A NEW POROUS MATERIAL BASED ON CENOSPHERES

A Thesis
Presented to
The Academic Faculty

by

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In Partial Fulfillment
of the Requirements for the Degree
Master of Science in the
School of Civil and Environmental Engineering

Georgia Institute of Technology
December 2007

A NEW POROUS MATERIAL BASED ON CENOSPHERES

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ACKNOWLEDGEMENTS

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SUMMARY

This thesis deals with the mechanical and physical investigations on a newly discovered porous material based on fly ash cenospheres. The process used to fabricate the material along with the physical properties of the material is first described. Under uniaxial compression, it is observed that the material exhibits a long load plateau that is typical of energy absorbing materials such as thin-walled metallic honeycombs. In tension, the material fractures similar to most traditional brittle materials such as glass and ceramics. As a result, several uniaxial compression and tension tests are performed on different samples to evaluate the influence of the different chemicals, the curing time, and the mass density on the 'plateau' strength. However, in addition to its low processing costs, the new material presents important properties that are desirable for discrete materials such as homogeneity and isotropy. Although its insulating properties were not quantified, it appears that the material can be used as an excellent heat barrier. Finally, metallic tubes as well as bamboo poles reinforced with the new material are tested to investigate the effectiveness of the reinforcement, showing highly improved structural performance.

CHAPTER 1

INTRODUCTION

Lightweight materials are of great interest, particularly in the automotive, aerospace and construction industries. They induce a decrease in the fuel consumption of a vehicle or a plane. Further, a building or structure that is constructed with strong lightweight materials has the potential to experience a reduced earthquake load. Another important property of lightweight materials is that they typically possess cellular structures. The advantage of a cellular structure is that unlike a solid, it fails due to collapse of the cells thereby giving the material the ability to absorb impact and shock energies. As well, a cellular media is a typical excellent thermal and sound absorber [1,2,3,4,5]. Unfortunately, lightweight materials are typically expensive so that they only find limited usage in a few select industries. Another drawback of such materials is reliability. For example, cellular materials such as metallic foams are non-homogeneous due to the foaming-induced gradients during fabrication, and they tend to exhibit a wide scatter in their mechanical properties [2,6]. Although other cellular materials such as honeycombs are reasonable because they are orthotropic, their main problem is that they are able only to absorb energy in one specific tubular direction [1,7]. In the field of construction engineering, efforts are being made to develop lightweight or pervious concrete. Although this type of material is relatively cheap, lightweight concrete is not a 'green' material, since it consumes 'virgin' materials (e.g. limestone) during manufacturing and releases a great amount of carbon dioxide in the atmosphere, which contributes in a great extent to global warming [4,9,10]. Thus, a need still exists for a cellular material that has the potential to become an everyday material: green, functional and cheap.

In this thesis, we will present physical and mechanical properties of a new cellular material that is not only cheap and multifunctional, but also green. The material we will be presenting is based on cenospheres from fly ash which is a by-product of coal gasification during power generation. As a pozzolanic by-product of the coal production, fly ash has been extensively used over the past decades in the concrete industry to partially replace cement [9,11]. A pozzolan is a siliceous or siliceous and aluminous material that in presence of moisture reacts with calcium hydroxide to form compounds having cementitious properties. Fly ash concrete shows very interesting properties: it reduces the peak temperature of the hydration reaction and increases the compressive strength and workability of the concrete [13,14,17]. At the same time, by replacing cement, it reduces the amount of 'virgin' materials needed and the volume of carbon dioxide released in the atmosphere, which makes it a 'green' material [7,10,16]. Two millennia ago, the Romans were already taking advantage of another pozzolanic powder, namely volcanic ash. They mixed volcanic ash with lime, aggregate and water to produce mortar and concrete. In the same way, fly ash is now mixed with portland cement, aggregate and water to produce concrete. At the microstructural scale, fly ash fills in the spaces originally occupied by water, therefore decreasing concrete permeability (cf. Fig. 1).
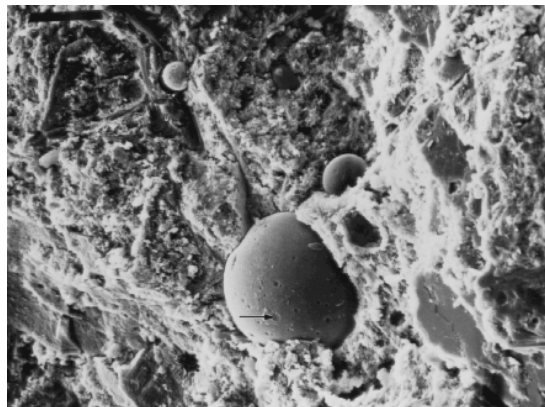
Figure 1: Fly Ash Concrete Microstructure. The microstructure is non-porous.

Whereas in private construction fly ash is not extensively used, the United States has used it for a long time, particularly in dam construction, where fly ash properties are crucial. The reason is that the use of fly ash in concrete reduces the heat generated during the cementitious reaction and therefore the risk of cracks due to thermal shrinkage. In the 1960s and the 1970s, as the international context became more tensed and the American supply in oil more problematic, the US decided to build a new generation of power plants, which made fly ash more available. Today, the United States produces about 63 million tons of fly ash per year, 20 % of which is used for concrete production [11].

In the coal production process, fly ash is a product of the cooling of incombustible liquefied minerals. Electric precipitators collect it, in a way that enables size and density segregation, therefore high-quality versus low-quality material segregation. Fly ash physical properties are indeed directly dependant upon such macroscopic factors. A couple of decades ago, in order to prevent acid rains, the coal industry was asked to reduce NO_x production. Such reduction technologies have a negative impact on fly ash quality, as they incorporate it with unburned carbon and other residuals, and also make its particles less spherical.

But there are methods to increase fly ash quality, which act on three factors: fineness, loss on ignition and carbon content. As fineness decreases, resistance to sulfates and long-term compressive strength increase, whereas loss on ignition, permeability and water demand decrease. Typically, the particle size can range from 15 to 35 μm to 2.5 to 4 μm. Such fine fly ash particles are called "ultrafine fly ashes" [11]. There are also other technologies to reduce carbon content and therefore loss on ignition, including one that simultaneously removes the ammonia from fly ash, by providing a sufficient combustor temperature. The ammonia present in fly ash is a product of the reaction that transforms NO_x. Fly ash is made of heterogeneous combinations of amorphous and crystalline phases. The former represents 60 to 90 % of the total mass, the latter 10 to 40 %. More

precisely, crystals are present within the glassy matrix or attached to the surface of glassy spheres. Such an arrangement makes fly ash structure quite complex.

There is not a single type of fly ash. ASTM C 618 differentiates class C and class F fly ash. This differentiation is based upon chemical composition criteria. In general, fly ash is made up of four main constituents: SiO_2, Al_2O_3, Fe_2O_3 and CaO. If the mass of the first three constituents exceed 70 % of the total mass, fly ash is designated as class F fly ash. Otherwise, it is called class C fly ash. SiO_2 comes from the clay minerals and the quartz in the coal. It is responsible for the pozzolanic reaction in concrete: SiO_2 combines with lime and water to form calcium silicate hydrate (CSH), the binder in concrete. Al_2O_3 comes from the clay in the coal, Al_2O_3 from the iron-containing materials, and CaO from the calcium carbonates and sulfates. The latter can be another means of classifying fly ash, since it influences the reactivity of the ash. Fly ash also contains some other elements. It is common to find MgO, SO_3, C and alkalis, which respectively come from organic constituents, pyrite and gypsum, incomplete coal combustion, and clay minerals and other sodium and potassium-containing constituents in the coal. It also contains in small proportions heavy metals, typically Ti, P, Pb and Cr.

Fly ash glassy constituents are determined by quantitative x-ray diffraction analysis (XRD). They directly influence the properties of the ash. Their amorphous structure is due to the rapid cooling of the unburned coal residue. Their composition depends upon the composition of the coal and the burning temperature. As well as the general content in glassy constituents, it determines fly ash reactivity. Among those constituents, calcium plays a key role. Fly ash reactivity increases with the amount of calcium present in the ash [11]. Then, the physical properties of fly ash depend upon the shape, size, particle-size distribution, and density of fly ash particles, insofar as these particle characteristics influence the water demand. The strength of concrete is inversely proportional to the particle size of fly ash. Fineness can vary to a great extent, from 1 μm to 1 mm. ASTM C 618 requires that less than 34 % of the particles be retained on the 45 μm sieve, i.e. that

more than 66 % of the particles have a diameter less than 45 μm. It has indeed been shown that strength, abrasion resistance, resistance to freezing and thawing are proportional to the percentage of the particles of diameter less than that value. Generally, performance increases with fineness. Another important factor is fly ash density, which typically ranges from 2.2 to 2.8 g/cm^3. But density is obviously related to fineness: the former and the latter increase together. The key reaction between fly ash, calcium hydroxide and alkali in concrete that generates the CSH bond and the calcium aluminate hydrates, consists in the breakdown and dissolution of the glassy structure of the ash by the OH$^-$ ions. One can summarize the influence of fly ash on the concrete mechanical properties as the following [17]:

- Better pumpability and workability;

- Slower setting time;

- Early strength loss. This drawback is one of the main reasons why fly ash has not been used extensively. However, it can be offset by the use of silica fume: the latter has a diameter 100 times smaller than fly ash that makes it much more reactive.

- Much later strength gain between 28 days and 90 days or more;

- Superior dimensional stability and resistance to cracking from thermal shrinkage and drying shrinkage (due to the decrease in the heat generated in the cementitious reaction and the lower w/cm ratio);

- Very high durability to the reinforcement corrosion, alkali-silica expansion, and sulfates attack;

- Creep decrease;

- Better bond between steel and concrete (due to the increase in the contact area between them);

- Smoother surface, sharper details.

CHAPTER 2

NEW MATERIAL BASED ON CENOSPHERES

Materials based on cenospheres

The material described in this paper does not need any cement whatsoever or 'virgin' materials, since it is mainly based on fly ash cenospheres. Cenospheres are the pale to mid grey hollow microspheres that constitute the 1-5% lightest part of fly ash. They can easily be recovered: since their specific gravity is lower than one, they will float on water. They are currently mostly used as fillers. It can hence be legitimately qualified as environmental-friendly material. Cenospheres inexpensiveness, lightness, fire resistance and insulating properties have already been used to make advanced materials. A Functionally Gradient Material (FGM) comprising cenospheres has for example been patented [17]. Functionally Gradient Materials are composites in which the material composition is varied spatially to optimize the performance of the material for a specific application. It consists of a polyester resin, a plasticizer and a plurality of cenospheres that are distributed nonhomogeneously in the matrix. The constant gradient of the material is achieved by the migration of the cenospheres towards the top of the mold used to make the material, as they have a lower specific gravity than the matrix. The use of such a composite is interesting to understand the physical phenomena associated with FGMs. Another material has been recently developed [18]. This composite is made of ASTM class C and/or relatively low lime ASTM class F fly ash, and recycled, post-consumer waste, chemically unmodified polyethylene terephthalate (PET) beverage bottle material as a resin (cf. Figure 2).
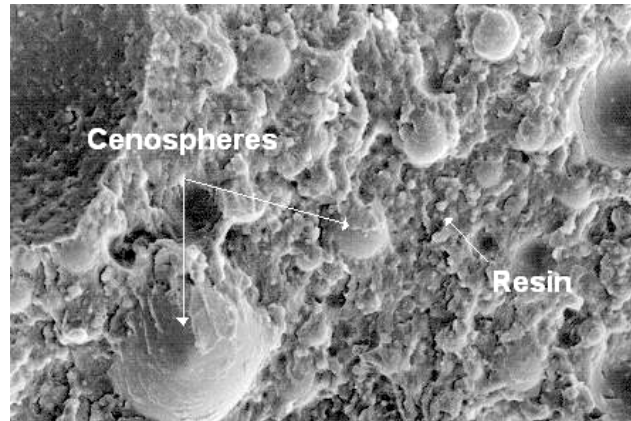
Figure 2: SEM picture of the PET-Cenospheres material (Patent #6583217) at a 1000 magnitude scale. The cenospheres are entrapped in the PET resin.

In this case recycling issues are the main purpose, but the material exhibits fairly good mechanical properties. Cenospheres lightness has been taken advantage of in another patented composite material, whereby a resin is adapted to bind the cenospheres into a solid mass and retain them in a desired shape into which the composite material is to be formed [19]. The composite material can be used to form constructional elements used in modular buildings and will provide them with higher wind and earthquake resistance.

In the same lightness purpose, a glass-fiber reinforced light-weight cementitious product has also been invented. It comprises a cement matrix, and aggregates consisting of substantially equal parts of fly ash cenospheres and silica fume and reinforced with chopped glass fibers [20]. Its tensile strength of 600 psi is higher than the tensile strength of usual lightweight concretes (200 psi).

Lightness and high mechanical strength are characteristic of another recently discovered material comprising cenospheres bonded together with clay and/or schist aggregates by a melamine-formol resin [21]. The high compression strength (20 MPa) together with a mass density close to 1 g/cc makes it suitable for marine applications.

The nuclear industry has also shown interest for cenospheres. A lightweight (0.3-0.6 g/cc) heat-resistant, acid-resistant, low-density open-cell porous (90% vol.) and permeable material made mainly from cenospheres has been developed [22]. Its

properties make it suitable for liquid radioactive waste, but also heat-resistant traps and filters, supports for catalysts, adsorbents and ion-exchangers. Contrary to the previous materials that incorporate the cenospheres within a matrix by mechanical processes or bind the cenospheres together by a chemical reaction, the cenospheres are here sintered together. The porosity is controlled by the use of gas evolving additives that foam the melting paste.

Finally, cenospheres' good insulation properties have been used in developing a thermally insulating and fire resistant material, where the matrix consists of a sodium silicate binder [23]. The composite material is capable of deformation at high temperatures (e.g. up to 1100°C) without fracture or loss of cohesion, which makes it useful in the protection of steel structures. Panels of this material can indeed be used to clad steel beams and columns and increase their fire resistance.

All those advanced composites are related to the newly discovered material, insofar as cenospheres' properties are being taken advantage of. However, the new material differs in the way it is fabricated. The fabrication processes of the advanced materials described above can be classified in three groups: mechanical processes incorporating the cenospheres in a matrix, chemical reactions binding the cenospheres together, and sintering (cf. Fig. 3).
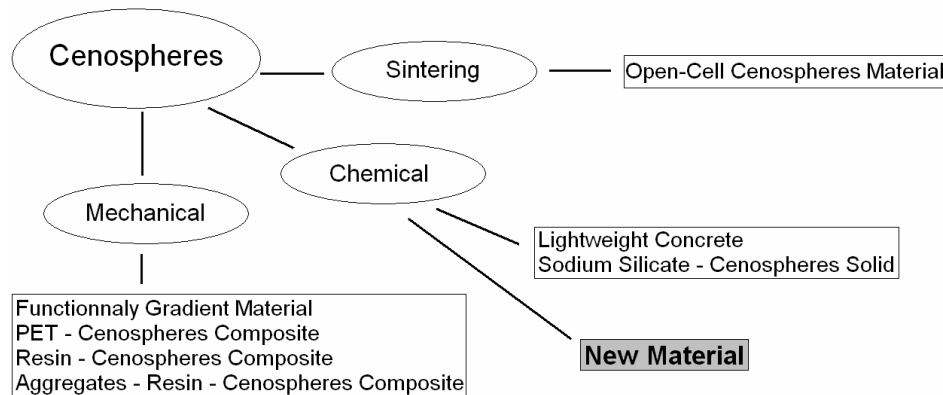

Figure 3: Cenospheres based materials' fabrication processes. The new material is fabricated using a chemical reaction, but the foaming of the paste is also an essential part.

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Mechanical processes have the disadvantage of not creating an actual bond between the matrix and the cenospheres, while sintering requires high temperatures. For example, temperatures of 850-1100°C are used to sinter the cenospheres together in the case of the open-cell porous material used in the nuclear industry described earlier. The material described in this thesis can be included in the group of materials that are based on chemical reactions, but have the originality of evolving into foams.

The chemical composition of the new material

In the new material the bond between the cenospheres is achieved by a chemical reaction that involves three different solutions.

Pure sodium hydroxide (NaOH) is a white solid available in pellets. It is produced via two main processes. The most common, one known as the choralkali process, involves the hydrolysis of an aqueous solution of sodium chloride (NaCl - also known as common salt), according to the chemical reaction:

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH.$$
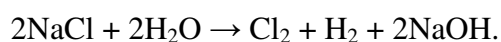
The second one is used mainly in North America because of the existence of natural calcium carbonate ores. The reaction is:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH.$$
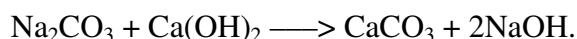
Sodium hydroxide is the most common base used in chemical laboratories to measure acid concentrations (titrations). It is also used in a wide range of industries, including the paper, soap, plastic, detergent products and aluminium industries. In the Bayer process, which is the principal industrial means to produce aluminium, crushed bauxite (the usual

aluminium ore) is indeed washed in pressure vessels with sodium hydroxide at temperatures from 150-200°C [24]. This converts the alumina to aluminium hydroxide according to the chemical equation:

$$Al_2O_3 + 2\ OH^- + 3\ H_2O \rightarrow 2\ [Al(OH)_4]^-.$$
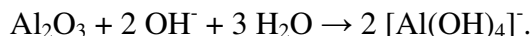
Further steps then transform the aluminium oxide to an almost pure aluminium metal.

Sodium silicate is a white solid that is soluble in water. It is a product of the reaction in solid phase between sodium carbonate (Na_2CO_3) and silica (SiO_2). There are many kinds of this compound. In the research we used an aqueous solution of orthosilicate (Na_4SiO_4). It is used in a wide range of applications, including timber treatment (timber treated with sodium silicate is flame-retardant and more resistant to insects attacks), concrete treatment (sodium silicate can decrease the porosity of concrete and act as a water-repellent barrier) and automotive repair (e.g. sodium silicate is used to seal eventual leaks in the cooling system) [25].

Finally, organosilicons are chemical compounds containing carbon silicon bonds. The raw material, silica (SiO_2), is reduced to elemental silicon in a smelting process:

$$SiO_2 + 2C \rightarrow Si + 2CO.$$
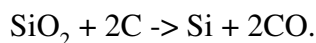
The polymerization of the silicon metal then involves a direct reaction with methyl chloride (CH_3Cl) in a fluid bed reactor that yields a complex mixture of methyl chlorosilanes, mainly $(CH_3)_2SiCl_2$ and CH_3SiCl_3 [26]. These chlorosilanes are distilled or purified, and the primary product (dimethyldichlorosilane, $(CH_3)_2SiCl_2$) is reacted with water through an electrolysis process to give polydimethylsiloxane oligomers

([Me$_2$SiO]$_n$), with typically n>4. In the research the particular organosilicon chosen was an aqueous solution of dimethylsiloxane of chemical formula [SiO(CH$_3$)$_2$]$_n$.
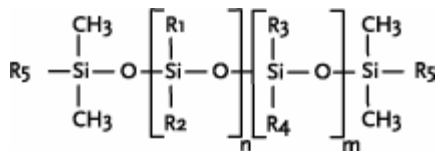
Figure 4: Polydimethylsiloxane chemical formula

In more details the structure consists of an inorganic backbone of alternating silicon and carbon atoms, each silicon atom bearing organic side chains. These side chains confer hydrophobic properties to the whole chemical. This property is used in water repelling coating agents for concrete. Other industrial applications include the painting and cosmetics industries, where siloxanes are used as emollients, antifoaming and viscosity-controlling agents [27]. The world annual consumption of siloxanes in 2003 was 0.85 million tons [28].

Those three chemicals are widely available and relatively inexpensive. However, basic safety precautions have to be taken when manipulating the sodium hydroxide as well as the siloxane.

As coal chemical composition differs from site to site, there will not be one single type of cenospheres. The ones used in this research were provided by Trelleborg Fillite, the world's largest producer of cenospheres [29]. Their chemical composition and physical properties were provided by the supplier and are given in the following tables.

Table 1: Cenospheres chemical composition. Silicium and aluminium oxides are the main constituents.

SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	K$_2$O	Na$_2$O	CaO	MgO	TiO$_2$
55 %	31 %	5 % max	5 %	1 %	0.5 %	1.5 %	1 %

Table 2: Cenospheres physical properties. The particle size shows a great variation, which increases the spheres packing.

| Specific gravity	Min particle size	Max particle size	Mean particle size
0.7 g/cc	5 microns	540 microns	130 microns

In the new material the bond between the cenospheres is an amorphous alumino-silicate gel [30, 31] formed by a chemical reaction including some alkali solutions with an organosilicon solution [32, 33]. The ternary diagram[1] below shows the composition of the pastes that were prepared and tested.
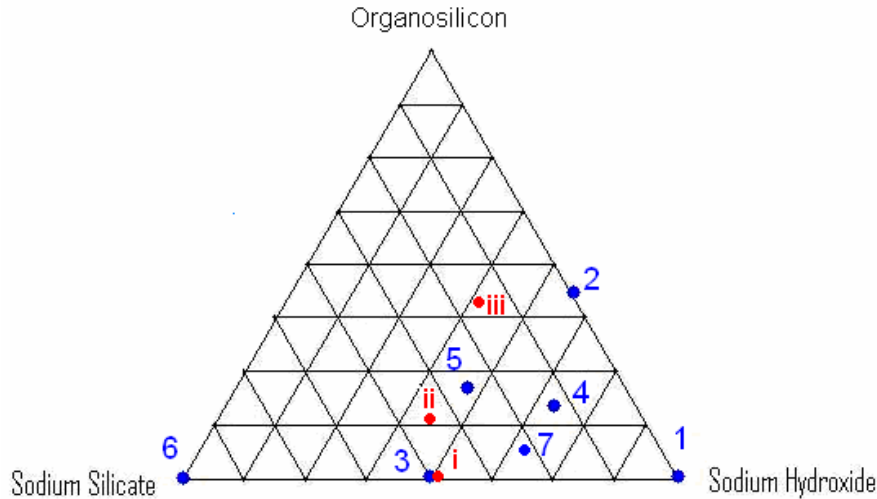
Figure 5: Pastes compositions used to investigate different parameters on the plateau strength. Pastes numbers 1 to 6 are tested to show the influence of the two alkali solutions and the organosilicon; pastes i to iii the influence of the curing time.

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[1] On the ternary diagram each segment corresponds to a proportion of 12.5% of the respective chemical. For example, apart from cenospheres, paste #1 has but sodium hydroxide; paste #3 50% of sodium hydroxide and 50% of sodium silicate; paste B 15% of organosilicon, 42.5% of sodium hydroxide and 42.5% of sodium silicate.

The mixture produces a paste that reacts and solidifies at curing temperatures in the range of 90-150°C over a time period of 10-30 hours. The proportion of the organosilicon solution determines the porosity of the material.
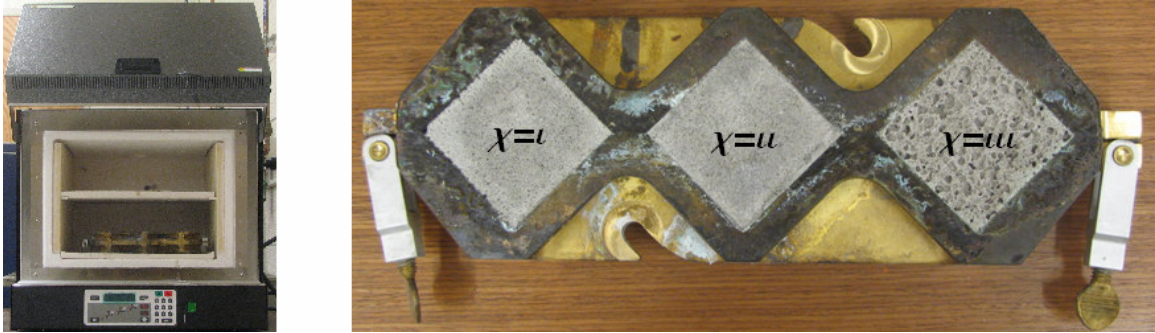
Figure 6: Heating and curing at 115°C (left); Specimens after curing (right). For the pastes composition, refer to Figure 6.

The paste viscosity is an important issue as far as industrial applications are concerned. The sodium silicate and the organosilicon have contrary effects: the former increases the viscosity, the latter decreases it. Another issue is the activation of the foaming and the homogeneity of the paste. Both are established by stirring the paste. The homogeneity of the material is due to the homogeneity of the paste and the heating. Therefore the metallic molds used to cure the paste need a top plate to ensure that homogeneous heating.

The resulting material is a pale grey microporous material with a mean specific gravity of 0.5 g/cc that can vary when one alters the porosity. It looks somewhat similar to a lightweight concrete, far lighter though. However, its mechanical behavior is quite different because of its microporosity and the hollowness of its constituents, the cenospheres. The figure below shows the range of porosity the new material can achieve.
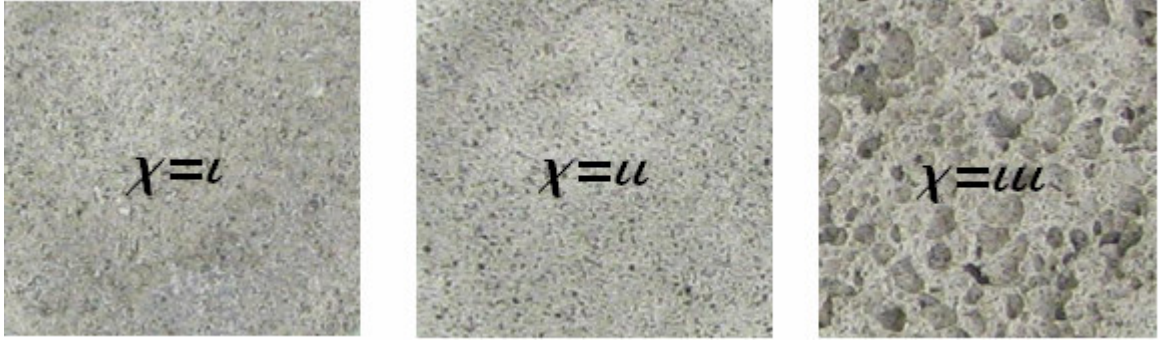
Figure 7: Samples with different porosities: 0% (left), 8% (middle), 30% (right). For the pastes compositions, refer to Figure 6.

The material was observed at a higher scale using a scanning electron microscope. A quarter of an inch cube of the new material was silver-coated and its microstructure observed using a Hitachi S-800 FE-SEM. The two pictures below show this microstructure at different scales.
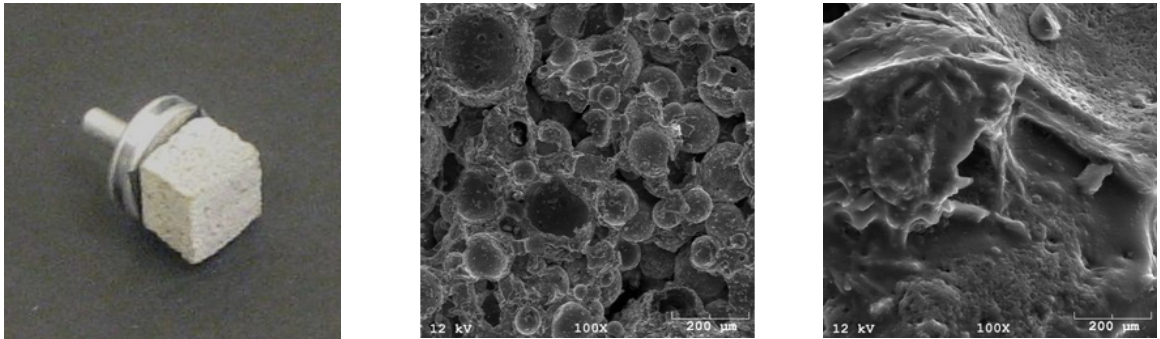
Figure 8: Sample used for the SEM (left); SEM pictures of the microstructure at magnitude scales of 100 (middle) and 1700 (right).

The first SEM picture witnesses the material porosity and cellular microstructure. Microspheres of different sizes are bonded together and leave space to many air pockets. The second picture focuses on the aluminosilicate bond between two cenospheres, a third one, smaller, being entrapped between the main two. Note that this cellular microstructure is quite different from fly ash concrete (cf. Fig. 1).

Uniaxial compression tests were performed on specimens having a porosity ranging from 0 to approximately 30% and mass density from 0.4 g/cc to 0.9 g/cc. Such variations were achieved by varying the different proportions of the alkali and organosilicon solutions. The effects of the different chemicals as well as the curing time were investigated by testing specimens that can be represented in the ternary diagram shown in Figure 5. The tests results are presented in Chapter 3.
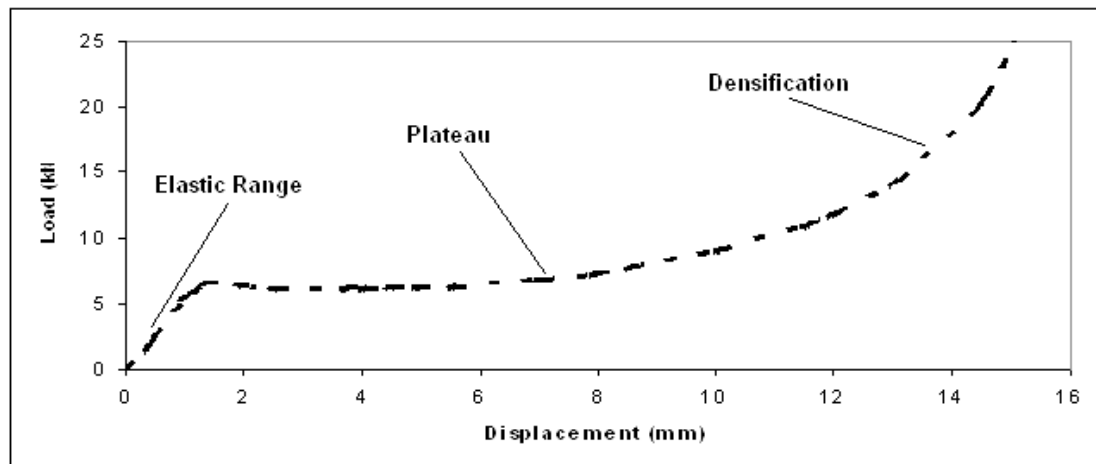
CHAPTER 3

THERMOMECHANICAL AND STRUCTURAL PROPERTIES

Behavior in Compression

A sample of the new material of dimensions 4.8cm*4.8cm*2.4cm was tested using an INSTRON 8800 testing machine. The uniaxial compression test was displacement-based, at a rate of 0.15 mm/sec. The test gave the following load vs. displacement curve.

Figure 9: Load vs. Displacement Curve in Uniaxial Compression. The material's behavior exhibits three different stages: a short elastic range is followed by a plateau. Finally, densification occurs.

The curve shows very interesting features characteristic of energy absorbers that can be related to the microstructural properties of the material. A linear elastic range is followed by a fairly horizontal deformation plateau. Finally, densification occurs. In the elastic phase the cenospheres are stretched elastically. The plateau load is believed to correspond to the first vertical crack due caused by the Poisson's effect. During the plateau the air pockets are closed and cenospheres progressively crushed. Finally, when the cenospheres

are crushed and the porosity reaches zero, the material cannot be compressed furthermore.

The interesting value in such a uniaxial compression test is the plateau strength, i.e. the stress at which the elastic range ends and the deformation plateau begins. As far as lightweight materials are concerned, the ratio of this strength divided by the specific gravity of the material is even more critical. The following table compares this value to concurrent materials, namely metallic honeycombs and traditional concrete. Since the new material mechanical properties can vary with its porosity, the composition that gave the best ratio was chosen.

Table 3: Comparison between the new material and other materials. The new material can potentially compete with them.

	Honeycombs	Concrete[2]	New Material
Specific gravity	3.1	2.4	0.4
Compressive strength (MPa)	2.45	40	1.6
Compressive strength/ specific gravity (MPa)	0.8	16.7	4.0

It turns out that the new material is a good competitor for metallic honeycombs. However, it is far more cost and energy effective. Whereas honeycombs are made of a metal, the new material is made of a by-product widely available. Furthermore, a temperature of $100^{\circ}C$ is enough to cure the paste that will produce it, whereas the honeycomb technology requires the melting of aluminum, which occurs at about $660^{\circ}C$, hence more energy.

The new material can in a certain extent be qualified as homogeneous foam, even if its porosity (0-30%) is smaller than metallic foams (90%).

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[2] Values for a traditional concrete, not for a high-strength, lightweight, pervious or foam concrete. Source: ACI.

Behavior in Tension

Tension tests were performed on the new material on the same testing machine. Specimens of dimensions 2.4cm*2.4cm*4,8cm and of similar chemical compositions to those tested in compression were glued to the surface of the bottom and top metallic plates. A slow displacement rate (0.3 mm/sec) was chosen to account for the small observed displacements. The experimental set-up proved to reproduce pure tension fairly well. The glue was considered infinitely stiff compared to new material. The test gave the following load vs. displacement curve.
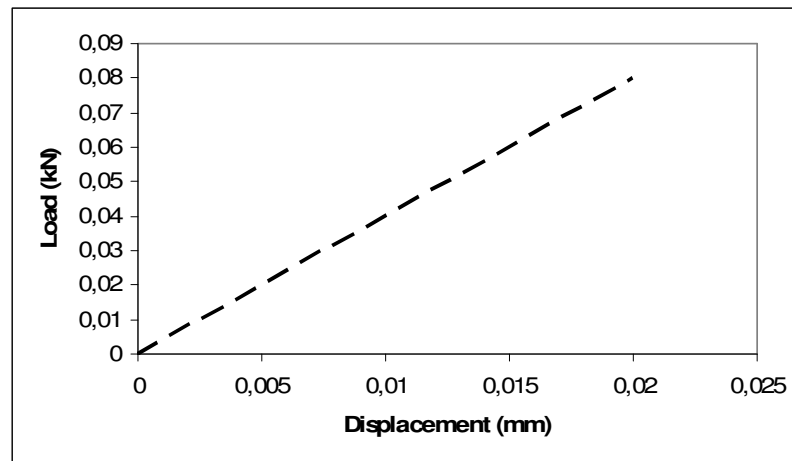
Figure 10: Load vs. Displacement Curve in uniaxial tension. The material's response is elastic. Failure is brittle.

After an elastic deformation where the cenospheres are stretched, a horizontal crack appears in the middle of the specimens. This occurs in a brittle fashion, which is believed to correspond to the brittleness of the alumino-silicate gel that bonds the cenospheres together. Once its tensile strength is reached, a crack is formed that is believed to propagate horizontally between the cenospheres. Since air pockets do not have any resistance, the tensile strength is again a factor of the material's porosity.

The influence of the different chemicals on the mechanical response

During the processing of the material, the organosilicon reacts with the cenospheres-sodium hydroxide mix to produce fairly stable foam. The proportion of this chemical will therefore influence the porosity of the material, which is then expected to influence the plateau strength. On the other hand, the sodium silicate increases the paste viscosity and therefore its cohesion.

Six pastes with different proportions of sodium hydroxide, sodium silicate and organosilicon were prepared and then cured at 115°C for twenty-four hours (cf. Fig. 6). It was observed that the absence of sodium silicate produces an uncured material similar to an unconsolidated soil with almost no cohesion. Conversely, a paste containing but sodium silicate will be too viscous and impossible to remold. The potential applications for the new material make this type of paste irrelevant. In addition, three representative pastes named i, ii and iii were cured for 14, 21, 28, 35 and 42 hours and then tested. Uniaxial compression tests were performed on specimens of dimensions 4.8cm*4.8cm*2.4cm. The load vs. displacement curves were then used to draw relationships between the plateau strength and tensile strength vs. mass density.
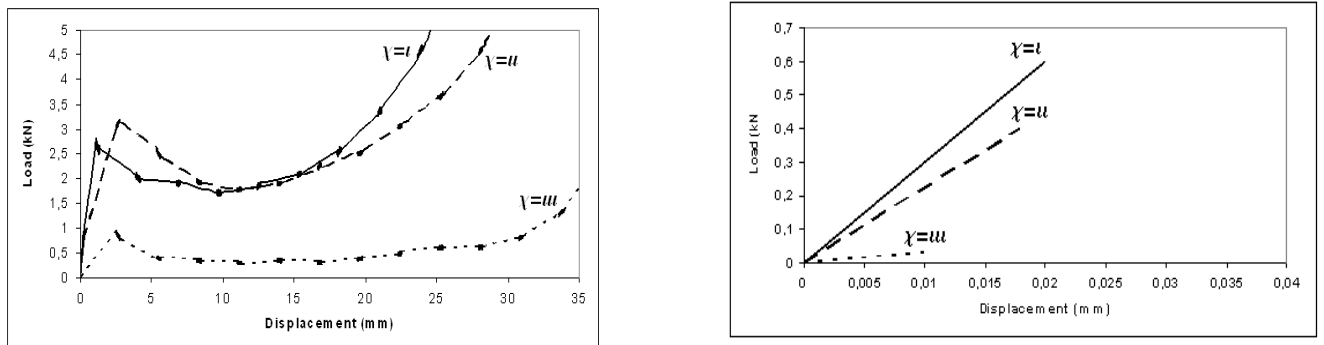

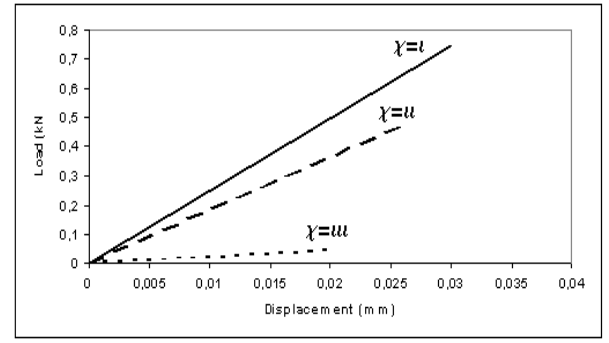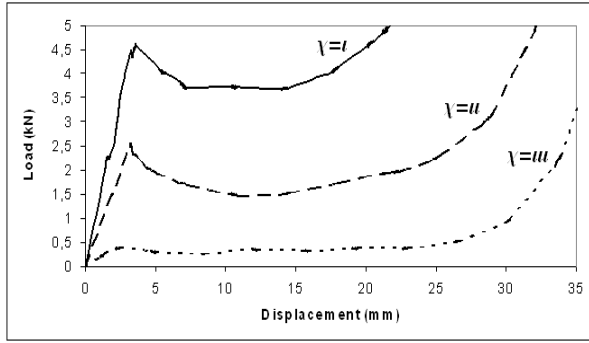**Figure 11: Load vs. displacement for curing time of 14 hours in compression (LEFT) and tension (RIGHT).**

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Figure 12: Load vs. displacement for curing time of 21 hours in compression (LEFT) and tension (RIGHT).

Figure 13: Load vs. displacement for curing time of 24 hours in compression (LEFT) and tension (RIGHT).

Figure 14: Load vs. displacement for curing time of 28 hours in compression (LEFT) and tension (RIGHT).
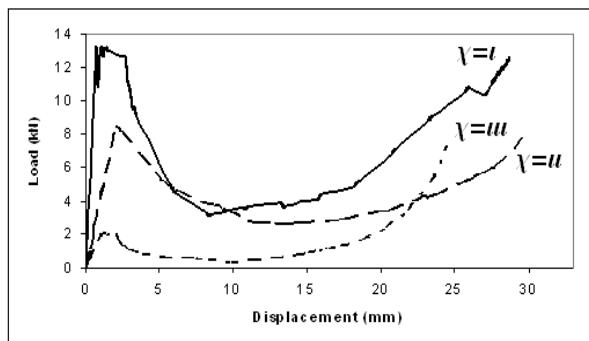
Figure 15: Load vs. displacement for curing time of 35 hours in compression (LEFT) and tension (RIGHT).
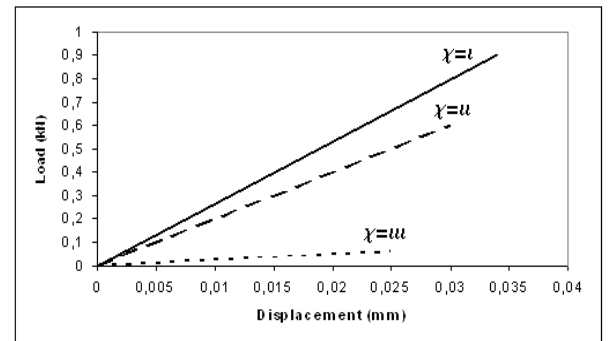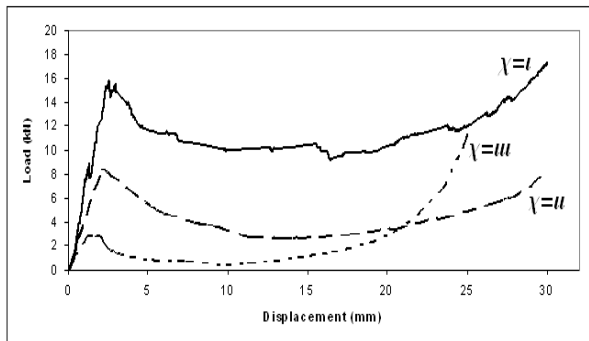
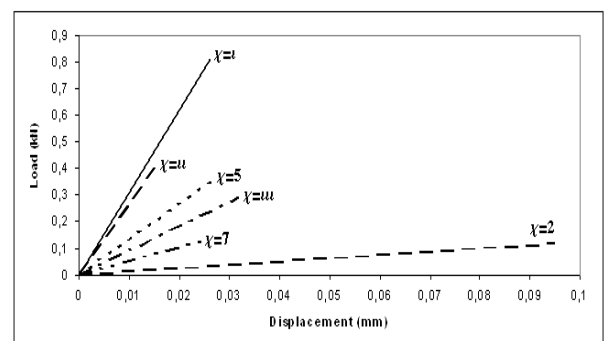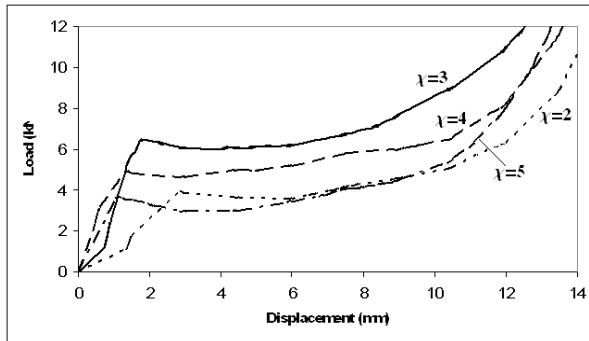**Figure 16: Load vs. displacement for curing time of 42 hours in compression (LEFT) and tension (RIGHT).**
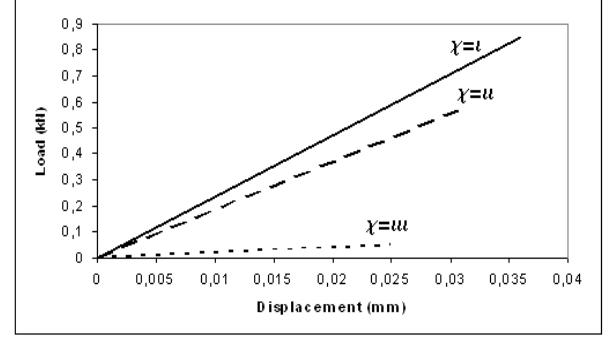

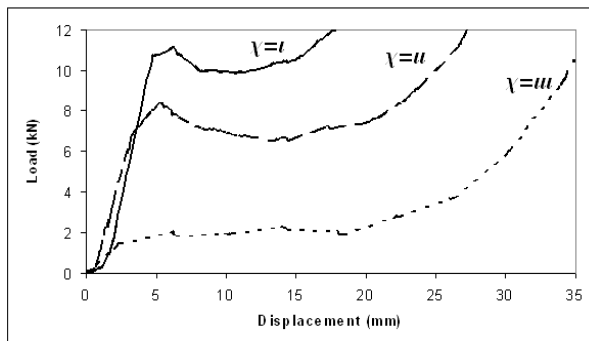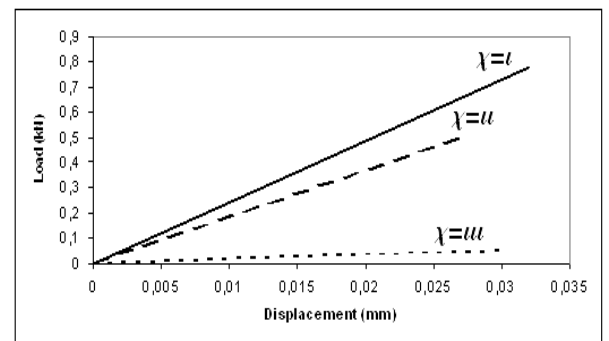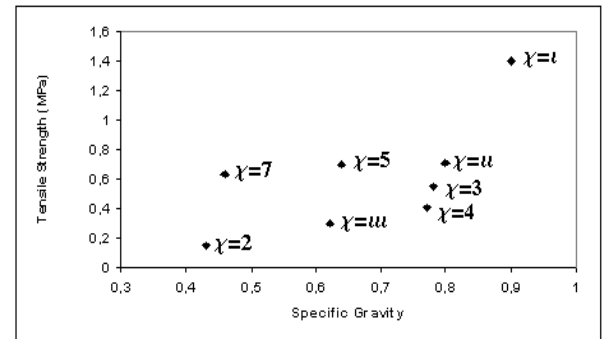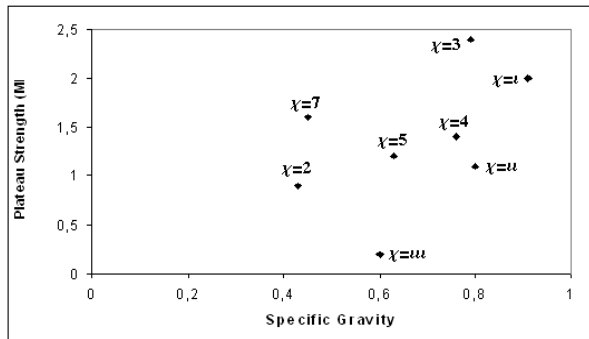**Figure 17: Strength vs. Specific Gravity. The relationship is not linear.**
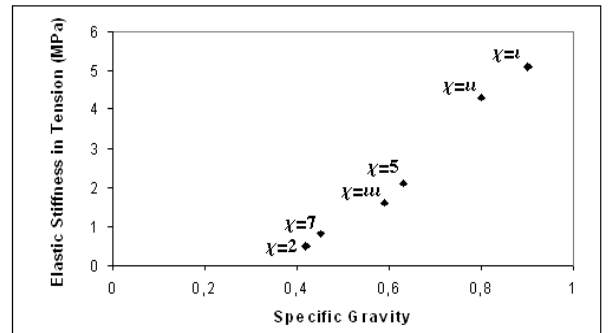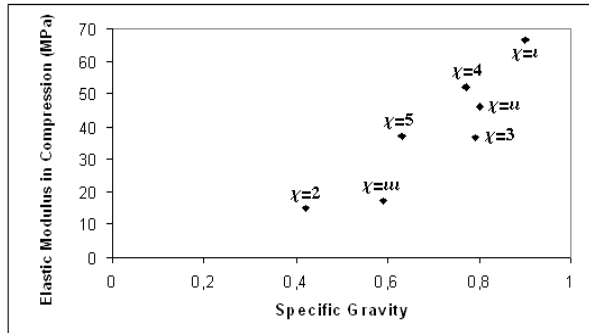
Figure 18: Elastic Modulus vs. Specific Gravity. The relationship is linear.
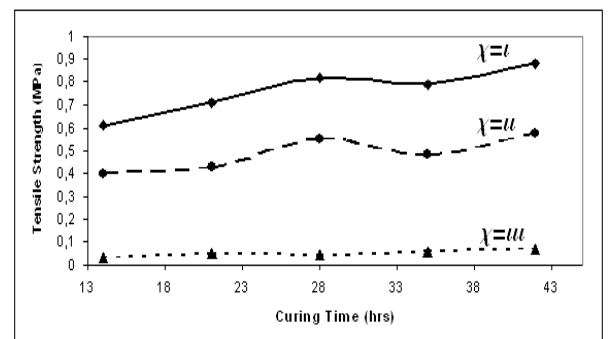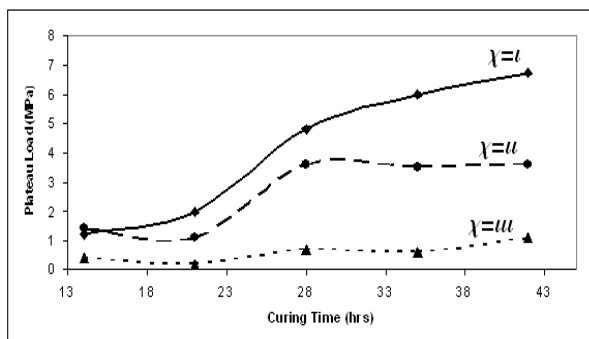
Figure 19: Strength vs. Curing Time. A plateau is reached.

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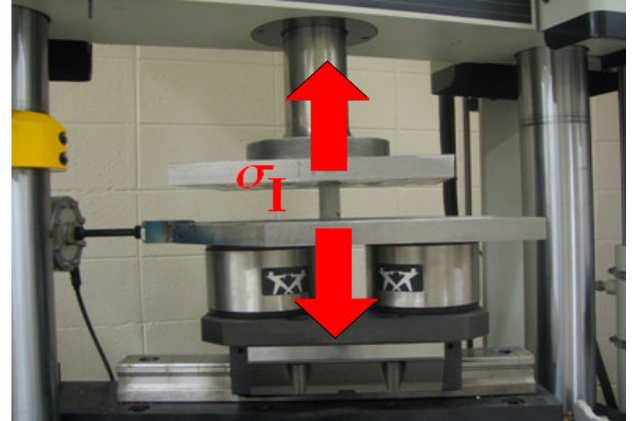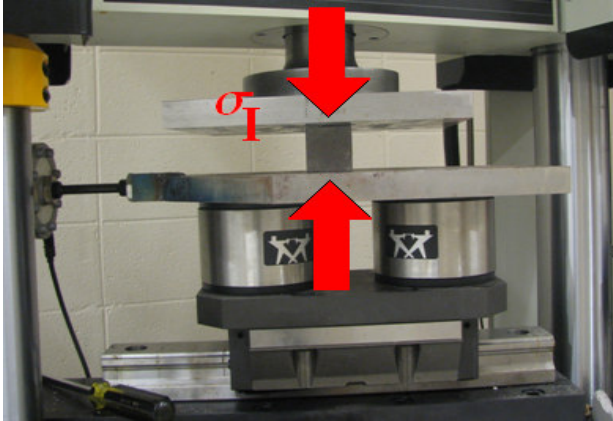
Figure 20: Experimental Set-up. The arrows represent the direction of the first principal stress.
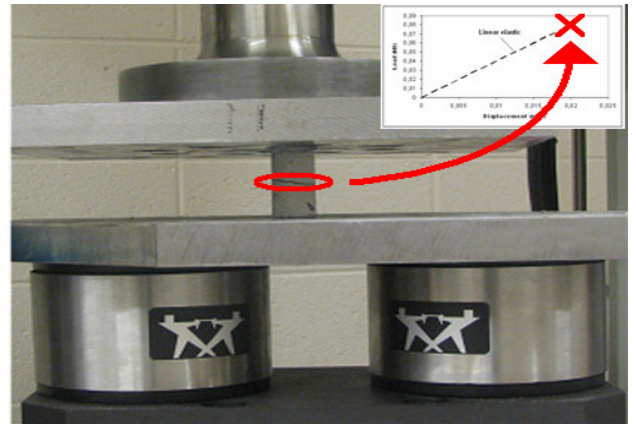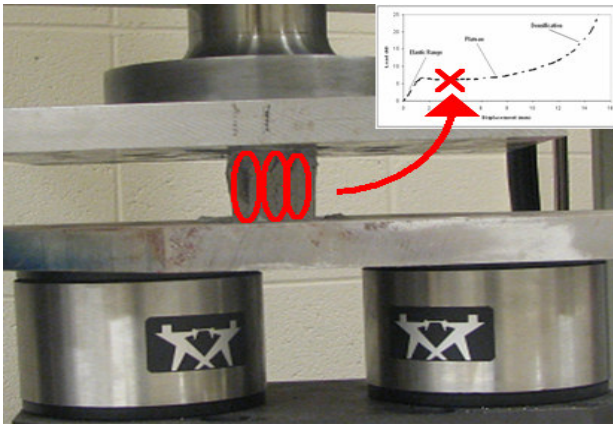
Figure 21: Material's failure through vertical and horizontal cracks respectively.

Comments

- The sodium silicate is responsible for the strength as well as the stiffness of the material, both in tension and compression.

- The organosilicon increases the material's porosity, therefore the length of the deformation plateau. However, the strength as well as the stiffness are decreased. A balance must therefore be found between the sodium silicate and the organosilicon.

- After a curing time of 28 hours, the deformation plateau is no longer flat. The material softens and the energy absorption reduced.

- The material's elongation in tension is very limited (up to 0.1%).

- The aluminosilicate bond gets stronger with a longer curing time. After a curing time of 28 hours a plateau is reached, except for the solid material.

- The relationships between the plateau and tensile strengths vs. mass density are not linear. In compression, the optimal strength to mass density ratio is obtained for paste 7 (cf. Fig. 5).

- The relationship between the stiffness vs. mass density is linear.

- The elastic modulus in tension is higher than the elastic modulus in compression.

The following tables show the mechanical properties for the different materials tested.

Table 3: Mechanical Properties for different pastes' compositions (S.I. units)

Composition	Mass density (kg/m3)	Plateau strength (MPa)	Elastic modulus in compression (MPa)	Tensile strength (MPa)	Elastic modulus in tension (GPa)
Curing time = 14 hours					
i	900	1,2	60	0,6	1,5
ii	800	1,4	28	0,4	1,1
iii	600	0,4	8	0,1	0,2
Curing time = 21 hours					
i	900	2,1	26	0,8	1,1
ii	800	1,1	16	0,5	0,7
iii	600	0,2	5	0,1	0,2
Curing time = 24 hours					
2	430	1,2	21	0,2	0,1
3	790	2,8	70		
4	760	2,1	77		
5	630	1,6	79	0,7	1,3
7	460	1,6	59	0,7	1,2
Curing time = 28 hours					
i	900	4,9	54	0,8	1,1
ii	800	3,8	47	0,5	0,8
iii	600	0,7	8	0,1	0,2
Curing time = 35 hours					
i	900	5,8	96	0,8	1,2
ii	800	3,7	61	0,5	0,8
iii	600	1,0	25	0,1	0,2
Curing time = 42 hours					
i	900	6,8	113	0,8	1,3
ii	800	3,7	82	0,5	0,8
iii	600	1,1	24	0,1	0,2

Table 4: Mechanical Properties for different pastes' compositions (U.S. units)

Composition	Mass density (pcf)	Plateau strength (psi)	Elastic modulus in compression (ksi)	Tensile strength (psi)	Elastic modulus in tension (ksi)
Curing time = 14 hours					
i	56,7	174	8,7	87	217,5
ii	50,4	203	4,1	58	159,5
iii	37,8	58	1,2	14	29,0
Curing time = 21 hours					
i	56,7	304	3,8	101	159,5
ii	50,4	159	2,2	58	101,5
iii	37,8	29	0,7	14	29,0
Curing time = 24 hours					
2	27,1	174	3,1	29	14,5
3	49,7	405	10,2		
4	47,8	304	11,2		
5	39,6	232	11,1	101	188,5
7	28,9	232	8,5	101	174,0
Curing time = 28 hours					
i	56,7	709	7,8	117	159,5
ii	50,4	550	6,9	79	116,0
iii	37,8	101	1,1	14	29,0
Curing time = 35 hours					
i	56,7	839	13,9	113	174,0
ii	50,4	535	8,9	72	116,0
iii	37,8	145	3,6	14	29,0
Curing time = 42 hours					
i	56,7	984	16,4	130	188,5
ii	50,4	536	11,9	72	116,0
iii	37,8	159	3,5	15	29,0

Other Parameters

The temperature of the curing is also believed to play a certain role in the compressive behavior of the material. It was observed that below 85°C the material cohesion gets close to zero, while above 150°C temperature has no more effect and can even deteriorate the bond.

Thermal Properties

Cenospheres are hollow ceramic spheres and are therefore good thermal insulators [34] that have already been used in the aerospace industry. It is hence believed that the new material is a good thermal insulator, all the more so as it entraps many air pockets. A simple and empirical test showed its effectiveness as thermal insulator. An inch and a half long sample was heated at one end and held at the other. It was possible to hold it for about a minute, which would be impossible for a metal or even for wood, as the latter would have burned. After a period of five seconds the other end it was also possible to hold the other end, which indicates a fast heat release.
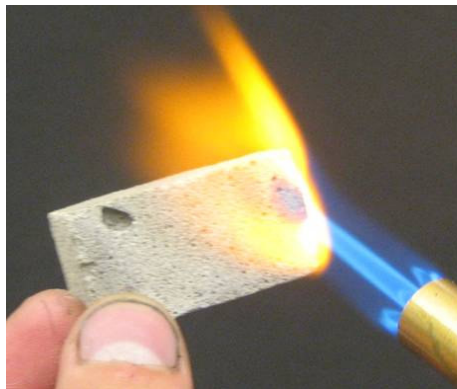
Figure 22: Fire resistance and low thermal conductivity of the material

This encouraging experiment led us to measure the new material's thermal conductivity at 25°C. The value of the thermal conductivity indicates the quantity of heat passing per

unit of time per unit area at a temperature drop of 1-degree C per unit length. The material was tested using the transient plane source method. Since this testing method requires expensive equipment, two specimens corresponding approximately to the most porous and less porous versions of the new material were shipped and tested by a testing company based in Canada [35]. The following table compares the result with other materials.

Table 5: Comparison between the new material's and other materials' thermal conductivity

Material	Mass Density (kg/m3)	Thermal Conductivity (W/mK)
New Material (low porosity)	750	0.154
New Material (high porosity)	450	0.141
Wood	500-900	0.10-0.40
Asbestos Cement Sheet	700	0.36
Brickwork	1700	0.84
Cast Concrete (dense)	2100	1.40
Cast Concrete (lightweight)	1200	0.38
Roof Tile	1900	0.84
Expanded Polystyrene	25	0.035
Phenolic Foam	30	0.040

It appears that the new material has a lower thermal conductivity than other construction materials (structural materials). However, this thermal conductivity is higher than typical insulation materials (polystyrene and phenolic foam). The new material therefore appears to be a multifunctional material.

Water Resistance and Permeability

The curing of the aluminosilicate gel plus the precipitation of the sodium silicate create a glassy bond along which water can run but not penetrate, provided porosity has been formed by the foaming due to the organosilicon. The porosity induced by the foaming of the paste and the random and homogeneous connection between the air voids are responsible for a fair permeability of the material, especially at high gas or water pressures. This property in conjunction with the material stiffness could lead to potential applications, including thin-walled vessels, gas or liquid storage tanks, as well as pervious pavement.

In the construction industry where permeability of structural or insulating materials is not wanted, dipping the new material into the same organosilicon can close up the pores and make the material hydrophobic, as shown on the figure below.

Figure 23: Hydrophobic treatment of the new material. The drop of water cannot penetrate the surface and forms a certain angle with it, characteristic of hydrophobic materials.

Non-Corrosiveness and Machinability

The new material is not a metallic material and therefore does not corrode. Unlike concrete, it is very easy to cut (e.g. using a regular band saw). As far as the construction industry is concerned, panels of appropriate dimensions can therefore be built and then transported on site at low cost.

Structural properties

One could think of basically three applications for the newly-discovered material. As availability of fly ash and therefore cenospheres is not questionable, these applications could be implemented at an industrial scale. The first one consists of large panels that could be reinforced with other environmental-friendly materials and then assembled on site to build a structure. Because of the material lightness, the panels could be transported by plane to regions devastated by natural disasters such as earthquakes, tsunamis or wars. Depending on the nature of the project the panels could be structural or isolating components. One could think of sandwich structures with layers of different porosities that could achieve both those functions.

Conversely, in the second one the new material would act as reinforcement for other materials. As far as the automotive industry is concerned, the material compressive behavior and lightness could be taken advantage of in reinforcing the front and side shock absorbers. This is an actual engineering issue, since the lightness as well as the balance between the front and the back of a vehicle are becoming critical issues for future cars.

Reinforced Metallic Tubes

Two thin-walled copper tubes were tested in compression. Their dimensions were the same: 47 mm long, 22 mm wide and 1 mm thick. One of them was reinforced with the new material. The different proportions of sodium hydroxide, sodium silicate and organosilicon were those that provide an optimal compromise between strength and porosity. The paste was poured into the tube and heated for 20 hours at 115°C. In real life applications, typically the automotive industry, a more complicated geometry of the metallic tubes could require pumping.

The specimens were tested in compression at a rate of 0.10mm/sec. The tests gave the following load vs. displacement curves.

Figure 24: (Un)Reinforced (crushed) copper thin-walled tubes
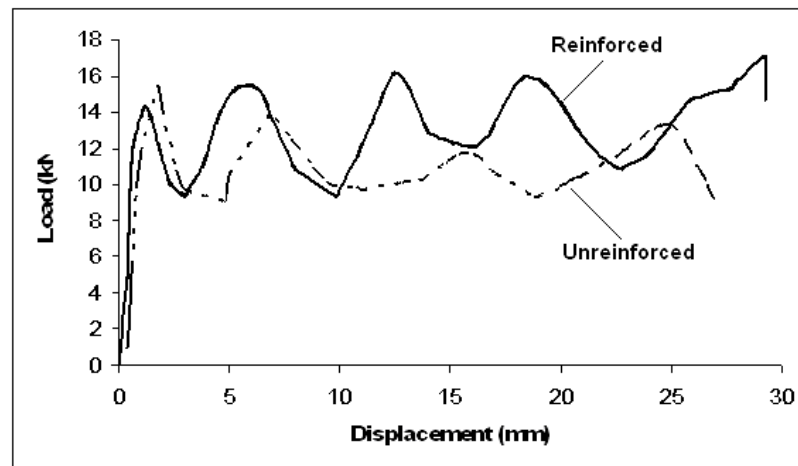
Figure 25: Load vs. Displacement curves - Effect of the reinforcement (Metal)

The two curves present several similarities. The initial phase is elastic, the most part of the axial stress being taken by the copper, since it has a modulus of elasticity superior than the one of the new material. After this elastic phase, local buckling occurs at different times, paving the way for softening phases. The buckling folds are orthogonal to one another (cf. Fig. 24). However, the third and fourth buckling loads are higher when the material is present as reinforcement. Therefore the reinforced copper tube can absorb more energy than an unreinforced one. In the automotive industry front shock absorbers would be made out of steel instead of copper, but the conclusion remains unchanged.

Reinforced Bamboo Poles

Following the same purpose, reinforced bamboo poles were tested in compression and compared to unreinforced poles. This experiment was motivated by the idea that as fiber material, bamboo is fairly good in tension but weak in compression. Bamboo reinforced beams and slabs are very common in the tropical architecture [36]. They are sustainable, cheap and have behaved very well [37]. However, bamboo columns behavior is more problematic, since they must sustain compression in the direction parallel to the fibers. The poles were 53.5 mm long, 17 mm wide and 3 mm thick. The tests gave the following load vs. displacement curves.
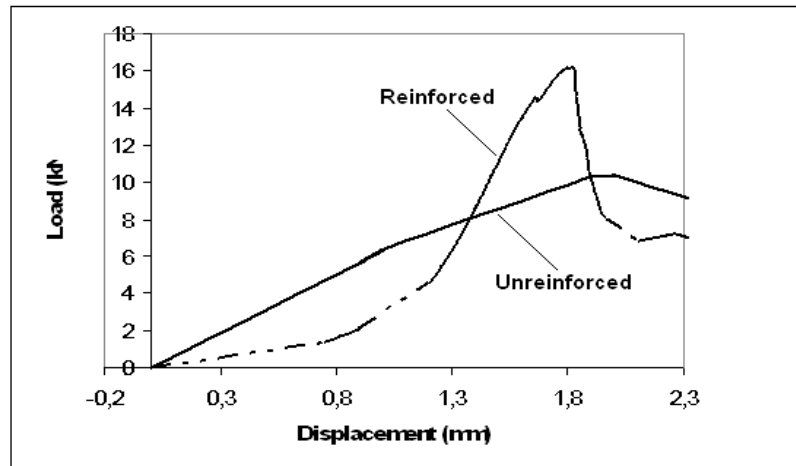
Figure 26: Load vs. Displacement Curve – Effect of the reinforcement (Bamboo)

Unlike ductile metallic tubes, bamboo has a brittle behavior, and one is therefore more interested in the peak crushing load than in the energy absorption. A reinforced bamboo pole (blue curve) surprisingly shows less stiffness but the crushing load is increased by 60%, which is a fairly good improvement given the low-cost and availability of the reinforcing material.

CHAPTER 4

CONCLUSIONS

The newly discovered material presents very interesting properties: it is a lightweight, homogeneous, isotropic, low-cost, environmental-friendly and thermal insulating material that can absorb a large amount of energy, which makes it suitable for the automotive and construction industries. Its porosity and therefore mass density, 'plateau' strength and thermal conductivity can be controlled by varying the amount of siloxane that acts as foaming agent. While patenting and licensing of the new material are currently underway, physical as well as chemical analysis should now be performed on a microstructural model to understand the mechanisms of its behavior under varied mechanical and thermal loads.

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