MINERAL FOAMS WITH IMPROVED PERFORMANCES

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1. INTRODUCTION

In a context of sustainable development and energy saving, there is a need for thermally efficient load-bearing materials in the field of restoration and construction.
Moreover, new standards enforce to reduce the use of fibrous compounds (e.g. rock wool and fiberglass) and of VOC-bearing polymers (e.g. PE and PU).
Hence, new types of building materials exhibiting the best compromise between insulating performances and mechanical properties must be developed. Hollow clay bricks for load-bearing walls are an interesting solution towards mechanical and thermal properties. Such cellular products can be optimized by:
– reducing the size of cells,
– increasing their number,
– and reducing their thickness.
This optimization step must remain compatible with the dedicated shaping techniques (e.g. extrusion, molding…). Cellular concrete is thus another quite good compromise. Its structure resembles the one of mineral foam whom cells' size is ranging from 0.2 to 2mm and whom wall thickness is around 0.1mm.
Some others solutions relying on environment friendly materials are being studied [ALL, 05]. Those environment friendly materials are hemp, reed, linen or wood-based composites. These materials are made of:
– vegetal hollow aggregates,
– mineral binders (e.g. lime, cement, gypsum…).
Most of these solutions are based on coupling of air filled cavities at different scales. They lead to products with quite low densities and thermal conductivities. In the same objectives, the development of mineral foams is an alternative solution that must be rediscovered.
After reminding the conditions that are needed to obtain foams in wet conditions, various foam production systems will be reviewed. Afterwards, some significant results obtained with gypsum-based binder will be presented. The influence of the formulation and of the forming conditions on the thermal and mechanical properties will be presented and discussed.

2. PRODUCTION OF FOAMS

2.1. Foam physics

An occlusion of gas bubble into a mineral binder is based on equilibrium between:
– The fluidity of the mix during shaping,
– The surface tension,
– The density,
– The pressure.
Foam shaping is based on physical principles [BRU 04] and [LAB 04], as expressed in the Laplace and Young relation see Eq. 1:

$$\Delta p = \gamma.(\frac{1}{R_1} + \frac{1}{R_2}) \quad \text{(Eq.1)}$$

Where:
– Δp is the pressure difference between the gas inside cells and the matrix binder

– and γ is the surface tension at the interface between the gas and the fluid.

R_1 and R_2 are the algebraic expression of the main radii of interface curvature (for spherical interface, $R_1 = R_2$).

For more precise explanation about these principles, see [BRU 04] and [LAB 04].

Foams can be obtained from different ways:

– Outgassing
– Modification of the solid/gas interface equilibrium, as example changing the surface tension by mean of wetting agent or changing air content…

2.2. Syntactic foam

Syntactic foam is a cellular composite material. Cavities are obtained with hollow-core aggregates, such as microspheres embedded in organic binders (e.g. epoxy, polyester, polyurethane, and polypropylene) (see. Fig. 1 left).

In some case of mineral binders (calcium silicate or gypsum-based binders), glass made hollow-core aggregates are used (see Fig. 1 right).

The foams that are made in such a way suffer weak mechanical performances induced by the hollow spheres. In the case of organic matrices, the foams are obtained by injection. In the case of mineral foams, an extra mixing step dramatically damages the spheres.

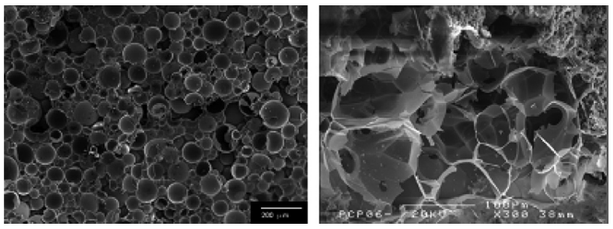

Figure 1: left: Syntactic foam made of hollow spheres embedded in an organic resin. (data obtained from wikipedia). Right: multi-celled glass hollow spheres embedded in a mineral matrix (Thermax CL product).

2.3. Foams obtained by in-situ outgassing

Releasing a gas in fluid suspension can promote foaming phenomena. This outgassing can be induced by different chemical reactions (see below). The carefully tailored synergy between outgassing and setting time is a key point for the good shaping of the considered foam.

The gas release can be induced, for example, by acid-base chemical:

– Addition of calcite to K-struvite cement [WAG 04] with release of CO_2
– Addition of perborates or percarbonates to strong bases (alkali-silicates for example releasing O_2 or CO_2).

In 1889, Hoffman was already reacting calcite in sulfuric acid to promote the release of carbon dioxide in lime-based mortars.

Other ways can be used, such as redox reactions, and foamed clays have already been obtained by mixing MnO_2, ovalbumine and H_2O_2 to clay pastes.

The most representative and known example of such materials is cellular concrete. This type of concrete is obtained by wet autoclave curing of lime/sand/ blends as demonstrated by W. Michaelis in 1880. Water resistant C-S-Hs are thus obtained (see Figure 2 left). In this case, foaming occurs when H_2 bubbles form concomitantly with the setting of the mineral matrix (Hoffmann 1889). The bubbling is due to the reaction of metal silicon, aluminum or zinc powders (J.W. Aylswoth and F.A. Dyer 1914) with the alkaline media, namely cement or calcic lime. When aluminum powder is added to calcic lime pastes, C_3AH_6 are formed while H_2 releases. Those hydrated phases are responsible for the setting of the mineral matrix. Further autoclave curing leads to the formation of tobermorite ($C_5S_6H_5$).

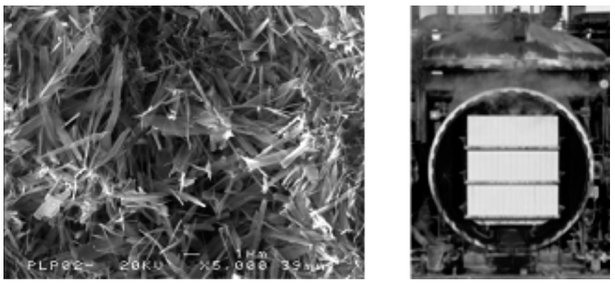

Figure 2: left: Structure of a calcium silicate matrix (Skamol product). Right: Post remolding autoclave curing (T = 180°C P = 10 atm.) - Febecel.

2.4. Effect of wetting agents

Adding wetting agents to the blend can improve the foaming ability of the paste. The surfactants:

– help to stabilize the gas-fluid interface,
– increase the pressure gradient between the liquid phase and the gaseous phase,
– affect the size of the bubbles.

Several chemical moieties can be used and are derived from the detergents and soaps chemistry (e.g. sodium lauryl sulfate, sodium laureth sulfate, cetyl trimethylammonium bromide, fluorosurfatants…).

Regarding the case of mineral foams, the surfactant must be carefully chosen: some of them can exhibit adverse effects towards the chemistry of mineral foams and binders (setting delay, lower mechanical strengths…).

The best compromise between the quantity of bubbles and the quantity of water will make this technique performs well or not. Indeed, water is required to create bubbles but excess water will dramatically affect the mechanical strengths of the hardened mineral foams. The main adverse effects that can be observed because of excess water are the too high dilution of the mineral phase and the coalescence of bubbles. This being written, one solution can consists in use of yielded fluid. In other words, stabilizing mineral foams is nothing less than entraining the highest quantity of air in a yielded concentrated suspension. A quite common solution is the use of a blender. Another solution consists in using a foam gun (see Fig. 3)

in synergy with water and specific surfactants. The obtained foam is then added to the mineral paste (see Fig. 4 left). This dissociated method performs quite well but its main disadvantage is the high amount water that is required.

Figure 3: Example of an industrial foam gun (stator and rotor details).

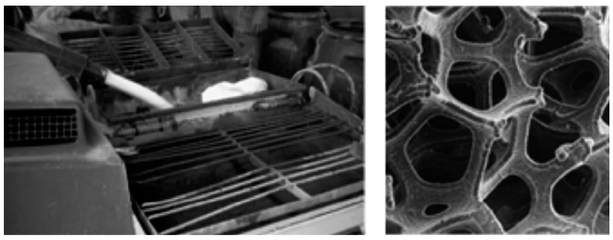

Figure 4: left: Adding foam in the gauging chamber of a mixer. Right: Foam deposit on a metal substrate (www.recemat.nl).

2.5. Effect of dispersive agents

Adding a dispersive agent to a mineral suspension can lead to the formation of stable foam. This can also occur when a plasticizer is added to the aqueous suspension. The molecules are adsorbed on the fine particles surfaces and help to break the flocks that form when water is added to charged particles. A strong steric hindrance effect occurs on the grains surfaces and the particles repel each other. If the particles size is fine enough, the surface tension will be modified at the air/fluid interface (see Fig. 5) and a stable bubble will form. In this case, the wall of the bubble is obtained without any extra-surfactant or increase of water as far as the dispersive agent behaves like a plasticizer. The so-called third generation superplasticizers, such as poly-carboxylate ethers, are of particular interest for hydrophobization of grains. Mineral foams can thus quite easily be obtained.

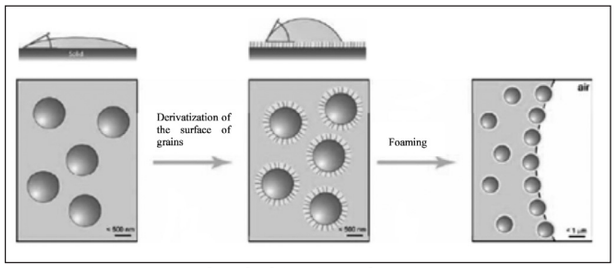

Figure 5: Hydrophobisation of grains [STU, 07].

2.6. Other methods

Other way to obtain foam does exist. Lightweight foams can be obtained by the deposit method (see Fig. 4 right). The raw material is usually foam with open cells (e.g. polyurethane.). Metal is then sputtered on the foam. The resulting 3D network is extremely porous. To the best of our knowledge, this method has not been applied yet to the case of mineral foam.

3. CASE OF GYPSUM ($CASO_4.2H_2O$)

3.1. Foam obtained by outgassing

Gypsum-foam can be easily obtained by adding a few percents of aluminum sulphate to a gypsum-plaster ($CaSO_4.0,5H_2O$) slurry. A chemical reaction occurs and leads to the formation of gas. A slightly plasticizing effect is also observed and the setting time of gypsum-plaster is shortened (setting occur within the first two minutes of the reaction). Gypsum foam is thus obtained. The bubbles size is about 1 mm (see Fig. 6 left) and the connectivity between bubbles is low. Chemical analyses of the exhausted gas revealed SO_3, i.e; a toxic gas. Considering health issues, this method is thus not safe and is of lab interest only. The SEM pictures (see Fig. 6 right) of the grains surfaces reveal that the crystallization of the gypsum is affected by the presence of aluminum. White deposits (see Fig. 6) are observed on the grain surfaces and are due to the presence of sodium carbonate (sodium salts are added to control the reaction rate and act as setting regulators).

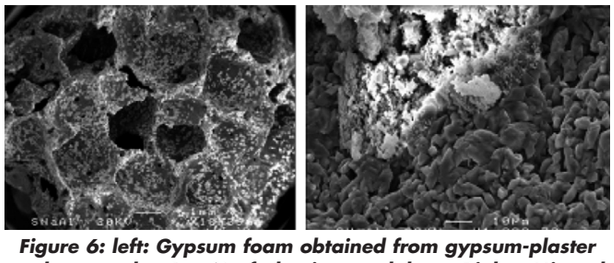

Figure 6: left: Gypsum foam obtained from gypsum-plaster and water plus 6 wt% of aluminum sulphate. Right : Mineral structure of the foam.

Those gypsum foams are hard to produce regarding the setting time that is not easily adjustable. Moreover, even if the voids are closed, they are too coarse to present satisfying properties.

3.2. Foams obtained with wetting agents and superplasticizers

Several foamed gypsum are formulated with different surfactants and superplasticizers. The binder is a mixture of 95 wt% of Kerysten® (anhydrous calcium sulphate produced by K&Co) and of 5 wt% of Portland cement (CEMI 52,5). Various surfactants are tested. Their contents are limited to the range advised by the suppliers. As mentioned by the

suppliers, a retarding effect of these admixtures is noticed and the setting of the gypsum foams is thus delayed. The selected superplasticizer is produced by K&Co: SemperActis™ SP20. This powder admixture containing polycarboxylate is well adapted to calcium sulphate. It is proportioned with less than 1%. Water proportioning is generally chosen between 30 and 35 % of the dry mass except when the foaming method is dissociated.

Various manufacturing processes of the foam are used: traditional mortar planetary mixer (Hobart Mixer), whisk mixer, foam generator (dissociated method of foaming). The mix method is adapted in order to obtain large density range of the gypsum foams. After mixing and foaming, the foam samples are abandoned in their mould until hardening. The form removal occurs within the first two hours after the setting. The specimens are cured at 20°C and 50 % HR.

Examples of foams obtained according to the considered foaming techniques are presented figure 7. The connectivity between the cells appears to be directly related to the thickness of the membrane between cells. If the membrane is too thin, the surface energy minimisation leads to the formation a "hollow disc" connection type. The thickness of the wall and the diameter of the hollow disc in the wall between two cells are directly related to the gradient of pressure between the two phases and the surface tension. Therefore the morphology of foam is only linked to the quantity of gas phase that is trapped in the liquid phase during the manufacture of foam. The optimization of the relation between the structure of the foam and the formulation thus remains difficult to control.

Considering the crystallization of the solid matrix, one can notice that the crystallites are more randomly oriented than in the case presented on the figure 6 right. The foams obtained starting from the same formulation present very similar mineral matrices. On the other hand the matrices of the foams obtained with the dissociated method are much looser.

3.3. Assessment of thermal and mechanical characteristics

Performances of various gypsum foams are compared. Tensile and compression strength tests are realized on different specimens (prismatic: 4x4x16 cm^3, cylindrical: ϕ = 11 cm). In addition, some thermal conductivity measurements are carried out using hot wire method.

Figure 8 presents a comparison of compression strengths obtained on gypsum foam for density ranging from 250 to 1600 kg/m^3. Results on other cellular materials (e.g. cellular concrete, more complex to produce) and environment friendly materials are indicated for comparison purpose. It is interesting to note that the considered foaming methods lead to gypsum foams with a weak water mixing rate and with a quite low density.

Some conclusions can be made from Figure 8:

– mechanical strength results of different gypsum foams fit well with a regular trend line,
– the more the binder is compact, the more the strength is high,

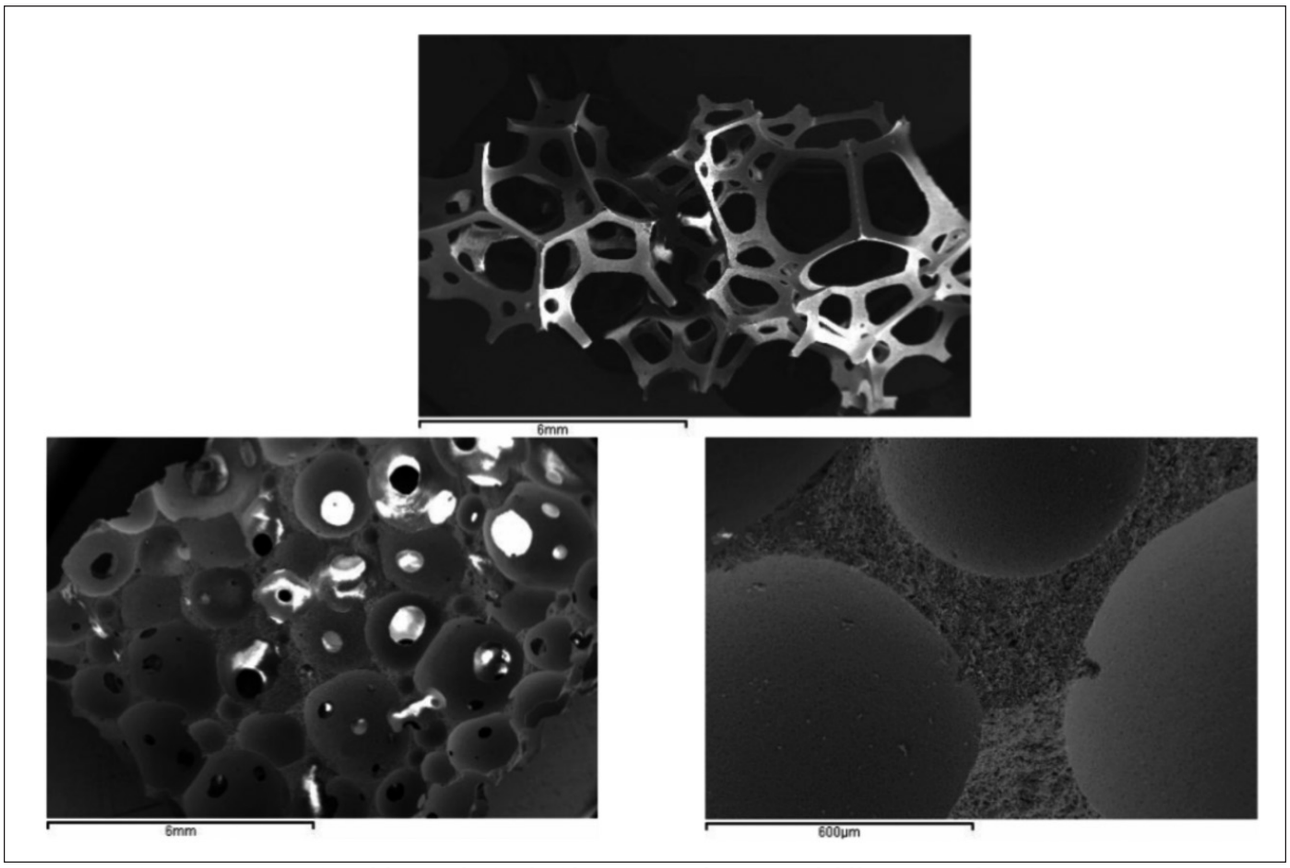

Figure 7. Various mineral foams obtained with various surfactants and different manufacturing processes.

– mechanical performances of gypsum foams and of cellular concrete are similar, and higher than hemp concrete ones.

Thermal conductivity results show a regular increase with density (figure 9). All the presented materials seems to have quite similar thermal performances. However, thermal conductivity values of tested gypsum foams appear lightly higher than the mean curve.

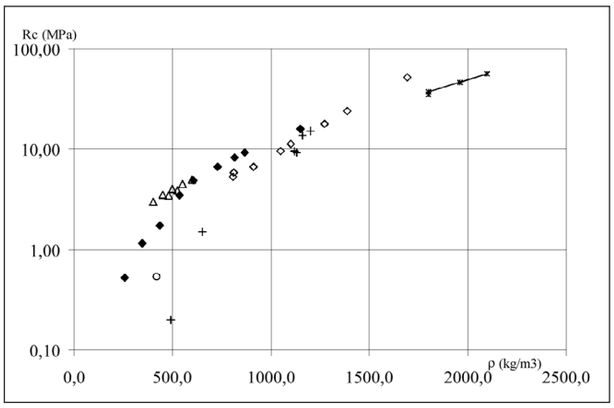

Figure 8: Compression strength vs density: rhomb : gypsum foams (dark mark : E/L = 0,30, white mark : E/L = 0,35), triangle : cellular concrete, circle : hemp concrete, cross : gypsum foam from dissociated method.

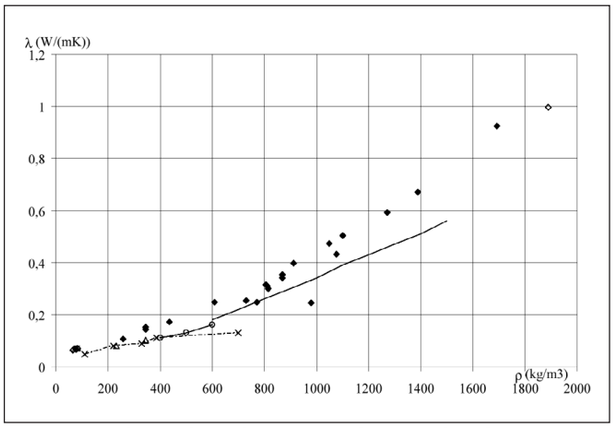

Figure 9: Thermal conductivity vs density: rhomb : gypsum foams, cross : hemp concrete and straw, circle : cellular concrete, triangle : polystyrene concrete, full curve : normalized conductivity values of plaster.

4. GENERALIZATIONS TO OTHER BINDERS AND CONCLUSIONS

The method of producing such paradoxical foams (lightweight foams based on dense mineral matrices) can be extended to other binders than gypsum. Figure 10 shows the structure of foams obtained with two distinct binders:

– the first one is full of insoluble micro-particles (Figure 10 left),
– the second one is made by coupling organic and mineral binders (Figure 10 right).

Bubble surface has got different characteristics without important structural modification.

The mineral foam optimization requires:

– an effective binder with a low gauging ratio, and at the same time, a rather good fluidity,
– an efficient technique to trap air into the matrix,
– a short setting time (or stiffening), so that foam structure remains stable.

Thermal and mechanical performances of these studied foams appear to be very relevant. So, applications of such mineral foams can evolve in the future by substituting some fibrous products.

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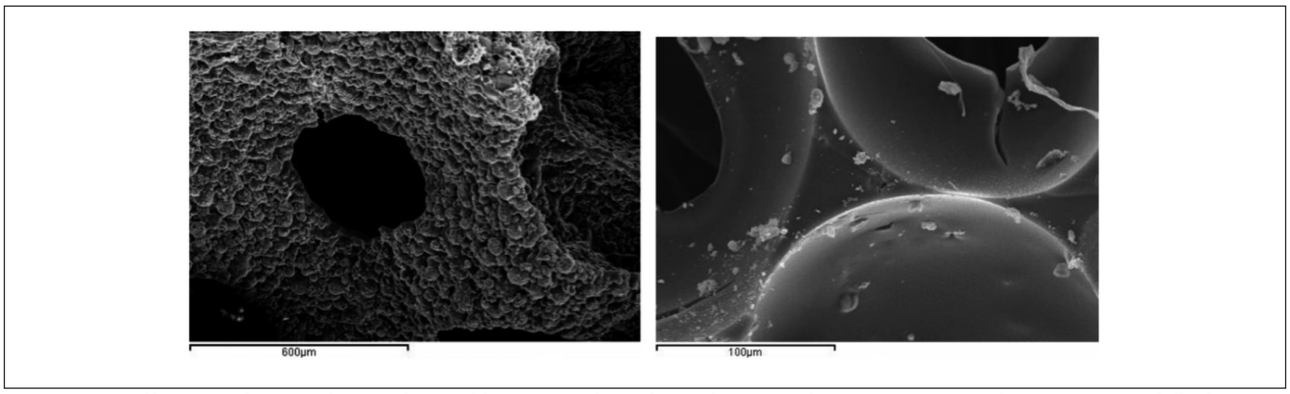

Figure 10: Different surface conditions obtained by various formulation but same foaming process: Left: a suspension full of micro-particles. right: a mix of organic and mineral binders.