P- AND S-WAVES TO DETERMINE RHEOLOGICAL PROPERTIES OF HETEROGENEOUS MATERIALS WITH EVOLVING PROPERTIES

L.Arnaud[1],
[1] National School of Public Works, ENTPE, Lyon, France

Abstract: The paper deals with the rheological measurements throughout setting and hardening periods of different heterogeneous civil engineering materials. Results on cellular concrete, mortar, hydraulic concrete and cold bituminous mixes are presented. Such materials are heterogeneous mixtures containing solid particles, binder, fluids and gas bubbles. For all these materials, we investigated the influence of parameters such as water content, binder proportioning and compaction level.
A non-destructive device allows the setting to be monitored and to be clearly characterized. This device makes it possible to simultaneously study the propagation of compressional and shear waves in the same sample of material. To prevent diffraction of waves from heterogeneities, a condition of long wavelength compared to the heterogeneity size is required, so low frequencies are used (20 - 1000 Hz). Velocity and damping coefficients versus time are deduced, then related to rheological viscoelastic properties by an inverse analysis.
The linear behaviour of these materials under small strains is proved and the measurements are very repetitive and sensitive to the nature and the component proportioning of the materials.
The rheological evolutions of the different materials are presented and compared. For example, it is shown that the normalised evolution of hydraulic concretes follows a single master curve for all the different formulations investigated. Similar results are established for cellular concretes and mortars.

Introduction: This paper focuses on the rheological evolutions of some materials in the field of the Civil Engineering during the hardening and the setting periods. The setting phenomenon results from various processes (chemical, physical, etc.) that bring the mixture from a fluid state that is favorable to easy placement, to that of a solid whose properties are necessary for the proper behavior of the material in service. Control of such phenomena is an important objective for economic as well as technical reasons. For example, one can mention for concrete, the determination of the right moment to remove formwork or to load a structure.
This paper proposes a synthesis of the works carried out for the rheological study of the materials throughout setting and hardening. Four materials with very different characteristics were successively studied: cellular concrete, mortar, hydraulic concrete and cold bituminous mix.

Setting designates the period in a material's evolution that precedes the moment when the solid particles become connected, either by means of a network of hydrates for cement-based materials, or by bituminous bridges in the case of cold bituminous mixes. After this transition the structure of the skeleton progressively reinforces itself: this is the *hardening* phase.

The study is complex, since this time-dependent structure evolves with the building of fragile links between the solid aggregates, these materials are highly heterogeneous (they consist of solid constituents, fluids and gas, the size of the heterogeneities varies from the millimeter to the centimeter), the evolution from fluid to solid is very pronounced from a mechanical point of view, and in addition, these processes are very sensitive to thermodynamic conditions. That is why very few measurements are achieved on « fresh » material, and when it exists the analysis remains most of the time purely comparative (slump or Vicat needle tests). Furthermore, for cellular concrete and cold bituminous mix, there are no tests to monitor mechanical evolution. For hydraulic concrete there is no generally accepted method to directly monitor setting and hardening.
For the study of concrete, tests have been performed with rheometers. Besides the problems of coherence of the results between these devices (Nachbaur 2001), the major drawback of these systems is that the large strains imposed lead to the destruction of the microstructure.
The basic idea for the design of the experimental device used in this paper is to study the propagation of P- and S-waves whose *wavelength is large compared to the size of the heterogeneity*. This is achieved by using very a low frequency (20Hz to 800Hz) (Boutin, 1995)(Arnaud, 1996, 2000). Indeed, at the beginning of the setting, the presence of gas bubbles leads to wave velocities C of the order of 100 m/s. Ultrasounds (frequencies f = 50kHz) are diffracted on heterogeneities and strongly

attenuated (Sayers 1993). Some tests have been performed on mortar and hydraulic concrete with signals presenting a wide frequency spectrum without any rheological analysis (Reinhardt 1996) or on degassed materials or in the absence of the biggest aggregates (mortar) by means of shear ultrasonic waves (Boumiz 1996).

In the first part of this paper, the main characteristics of the studied materials and of the experimental device are briefly presented. Then in the second part, the measurements are presented and the linear behaviour of these materials under small strains is proved. The third part aims to present the inverse analysis conducted. The measurements of velocities and damping coefficients are related to the rheological viscoelastic properties of the materials. The rheological evolutions of the different materials are presented and compared.

Results : The interest of this study is to present rheological measurement on materials with very different characteristics, although they are all composed of solid aggregates, water, binder and gas bubbles. The usual mix proportions of these materials are listed in Table I.

<table>
<tr><th colspan="2">Material</th><th>Cellular concrete</th><th>Mortar</th><th>Hydraulic concrete</th><th>Cold bituminous mix</th></tr>
<tr><td colspan="2">Use</td><td>Building</td><td>Building</td><td>Civil engineering</td><td>Road pavement</td></tr>
<tr><td rowspan="2">Setting</td><td>process</td><td>Hydration of binders</td><td>Hydration of cement</td><td>Hydration of cement</td><td>Electrical and evaporation</td></tr>
<tr><td>duration</td><td>4 h</td><td>8 h</td><td>8 h</td><td>30 days</td></tr>
<tr><td colspan="2">Fresh density (kg/m^3)</td><td>950</td><td>2200</td><td>2300</td><td>1840</td></tr>
<tr><td rowspan="4">Content in mass for 1 m^3</td><td>Aggregates (kg)</td><td>265</td><td>1723</td><td>1784</td><td>1666</td></tr>
<tr><td>Water (kg)</td><td>550</td><td>228</td><td>190</td><td>102</td></tr>
<tr><td>Binder (kg)</td><td>Cement + Lime 152 + 37</td><td>Cement 380</td><td>Cement 380</td><td>Asphalt 72</td></tr>
<tr><td>Air cont. (in vol. %)</td><td>> 50</td><td>5</td><td>1</td><td>20</td></tr>
<tr><td rowspan="2">Device</td><td>Heterogeneity Size</td><td>1 mm</td><td>5 mm</td><td>20 mm</td><td>20 mm</td></tr>
<tr><td>P - S -Wave freq.</td><td>200 – 20 Hz</td><td>800 – 100 Hz</td><td>800 – 100 Hz</td><td>800 – 100 Hz</td></tr>
</table>

Table I. Characteristics of the tested materials

The fresh *cellular concrete* is characterized by very fine sand particles of quartz and gypsum (< 80µm in diameter) and a large volume of the gas phase (about 50% of the total volume). Due to the aluminium powder reaction, small hydrogen bubbles (about 1mm in diameter) are created. They remain blocked in the viscous suspension of sand, cement and lime that is very concentrated. After thirty minutes, the gas volume represents more than 50% of the total volume. Then during the next four hours, with the hydration of first the lime and then the cement, hydrates are created. At first they are not connected, and the concentration of the suspension is gradually increasing. The continuation of the process leads to the percolation threshold: this is the transition between fluid and solid states. Then, gradually, the solid skeleton consolidates with new hydrates created: the material hardens. After approximately four hours, the fresh cellular concrete is carved and then submitted to a high-pressure steam curing. This study deals only with the fresh cellular concrete evolution before autoclaving.
Different conditions for cellular concrete were tested involving different initial temperatures (40-50°C), different water contents (ranging from -5.8% to +11.6% in volume) and binder contents (ratio cement/lime).

Compared to cellular concrete, *mortar* and *hydraulic concrete* are characterized by coarse aggregates (maximum diameter 5mm for mortar and 22mm for hydraulic concrete) and a lower volume of the gas phase due to the air bubbles that are trapped during the mixing process (about 5% for mortar and 1 or 2% for hydraulic concrete). Setting and hardening result from the chemical reactions of cement hydration. The different stages described for cellular concrete remain the same but the resulting microstructure is very different due to the differences in aggregate size. Seventeen experiments were carried out on hydraulic concretes and five other on mortar. Several parameters were modified: the W/C ratio (in-between 0.4 – 0.6) and the casting temperature from 10 to 30°C. On mortar, some additives have been tested (plasticizer, air entraining and retarding agents). The different mix proportions are presented with some results (see section 3) in the table II.

Campaign	Name	W/C ratio	Ti (°c)	Waves	Co (m/s)	τ (s)
CALIBE	B04-10	0,4	11,5	P	164	141
	B06-10	0,6	12,5	P	140	149
	B04-20	0,4	21,8	P	194	105
	B06-20	0,6	19	P	118	127
	B04-30	0,4	30,4	P	185	85
	B06-30	0,6	28,5	P	146	100
BSP	BSP1	0,43	20,8	P - S	118	100
	BSP2	0,41	20,9	P - S	140	149
	BSP3	0,55	25,4	P - S	114	109
	BSP4	0,55	26,9	P - S	100	88
RE	M-re3	0,6	26,4	P	121	130
	M-re4-P	0.5	25,2	P	109	133
	M-re9-P	0.5	23,9	P	125	172
	M-re6-AE	0.55	24,1	P	112	120
	M-re5-R	0.6	23,8	P	85	204

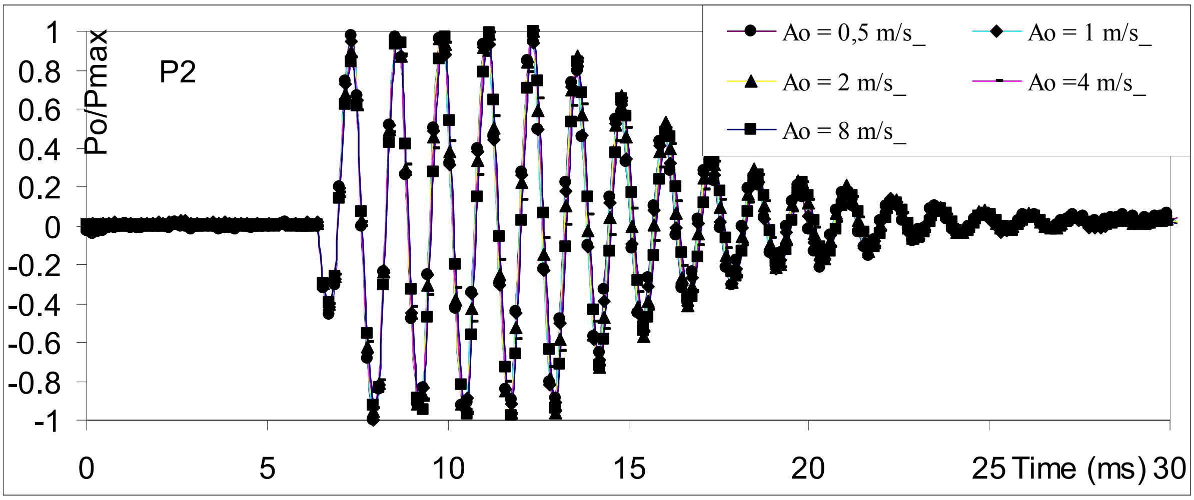
Table II. Parameters of experiments on hydraulic concrete.

The *cold bituminous mix* consists of solid aggregates (different aggregate gradings from 0 to 14 mm) mixed in a cold asphalt emulsion. For that material, the setting and hardening result from the evolution of the emulsion. Due to different electrical charges, at the beginning of the mixing, asphalt droplets are attracted and adhere to the aggregates. This is the breaking of the emulsion. After the compaction process, due to the evaporation of the emulsion water, asphalt droplets coalesce and asphalt links are created between the solid aggregates. The material is hardening. This process ends after about one month depending on the compaction level. More details on these phenomena are given in (Isacsson1986) and (Thinet 2000). Results of four experiments are presented for initial compaction levels from 54 to 84%, so the initial air

The principle of the device is based on compressional (P) and shear (S) waves propagation through a sample of material. It senses the large variations of macroscopic compressibility and shear modulus, which cause large variations of P- and S-wave velocity and damping as the material changes. The device is extensively presented in (Boutin1995)(Arnaud 1996, 2000, 2003). The main characteristic is the use of low frequency which ensures a good scale separation between wavelength and heterogeneity size. The characteristics of each material require a special value fp (see Table II). For *compressional waves*, referring to the case of cellular concrete, the actual initial velocity Cp is about 20m/s. Large wavelengths ($\lambda \approx 10$ cm) in comparison with the heterogeneity size ($h \approx 1$mm) are then achieved when using low frequencies $fp \approx 200$Hz. Consequently, waves are not scattered on the heterogeneities. For *shear waves*, very low frequencies ($fs \approx 20$ Hz) are used. On the one hand, large wavelengths are generated, a good scale separation is obtained; on the other hand, the thickness of the viscous layer, when the material is in a fluid state (very viscous), is large enough in comparison with the size of a representative volume of the material.

Transient plane (compressional or shear) waves are composed of five sine oscillations at constant amplitude followed by attenuated sine at the given frequency. P-waves and S-waves are successively generated and sensed by the transducers. Between each load, we wait until no signal is detected. From these signal recorded, we determine the wave velocities (Cp and Cs), the damping coefficients.

Low levels of load, pressure, strain and rates of strain are imposed, so that the test is non-destructive. This property is verified experimentally by successively applying proportional loads ranging from 0.15 to 2.5 times the usual load. We propose two examples of result concerning these measurements. Fig.1 is a plot of the signal recorded for the different loads ($0.75 < A < 12 m/s^2$) in the case of hydraulic concrete. These tests were performed at different moments during setting and hardening. We observe that the materials always behave linearly. Under small harmonic loads in the range of load tested, we can conclude that the behavior remains linear and that this test is non-destructive.



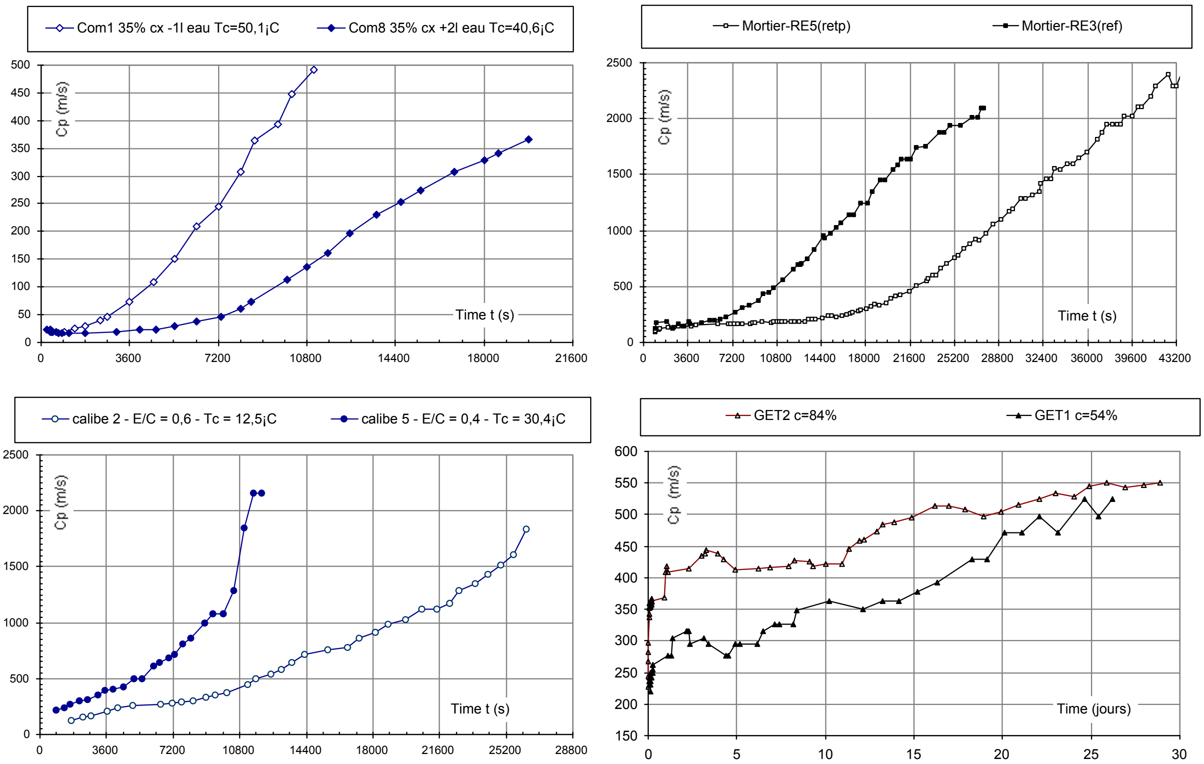


Fig.2: Velocity versus time, two different experiments for each material (Com=Cellular concrete, Mortier=Mortar, calibe=Concrete, GEB=Cold bituminous mix)

The evolutions versus time of the P-wave velocity are shown in Fig.2, for two different mix proportions of each material. From the simple measure of velocity, the mechanical evolution of the materials is monitored in a wide range. Depending on the material, the velocity ranges from 20 to 3000 m/s. The different stages are clearly identified in the material evolution. For cement based materials, two stages are observed. During the first one, the mechanical evolution is slow but is not nil. During this second period (hardening period), the velocity is strongly increasing. This transition can be linked to the threshold percolation.

In the case of cold bituminous mix, velocity increases quickly at the beginning: asphalt droplets are attracted to the solid aggregates. Then the material evolves slowly. Velocity increases slowly for 20 days with the evaporation of water and the construction of a bituminous skeleton between the aggregates.

In addition, for each material, the device is sensitive enough to distinguish two different mixes. In practice, it is also possible to use the device to measure variations in the mix such as those due to a change in the initial temperature, in the W/C ratio, in the binder content, or in the compaction level (see Fig.2). Conventional influences are observed: for instance with an increase of the W/C ratio, setting is retarded, and the delay is characterised from a qualitative and also quantitative point of view with the device. Another example is given for the cold bituminous mix. A higher initial compaction leads to an increase of the macroscopic rigidity at the beginning. But due to a lower void ratio, the evaporation phenomenon is slower (see Fig.5) [Villain 1997], [Thinet 2000] and [Arnaud 2002].
According to the shear waves' propagation, a comparison between the P-wave velocity and the S-wave velocity is given versus time in Fig.3 for two experiments on cellular concrete with similar mix proportions and initial conditions. We observe first a good repeatability of the measurements and second that the transition between the two stages is detected approximately at the same moment.

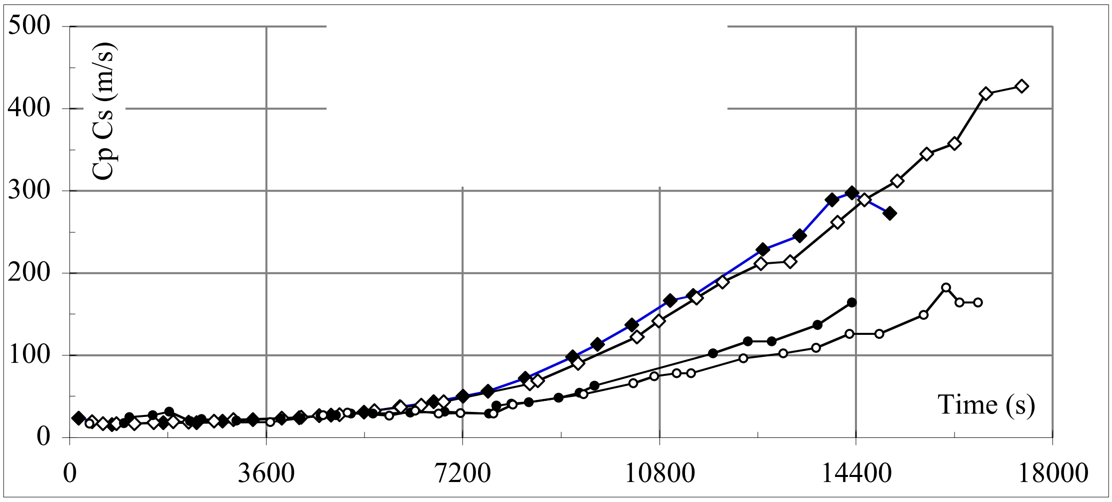


Fig.3: Comparison of P- and S- wave velocity versus time (celular concrete, two experiments, same mix proportions)

From the plots of P-wave velocity versus time, two periods (slow then rapid) are clearly identified. The evolution is close to an exponential increase. Therefore we define the optimal exponential curve fitting the evolution of C_p normalized by the initial velocity (C_p^O). This description leads to define a characteristic time τ: $C_p = C_p^O \exp(t / \tau)$. The evolution of the normalized velocity (C_p / C_p^O) as a function of the normalized time (t / τ), and the comparison of all the normalized evolutions are presented in Fig.4. An interesting result is then observed. All the "fresh" hydraulic concretes and mortars, whatever their formulation (25 experiments), roughly follow the same master curve. So the physical significance of this observation is that the second parameter C_p^O represents well the initial rigidity of the arrangement of the aggregates and air bubbles with water. The ratio C_p / C_p^O is then linked to the gain in compressibility due to the setting process. Table II lists the values of C_p^O and τ of the initial conditions for the experiments for mortar and concrete. *The parameter τ constitutes a good time base for the mechanical evolution.* It is clear that the mechanical evolution is related to the progress of the cement hydration. In order to better understand the possible link between the mechanical and chemical evolutions, we represent the normalised temperature evolution versus normalised time and we observe that the curves are not superimposed: temperature fits *chemical* evolution whereas τ is a good time base for the *mechanical* one during setting.

Inverse analysis: As the test of wave propagation is non-homogeneous, the rheological parameters are obtained from the measurements by means of an inverse analysis. By assuming a behaviour law for the material, the main characteristics of the propagation of plane waves in such a medium is related to the measurements at any moment. The analysis presented here is based on the measurement achieved with P-wave propagation. Then the rheological parameters are plotted versus time and the rheological evolution is discussed for each material.

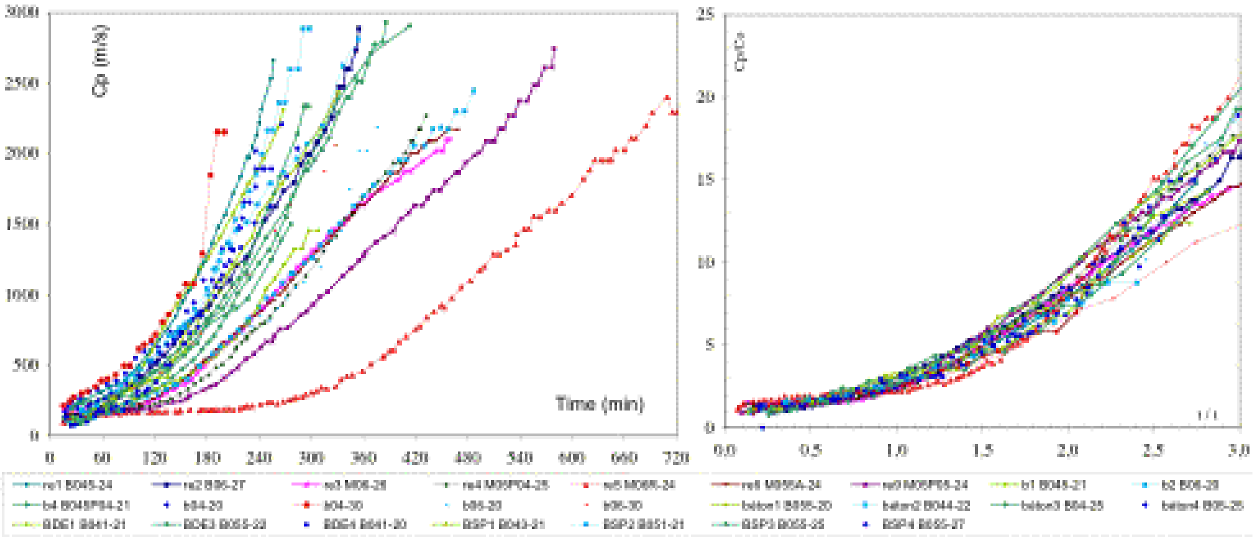


Fig.4: Comparison of P-wave velocities versus time (left side) and versus normalised time (right side) for 25 mixes of concrete and mortar (differences of water/cement ratio, admixture, initial temperature,…)

Discussion : As the test of wave propagation is non-homogeneous, the rheological parameters are obtained from the measurements by means of an inverse analysis. These materials present time-dependent properties because of the setting and hardening processes. At each instant, the material is assumed to be a suspension of gas bubbles (c is the finite gas concentration and $1/Kg$ its compressibility) in a viscoelastic time-dependent matrix (density ρm, its complex viscoelastic shear modulus Mm and its compressibility $1/Km$). By means of the homogenisation technique, we determine the isotropic macroscopic behavior of the equivalent medium submitted to small harmonic loads (Arnaud 2000): $\sigma = (K + aMm\ div(\mathbf{u})).I + 2bMm\ \varepsilon(\mathbf{u})$. σ is the macroscopic stress tensor related to $\varepsilon(\mathbf{u})$ the macroscopic strain tensor. The scalars a and b are form factors which only depend on the local geometry, which enables us to adapt the modelling to the study of the different materials. This modelling describes a *viscoelastic compressible medium*. The matrix only appears via its shear modulus Mm and the macroscopic moduli (shear and volume) are proportional to Mm by form factors a and b. The contribution of the gas appears in the effective compressibility $K(= \gamma Pg/c$ where $\gamma = 1.4$ is the ratio of specific heat coefficients, the gas phase remains in quasi-adiabatic conditions because for the frequency used, $Pg = 10^5\ Pa$). c, the gas phase concentration, is measured precisely (about 1 to 3% for hydraulic concrete, 5% for mortar, 20% for cold bituminous mix and 50% for cellular concrete). It is important to note that due to the presence of air bubbles, even under macroscopic purely **isotropic strain**, it is the **shear properties** of the interbubble matrix which act. So, the role of gas bubbles is fundamental even when the gas volume is low, as it is the case for hydraulic concrete. As the macroscopic compressibility $1 / K$ can be evaluated, the advantage of this analysis is to obtain rheological measurements directly linked to the time-dependent matrix properties (Mm).

For two experiments of all materials, the evolutions of $E = |E|\ e^{i\phi} = K+(a+2b)Mm$ are plotted in Fig.5. as function of t. Due to the volume of the gas phase, at the very beginning the order of magnitude of K and $(a+2b)Mm$ are of the same order of magnitude ($10^7\ Pa$). Despite this difference, the previous physical analysis remains valid with the different stages: creation of unconnected hydrates which leads to an increase in the matrix viscosity (ϕ goes from 45 to $90°$), then percolation threshold of hydrates followed by the hardening process (increase in the modulus, important decrease in the viscoelastic phase).

For the cold bituminous mix, the evolution is significantly different. The setting and hardening results from the strong difference in the shear modulus of asphalt as compared to water. The water content has a strong influence on the mixing process and also on the compaction process. There is optimum water content for the mix, and at this optimum the highest density ratio would be obtained. And when the density is at its maximum for a given mix proportion, the resulting properties of the pavement would be better, but the evaporation phenomenon could be blocked. So the water content is limited, and these mixes are very « dry » compared to concrete. Compaction requires a great amount of work. The resulting aspect of the paste is a compact arrangement of solid particles $(|E| \approx 5\ 10^7\ Pa)$. After 30 days, the modulus is only multiplied by a factor of *10*. The first results presented here show the influence of the compaction level on the setting kinetics. It seems that, for the same mix proportion, an increase in compaction tends to accelerate the early age evolution but the coupled effect is to reduce the porosity of the paste and consequently to reduce the rate of evaporation, so that, afterwards, the material evolves more slowly.

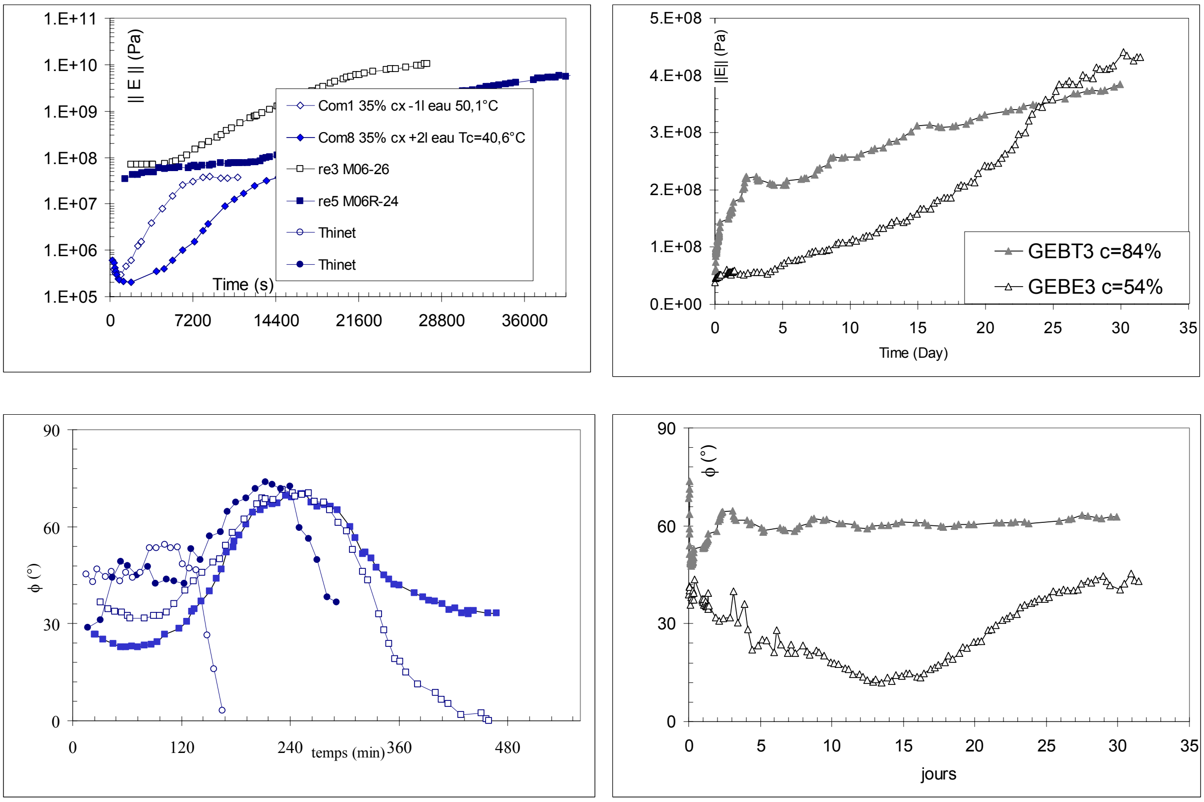


Fig. 5: Evolution of complex œdometric modulus $E = |E|\ e^{i\phi} = K+(a+2b)Mm$ versus time, modulus (top), phase (bottom), two examples of each material (cement based materials, left side, cold bituminous mixes, right side).

Conclusions : This article focuses on experimental measurements on very different materials (cellular concrete, mortar, hydraulic concrete and cold bituminous mix) when they are setting and hardening. Such materials cover a wide range of properties of materials that are used in the civil engineering field. By means of an experimental device based on the propagation of compressional and shear waves at low frequency (20 to 800Hz), non destructive tests makes it possible to monitor the mechanical evolution of such different materials. This device is of interest since very few mechanical measurements can be achieved on « fresh » material while it is setting and hardening. The first measurements are obtained only 15 minutes after the end of mixing needed for the placing of the material inside the test container.

These experimental data obtained from the device are then used to calculate rheological parameters attached to the time-dependent materials by means of an inverse analysis. Different levels are presented to characterise the viscoelasticity of the bulk medium and then the viscoelasticity of the interbubble matrix. The oedometric complex modulus is first calculated then the shear complex viscoelastic modulus is determined for each material. The usual influences of the initial temperature, the Water/Cement ratio and the compaction level on the setting and hardening periods are observed and discussed. It is important to note that these influences can be quantified.

Some results have been established. On mortar and hydraulic concrete, from the (P or S-) wave velocity, a characteristic time is defined by approximating the velocity evolution curve as best as possible with an exponential function. This parameter constitutes a relevant time base for the mechanical evolution for fresh material, whatever the mix proportion tested. This characteristic time is shown to be very different from the chemical evolution of the material. It is also observed that the velocities of mortar and hydraulic concrete, normalised by the initial velocity, follow the same master curve.

For all the cellular concrete mix proportions tested, it appears that the relationship between real and imaginary parts of the shear viscoelastic modulus follows roughly the same curve which characterises the rheological evolution of the matrix (time appears only as a parameter). This leads us to consider that the evolving microstructure presents identical rheological states even if the setting kinetics differ. Significant differences are observed between mortar and cellular concretes.

The device is used to analyse the influence of admixtures on the behavior of fresh concrete. This approach can also be adapted to the study of other time-dependent heterogeneous materials during their mechanical evolutions in civil engineering and also in other fields involving different time-dependant processes.

References : Arnaud L., Boutin C., Villain G. (1995) The setting of cement pastes followed up by the vibroscope" Proc. of the Int. Symp. on Non-Destructive Testing in Civil Engineering (NDTE) ed. by Schickert and Wiggenhauser, Berlin Germany, Sept. 95, P 1323-1330.

Arnaud L., Thinet S. (2000) A device to monitor continuously the setting of concrete, Proc. of *15th World Conf. On Non Destructive Testing* – Rome 15-21/10/2000.

Arnaud L., Thinet S. (2003) Rheology of concrete during setting and hardening. Experimental approach and rheological measurements., *Materials and structures*, Vol. 36, july 2003, pp 355-364.

Arnaud L., Villain G., Boutin C. (2000) Mesures rhéologiques sur matériaux en cours de prise, *C. R. Acad. Sc. Paris*, t. 328, Série II b, 217-223.

Arnaud L., Villain G., Boutin C. (2000) Rhéologie des matériaux en cours prise : II. Approche théorique, C. R. Acad. Sc. Paris, t. 328, Série II b 855-862.

Boutin C., Arnaud L., Mechanical characterization of heterogeneous materials during setting, *Eur. J. Mech. A/Solids,* 14, 4, pp. 633-656, (1995).

Boumiz, A., Vernet, C., Tenoudji, F. C. (1996) *Advanced Cement Based Materials* 3, Nr. 3/4, S. 94-106.

Grosse C.U., Reinhardt H.W. (2000) Ultrasound technique for quality control of cementitious materials, Proc. of *15th World Conf. On Non Destructive Testing* – Rome 15-21/10/2000.

Isacsson U. (1986) Une synthèse des méthodes de laboratoire pour étudier la stabilité des émulsions bitumineuses, *Bull. Liaison du LCPC,* 141, p. 67-80.

Nachbaur L., Sedran T., de Larrard F. (2001) Rhéométrie du béton. Comparaison de rhéomètres, Rhéologie du béton hydraulique en cours de prise, Proc. of 36ème Coll. du GFR – Paris 10-12/10/2001.

Reinhardt H.-W., Grosse C. U. (1996) Setting and hardening of concrete continously monitored by elastic waves, Proc. of the Int. RILEM Conf., Paisley/Schottland, pp. 415-425.

Sayers C.M., Dalhin A. (1993) Propagation of ultrasound through hydrating cement pastes at early times, *Adv. cement based materials*, 1, pp. 12-21.

Thinet, S. (2000) *Caractérisation rhéologique de matériaux hétérogènes évolutifs par propagation d'ondes acoustiques*, Thèse Eccole MEGA (ENTPE/INSA), 264 p.

Villain G. (1997) *Caractérisation de la prise des matériaux à base de ciment par propagation d'ondes acoustiques et ultrasonores*, Thesis ENTPE/INSA, 326 p.