree of embrittlement of the bituminous mastics: the stiffening power of the Ud filler should be considered during the mix design process. This data can be related to the different displacement at failure for ITS tests (3.19 mm for PA F vs. 2.39 mm for PA Ud).

6. Analysis of vertical permeability

Three specimens for both PA mixtures were tested. According to EN 12697-19, was used a particular apparatus which can keep a constant water column on cylindrical specimens. The specimens are sealed sideways and fit snugly with the plastic tube to allow the water flow through the PA into a container. The vertical flow Q_v of the water through the specimen in calculated according to the following formula:

$$Q_v = \frac{(m_2 - m_1)}{t} \cdot 10^{-6}$$

where m_1 is the mass of the empty container, m_2 is the mass of the filled container and t is the time of collecting the water (60 s).

From this result, it is possible calculate the vertical permeability K_v, according to Darcy's equation:

$$K_v = \frac{4 \cdot Q_v \cdot l}{h \cdot \pi \cdot d^2}$$

where l is the thickness of the specimen, h is the height of water column (30 cm) and d is its diameter.

Results are shown in Fig. 9.

There is not a significant difference in the vertical permeability of the two different porous asphalts. The substitution of limestone filler with digested spent bleaching clay within the mixture seems not to worsen noticeably the drainage capacity of the porous asphalt. The higher average values of the PA F is probably related to the higher air voids content of the mixture if compared to PA Ud. Both permeability values comply the limit imposed by the Italian technical specifications for porous asphalt ($K_v \geqslant 0.5 \cdot 10^{-3}$ m/s).

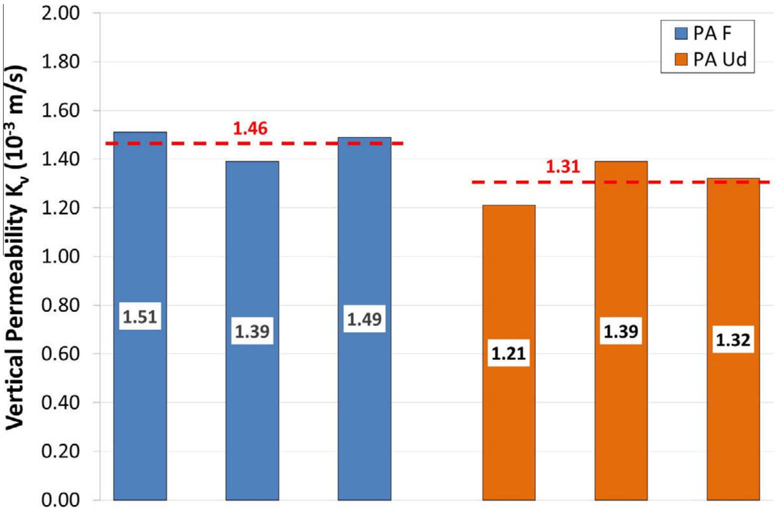

Fig. 9. Vertical permeability for PA F and PA Ud.

Table 8
Test results and differences between PA F and PA Ud.

Test	Unit	PA F	PA Ud	Difference (%)
Air voids content (Va) EN 12697-8	%	15.4	14.5	−5.8
ITS EN 12697-23	MPa	0.92	0.98	+6.5
ITSM 12697-26 @ 5 °C	MPa	7669	11949	+55.8
ITSM 12697-26 @ 20 °C	MPa	3390	5554	+63.8
ITSM 12697-26 @ 35 °C	MPa	821	2091	+154.6
ITSR EN 12697-12	%	88	83	−5.6
RLAT EN 12697-25 dry condition	%	0.43	0.27	−37.2
RLAT EN 12697-25 wet condition	%	0.43	0.25	−41.8
Cantabro EN 12697-17	%	7.60	15.10	+98.6
Vertical permeability EN 12697-19	10^{-3}m/s	1.46	1.31	−10.2

7. Conclusions

Table 8 summarises the results obtained for each test carried out during the research.

Based on the experimental data presented in this study, several conclusions can be drawn:

- The substitution in volume of limestone filler with digested spent bleaching clay does not modify substantially the aggregates gradation of a traditional porous asphalt. The Ud filler does not worsen the compactability of the bituminous mixture: the PAs in the study achieve very similar densities at the end of compaction. There is not a significant difference in terms of voids content (Va, VMA, VFA) between the two PA mixtures.
- From the analysis of ITS and ITSM data, the presence of Ud filler involves a slight increase in Indirect Tensile Strength and a significant one in stiffness, if compared to the mixture with limestone filler. This can be attributed to the volumetric characteristics of Ud: the high Rigden Voids lead to an increment in the stiffness of the bituminous mastic, due to the increase of the quantity of fixed bitumen. The rise in stiffness is evident at high temperatures and it should lead to an improvement of the durability and resistance to permanent deformations.
- The presence of Ud filler within the mixture does not lead to a worsening of the water susceptibility of the PA mixture. From the analysis of the ITSR there is not a significant variation in the reduction of Indirect Tensile Strength in wet conditions. From the results of the dynamic creep test at 40 °C in wet and dry conditions, it is possible to conclude that the substitution of the limestone filler with Ud does not determine a worsening of resistance to permanent deformations, which, however is substantially improved.
- In scientific literature, the mass loss in Cantabro test is usually related to the air voids content and the ITS resistance of PA. In the case under study despite the air voids content and ITS resistance values are very similar for both mixtures, PA Ud shows an higher percentage of mass loss. This aspect should be further examined. However, the percentage of mass loss is anyway significantly lower than the limits imposed by some technical specification for PA mixtures.
- There is not a significant difference in vertical permeability between the two tested PA mixtures. This data fit with the results of the volumetric analysis. However, the vertical permeability is higher than the limits imposed by common technical specifications for PA mixtures.
- On the basis of the experimental results here presented, the substitution of traditional limestone filler with digested waste bleaching clay seems to be possible for PA layers, and it can lead to an improvement of the mechanical properties of the mixture. Further work is necessary to examine in depth the fatigue performance of this alternative PA mixture.

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Preliminary Research on the Physical and Mechanical Properties of Alternative Lightweight Aggregates Produced by Alkali-Activation of Waste Powders

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Abstract: There is growing interest in construction field issues related to environmental protection, energy saving and raw materials. Therefore, the interest in recycling waste materials to produce new construction ones is constantly increasing. This study proposes a new methodology to produce lightweight aggregates (LWAs) by alkali-activation of two different waste powders: a digested spent bentonite clay and a basalt powder. Metakaolin, as secondary precursor, was added to the mixtures according to mix-design proportions, to improve the mechanical properties of the final materials, while a specific activators mix of Sodium Silicate and Sodium Hydroxide enabled the alkali-activation. The expansion process, on the other hand, was obtained using Peroxide within the liquid mix. The experimental LWAs were analyzed and tested in compliance with the EN 13055-1 standard. A more in-depth analysis on LWAs' air voids content and porosity was also carried out by the means of Mercury Intrusion Porosimetry and Nuclear Magnetic Resonance. The results were compared with those obtained from commercial Lightweight Expanded Clay Aggregate, which represents one of the most common LWAs in the construction field. According to the presented preliminary results, the use of alkali-activated waste powders seems to be a suitable solution for the production of eco-friendly LWAs by allowing the recycling of waste materials and energy saving for their production.

Keywords: alkali-activated materials; lightweight aggregates; nuclear magnetic resonance; expanded clay

1. Introduction and Background

Light Weight Aggregates (LWAs) are granular materials characterized by high porosity and low density. The European Standard EN 13055-1 [1] refers to LWAs as construction materials which present bulk density values lower than 1.2 Mg/m^3 and particle density values lower than 2.0 Mg/m^3. When used in the construction industry, LWAs offer functional and economic advantages. The pores of these materials determine favorable thermal and acoustical insulation properties and permit an overall reduction of the self-weight of the final products. LWAs can be found in nature, but most commonly they are artificially produced, either from natural raw materials or from industrial by-products [2]. In the latter case, source materials are subjected to specific treatments, which can be set to control the physical and microstructural properties of the resulting artificial LWA. The most widely used artificial LWAs are based on the processing of clay, slate, perlite, vermiculite, waste glass and ash. Among these, the use of Lightweight Expanded Clay Aggregate (LECA) is probably the most popular. LECA is a widely available and normed material that can be used in various applications including civil engineering projects. The production process of clay LWA comprises the pre-treatment of the raw dried clay and its consequent firing inside a rotary kiln. During the first stages of the process, the raw clay is finely grouted and formed in granules through the addition of water. The pelletized clay consequently undergoes drying and sintering at temperatures typically between 1050 °C and 1250 °C. The heating and rotating action of the rotary kiln leads to decomposition processes and the generation of gases. These are mainly released by the decomposition and reduction of ferric oxides, by the combustion of organic particles, the blowing of entrapped water molecules and the decomposition of carbonates [3]. The formed gases act like blowing agents and expand the clay matter, which swells forming granules with volumes up to five times the initial pellets' dimensions. The granules are characterized by a porous inner structure and an outer hardened shell and result in an optimized weight-to-strength relationship. The physical and mechanical characteristics of LECA vary depending on the raw materials' composition, the firing temperature, and the rotation speed. Materials used in construction industry can present a compressive strength up to 4.5 N/mm^2 and a density of approximately 0.6 Mg/m^3, with figures varying slightly according to the different producers.

Notations are listed in Table 1.

Table 1. Table of notations.

Notation	Description
LWA	Light weight aggregate
LECA	Lightweight expanded clay aggregate
AAM	Alkali-activated material
L/S	Liquid-solid ratio
NMR	Nuclear Magnetic Resonance
TD-MRR	Time Domain Nuclear Magnetic Resonance Relaxometry
PSD	Distribution of pore sizes
MIP	Mercury Intrusion Porosimetry
Ud	Digested spent bentonite clay
B	Basalt powder
MK	Metakaolin
SS	Sodium silicate
SH	Sodium hydroxide
HP	Hydrogen peroxide
A/P	Activator-precursor ratio
IR	Standard Inversion-Recovery
CPMG	Carl-Purcell-Meiboom-Gill sequence
SSD	Saturated and surface-dried

In recent years, increasing effort has been invested into finding new ways to reuse waste materials [4–6] to produce LWAs. The main benefits are represented by the reduction of the production impacts, due to the replacement of natural raw materials, and by the reuse of considerable volumes of wastes. LWAs produced from industrial by-products, such as fly-ash, sludge, and other more unconventional raw materials, can be obtained from similar production processes that are fundamentally based on the sintering of materials at high temperatures between 1000 °C and 1200 °C. Despite the beneficial incorporation and reuse of waste materials in LWAs, the energy demand of traditional production processes still represents a detrimental fact. To meet the deeper ecological goals, the cold-bonding agglomeration process is a valuable technique to produce artificial LWAs without the need of high-temperature sintering. The process is based on the use of a sloping rotary disc, where the wetting agent is added by drops and the material is pelletized by the action of scrapping blades [7,8].

In the context of an increasing sustainability, the possibilities offered by alkali-activation (AA) are gaining relevance. Alkali-activated materials (AAMs) are alternative cementitious materials that result from the chemical reaction between silica and alumina-rich sources and strong alkali solutions [9–12]. The alkali solutions are composed of hydroxides or silicates, or by a combination of both. The most commonly used activators are potassium or sodium hydroxide and sodium silicate. The reaction can conceptually be split into three main steps, which take place almost contemporarily: dissolution, condensation and reorganization [13,14]. During the first stage, the alkali media induces the leaching of the aluminum and silicon ions contained in the precursors. These ions then interact and condensate resulting in the formation of an intermediate complex, which is often defined as a gel. Finally, with the increase in connectivity of the gel, a condensed reorganized structure is formed, typically composed of highly connected silica and alumina tetrahedra [15]. The reaction products are mainly amorphous binders, which show remarkable features in terms of mechanical strength, chemical stability, and fire resistance. A crucial fact in the reaction kinetics is determined by the precursors' composition, and secondarily, by the type and concentration of the alkali-activators. It is proved that a higher alkali content leads to a higher reactivity of the compounds. Nonetheless, strict control needs to be exercised on the liquid to solid ratio (L/S) of the mixture, to prevent the formation of a weak structure. A reasonably low L/S ratio, combined with a curing treatment at temperatures lower than 100 °C, is likely to give the most favorable results [16,17]. AA is quite a recent research field and because many industrial by-products present chemical compositions that match the requirements of AA, a wide range of materials are currently investigated as possible precursors.

The development of lightweight AAMs is drawn from the knowledge of cellular cement. Voids inside the cementitious binder can either be produced by adding a pre-foamed foam to the paste or by using chemical blowing agents, which release gas during the mixing phase. The addition of reactive metal powders, such as aluminum powder, liberates hydrogen gas, while a blowing agent such as hydrogen peroxide exhibits the expansion through the release of oxygen gas. The foaming technique and the mixture composition, as well as the curing conditions, differently influence the porosity and strength of the foamed materials. The combination of the alkali concentration and the L/S ratio determine both the reaction rate and the viscosity of the AA paste, which are fundamental for a stable foaming. Experience on the expansion through hydrogen peroxide showed that a correct manipulation of the AA mix permits the generation of a controlled and stable foaming. Attempts in the production of AA LWAs comprise techniques such as the granulation of hardened AAMs [18] or the cold-bonding pelletization process [19]. More recently, favorable results were achieved using a high-shear granulator, where the AA mass is mixed inside the rotating device resulting in porous granules of different grain sizes [20,21].

In this study, hydrogen peroxide is used to produce AA LWAs, which are obtained from the alkali-activation of two different waste powders, originated from different industrial processes, combined to a certain amount of metakaolin. The activator is a specific solution of sodium hydroxide and sodium silicate.

Furthermore, and likely for the first time, LWAs materials were also studied with the Time Domain (TD) Nuclear Magnetic Resonance (NMR) Relaxometry of protons (^{1}H TD-MRR). This technique is an important non-destructive and non-invasive tool for analyzing the structure of porous media, ranging from biological systems [22] to cement [23]. TD-MRR is characterized by two relaxation parameters, the longitudinal relaxation time (T_1), the transverse relaxation time (T_2) and by a magnetization vector (the sum of the polarized nuclear magnetic moment associated to the ^{1}H spins). Since a permeable porous medium is made of a network of interconnected pores of different shapes and sizes, when the TD-MRR experiment is performed on porous media fully saturated with water (or other fluid containing ^{1}H as for example oil) the relaxation times will be influenced by the presence of the pore walls. Because of the auto-diffusion, a molecule of the saturating fluid continuously moves in the pore network and hits the pore walls, and so the NMR magnetization intensity relaxes back to the equilibrium over a region that is larger than a single pore (the so-called diffusion cell) [24]. TD-MRR data will therefore be averaged over the diffusion cell giving a local average information on pores. If the molecular diffusion is fast enough to maintain the magnetization uniform within the diffusion cell, then T_1 and T_2 show distributions of relaxation times that could be related to the distribution of pore sizes (PSD).

To obtain the PSD of a sample via TD-MRR, the surface relaxivity of the sample should be known. Many techniques can be used to obtain it, each one with its own advantages and disadvantages. Here we used the comparison with the porosity analysis carried out with the classical Mercury

Intrusion Porosimetry (MIP) method. Numerous experiments have shown that in many cases the T_1 or T_2 relaxation time distribution curves could be very similar to the pore size distribution curves obtained by MIP [25].

Results demonstrate a significant correlation between the data obtained with NMR and the outcomes from MIP analysis.

This study proposes a new procedure to produce LWAs by AA of two different waste powders. An in-depth analysis on LWAs' air voids content and porosity was also carried out by the means of MIP and NMR, providing practitioners and researchers with an alternative methodology to assess these characteristics.

2. Materials and Experimental Program

The AA process involves specific precursors and activators in a chemical reaction that leads to the development of cementing materials. In the present work, two different waste materials were used as precursors: a digested spent bentonite clay (named Ud) and a basalt powder (named B). These waste compounds were mixed with metakaolin (M) to ensure adequate chemical properties and mechanical performances to the final mix. The liquid compounds needed for the AA process were sodium silicate (SS) and sodium hydroxide (SH), according to a specific mix-design. A commercial LWA (named LECA) was used as reference material through the research.

2.1. Precursors

2.1.1. Digested Spent Bentonite Clay

Ud used in the presented research is a waste from the food industry. The original material is a bleaching clay, which, thanks to its properties of capturing impurities from oils, is normally used for the decoloring process of oils. As a result of anaerobic digestion for biogas production, the waste materials is disposed of in a dump, with a residual oil content up to 1% by the weight of particles. After some preliminary experimental applications made by the authors for the production of AAMs with Ud, it was found that initial calcination was helping the AA reactions. In fact, the heat treatment allows the material to better interact with the activators for the AA process.

2.1.2. Basalt Powder

The basalt powder is a residual from the extractions and productions processes in basalt quarries. Basalt deposits are present in almost every country and this material is widely used in the constructions field for its mineralogical, chemical, and physical properties. The extensive use of this material for bituminous mixtures and concretes leads to the production of huge quantities of powder during the preparation of aggregates. Different studies and researches have been done for the recycling and reuse of this waste powder in replacement of raw aggregates for the production of construction materials [26]. Some researchers have also verified the AA of the basalt powder, with positive outcomes [27].

2.1.3. Metakaolin

The use of metakaolin (MK) to produce AAMs is common. The chemical properties of this material makes it extremely suitable for the alkali reaction process, as verified by several applications. Metakaolin is a dehydroxylated form of the clay mineral kaolinite and it is obtained by heat treatment (around 700 °C) of a natural kaolin [28].

Table 2 summarizes the precursors' physical properties, while Table 3 shows their chemical composition.

Table 2. Ud, B and M physical properties.

Test	Unit	Ud	B	MK
Size distribution (EN 13043)	%	100 P_{50um}	100 P_{50um}	95 P_{80um}
Water content (EN 1097-5)	%	1.12	0.04	0.12
Particle density (EN 1097-7)	Mg/m^3	1.86	2.70	2.40

Table 3. Precursors' chemical composition.

Compound	Unit	Ud	B	MK
SiO_2	% p/p	43.9	45.3	55.2
CaO	% p/p	2.2	8.8	0.2
Na_2O	% p/p	1.2	1.7	0.6
Al_2O_3	% p/p	9.7	21.6	40.3
Fe_2O_3	% p/p	5.4	8.5	1.4
SO_3	% p/p	1.4	<0.1	0.2
MgO	% p/p	5.7	2.0	0.1
P_2O_5	% p/p	0.7	0.7	<0.1
TiO_2	% p/p	0.8	0.2	1.5
ZnO	% p/p	<0.1	<0.1	<0.1
K_2O	% p/p	0.8	9.7	0.2

According to scientific bibliography, the chemical composition of basalt powder is particularly suitable for its alkali-activation, as verified during the mechanical characterization of the AAMs.

2.2. Activators

2.2.1. Sodium Silicate

SS (Na_2SiO_3) also commonly named as waterglass, is an aqueous solution of sodium oxide (Na_2O) and silicon dioxide (SiO_2) mixed according to specific proportions. Modifying the ratio between SiO_2 and Na_2O one can obtain a solution with different properties, which is suitable for several applications, from the construction to the food field. The SS employed in this experimentation is a commercial product, with a SiO_2/Na_2O ratio of 1.99 and a viscosity of 150–250 MPa·s at 20 °C.

2.2.2. Sodium Hydroxide

SH (NaOH) is a solution employed to dissolve aluminosilicate, increase the pH and to compensate the electric charge of the aluminates in the mixture. It is an inorganic compound that is a highly caustic base and highly soluble in water. A 10 M SH was used in the present work. According to scientific bibliography, the SH suggested molarity for AAMs, ranges between 8 and 12 M [29,30].

2.3. Foaming Agent

Hydrogen peroxide (HP) was used as chemical foaming agent in this research. The HP reacts to produce oxygen gas, and the expansion process of the AAMs' paste is due to the bubbles of O_2 that are trapped into the mixture. It can be directly added to the AA mixture before curing, immediately developing the foaming process due to its sudden decomposition into water and oxygen gas. In this research, an HP solution 30% *w*/*w* (110 vol.) was adopted.

2.4. Experimental Program and Methods

The experimental program was divided into three main steps. The first one was related to the alkali-activation synthesis and to the mechanical characterization of the AAMs. In this step, no foaming agent was added to the mixtures, which were characterized by their workability and compressive strength resistance [31]. The second phase of the research program was related to the production of LWAs. The correct amount of HP needed for the expansion process was evaluated and at the same time the mixing, casting, and curing procedures of the LWAs were defined. The third step focused on the LWAs characterization. The EN 13055-1 standard [1] specifies the properties of light aggregates either obtained through natural processes or artificially produced from natural or recycled materials, used in concrete, mortar and grout in buildings, roads, and other civil engineering applications. A set of tests was selected to investigate the most relevant properties of the LWAs, with the aim of evaluating their suitability to be used as construction materials. Different tests were carried out to characterize the alkali-activated LWAs. The geometrical properties were assessed based on the particle size distribution [32]. The physical characteristics were evaluated according to the loose bulk density [33], the water content [34] and the particle density and water absorption tests [35]. According to each reference standard, a specific number of samples was tested to have significant results.

A detailed analysis of porosity and pore size distribution of LWAs were also conducted by means of both MIP and NMR techniques.

The preparation of samples measured with TD-MRR was conducted as follows. The LWAs were dried in an oven at 60 °C for 8 h and weighted (dry weight). Then the dried samples were saturated under vacuum with fresh water and weighted (saturated weight). To remove liquid from the outer surface of the aggregates (extrapellet liquid), shortly before TD-MRR analysis the LWA were removed from the liquid and rolled over a pre-soaked filter paper that ensures the liquid is not removed from the pores during the process. With the saturated and dry weights, it is possible to classically evaluate the quantity of absorbed water and therefore roughly check the quality of TD-NMR analysis. In fact, the intensity of the acquired TD-MRR signal is proportional to the amount of saturating water.

A few 20 mm internal-diameter test tubes were filled to a height of 30 mm (sensitive volume of the NMR probe) with the saturated LWAs and sealed with parafilm. TD-MRR relaxation signal curves were acquired with a console and a probe (equipped with a 25 mm internal-diameter coil) both manufactured by Stelar (Mede, PV, Italy), and using a permanent 0.18 T magnet (ESAOTE SpA, Genova, Italy).

Standard Inversion-Recovery (IR) and Carl-Purcell-Meiboom-Gill (CPMG) sequences [36] were used to acquire the T_1 and T_2 relaxation decay curves, respectively.

T_1 and T_2 relaxation decay curves were inverted to produce quasi-continuous relaxation time distributions by means of UpenWin (http://software.dicam.unibo.it/upenwin) a software that implements the 1D version of the inversion algorithm Upen [37]. Upen was specifically designed not to provide distribution details that are not supported by data, which might be misinterpreted, for example, as physically meaningful resolved pore compartments. To synthesize a complex distribution of values with only one single more manageable value, various scalar parameters (as for example, different kind of averages) could be computed from the relaxation time distribution itself. Distribution peaks position ($T_{(1,2)pk}$) and geometric weighted average ($T_{(1,2)g}$) are among these.

MIP experiments were performed by means of the mercury porosimeters PASCAL 140, measuring range 3.8 µm–116 µm, and PASCAL 240, measuring range 7.4 nm–15 µm (ThermoFisher Scientific, Waltham, Massachusetts, USA), where 5 g of the samples were measured using a mercury pressure range from 0 to 200 bar. The MIP data were analyzed by means of the SOL.I.D software (1.3.3, ThermoFisher Scientific, Waltham, Massachusetts, USA).

The results obtained during the characterization of the experimental aggregates, were always compared to values refer to traditional LECA.

3. Lightweight Aggregate Characterization

3.1. Alkali-Activated Material Characterization

Two different mixtures were studied using the waste materials as precursors, combined with MK according to several proportions, to achieve adequate mechanical properties. In the mix-design step, different mixes were prepared varying the following variables:

- Ud/MK and B/MK;
- SS/SH;
- Activators/Precursors;
- Curing method.

The correct mix designs and curing method were chosen according to the workability of the alkali-activated pastes and the compressive strength of the cured mixtures. In the light of the above, the optimized mix designs for the two AAM are presented in Table 4 (precursors are in percentages on the weight of the mixtures).

Table 4. Mix design for AAM_Ud and AAM_B.

Mixture	Ud (%)	B (%)	MK (%)	SS/SH	A/P
AAM_Ud	50	0	50	3	1
AAM_B	0	70	30	4	0.45

The higher amount of MK in the AAM_Ud is adopted to achieve consistent compressive strengths. As mentioned before, the chemical composition of B makes this waste material suitable for the alkali activation process. The presence of MK is needed to optimize the mechanical properties of the AAM_B. Both mixtures had the same workability and the different A/P ratio is mainly due the different absorption power of the mix of precursors. The performances in terms of compressive strength of both mixtures are shown in Figure 1 (avg. values of three samples). The tests were carried out on cubic samples (40 × 40 mm) initially cured for 12 h in the oven at 70 °C and then kept at ambient temperature and humidity in the laboratory.

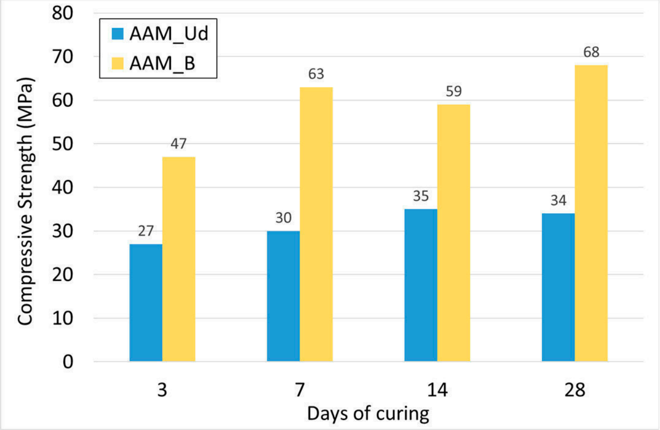

Figure 1. Compressive strength average results for AAM_Ud and AAM_B after 3, 7, 14 and 28 days of curing.

The different mechanical resistance of the two AAMs is clear. Despite the higher presence of MK into the AAM_Ud, the compressive strength for this mixture is almost half of the AAM_B one. This is mainly due to the chemical composition of Ud, which has an Al_2O_3 content lower than basalt. According to scientific literature, a considerable amount of Al_2O_3 and SiO_2 is favorable for the formation of a resistant microstructure during the AA process. As an overall result, it is worth noting that both mixtures reached significant compressive strength levels, if compared to other AAMs tested in several experimental applications [38–42] or traditional construction materials (cement concretes).

3.2. LWA Synthesis and Production

LWA synthesis starts from the addition of the expansion agent to the mixture after the mixing of precursors and activators for 10 min. The quantity of HP to be added to the AAMs was chosen to obtain a high workability and a good level of expansion. A specific amount of HP was added to each mixture, due to the different composition of the two experimental AAMs. Several LWAs were produced with a HP concentration between 2% and 10% by the weight of the activators. As soon as the expansion process starts, the alkali-activated samples are produced by extruding the paste from a syringe and rolling the material to form the aggregate. After being placed at 70 °C for 12 h, the samples were weighted and crushed for a preliminary analysis of their mechanical resistance.

Table 5 shows the final mix design of both mixtures, in which the amount of HP is expressed in percentage on the weight of the activators. For the LWA_Ud, the quantity of MK was also increased from the original mix design to achieve a higher mechanical strength.

Table 5. Mix design for LWA_Ud and LWA_B.

Mixture	Ud (%)	B (%)	MK (%)	SS/SH	A/P	HP (%)
LWA_Ud	40	0	60	3	1	5
LWA_B	0	70	30	4	0.45	7

Figures 2 and 3 show the external and internal structure of the experimental LWAs and of the LECA one.

Figure 2. External shape of LWA_B (**left**), LWA_Ud (**center**) and LECA (**right**).

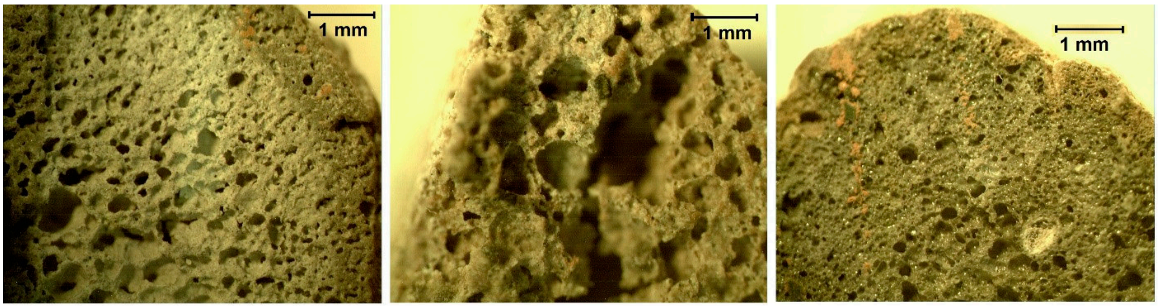

Figure 3. Inner structure of LWA_B (**left**), LWA_Ud (**center**) and LECA (**right**) by optical microscope.

The difference in terms of external shapes between the three samples is due to the different production methods: while the experimental LWAs are handcrafted in this preliminary research stage, the LECA is produced by heat treatment. This makes the external shape irregular and the inner structure rich in small voids. From the comparison of the pictures in Figure 3, it is almost clear the difference in terms of voids between the three different samples. The LWA_Ud seems to have the largest and irregular pores, while the LECA sample shows small and well distributed voids, as confirmed by the porosity analysis shown below.

3.3. LWAs' Geometrical and Physical Properties

The third stage of the research program is based on the LWA characterization. To evaluate the geometrical, physical, and mechanical characteristics of the experimental materials, laboratory tests were performed on samples in compliance with the EN 13055-1 standard [1]. The physical properties of the experimental LWAs and the reference one were assessed through the following tests:

- Particle size distribution [32];
- Loose bulk density and air voids [33];
- Water content [34];
- Particle density and Water absorption [35].

The physical analysis of LWAs was corroborated by means of NMR and MIP tests.

3.3.1. Particle Size Distribution

The determination of the particle size distribution of aggregates follows the EN 933-1 standard [32]. The test consists of dividing and separating the material into several particle size classifications of decreasing sizes by means of a series of sieves. The particle size distribution test is applied to every aggregate, including lightweight ones. Figure 4 shows the grading distributions of the three LWAs.

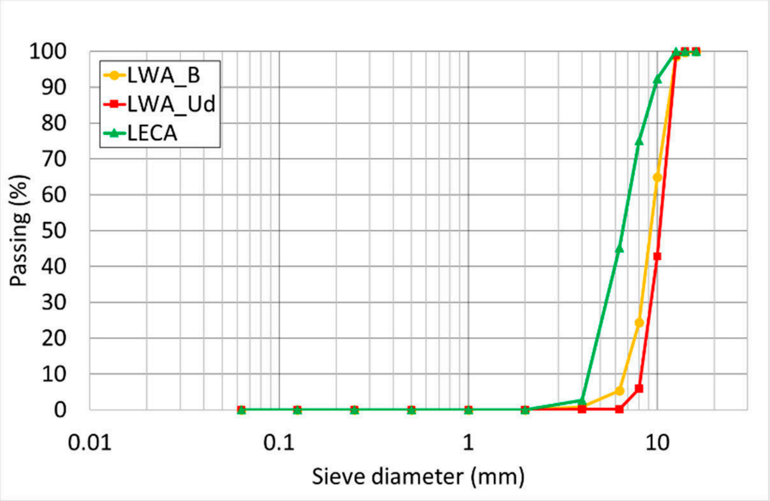

Figure 4. LWAs size distributions.

The particle sizes of the experimental aggregates are similar and can be classified as a 4/12.5 mm designation. The LECA grading distribution, even if classified according to the same class, is characterized by the presence of finer particles (Table 6).

Table 6. Passing material for LWA_B, LWA_Ud and LECA.

Sieve (mm)	Passing LWA_B (%)	Passing LWA_Ud (%)	Passing LECA (%)
16	100.00	100.00	100.00
14	99.71	100.00	100.00
12.5	98.57	98.99	100.00
10	64.90	42.84	92.39
8	24.40	5.88	75.04
6.3	5.39	0.17	45.11
4	0.86	0.06	2.64
1	0.00	0.00	0.00
0.5	0.00	0.00	0.00
0.063	0.00	0.00	0.00

3.3.2. Loose Bulk Density and Air Voids

According to the EN 1097-3 standard [33], the loose bulk density calculated as the ratio between the mass of dry aggregates filling a specific container without compaction, and the capacity of that container. From the calculation of the loose bulk density, the air voids content is evaluated as the air-filled space between the aggregates filling the container. In compliance with the standard, a 5 L container was used considering the particle size distributions of the LWAs. Results are presented in Table 7.

Table 7. Loose bulk densities and voids content for the LWAs.

	LWA_B	LWA_Ud	LECA
L.b.d.—Sample 1 (Mg/m^3)	0.701	0.473	0.422
L.b.d.—Sample 2 (Mg/m^3)	0.703	0.476	0.420
L.b.d.—Sample 3 (Mg/m^3)	0.702	0.475	0.424
Avg. L.b.d. (Mg/m^3)	0.702	0.475	0.422
Avg. Air voids (%)	44.3	36.0	43.5

The loose bulk density for the LWA produced with basalt is higher if compared to the other LWAs, and this is due to the higher mass of the samples. It is worth noting that the EN 13055-1 standard [1] classifies as lightweight the aggregates with a loose bulk density not exceeding 1.20 Mg/m^3. There is not significant difference between LWA_Ud and LECA. If the air voids are taken into account, the different results are mainly related to the grading curve of each material and the related particles shape. The standard does not specify any limits or range of values for this parameter.

3.3.3. Water Content

According to the EN 1097-5 standard [34], the water content of aggregates is evaluated by successive weighing of samples placed in a ventilated oven (110 ± 5 °C) until a constant mass is reached. The water content is determined as the difference between the wet and the dry mass and it is expressed as a percentage of the dry mass of the test portion. Table 8 shows the results.

Table 8. Water content for the LWAs.

	LWA_B	**LWA_Ud**	**LECA**
Water content (%)—Sample 1	1.27	4.10	0.19
Water content (%)—Sample 2	1.27	4.44	0.17
Avg. Water content (%)	1.27	4.27	0.18

The water content varies from 4.27% of LWA_Ud to 0.18% measured for the LECA samples. The results are highly influenced by the storing condition of the samples. All the material were kept at ambient temperature inside the laboratory, stored in plastic bags. Both tests on basalt and expanded clay aggregates were performed during a dry season, whereas the tests on Ud specimens were performed when climate conditions were more humid. In the light of the above, further test are needed to verify the water content of LWAs on similar storing conditions. It shall be mentioned that EN 13055-1 [1] does not specify any water content limit for the LWAs.

3.3.4. Particle Density and Water Absorption

The EN 1097-6 standard [35] describes the pycnometer method for the evaluation of three different density parameters and the water absorption values for LWAs. According to the standard, the particle density is given by the ratio of mass to volume. Based on the conditions of weighting the test portion, the density is considered in saturated, saturated, and surface-dried (SSD) and in the oven-dried condition. The water absorption is then calculated using a soaking time of 24 h. Average results are presented in Table 9.

The densities of the three LWAs are different because of the inner structure given by the expansion process. LECA is the lightest material while LWA_B is the heaviest one. It is worth noting that according to the EN 13055-1 standard [1] the aggregates with a particle density not exceeding 2.00 Mg/m^3 are classified as lightweight. The water absorption values are strictly connected to the pores dimensions. Further observations on particle densities and porosity are shown in the porosity analysis section of this paper.

Table 9. Apparent, oven-dried, SSD particle densities and water absorption values for LWAs.

	LWA_B	**LWA_Ud**	**LECA**
Apparent particles density (Mg/m^3)	1.69	1.18	0.87
Oven-dried particles density (Mg/m^3)	1.26	0.74	0.75
SSD particles density (Mg/m^3)	1.52	1.11	0.85
Water absorption after 24 h (%)	20	50	17

3.3.5. Analysis of Porosity

To obtain the relaxation time distributions, the relaxation decay curves were inverted by means of UpenWin.

At first sight, the T_2 distributions (not shown) encoded at different echo time, allow us to state that there are not evident diffusion effects, more precisely, the T_2 distributions do not change varying the echo time. Therefore, the relaxation time distributions are strictly related to the local diffusion cell and consequently they are representative of the PSD. In Figure 5 the T_1 distributions of samples are shown. All the distributions show a well-defined and narrow peak at long times (around 1 s) followed by long tail with a hump at shorter times. The areas under the relaxation curves are proportional to the NMR signals which, in turn, are proportional to the amount of saturating water.

The T_{1pk} of the three distributions are respectively: 1108, 1417 and 1519 milliseconds. Table 10 summarizes the weights and the NMR signal intensity computed on the distributions. The good proportionality of column 4 and 5, the maximum percentage discrepancy of their ratio (column 6) is approximately 7%, allows us to state that the TD-MRR measurements were significant and reliable.

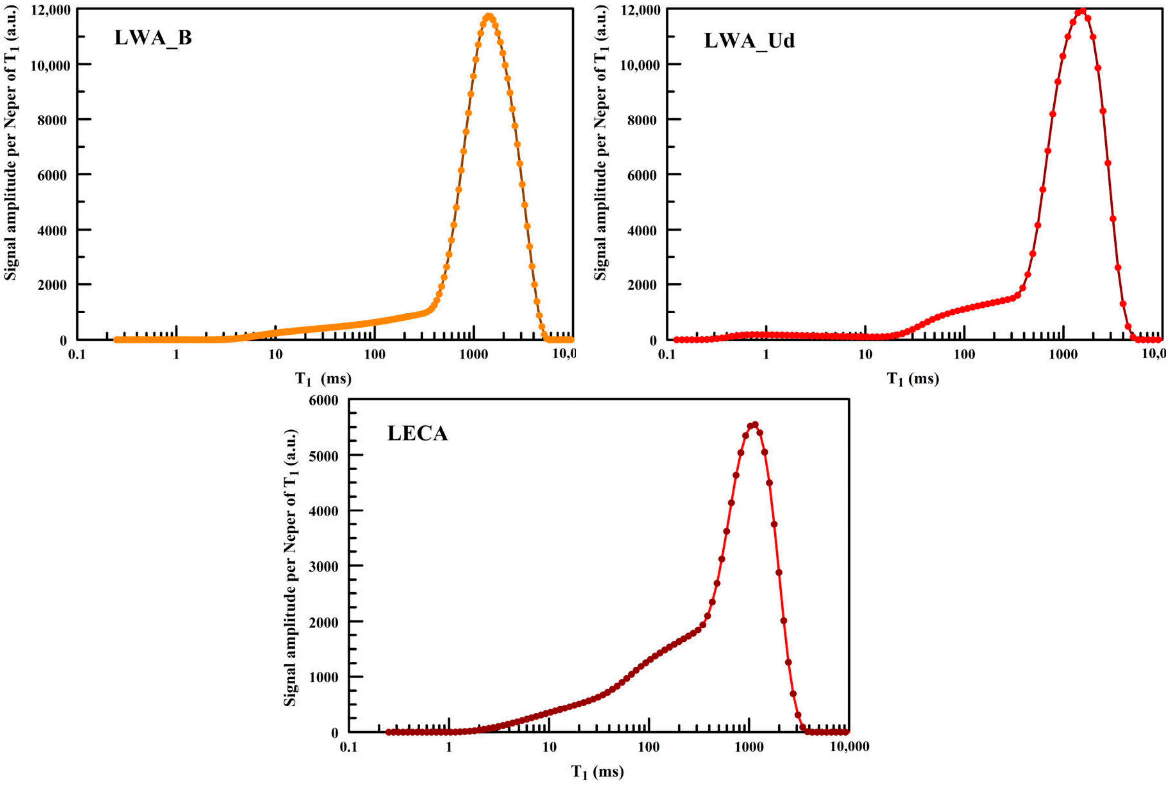

Figure 5. T_1 distributions for LWA_B, LWA_Ud and LECA.

Table 10. Weight of the samples used for the NMR measurements and the total NMR signal of the T_1 distributions.

Sample	Dry Weight (g)	Saturated Weight (g)	Absorbed Water (g)	T1 Total Signal (Arbitrary Unit)	Ratio [-]
LWA_B	5.7	8.9	3.2	19,050	5953
LWA_Ud	4.1	7.7	3.6	21,290	5914
LECA	4.4	6.5	2.1	11,690	5567

The TD-MRR PSDs obtained by calibrating the TD-MRR relaxation time distributions with MIP results are shown in Figure 6. The samples have significantly different PSDs. In particular, small pores in the range from few nanometers to some micrometers characterize the LECA aggregates. LWA_B and LWA_Ud have larger pores in the range of 0.1–200 mm. If the two experimental aggregates are compared, the LWA_Ud has the larger pores, with a consistent density of pores whose size ranges between 100 and 200 mm. Moreover, form the analysis of the area under the distribution curves, both experimental aggregates are characterized by a more homogeneous pore size distribution. These results are in line with that verified from the optical microscope images shown in Figure 3. The inner structure of LECA consists of small pores if compared to the experimental aggregates, while the Ud one has the largest diameter voids.

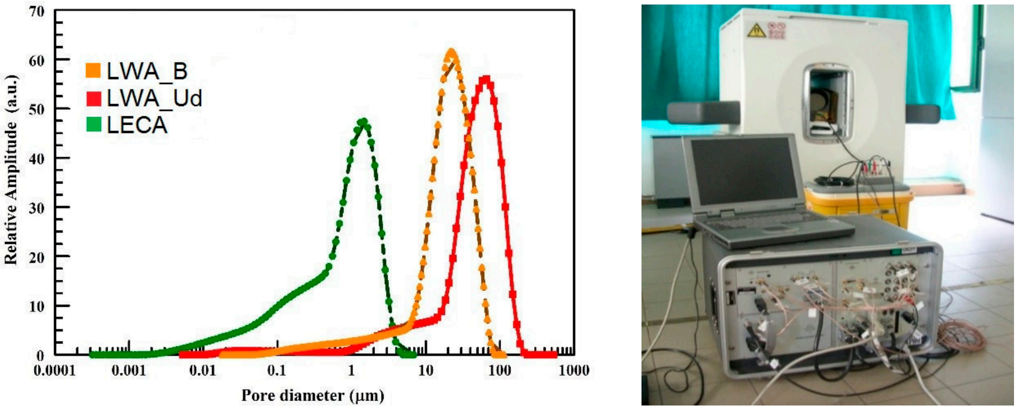

Figure 6. TD-MRR PSDs for LWA_B, LWA_Ud and LECA (**left**) and NMR equipment (**right**).

3.4. LWAs' Mechanical Properties

The mechanical characterization of LWAs is made through the evaluation of their crushing resistance. The EN 13055-1 standard [1] specifies the apparatus and two different test procedures related the loose bulk density of the LWAs. Based on previous results, the procedure n.2 was adopted. According to the standard, three test specimens were prepared by filling a specific steel cylinder with aggregates. When compacted, the LWAs surface was leveled to the top rim of the container, which was then subject to a force given by a piston set to reach a compression of 20 mm in approximately 100 s. The crushing resistance for each test specimen was than calculated using an equation that considers the load exerted by the piston, its area and the compression force and the area. Average results are shown in Table 11.

Table 11. Compression force and crushing resistance for LWA_B, LWA_Ud and LECA.

	LWA_B	LWA_Ud	LECA
Compression force (N)	51,100	12,150	38,050
Crushing resistance (N/mm^2)	4.44	1.07	3.31

Comparing the results, LWA_B shows the highest mechanical performance: its crushing resistance is three times that of LWA_Ud. If LECA is taken into account, the increase in crushing resistance for LWA_B is about 34%. As general remark, it must be noted that the standard does not specify any limits or range of results in terms of crushing resistance for LWAs. However, considering the wide field of applications of these materials, a minimum value of crushing resistance is required for LWAs to be used as construction materials. Generally, according to the different uses in the civil engineering field, the threshold limit is set at 0.7 N/mm^2. As an example, for foundation layers between the floor and the finishing flooring, for the thermal and acoustic insulation of a building, a crushing resistance between

0.7 and 1.5 is generally required. For structural lightweight concrete, this range is raised to a minimum of 4.5 N/mm^2 while for lightweight asphalt concretes the Italian technical specification requires a crushing resistance higher than 2.7 N/mm^2. In the light of the above, both the experimental LWAs meet the required minimum mechanical properties for their applications in the civil engineering field.

4. Conclusions

The study presented in the paper shows a new method to produce alternative LWAs by AA of two different waste powders. Two experimental alkali-activated LWAs have been developed using a basalt powder and a digested spent bentonite clay as main precursors. Based on the data presented in this work, several conclusions can be drawn which corroborate the validity and the smartness of the proposed solution for the production of alternative LWAs:

- The adopted waste materials were suitable for the AA process. The addition of HP to the pastes allowed the production of lightweight aggregates in the laboratory. The optimum quantity of the foaming agent was determined to obtain a workable paste and final aggregates with a good porosity-to-strength ratio.
- Because of the physical characterization of the LWAs, both the experimental materials showed appropriate properties to be classified as lightweight aggregates according to the EN 13055-1 standard [1]. LWA_B and LWA_Ud have densities lower than 2.00 Mg/m^3 and a loose bulk density not exceeding 1.20 Mg/m^3.
- Mechanical characterization was performed through the crushing resistance test. Even if the EN 13055-1 [1] does not specify any limits for LWAs, a specific crushing resistance value is required for their application as construction material. LWA_Ud has a crushing resistance (1.07 N/mm^2) higher than the lower limit usually specified for the application of LWAs in civil engineering projects. LWA_B has the highest mechanical resistance (4.44 N/mm^2) even if compared to the structural expanded clay, LECA, used in this research as reference lightweight construction material. These results are in line with the values recorded during the preliminary mechanical characterization of the alkali-activated paste materials and are mainly dependent on the chemical composition of the wastes used as precursors.
- The voids of the LWAs materials were studied by means of the Time Domain NMR Relaxometry of protons (^{1}H TD-MRR). The TD-MRR results were then compared with the porosity analysis carried out with the MIP method. In this work, the relaxation time distributions are strictly related to the local diffusion cell and effectively represent the distribution of pore sizes (PSD). From the correlation with MIP results, the TD-MRR PSD shows a structure rich in small voids for LECA samples, while larger and more size-homogeneous pores characterize the experimental aggregates. These results are corroborated by the visual analysis of the optical microscope images, which confirm the presence of larger voids for LWA_Ud if compared to LWA_B and LECA. Small pores instead characterize the latter.

In light of the above, the expansion of these AA waste materials seems to be a viable solution for the production of lightweight aggregates, allowing the recycling of materials otherwise dumped or sent to landfill. Moreover, the results confirm and validate the analysis of pore sizes and their distribution in lightweight aggregates according to TD-MRR and MIP methodologies.

Further investigations and tests are planned to back up these preliminary conclusions and to confirm the use of AA LWAs as construction materials. Additional research will focus on the Life Cycle Analysis of the proposed solution to justify their development on an industrial scale.

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EXPERIMENTAL APPLICATION OF SYNTHETIC LIGHTWEIGHT AGGREGATES FOR THE PRODUCTION OF SPECIAL ASPHALT CONCRETES

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Abstract

This paper presents the results of a laboratory research on asphalt concretes made with synthetic expanded aggregates produced from waste materials. In the last years, the use of wastes for the production of new construction materials is constantly increasing. In the present research, through the alkali-activation process, two different wastes are used for the production of synthetic lightweight aggregates: a digested spent bentonite clay and a basalt powder. Both experimental aggregates have been fully characterized in compliance with the reference standards for lightweight aggregates. Taking as a reference some Italian specifications for special wearing course asphalt concretes, the physical and mechanical properties of two different experimental asphalt mixtures have been evaluated. For this purpose, a mixture prepared with traditional expanded clay aggregates was used as reference material.

The presented preliminary results indicate that the use of alkali-activated lightweight aggregate in total substitution of the expanded clay does not negatively affect the performances of the asphalt mixture. Moreover, the alkali-activation of these waste materials seems to be a suitable and sustainable solution for the production of lightweight aggregates for this and other purposes.

Keywords: Lightweight aggregates; alkali-activated material; special asphalt concrete; expanded clay.

1. INTRODUCTION

According to EN 13055-1 standard, a lightweight aggregate (LWA) is a granular material with a bulk density lower than 1.2 Mg/m^3 and a particle density lower than 2 Mg/m^3. Earlier LWAs used in the engineering field as construction materials were of natural origin, generally volcanic [1]. Due to the limited availability of these natural aggregates and their changing properties, natural LWAs are not used anymore [2]. Moreover, the production of artificial lightweight materials allowed a better control of their properties and the marketing of different products all over the world. Today their applications as construction materials is widespread due to their thermal and acoustical insulation characteristics as well as for their mechanical properties, combined with the possibility of reducing the self-weight of the final product.

During years, several technologies have been developed to produce LWAs from both natural raw materials (clay, shale, slate, etc.) and industrial by-products (fly ashes, blast furnace slag, etc.). The Lightweight Expanded Clay Aggregate (LECA) is certainly the most used and widespread lightweight material that is suitable for civil engineering applications. Due to its physical and mechanical properties, LECA is used in the construction filed for the production of lightweight concretes as well as for blocks and precast elements [3]. Some other applications are also known for water treatment and in the agriculture sector. In the infrastructures field, LECA is used in road and railway structures as light fill material to limit subgrade settlement and to increase the stability of structures and road embankments on weak grounds. In the last years, LECA has been also used for the production of Asphalt Concretes (ACs) with specific properties such as improved drainability or high skid resistance [4, 5]. The production of LECA takes place in rotary kilns where a special plastic clay is heated and sintered at high temperatures (1050-1250 °C). From a sustainable and eco-friendly perspective, in recent years relevant efforts have been made into finding solutions to use wastes for the production of alternative LWAs. The final aim was to limit the use of raw materials and define a functional intended use for materials otherwise disposed into landfills.

In the light of the above, in the present research two different wastes were used to produce synthetic LWAs through the so called alkali-activation process. The growing interest of researches into finding alternative and sustainable technique for the production of construction materials, lead to the development of alkali-activated materials [6, 7]. These are alternative cementitious materials, which can be synthesized by combining wastes rich in silica and alumina into a strong alkali environment. The result is the development of a strong amorphous binder, with similar or even better performances than those of traditional Portland cement, in terms of mechanical and chemical properties and fire resistance [8]. It is worth noting that from an environmental point of view, this technology involves a reduction in CO_2 emissions, if compared to the Portland cement production process, and a potential solution for wastes disposal and recycling [9]. Two different wastes were here used for the alkali-activation process: a digested spent bentonite clay (WBC) and a basalt powder (BP). Following some Italian specifications for special wearing course ACs, the produced synthetic LWAs were used in total substitution of LECA to confer a high skid resistance to the bituminous mixture.

2. MATERIALS

The alkali-activation synthesis involves two main group of materials, precursors and activators, in a chemical reaction that leads to the development of a strong amorphous binder. In the present research, the WBC and BP were used as precursors, together with a specific amount of metakaolin which confers suitable mechanical properties to the final product. A liquid mix made with sodium silicate and sodium hydroxide in specific proportions was the activator adopted for the alkali-activation synthesis.

The expansion agent used in this research was hydrogen peroxide. This foaming agent enables the expansion of the alkali-activated paste through the production of O_2. The liquid was added, in a pre-defined amount, to the mixture before curing.

A traditional LECA was used as reference material for both the LWAs characterization and for the production of special ACs.

2.1 Waste materials

WBC is a waste from the food industry process. The original material is a bleaching clay adopted for the decolouring process of vegetable oils that is subsequently processed through an anaerobic digestion for the production of biogas. At the end of this stage, the material is landfilled. After first attempts to directly use this waste into an alkali-activation process, the authors verified that a thermal treatment (calcination) improved the material reactivity [10].

The BP is a waste from the extractions and productions processes in basalt quarries. The material adopted in this research is completely passing through the 0.5 mm sieve. Due to its physical characteristics, basalt is widely used as construction material and its chemical properties make it suitable for the alkali activation process [11].

3. EXPERIMENTAL PROGRAM AND METHODS

The experimental program was divided in two consecutive steps. The first one was a preliminary characterization of the experimental LWAs. The two waste materials were used for the production of two kind of LWAs, labelled WBC_LWA and B_LWA. Taking as a reference the EN 13055-1 standard, which specifies the physical and mechanical properties of LWAs suitable for the production of construction materials, the characteristics of the synthetic aggregates were assessed and compared to the LECA ones.

The second and main step was related to the characterization of special ACs with high friction properties and produced with LWAs. Three different ACs mixtures were tested: two with the experimental LWAs (labelled WBC_AC and B_AC) and a reference one with LECA (LECA_AC) which was designed in compliance with the Italian technical specifications. The experimental program allowed the physical and mechanical analysis of the mixtures. The volumetric analysis (EN 12697-8) was carried out on three samples for each mixture that were prepared using a gyratory compactor and in accordance with the EN 12697-31 (compaction pressure of 600 kPa and 120 revolutions).

The mechanical analysis was carried out by the means of static and dynamic tests. In compliance with the EN 12697-23 standard, the Indirect Tensile Strength was evaluated at 25 °C on three SGC samples (80 gyrations) for each mixture and the reduction in ITS (EN 12697-12) after water immersion was studied on other three samples placed in water at 40 °C for 72 hours. The dynamic analysis was based on the evaluation of the Indirect Tensile Stiffness Modulus (ITSM, EN 12697-26) at three temperatures on three SGC samples (80 gyrations). The durability of the ACs was assessed by means of the Cantabro test (EN 12697-17) carried out on four Marshall samples (EN 12697-30, 50 blows) for each mixture. Finally, the surface properties of the mixture was verified measuring the skid resistance of the three ACs, in compliance with the EN 13036-4 standard.

The results obtained for the experimental LWAs and mixtures were always compared to those obtained from the traditional LECA during each step of the research.

4. LIGHTWEIGHT AGGREGATES CHARACTERIZATION

Taking as a reference the EN 13055-1 standard, which refers to LWAs that are suitable for construction materials, a full characterization of the experimental aggregates was carried out. Data were always compared with values obtained for LECA. Table 1 summarizes the average results for each test.

Table 1: Tests and results for the experimental LWAs and LECA.

Test	Unit	WBC_LWA	B_LWA	LECA
Size distribution (EN 13043)	mm	0/14	0/16	0/12.5
Loose bulk density (EN 1097-3)	Mg/m^3	0.475	0.702	0.422
Air voids (EN 1097-3)	%	36.0	44.3	43.5
Water content (EN 1097-5)	%	4.27	1.27	0.18
Particle density (EN 1097-6)	Mg/m^3	1.18	1.69	0.87
Water absorption (EN 1097-6)	%	50	20	17
Crushing resistance (EN 13055-1)	N/mm^2	1.07	4.44	3.31

From the analysis of the results, both the experimental LWAs seem to have appropriate properties to be classified as lightweight aggregate suitable for applications as construction material. The two alkali-activated LWAs have densities lower than 2.00 Mg/m^3 and a loose bulk density not exceeding 1.20 Mg/m^3, in compliance with the limits imposed by the EN 13055-1 standard. In terms of mechanical properties, even if the aforementioned standard does not specify any limit, other technical specifications generally require a minimum value of crushing resistance equal to 1.00 N/mm^2. Both experimental LWAs exceed this threshold limit and B_LWA shows the highest crushing resistance, even if compared to the reference LECA. These results are strictly dependant on the chemical properties of the waste materials used as precursors that affect the final properties of the alkali-activated material.

5. ASPHALT CONCRETES CHARACTERIZATION

Once the physical and mechanical properties of the synthetic LWAs have been defined, two experimental ACs were prepared. Results were always compared with data obtained from a reference mixture containing LECA.

5.1 Mix Design

In compliance with relevant Italian technical specifications, a standard ACs prepared with LECA (12 % by the weight of aggregates) was taken as a reference mixture. Considering the different LWAs particles size distribution, a specific mix design was designed for each ACs, in order to have a constant amount of LWAs (12 % on the weight of aggregates) and the same grain-size distribution (Figure 1). A traditional 50/70 penetration grade bitumen was used as a binder; its rheological properties are given in Table 2.

Table 2: Rheological properties of asphalt 50/70 pen binder.

Test	Unit	Characteristic value
Penetration @ 25°C (EN 1426)	dmm	50 – 70
Soft. Point (EN 1427)	°C	50
Dynamic Visc. @ 60°C (EN 12596)	Pa·s	≥145

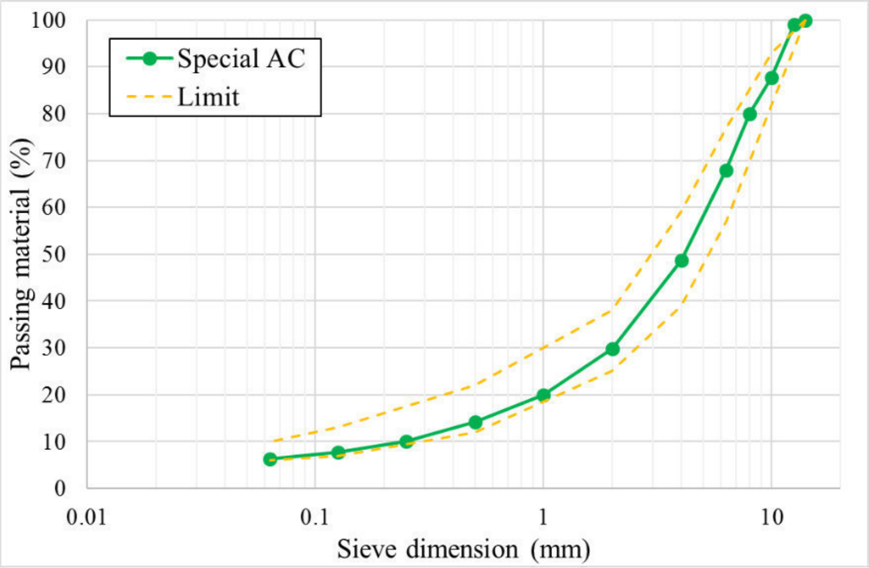

Figure 1: ACs particles size distribution.

The amount of binder was fixed according to 6 % on the weight of aggregates.

5.2 Air voids content analysis

Once the mix design of the AC was completed, three samples for each mixture were compacted by the means of gyratory compactor (EN 12697-31). To evaluate the workability properties of the mixtures and their physical properties, the air voids content (EN 12697-8) was assessed at different compaction energies corresponding to 10, 80 and 120 gyrations. Table 3 summarizes the average results.

Table 3: Average air voids content for each mixture.

Air voids content (EN 12697-8)	WBC_AC	B_AC	LECA_AC
@ 10 gyrations (%)	22.6	21.4	20.1
@ 80 gyrations (%)	17.1	14.8	13.9
@ 120 gyrations (%)	16.1	13.7	12.7

From the analysis of the results, mixtures have a high air voids content. The variation in porosity between the ACs is probably due to the different LWAs particles size distribution. The following mechanical tests will evaluate if the high air voids content has a detrimental effect on the properties of the final bituminous mixtures.

5.3 Indirect Tensile Strength and water susceptibility

The mechanical analysis was carried out by means of static and dynamic tests. The evaluation of the level of tenacity reached by the aggregates-filler-bitumen bond is generally given by the Indirect Tensile Strength (ITS) test. In compliance with the EN 12697-23 standard, three SGC samples (80 gyrations) were produced for each mixture and tested after conditioning for 4 hours at 25 °C. In order to evaluate the detrimental effect of water on the mechanical properties of the ACs, their reduction in ITS values (ITSR, EN 12697-12) was also assessed. Three additional samples for each mixture were prepared with the same compaction energy. These specimens were then kept in a water bath at 40 °C before testing at 25°C. The average results are shown in Table 4.

Table 4: Average ITS and ITSR values.

Mixture	ITS (MPa)	ITS_{wet} (MPa)	ITSR (%)
WBC_AC	0.88	0.61	69
B_AC	0.77	0.69	90
LECA_AC	0.70	0.69	98

From the analysis of results, the experimental ACs showed higher ITS values if compared to the reference mixture. This might be due to the different absorption of the synthetic LWAs, related to their porosity and to the higher specific surface. It is worth noting that the considered Italian technical specifications suggest an ITS value between 0.70 and 1.20 MPa for this kind of mixtures. Both the ACs prepared with the synthetic LWAs have suitable mechanical properties, despite the porosity of the samples. On the contrary, the high air voids content affects the performance of the mixture after the water saturation of samples. For each mixture, the reduction in ITS follows the increase in air voids content. WBC_AC, which has a significant porosity, registered the highest ITS decrease.

5.4 Indirect Tensile Stiffness Modulus evaluation

The mechanical characterization was also supported by the evaluation of the Indirect Tensile Stiffness Modulus (ITSM) according to the EN 12697-26 standard. Moreover, the thermal sensitivity of the mixtures was assessed by testing the material at three different temperatures: 10, 20 and 30 °C. For this purpose, three SGC specimens (80 gyrations) were prepared for each AC. Average results are shown in Table 5.

Table 5: Average ITSM results.

Mixture	ITSM (MPa) @ 10 °C	ITSM (MPa) @ 20 °C	ITSM (MPa) @ 30 °C
WBC_AC	7981	4952	2328
B_AC	7942	5213	2291
LECA_AC	6222	3761	1508

As overall result, all the ACs show adequate stiffness at each testing temperature. In compliance with ITS results, the experimental mixtures exhibit better mechanical properties if compared to the reference one, despite the samples high air voids content. There is not large difference in ITSM values between the experimental ACs. In terms of thermal sensitivity, the substitution of traditional LWA with synthetic materials does not affect the behaviour of the final bituminous mixtures.

5.5 Cantabro test

According to the EN 12697-17 standard, the Cantabro test was used to assess the ravelling resistance of the bituminous mixtures. The particles loss weight is traditionally one of the different method adopted to estimate the durability of ACs. For this purpose, four Marshall samples (50 blows) were prepared and kept at 20 °C for 4 hours before testing. The average results are shown in Table 6.

Table 6: Average Cantabro test results.

	WBC_AC	B_AC	LECA_AC
Particle loss (%)	5.4	6.3	8.2

The results are in line with the ITS values: the experimental mixtures show the best results if compared to LECA_AC. Once again, the high porosity of the synthetic ACs does not affect the behaviour of the bituminous mixtures. The Cantabro test results support the hypothesis of a strong aggregates-filler-bitumen bond for the experimental ACs conferred by the higher specific surface of the synthetic aggregates.

5.6 Skid resistance evaluation

The high surface friction is probably the most important functional property of the designed special AC. The EN 13036-4 standard describes a method for the laboratory evaluation of the skid resistance of bituminous surfaces. Three samples for each mixtures were tested and the average results are shown in Table 7, in terms of Pendulum Test Value (PTV).

Table 7: Average skid resistance results.

Skid resistance	WBC_AC	B_AC	LECA_AC
PTV	73	70	69

As overall results, each tested AC show a consistent skid resistance. The Italian technical specifications suggest a PTV greater than 55 after laying. The WBC_AC has the highest skid resistance, while similar values are registered for B_AC and for the reference mixture. The substitution of traditional LWAs with synthetic aggregates does not negatively affect the friction properties of the bituminous surface, which are actually improved.

6. CONCLUSIONS

On the basis of the presented results, the following conclusions can be drawn:

- The adopted waste materials seem to be suitable for the production of synthetic LWAs with adequate properties so to extend their use as construction materials.
- The substitution of traditional LECA with the experimental LWAs within a special AC needs for a specific mix design. Moreover, the dimensions of the synthetic aggregates must be taken into account since the porosity and the specific surface affect their absorption properties. This could have a negative effect on the workability and compactability characteristics of the final bituminous mixture.

- The experimental ACs show the highest mechanical performances (ITS, ITSM and Cantabro test). This is probably related to the stronger bond between aggregates and bitumen, due to the higher absorption power of the synthetic aggregate. The thermal sensitivity of the bituminous mixtures is not negatively influenced. On the other hand, as a result of the high ACs internal porosity, the mechanical properties are detrimentally affected after the saturation in water. Additional durability tests are needed.
- An increase in skid resistance is registered for the experimental ACs, more likely due to the different surface texture given by the specific LWAs dimensions.

In the light of these preliminary results, the application of synthetic LWAs within bituminous mixtures seems to be a viable solution for the production of special ACs. However, a more specific mix design needs to be optimized to decrease the air voids content.

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