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Some examples of mineral eco-materials

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Abstract

Eco-materials are materials which can minimize environmental impacts, can be manufactured from recycled materials, or are beneficial for human wellbeing. This paper will illustrate these three aspects on mineral-based eco-materials through research that has been developed in our ceramic institute: preparation of dense tapes of cementitious materials at room temperature by tape casting, valorization of dam sediments as raw materials for sintering of Portland clinker, monitoring the microstructure of plaster boards for improving the acoustical insulation in houses.

Keywords

Eco-materials, cements, dam sediments, plaster, recycling, tape casting, clinker

Introduction

If one looks for ‘ecomaterials’, the Mostar Bridge in Central Europe is a superb example. In order to replace a wooden bridge, Suleiman the Magnificent in the 16th Century commissioned a new bridge [1]. Hayruddin, the architect and builder who supervised its construction, committed suicide on the day the scaffolding was removed from the complete structure. He was scared that the bridge would collapse, stimulating the anger of Suleiman. The truth is, despite the fact the bridge was constructed on a seismic zone, it resisted many centuries until it was bombed in 1993 during the Croatia-Bosnia war. Thanks to a project lead by UNESCO, the bridge was reconstructed by replicating the original materials composition and construction, and was inaugurated in 2004. Beyond the symbolic meaning of reconstructing this bridge, there were some very interesting findings on the materials themselves. The engineers in charge of the bridge reconstruction found that the remains of the original bridge contained various mineral materials and a mortar with horse hair, egg shell. These components gave the bridge a remarkable durability. This is to point out that recycling or valorization of by-products to make new materials, which could be qualified nowadays as ‘eco-materials’, is quite an old concept.

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In the late 90's and at the beginning of the 21st century, eco-materials were defined as materials that could enhance environmental improvement through the whole life cycle, while maintaining accountable performances [2]. These materials should respect the principles of sustainable development. In this short paper, the presented examples, which correspond to research carried out in our laboratory, will illustrate three points: (1) an eco-material can present similar performances to a 'classical' ceramic material, (2) it should contribute to decrease the environmental impact through recycling and/or valorization of waste minerals, (3) it should permit to improve the home comfort of people in their house.*

Tapes of dense calcium aluminate cement obtained without any firing step

For those who are not familiar with cementitious materials, figure 1 is a simplified composition diagram showing two families of cements: Portland cements containing calcia and silica, and calcium aluminate cements (CAC), which are alumina rich.

The idea of our research was to see whether it was possible to make a dense aluminous cementitious material that could have some properties of 'classical' alumina but without a firing step. We prepared a slurry that could be used in tape casting or surface coating. The first requirement was to make a well dispersed suspension. Figure 2 presents the rheology of a slurry prepared from a calcium aluminate cement (Secar 71, table 1. The grain size ranges between 1 to 100 µm with d_{50} around 10 µm) [3] mixed with water (water over cement weight ratio, w_{water}/w_{cement} = 0.3) and containing increasing percentages of additive [4]. The best results, in terms of lowest viscosity, were obtained with the addition of acetic acid. The content which gives the smallest viscosity is $w_{additive}/w_{cement}$ = 0.005.

The next step was to examine the setting time when increasing quantities of acetic acid were added in the water (Figure 3). For a cement paste with no addition of acetic acid, the setting time was quite variable since it ranged between 2 h or 3 h up to 24 h. We found that this variability was due to external parameters such as storage conditions, and ageing of the cement when exposed to the ambient atmosphere. The corresponding pH is alkaline which is quite normal for a cement paste. For a percentage less than 1%, the setting time was very long. However, beyond this value, the setting time drops to 2 h and is very regular. The pH is also acid during the first 15 min. These variations were explained as follows: acetic acid can adsorb at the surface of cement grains, forming surface complex molecules $CaOAc^{+}_{surface}$ thus delaying the dissolution of anhydrous calcium aluminate grains and subsequently the formation of hydrates. When the

* This paper is based on an invited talk presented at the 7th International Congress on Ceramics, ICC7, organized in June 2018 at Foz do Iguaçú in Brazil.

quantity of acetic acid is increased, calcium acetates and gibbsite precipitate and the setting time is very regular. In a sense, addition of acetic acid permitted to get rid of the variability of setting time of the cement.

The second set of data concerns the density and the open porous volume as a function of acetic acid content after 4 days or 6 months ageing (Figure 4). First of all, the additive helps the densification of the hydrated cement since the density goes from 2.3 to 2.5 g/cm^3. Secondly, the open porous volume goes down from 35 to 25 vol% at 4 days and drops to less than 8 vol% after 6 months. The presence of the additive leads to a decrease in pore size and pore volume (Figure 5). In a 6 months old cement, with no additive, there are 2 populations of pores. With acetic acid, the micron size pores progressively disappear and the remaining pore are nanometric pores. The explanation is the following: the presence of acetic acid leads to a good dispersion of cement particles and contribute to a better densification compared to pastes with no addition. Moreover, calcium acetates and gibbsite can fill in the pores and thus contribute to the disappearance of micrometric pores.

Tape casting was used to prepare calcium aluminate cement tapes and the steps are described in figure 6. Table 2 gives the composition of the cement slurry and the role of each component. The principle of the process is the following: a slurry with adequate rheology is poured into a container which moves on a support and a tape is deposited. It is interesting to compare the process with the case of tape casting of alumina (Figure 6). The main differences between tape casting of a technical ceramic, such as alumina, and a calcium aluminate cement (which contains 72 wt% of alumina) is the removal of organic additives and the firing step: (i) with the cement, the removal of organic additive (also called ‘debinding’) is obtained by leaving the set tape in water for 24 h while it requires a heat treatment in the case of alumina, (ii) no sintering is necessary to obtain a dense material in the case of cement. The final materials (4 days old samples) presented similar dielectric constants (of the order of 10) and thermal expansion coefficients (of the order of 7.10^{-6} °C^{-1} between 25 and 1200 °C) [5]. The last interesting feature about our cement tapes was their surface roughness (of the order of 400 nm), lower than the surface roughness of an alumina substrate prepared by tape casting (of the order of 600 nm). Such a low roughness leads to a very smooth and glossy surface (Figure 7) which contains a mixture of calcium acetate and gibbsite. Michael Eden [6] coated his artworks with our slurries colored with a dye because our slurries gave the glossy aspect he was looking for (Figure 8).

This first example on a cementitious material shows it is possible to obtain at room temperature a fairly dense material which can find applications for making substrates or coating surfaces.

Valorization of dam sediments as raw materials for synthesis of Portland cement clinker

This second example will illustrate how dam sediments, instead of being disposed waste, could be valorized in the cement industry. Hydroelectric power generation represents 71% of renewable electricity all around the world [7]. Reaching 1,064 GW of installed capacity in 2016, it generated 16.4% of the world's electricity output. Some countries account for a significant percentage of the global installed capacities (in 2015, China, USA, Brazil and Canada represented respectively 26%, 8.4%, 7.6% and 6.5%). The immediate problem linked with the dams is the accumulation of sediments that get trapped in the reservoirs behind the dams instead of flowing into the river downstream. This can affect the efficiency of hydroelectric plant. Figure 9 gives a schematic representation on how sediments tend to accumulate in the reservoirs.

Due to watershed erosion, solid particles are transported by the watercourse. The biggest particles can deposit in the highest part of the reservoir while the finest particles (silts and clays) are transported in suspension and can accumulate with time. These accumulation of fine particles can have several potential impacts: for the operator, a reduction of the reservoir capacity and on the recreational activities. To avoid these impacts, it is necessary to have an adequate and sustainable management of these sediments.

Apart from the downstream transfer of the sediments, which is usually managed by the dam operator, there is an incentive to find alternative solutions because these sediments have to be considered as waste when they get extracted from a reservoir and are on-land-managed. Among the possible uses, a specific route we explored in a circular economy approach was the use of these sediments in the cement industry either as alternative materials for the manufacture of clinker (which is the raw material for cement production) or as pozzolanic addition to ordinary Portland cement. Using waste material in Portland cement clinker production is a relevant eco-friendly solution: it limits the mineral extraction in quarries (clays and marls mainly) and, at the same time, it alleviates the tonnages of landfilled waste [8]. Blending Portland cement with an alternative pozzolanic material has an additional advantage which is a limitation of the carbon dioxide emissions by ton of manufactured cement. Using life-cycle analysis, the CO_2 emission reduction using blended cement was found to be around 22 % compared to Ordinary Portland Cement [9] since less clinker is required in the formulation.

In this respect, we studied sediments extracted from dams operated by Electricité de France (EDF). They contain different minerals, typically quartz, carbonates, clay minerals and feldspars (Figure 10). Table 3 presents the range of chemical composition of the sediments located in the French Alps. Their silica, alumina, iron oxide and calcium oxide are compatible with their use as raw materials to prepare a Portland

clinker. In order to obtain a suitable clinker, the mix composition was adjusted so that three parameters, the lime saturation factor (LSF), the silica-ratio (SR) and the alumina ratio (AR) were within appropriate range as shown in table 4 [8, 10, 11, 12]. These three factors are defined below.

$$LSF = \frac{\%\ CaO}{2.80 \times \%\ SiO_2 + 1.20 \times \%\ Al_2O_3 + 0.65 \times \%\ Fe_2O_3} \quad (1)$$

$$SR = \frac{\%\ SiO_2}{\%\ Al_2O_3 + \%\ Fe_2O_3} \quad (2)$$

$$AR = \frac{\%\ Al_2O_3}{\%\ Fe_2O_3} \quad (3)$$

Therefore, we mixed the sediments with limestone in order to synthesize a clinker at 1450 °C, which is the typical temperature for Portland clinker manufacture [13]. By assuming the stoichiometric composition of synthesized phases, the mineral clinker phase fractions, namely alite (C_3S), belite (C_2S), aluminate (C_3A) and ferrite (C_4AF)[†] were calculated using Bogue's empirical formula [14]:

$$C_3S = 4{,}0710\ CaO - 7{,}6024\ SiO_2 - 6{,}7187\ Al_2O_3 - 1{,}4297\ Fe_2O_3 \quad (4)$$

$$C_2S = -3{,}0710\ CaO + 8{,}6024\ SiO_2 + 5{,}0683\ Al_2O_3 + 1{,}0785\ Fe_2O_3 \quad (5)$$

$$C_3A = 2{,}6504\ Al_2O_3 - 1{,}6920\ Fe_2O_3 \quad (6)$$

$$C_4AF = 3{,}0432\ Fe_2O_3 \quad (7)$$

The average percentages of each of these phases – determined by a Rietveld analysis - for a suitable Portland clinker should be 60-65 wt%, 20-25 wt%, 8-12 wt% and 8-10 wt% for C_3S, C_2S, C_3A and C_4AF, respectively, which is what we obtained in our mixtures [15]. Figure 11 shows a typical micrograph of a clinker we prepared by mixing adequate amounts of one sediment coming from the French Alps (27 wt%) with limestone (73 wt%) and synthesized at 1450°C. The porosity represents about a third of the total clinker grain volume, which can be explained by the granulation step of the powder mixture prior to synthesis. The observations show that the typical phases of a Portland clinker are present: calcium silicates (C_3S and C_2S), interstitial calcium aluminate phases (C_3A, C_4AF) [15].

This second example of eco-materials shows that the valorization of mineral waste is technically feasible and avoid the exploitation of new quarries. Nevertheless, for a large scale implementation, the sediment source should not be far from a cement industrial kiln since transport in this industry should be minimal.

Plaster to improve acoustic insulation in houses

According to a survey, a fair number of persons are bothered by noise in their housing [16]. The reduction of noise is a public health issue and it concerns different sector, especially new construction or rehabilitation of

[†] In cementitious notations, A, C, F and S correspond respectively to Al_2O_3, CaO, Fe_2O_3 and SiO_2.

dwellings. In order to understand acoustic insulation, two parameters should be considered. The first one is the sound transmission loss, STL; it corresponds to the loss of noise when it goes from one room to another room (Figure 12). An efficient acoustical insulation implies that STL, which corresponds to the difference in noise level, should be as high as possible. In general, STL increases with the frequency [17].

The second parameter is the critical frequency. For a specific frequency of noise called the critical frequency (f_c), the sound transmission loss curve shows a dip (Figure 13). This phenomenon can lead to a notably reduced acoustic insulation, especially if the dip of STL affects the midrange frequencies (The human hearing range is commonly given as 20 Hz to 20 kHz but the human ear is most sensitive in the midrange frequencies from 350Hz to 1500 Hz). Amongst the different possible materials for acoustic insulation, there is gypsum, $CaSO_4.2H_2O$ (commercially called 'plaster'). In fact, gypsum boards either alone or in a multilayer configuration are increasingly used as facing materials for interior walls and ceilings because of their acoustic properties, their good fire endurance, and thermal insulation characteristics. Our contribution was to examine to which extent the acoustic characteristics could be improved or not and how the microstructure could influence on the acoustic properties of gypsum.

In this respect, we prepared gypsum specimens with additive to modify the microstructure. The gypsum boards (thickness: 14 to 18 mm, width: 60 mm and length: 610 mm) were prepared from a mixture of calcium sulfate hemihydrate ($CaSO_4.½H_2O$), water (water over $CaSO_4.½H_2O$ weight ratio, W/P = 0.6) and in some cases addition of citric acid (0.1 to 4 wt% with respect to water) [18]. The sound transmission loss as a function of frequency was measured with the mechanical impedance method (MIM) described in the International Standard ISO 1694 [19]. Figure 14 presents these variations and the microstructure of the corresponding gypsum boards.

The effect of citric acid is remarkable since it shifts the critical frequency towards high values, further away from the human ear sensitive range. The microstructures are also different: gypsum with no additive presents the usual needle like crystals, while citric acid leads to platelets like crystals. Citric acid molecules present interatomic distances between the oxygen atoms of 4 Å, which is the interatomic distance between calcium in (120) and $(\bar{1}11)$ planes in gypsum. Finot et al. [20] confirmed that these faces exhibit the highest surface reactivity for adsorbing organic molecules. Therefore, citric acid molecules behave like a surfactant and can adsorb on these faces and slow down their growth, thus leading to a different morphology.

The consequence on the shift of the critical frequency can be explained as follows: the critical frequency, f_c is given by equation (8).

$$f_c = \frac{c_0^2}{2\pi} \times \sqrt{\frac{12 \times M_s}{E \times e^3}} \quad (8)$$

c_0 is the speed of sound in air (340 m s^{-1} at 20 °C), e is the thickness of the board, M_s is the mass per unit area of the gypsum board and E Young's modulus, which we determined by the pulse echo technique [21]. Table 5 presents the data for increasing percentages of citric acid. The parameter which influences on the f_c value is Young's modulus: the higher the citric acid content, the lower E is. Values of Young's modulus E are divided by 6 when the citric acid percentage goes from 0 to 4 wt%. A calculation of the number of contacts between the crystals [22] shows that it also decreases by a factor 6. Less contacts induce less rigidity of the material.

To conclude on this example, it shows that monitoring the microstructure enables to obtain gypsum boards with improved acoustic insulation capabilities.

Conclusion

These three examples show that the concept of 'eco-materials' offers interesting technical solutions to manufacture products. The example of calcium aluminate cement tape shows it is possible to obtain at room temperature a material close to sintered alumina tapes. Dam wastes, whose composition is close to clay minerals, could be valorized as raw materials in the cement industry, thus lowering the carbon footprint of cement manufacture. The third example shows that the presence of an additive modifies the microstructure of gypsum crystals and gives a material with improved acoustical insulation compared to gypsum with no addition. These three examples illustrate that these materials could fulfill some needs, like energy savings, waste management, and comfort in housing. Nevertheless, to go further into their wide implementation, there is a necessity to go beyond these scientific solutions and to build network between different actors: academic laboratories, industries, governmental agencies and above all the citizens who will be the consumers of these products [23]. The development of these eco-industrial networks will help to address environmental issues and participate in the social acceptability of different solutions.

Acknowledgments

The authors would like to thank all the contributors to these three topics and who are cited in the corresponding references.

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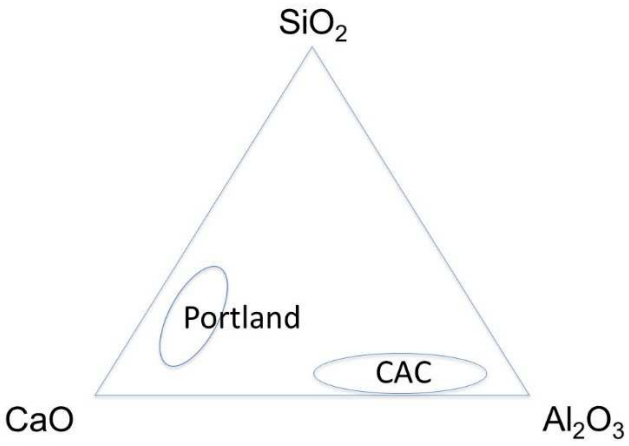


Figure 1: composition range of calcium aluminate cements compared to Portland cements

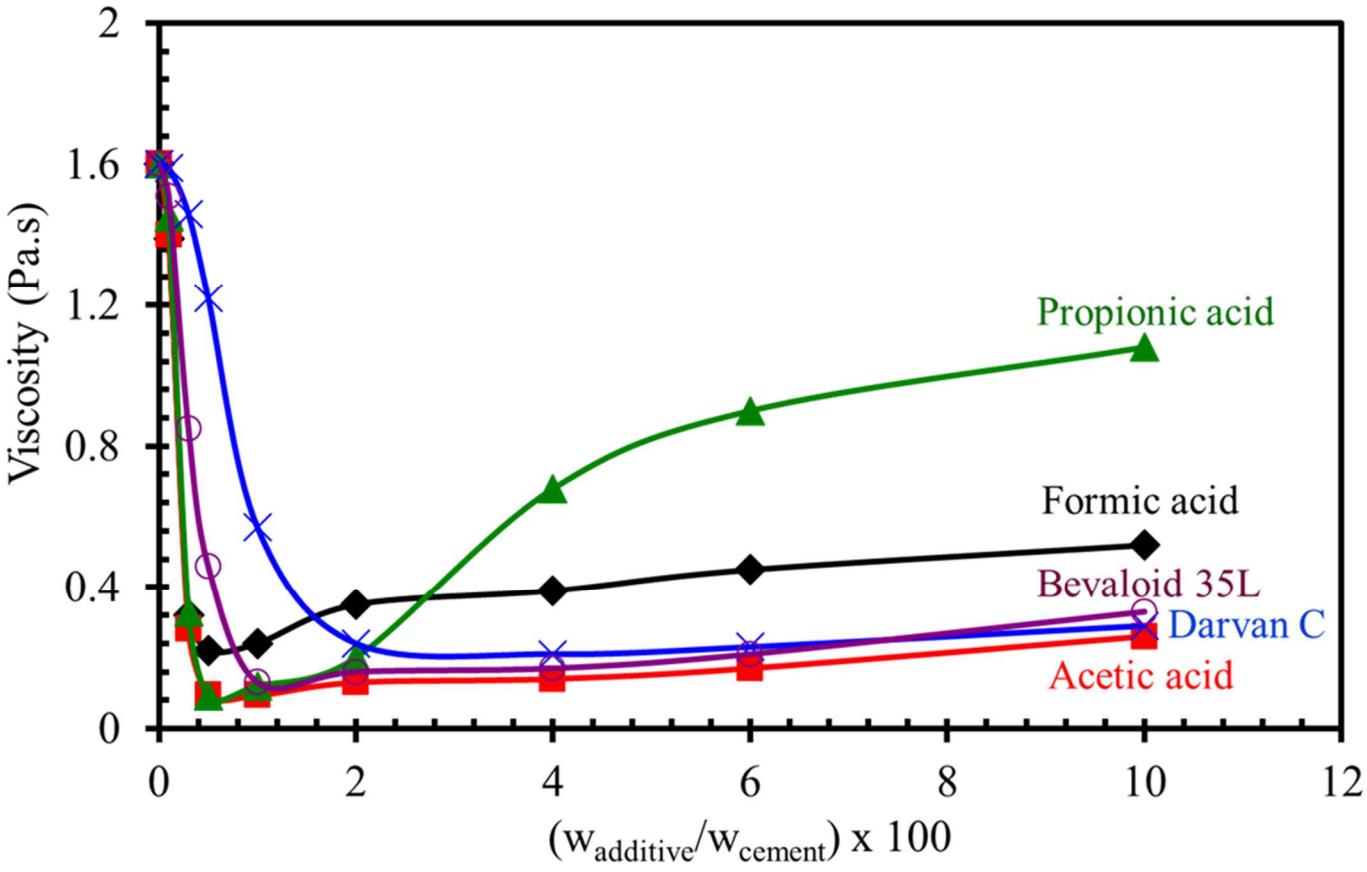


Figure 2: Viscosity, η (in Pa.s), calculated from the $\tau - \dot{\gamma}$ curves for $\dot{\gamma} = 20\ s^{-1}$ (typical value for tape casting). The cement pastes were prepared with a water over cement weight ratio, w_{water}/w_{cement}, equal to 0.3. The water contained increasing quantities of the five tested additives, namely

- a polyacrylate: Darvan C (RT Vanderbilt Company, Inc., USA),
- a sulphonate: Bevaloid 35L (Rhodia, UK),
- three carboxylic acids: formic, acetic and propionic acids (PROLABO, France).

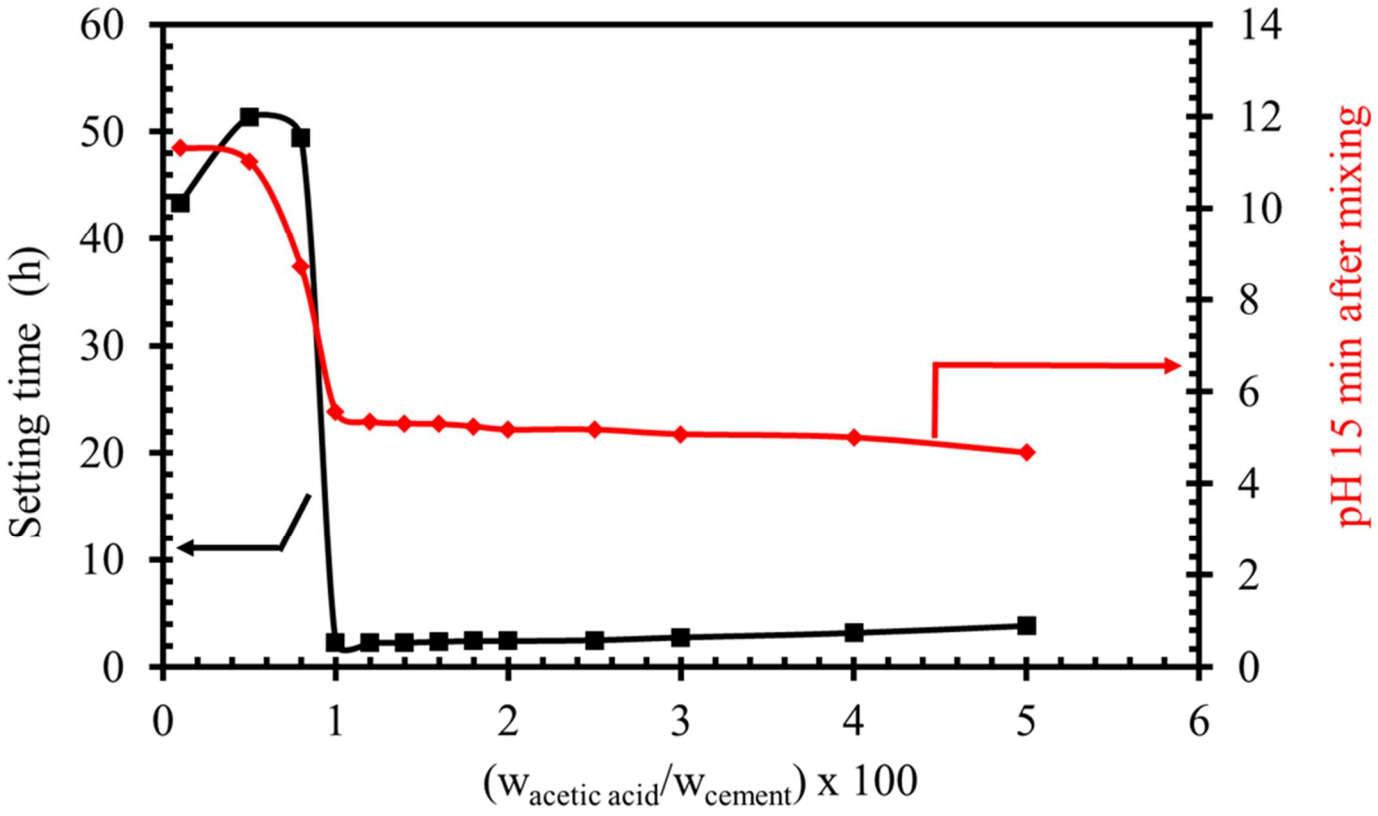
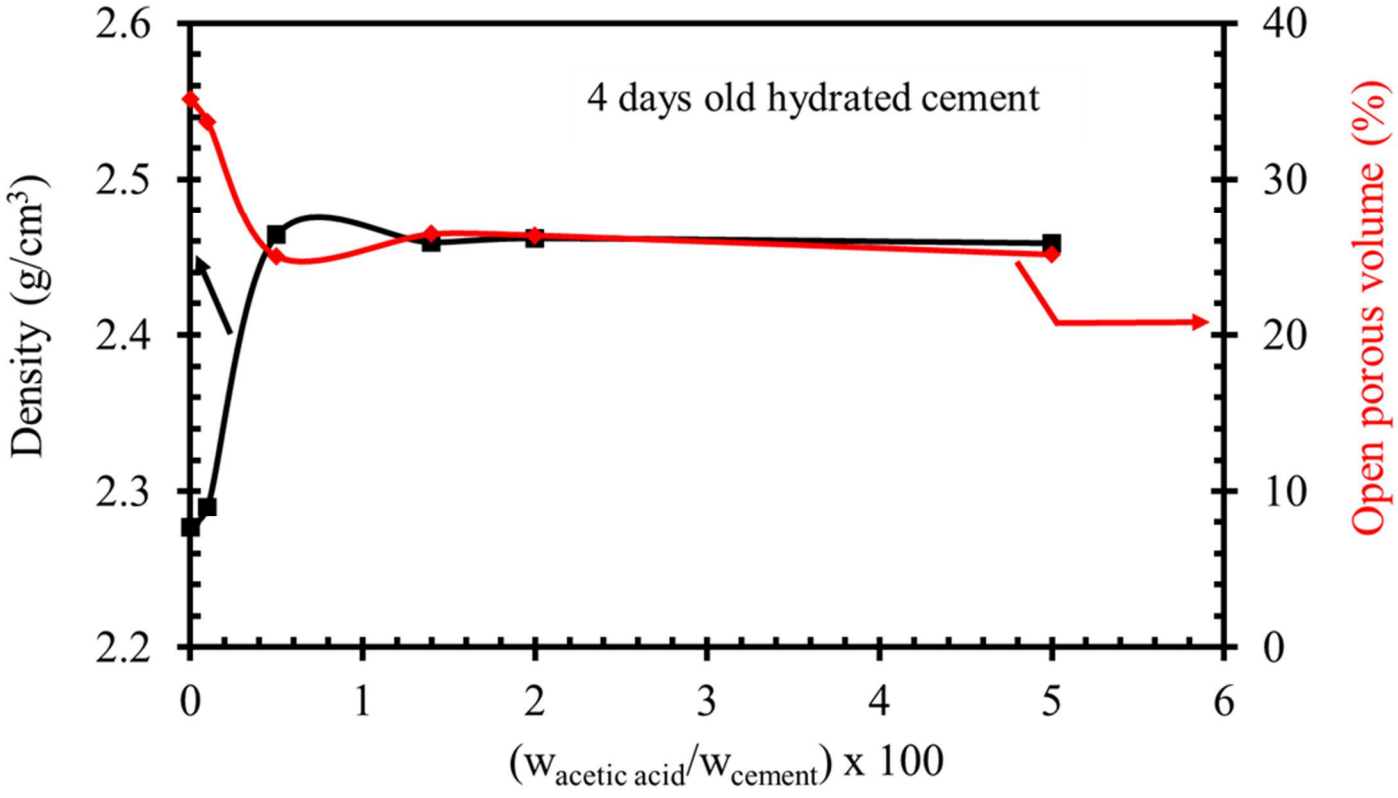
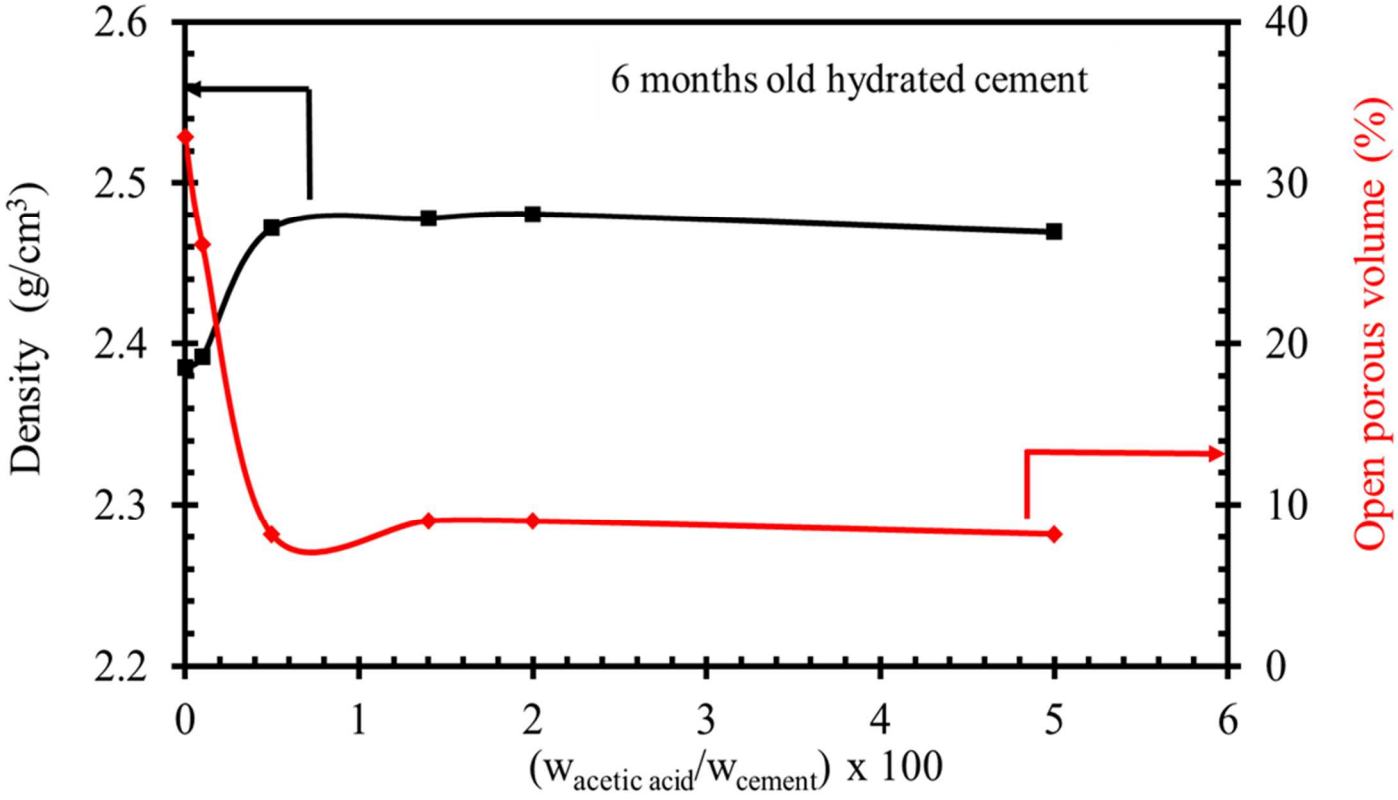


Figure 3: setting time and pH after 15 min mixing water with cement (w_{water}/w_{cement} = 0.3 and $w_{acetic\ acid}/w_{cement}$ ranges between 0 and 0.05).


4 days old hydrated cement
Density (g/cm3)
Open porous volume (%)
2.6
2.5
2.4
2.3
2.2
40
30
20
10
0
0
1
2
3
4
5
6
(wacetic acid/wcement) x 100

(a)



(b)

Figure 4: density and open porous volume of a cement paste (w_{water}/w_{cement} = 0.3 and $w_{acetic\ acid}/w_{cement}$ ranges between 0 and 0.05) after 4 days (a) and 6 months (b) ageing.

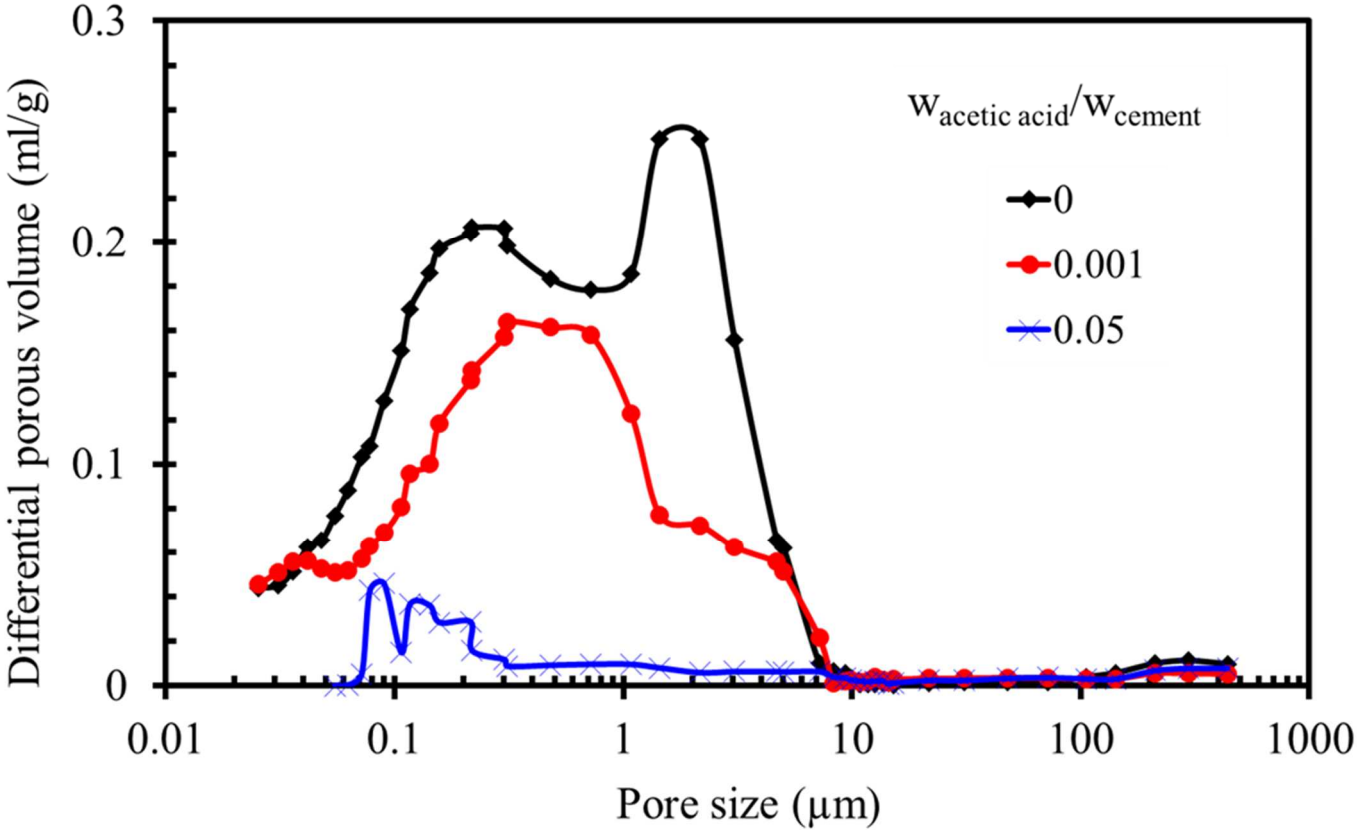


Figure 5: pore size and pore volume distribution in a 6 months old cement paste (w_{water}/w_{cement} = 0.3) containing 0, 0.1 and 5 % of acetic acid with respect to water.

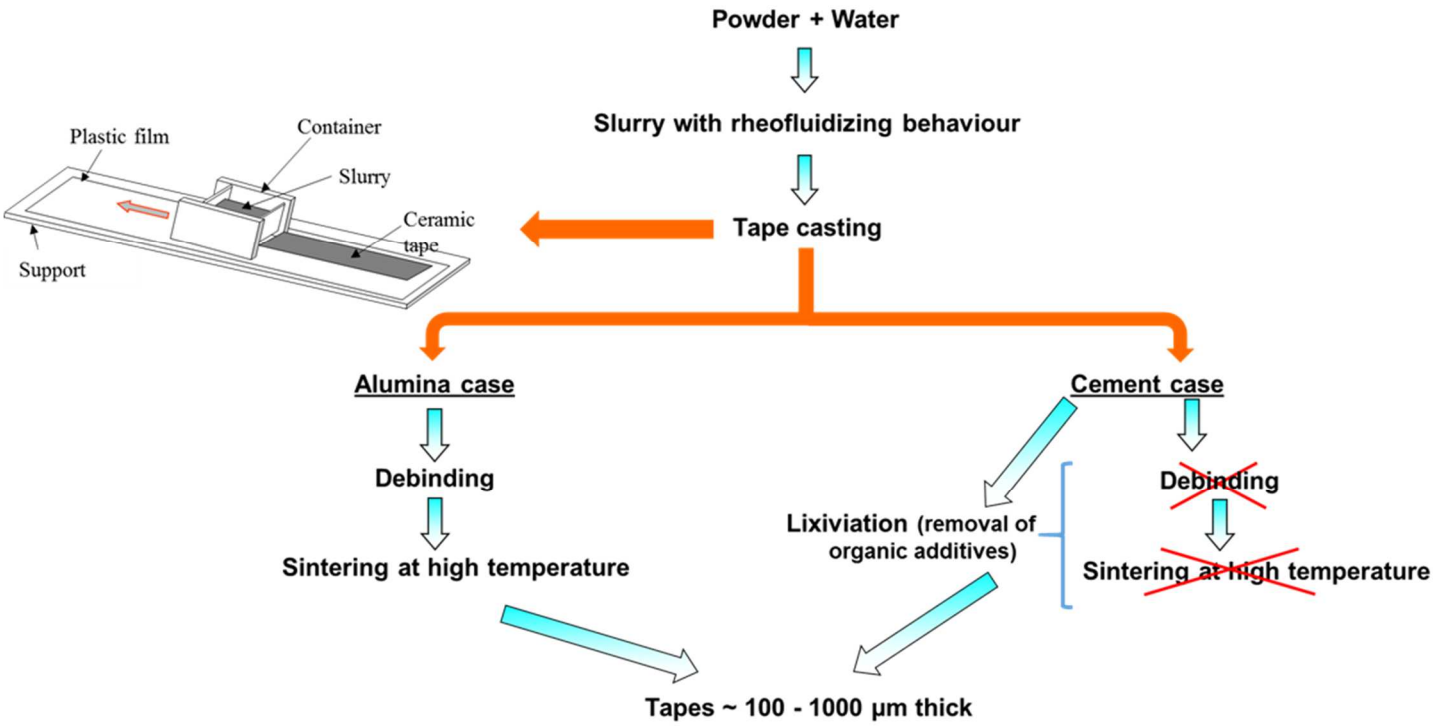


Figure 6: main steps of tape casting in the case of alumina and a calcium aluminate cement.

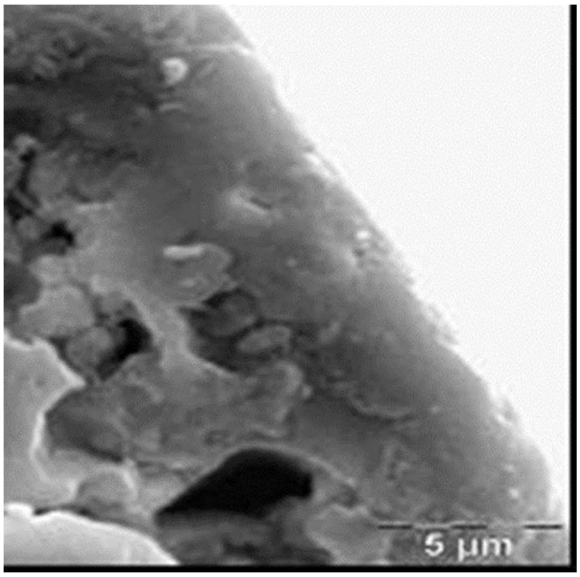


Figure 7: micrograph of the surface of the cement tape showing a dense and smooth surface.



Figure 8: The Wedgwoodn’t Tureen 2010 Michael Eden. Collection of Musée des Beaux-Arts, Montréal, Canada. Photo courtesy of Adrian Sassoon, London.

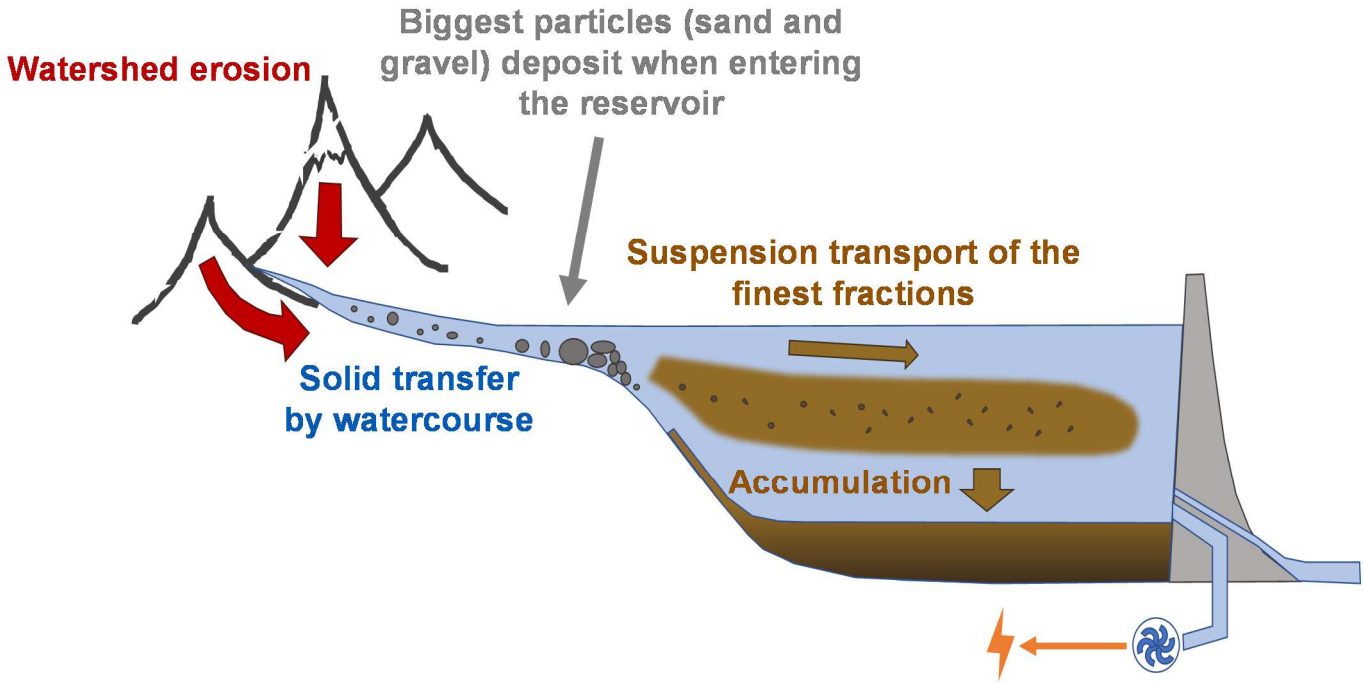


Figure 9: schematic representation of sediment deposition in hydroelectric reservoirs.

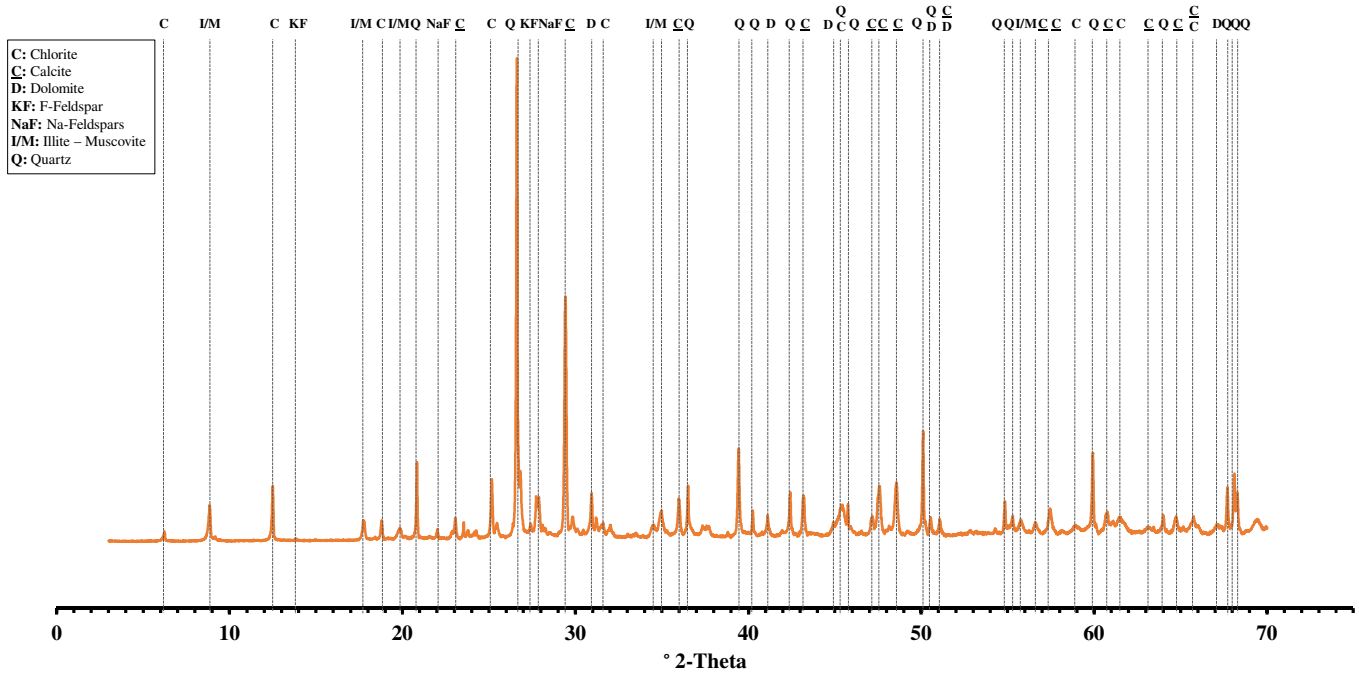


Figure 10: Typical X-Ray Diffraction analysis of a carbonated sediment from French Alps.

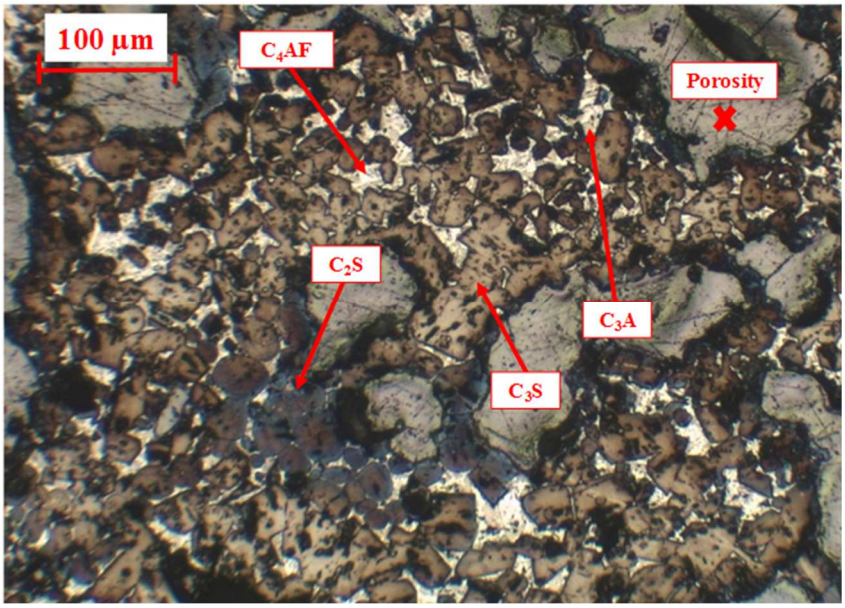


Figure 11: polished surface of a clinker prepared with an alpine sediment and etched with a NaOH solution followed by an ethanol-HNO_3 solution (nital), in order to successively reveal and color the interstitial aluminates and the silicate phases [11]. C, S, A and F stand for CaO, SiO_2, Al_2O_3 and Fe_2O_3 (from [15]).

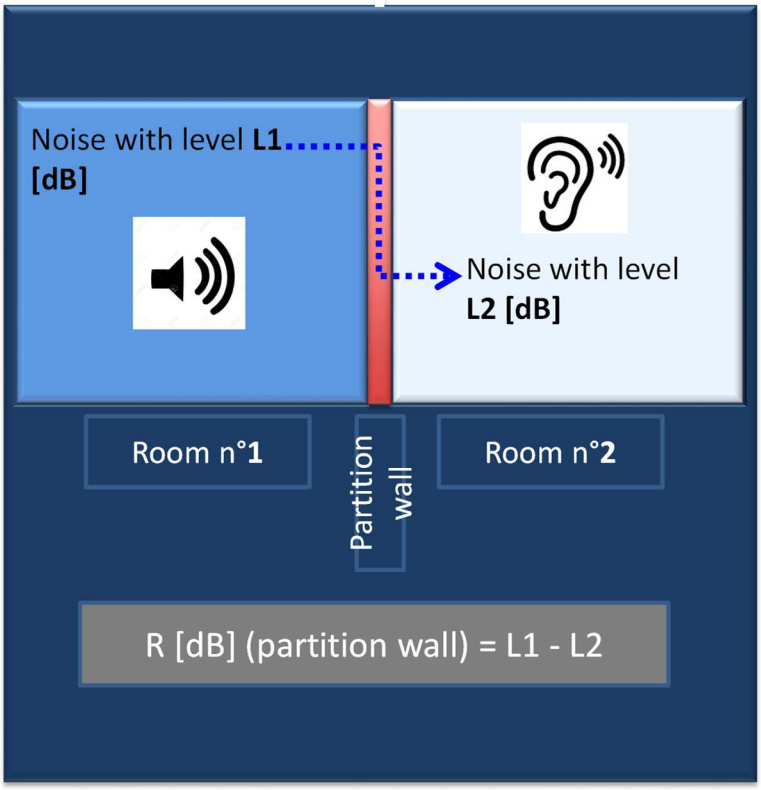


Figure 12: schematic representation of the sound transmission loss, R, through a partition wall.

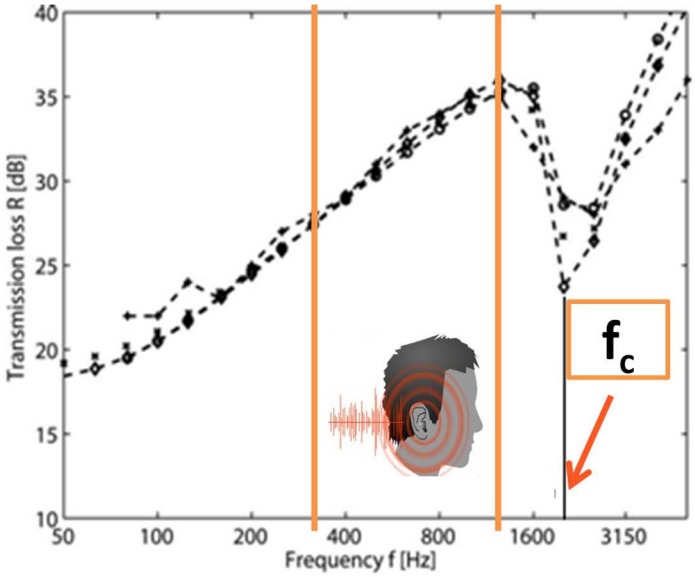


Figure 13: typical transmission loss as a function of frequency. At a critical frequency, f_c, the transmission loss decreases sharply and the acoustic insulation as well. 350 Hz to 1500 Hz is the range where the human ear is most sensitive.

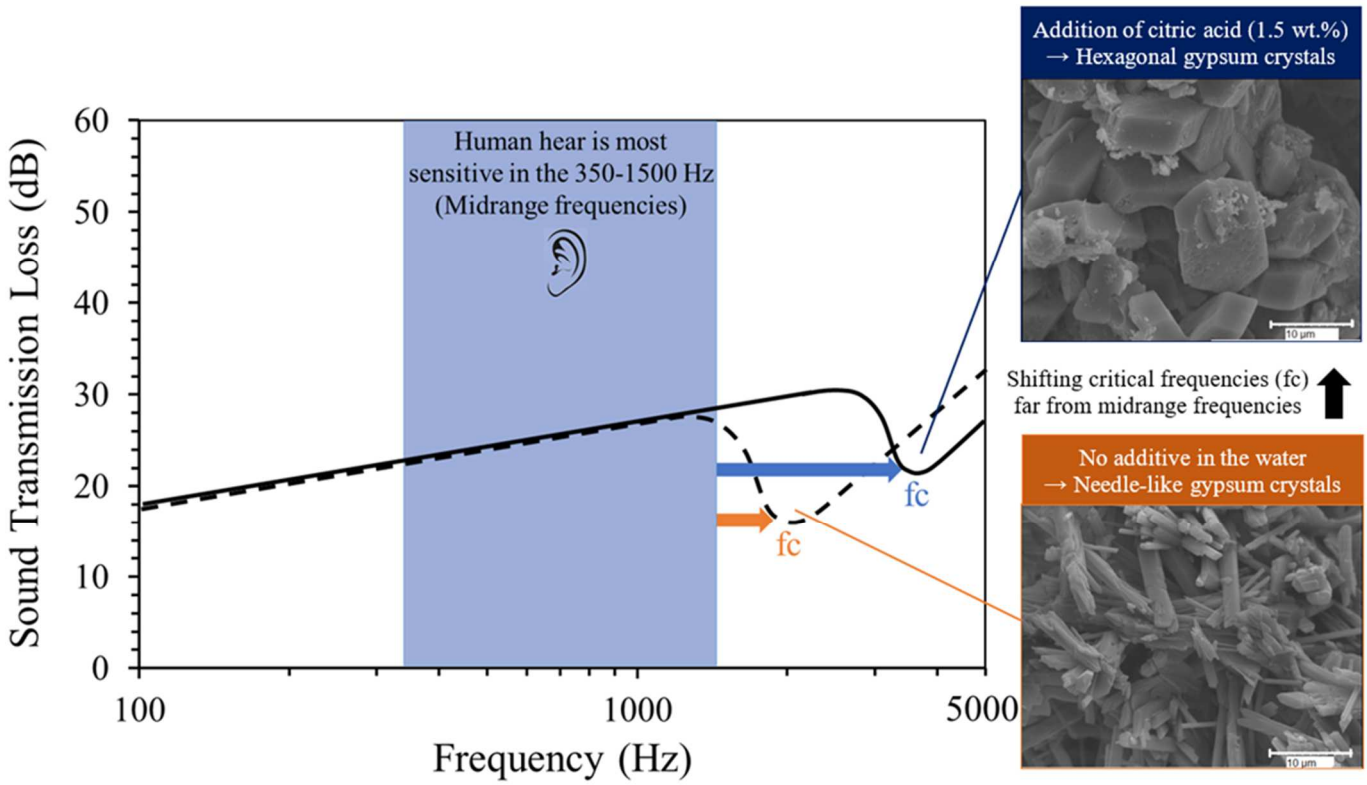


Figure 14: sound transmission loss as a function of frequency for gypsum boards (water over $CaSO_4.½H_2O$ weight ratio, W/P = 0.6) prepared with no additive in water or with the addition of citric acid (1.5 wt% with respect to water).

Mineralogical constituent	**Weight percentage (%)**
CA	56
CA_2	38
$C_{12}A_7$	<1
A	6
Oxide composition	**Weight percentage (%)**
C	28
A	72

Table 1: mineralogical and oxide composition of Secar 71.

C and A correspond to CaO and Al_2O_3 in cementitious notations.

Constituent	**Function**	**Weight percentage (%)**
Cement (Secar 71)	Powder	-
Water	Solvent and binder	33 - 35
Bevaloid 35L	Dispersant	0.05 - 2
PEG 300	Plasticizer	4 - 8
Acetic acid	Dispersant	0.3 - 2

Table 2: composition of the calcium aluminate cement slurry. The percentages are relative to the weight of cement.

Oxide	Composition range (wt%)
SiO_2	42.70 – 49.60
Al_2O_3	7.50 – 13.70
Fe_2O_3	3.00 – 5.80
CaO	12.10 – 15.60
TiO_2	0.40 – 0.70
MnO	0.05 – 0.16
P_2O_5	0.13 – 0.29
SrO	0.04 – 0.08
Na_2O	0.65 – 0.90
K_2O	1.60 – 2.70
SO_3	0.10 – 0.35
Ignition loss	< 20

Table 3: range of chemical compositions of the dam sediments located in the French Alps.

Ratio	Taylor [8]	Moir [10]	Locher [11]	Gani [12]
LSF	0.92 – 0.98	0.95 – 0.97	0.90 – 1.04	0.92 – 0.96
SR	2.0 – 3.0	2,4 – 2,6	1.6 – 4.1	2.3 – 2.5
AR	1.0 – 4.0	1.5 – 1.8	1.4 – 3.7	~ 2.0

Table 4: typical ranges of lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR) for a Portland clinker.

w/p ratio	Citric acid (wt%)	Ms (kg/m^2)	e (mm)	E (MPa)	fc (Hz)
0.6	0.1	14.7 ± 1.1	15 ± 0.1	3040 ± 360	2342 ± 224
0.6	0.5	16.3 ± 1.0	16 ± 0.1	2850 ± 330	2380 ± 223
0.6	1.2	14.7 ± 1.1	14 ± 0.1	1840 ± 220	3417 ± 334
0.6	1.5	15.0 ± 1.1	14 ± 0.1	1730 ± 210	3695 ± 363
0.6	3	14.3 ± 1.1	13 ± 0.1	1300 ± 160	4067 ± 402
0.6	4	14.1 ± 1.0	13 ± 0.1	490 ± 60	6936 ± 483

Table 5: physical parameters of gypsum boards and critical frequency (calculated from (8)) as a function of the quantity of citric acid added in the water + plaster mix.