JOURNAL OF MATERIALS SCIENCE **37** (2002) 3847–3853

Ultrasonic characterization of model mixtures of hydrated aluminous cement

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In an aluminous cement, which mainly consists of CA, the stable phases arising during hydration are C_3AH_6 and AH_3. This communication presents a chemical route for the synthesis of C_3AH_6 which is based on hydration of C_3A. Mixtures of CA, C_3AH_6 and AH_3 are characterised by ultrasonic testing. The ultrasonic velocity obtained on these mixtures is lower than what is observed in hydrated aluminous cement of similar chemical composition. Interfaces are thought to play a significant role in the ultrasonic response of aluminous cements. © *2002 Kluwer Academic Publishers*

1. Introduction

Aluminous cements consist mainly of calcia and alumina which combine to give anhydrous phases, the major being $CaO \cdot Al_2O_3$ noted CA[†]. On mixing with water and depending on the experimental conditions such as temperature, relative humidity and setting time, different hydrates are formed, namely CAH_{10}, C_2AH_8, C_3AH_6 and AH_3 [1–6]. The stable phases are C_3AH_6 and AH_3 and the other hydrated phases inevitably convert to these at a rate that depends on time, temperature and/or relative humidity. One of the key issue with such materials is to be able to predict the long-term behaviour of set systems. The most obvious approach in order to predict the mechanical behaviour of set aluminous cement is to examine simpler systems in terms of chemical composition such as single hydrates or a mix of hydrates with CA. In this paper, we wish to examine to mechanical behaviour of a three-phase system containing CA, C_3AH_6 and AH_3. The first part is devoted to the description of the preparation and characterisation of the single hydrate C_3AH_6, and the second part concerns with the mechanical characterisation by ultrasonic testing of the different mixes. The use of experimental design to predict the longitudinal wave velocities (V_L) and the influence of each constituent on it will be presented.

2. Synthesis and characterisation of C_3AH_6

C_3AH_6 is usually obtained from the hydration of C_3A. The synthesis of C_3A is derived from the method described in the literature [7–9]. It is based on the combustion of calcium and aluminium nitrates with citric acid according to reaction (1):

$$3Ca(NO_3)_2 + 2Al(NO_3)_3 + 10/3C_6H_8O_7 \rightarrow 20CO_2 + 6N_2 + (CaO)_3Al_2O_3 + 40/3H_2O \quad (1)$$

The final product has been characterised by X-rays diffraction, XRD (INEL CPS 120 curved diffractometer) and it is composed of C_3A exclusively (Fig. 1); it is called 'C_3A powder'. C_3A powder is mixed with water. For clarity, the resulting mixture is called 'the paste'. In theory, C_3A reacts with water to give C_3AH_6 according to reaction (2):

$$C_3A + 6H \rightarrow C_3AH_6 \quad (2)$$

Fig. 2a to c presents the XRD spectra of this mix at increasing times after mixing. If we look at 2 min after mixing (Fig. 2a), the only crystalline phase, which is detected, is C_3A. Moreover, some interesting observations can be done comparing Fig. 2a and Fig. 1. The recorded areas (number of counts in arbitrary unit) for the five most intensive peaks have notably decreased compared to the initial product (Table I). For example, the number of counts for the (440) plane falls from 19463 to 14438 for the starting powder and at 2 min after mixing sample, respectively. This result suggests that some C_3A powder has already started to react with water. In addition, if we consider the diffraction pattern of Fig. 2a at the lowest 2θ values ($2\theta < 20°$), we can observe a slight dome in the XRD pattern. This can be attributed to the existence of an amorphous phase. Fig. 3 shows the temperature recorded inside the paste just after mixing C_3A powder with water in the stoechiometric amounts. We can note an important increase in temperature at the beginning of the experiment. Since no other crystalline phase apart from C_3A is detected, it means that an amorphous material, possibly with the composition C_3AH_6, has been formed and this reaction is associated with an important heat exchange. At 24 and 72 h after mixing the constituents, crystallised C_3AH_6 is detected by XRD (Fig. 2b and c). This transformation between

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[†] Shorthand notation is used: C = CaO, A = Al_2O_3, H = H_2O.

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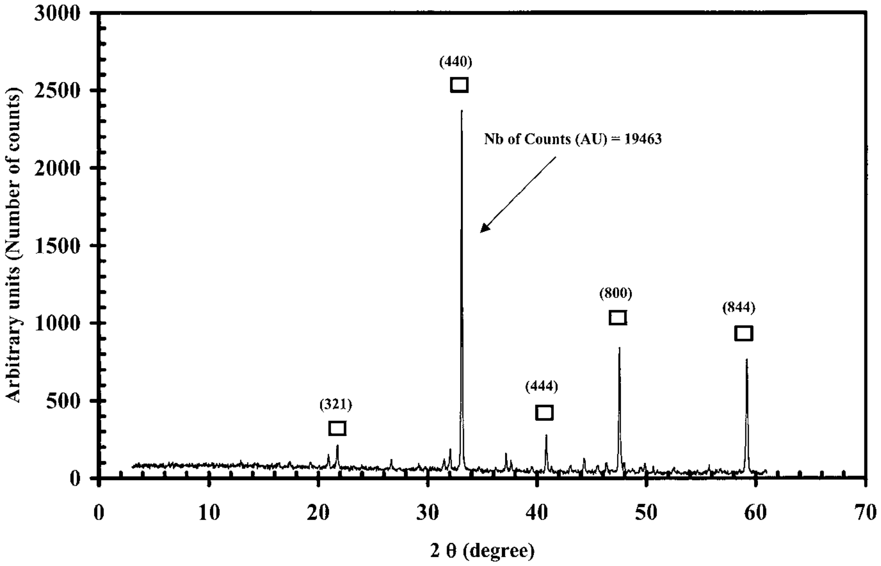
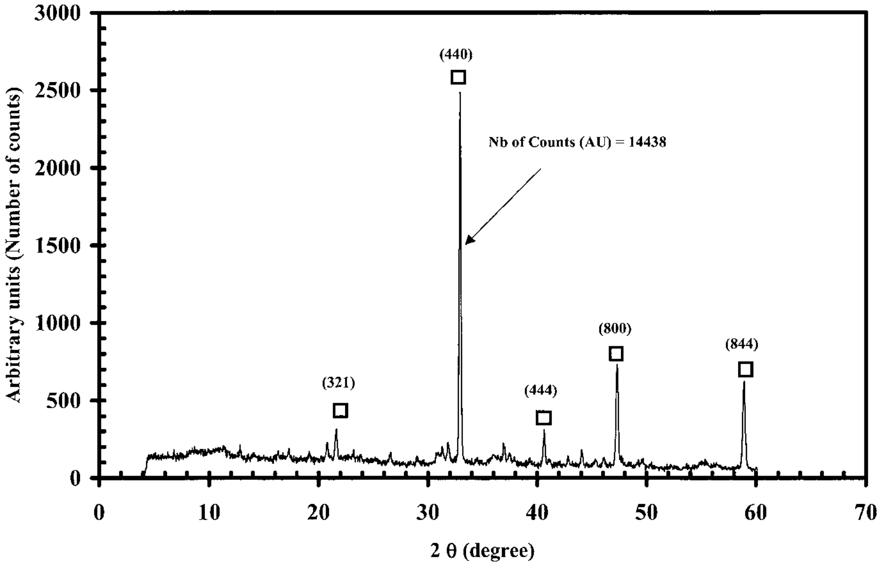
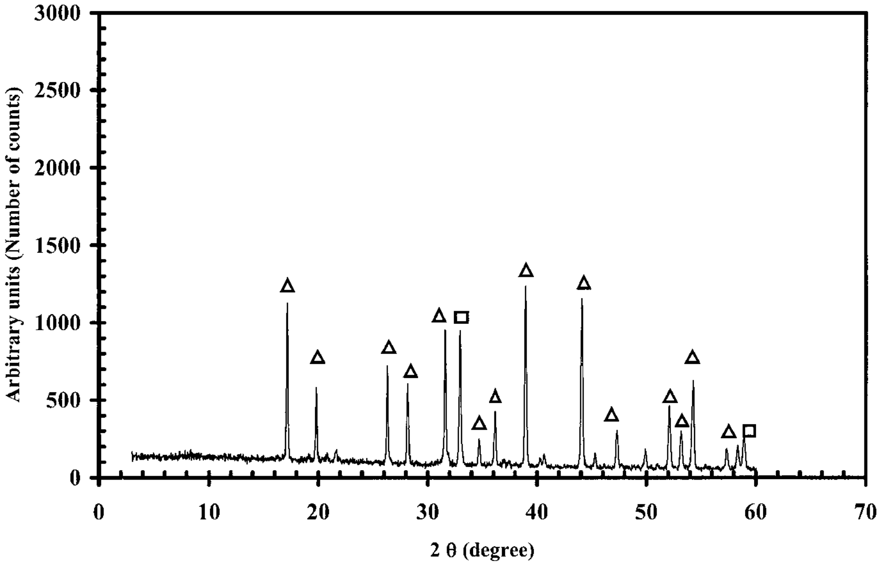


Figure 1 XRD spectra for C_3A powder. The most intensive diffraction peaks with the corresponding (*h k l*) planes are labelled.

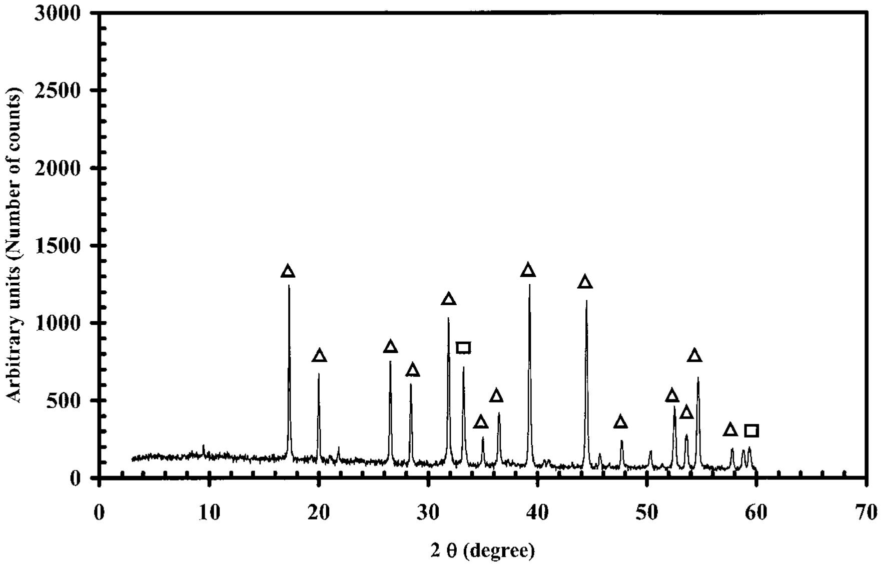


(a)



(b)

Figure 2 XRD spectra for the paste at different times after mixing with water; 2 min (a), 24 h (b) and 72 h (c). Symbols: □ C_3A, △ C_3AH_6. (*Continued.*)



(c)

Figure 2 (*Continued*).

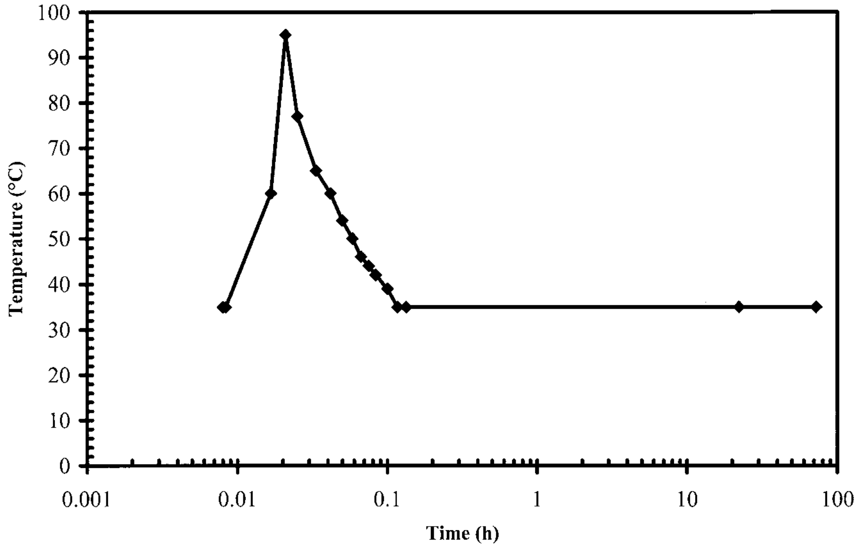


Figure 3 Temperature inside the paste as a function of setting time elapsed after mixing C_3A powder with water.

TABLE I Values of the number of counts (AU) for the fives most intensive XRD peaks in the case of C_3A powder alone and at 2 min after mixing C_3A with water. The number of counts corresponds to the surface area underneath the peak

	C_3A powder (Fig. 1)	C_3A + water 2 min after mixing (Fig. 2a)
(*hkl*) Plane	Nb of counts (AU)	Nb of counts (AU)
(321)	4536	2276
(440)	19463	14438
(444)	3802	2275
(800)	9053	6629
(844)	7817	6119

amorphous and crystalline forms is without any modification in the temperature.

The quantity of unreacted C_3A, which is still present in the paste just after mixing C_3A powder and water, has been quantified by X-rays dosage. Reference media have been prepared by mixing intimately ZnO ($m_{ZnO} = 0.04$ g) with increasing quantities of C_3A ($m_{C_3A} = 0.012$ to 0.04 g). Each sample is analysed by XRD. By measuring the area of the most intensive peak for ZnO and for C_3A (namely I_{ZnO} and I_{C_3A} for (101) at $2\theta = 36.253°$ and (440) at $2\theta = 33.169°$, respectively), we define a ratio as follows:

$$I = 100\frac{I_{C_3A}}{I_{ZnO}} \qquad (3)$$

and the corresponding reference curve is shown in Fig. 4.

At different times after hydration, 0.04 g of the paste is analysed by XRD. It is then mixed with 0.04 g of ZnO. It is calculated according to (3) and the weight percentage of unreacted C_3A still present in the paste is deduced from Fig. 4. Results are summarised in Table II. These data show that 2 min after mixing, 37 wt% of unreacted C_3A remains in the paste and consequently the rest of C_3A has converted into amorphous material. Its transformation into crystalline C_3AH_6 occurs over longer period of time. For instance, at 72 h after mixing,

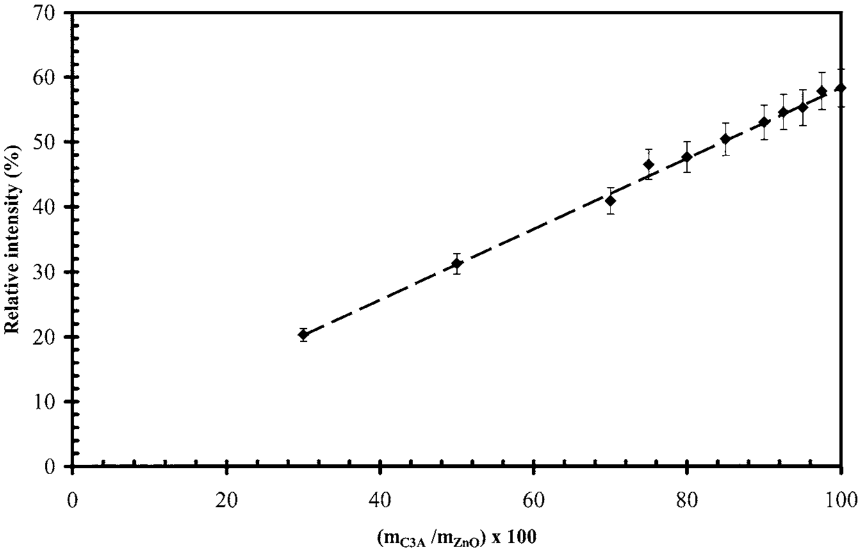


Figure 4 Reference curve for quantitative dosage of C_3A.

TABLE II Quantitative determination of C_3A inside the paste at increasing times after mixing C_3A powder with water

Time after mixing	Relative intensity (%)	C_3A weight%
2 min	24.1	37.00
2 h	22.9	35.00
6 h	23.0	35.00

unreacted C_3A is still present in the paste (Fig. 2c). A complete transformation of C_3A into C_3AH_6 requires a modification of the experimental procedure. C_3A powder has to be mixed with an excess water, heated at 120°C under 3 bars for 72 h. After this hydrothermal synthesis, only crystalline C_3AH_6 is detected by XRD.

3. Ultrasonic characterisation of CA, C_3AH_6, AH_3 and prediction of longitudinal waves velocity

Seven compositions containing different amounts of CA, C_3AH_6 and AH_3[‡] have been studied (Table III). C_3AH_6 and AH_3 correspond to the crystalline forms of the hydrates. These compositions are chosen according to an "optimal" experimental design in order to establish a polynomial model of the ultrasonic velocity. The CA compound has been prepared by mixing $CaCO_3$[§] and Al_2O_3[§] in the 1 : 1 molar ratio. The starting powders have been milled by attrition in propanol for three hours. After solvent removal, the resulting mix has been treated in air at 1400°C for 2 hours. This temperature is necessary to obtain a crystallised CA phase. CA is then ground to get the final CA powder with a particle size that ranges between 1 and 100 μm. Prior to mixing the CA powder with water, a thermal treatment at 300°C (calcination), already studied by Gessner *et al.* [10], for 1 hour has been carried out to insure a complete desorption of gases such as carbon dioxide and water that can be adsorbed at the surface of the particles during storage. For each composition, disks of various densities are prepared by uniaxial pressing (diameter: 30 mm; thickness, d: 8 mm; compaction pressure: 1 to 6 bars). The density, and consequently the porosity, is deduced from mass and volume measurements. Ultrasonic measurements have been carried out on the different disks. The velocities of longitudinal wave have been measured according to the pulse transmission method [11–14]. A Pulse generator/receiver system (Panametric 5072PR) and two piezoelectric transducers (Ultran W038 10 MHz) have been used. One transducer (transmitter) is applied on one face of the disk and sends directly ultrasonic waves across it. A second transducer (receiver) collects the waves on the other face. The received signal is recorded and analysed on a digital oscilloscope (Lecroy wave runner LT 322). The transit time, τ, is measured and is related to the longitudinal wave velocity, V_L, as follows:

TABLE III Compositions tested by ultrasonic measurements

Composition	CA (weight%)	AH_3 (weight%)	C_3AH_6 (weight%)
1	2.50	2.50	95.0
2	95.00	2.50	2.50
3	2.50	95.00	2.50
4	48.75	2.50	48.75
5	48.75	48.75	2.50
6	2.50	48.75	48.75
7	33.33	33.33	33.33

$$V_L = \frac{d}{\tau} \tag{4}$$

The experimental setup is described on Fig. 5. Fig. 6 shows a typical curve of V_L as a function of porosity (in vol%). From the data collected on the seven compositions, we can estimate for a given porosity the ultrasonic longitudinal velocity of any composition within the ternary phase diagram CA, C_3AH_6 and AH_3 by using a software (NEMROD) for experimental design [15, 16]. Fig. 7 presents a map of ultrasonic velocities for a material which has a porous volume fraction of 0.20. The used polynomial model is a "reduced order 3" model. The values range between 1400 to about

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[‡] AH_3 Rectapur from PROLABO.

[§] Aldrich.

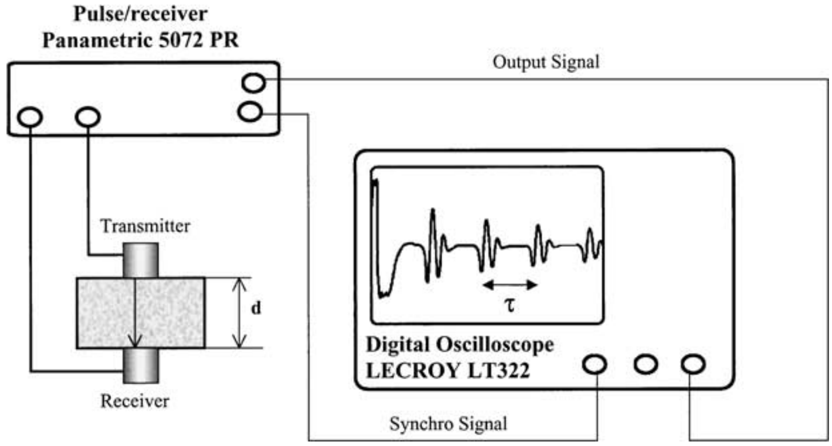

Figure 5 Experimental setup for measuring the ultrasonic velocity inside the different samples presented in Table III.

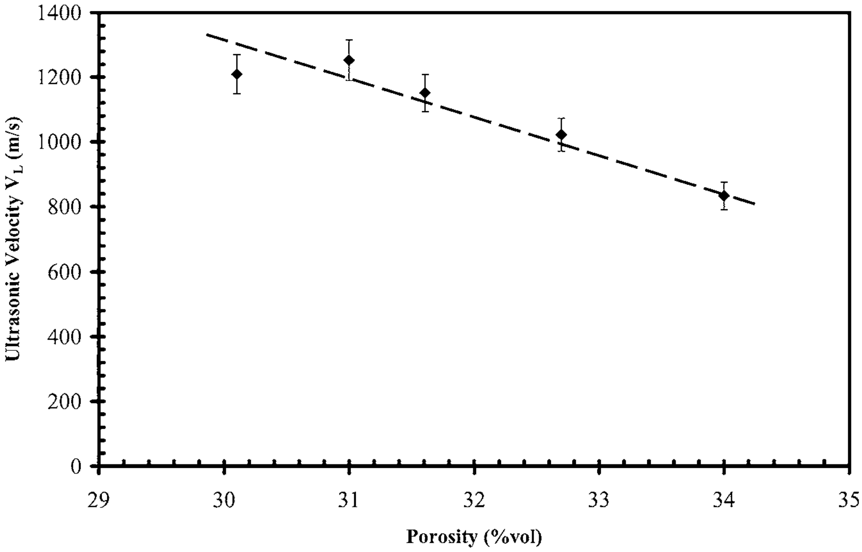

Figure 6 Ultrasonic velocity (in m · s^{-1}) as a function of porosity (in vol%) for mixture n°7.

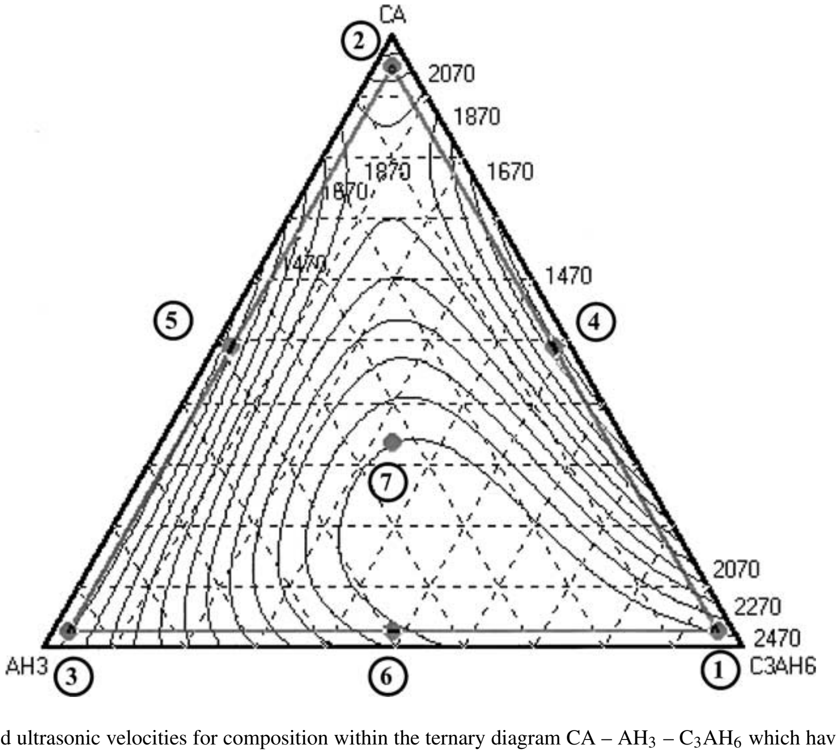

Figure 7 Map of predicted ultrasonic velocities for composition within the ternary diagram CA – AH_3 – C_3AH_6 which have 20 vol% porosity. The compositions of Table III are noted on the diagram. The points correspond to the experimental measurements.

$2500\ \mathrm{m \cdot s^{-1}}$. These values are lower than what is obtained on a cementitous material of similar porosity and which contains the same chemical constituents. For an aluminous cement, which is 24 h old and has been kept at 60°C and 95% relative humidity and where the mineral constituents are CA, C_3AH_6 and AH_3, the recorded velocity is equal to $3800\ \mathrm{m \cdot s^{-1}}$, C_3AH_6 and AH_3 are crystalline [17]. It shows that predicting the ultrasonic properties of a cementitous system from the behaviour of a porous material where the different constituents are not interacting with each other is not sufficient. In particular, the chemical interfaces between the different components probably play a role in the propagation of ultrasonic waves. To our knowledge, the role of pore morphology on the elastic properties of porous ceramics has been modelled [17, 18] but not the role of chemical interfaces or grain boundaries between phases. Nevertheless, despite the fact that the calculated velocities are lower than what is measured experimentally in the final product, it is interesting to exploit further the data of Fig. 7 in order to estimate the contribution of each constituent on the value of V_L. The methodology consists in choosing a reference composition on the ternary diagram, then plotting a line that goes through one apex and a reference composition. Such line is known as Cox or Pieppel line in an experimental mixture design [16]. Finally, for the different compositions along this line, the ultrasonic velocity (V_L) can be estimated. In the present study, the chosen reference composition is N°7 (Table III). Fig. 8 presents one line that passes through

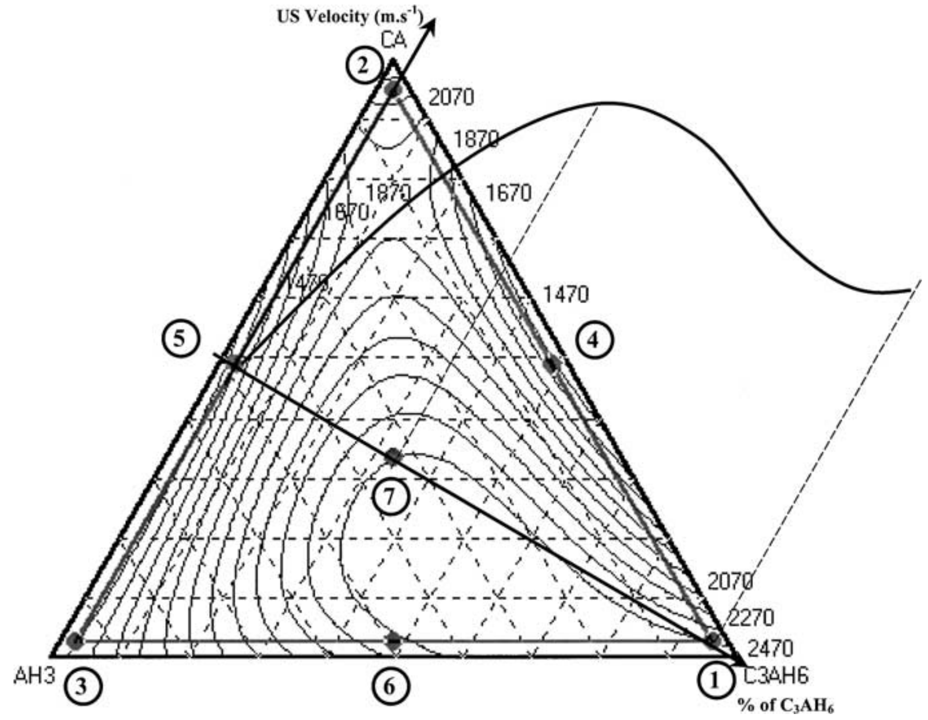

Figure 8 Map of predicted ultrasonic velocities for composition within the ternary diagram CA – AH_3 – C_3AH_6 (20 vol% porosity). The curve corresponds to the contribution of the % of C_3AH_6 on the evolution of the ultrasonic velocities. The chosen reference composition is N°7 (Table III).

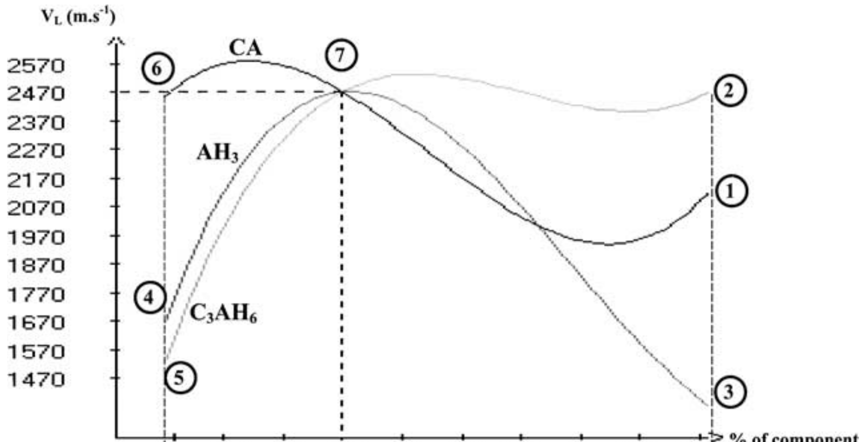

Figure 9 Contribution of the percentage of each constituent on the evolution of the predicted ultrasonic velocity deduced from the ternary diagram CA – AH_3 – C_3AH_6 (20 vol% porosity). The chosen reference composition is N°7 (Table III). The other compositions of Table III are noted on the diagram.

the C_3AH_6 apex; along this line, the ratio of the other two constituents (CA and AH_3) is constant. The variations of V_L are plotted on this figure for increasing percentage of C_3AH_6. The same procedure has been carried out for lines going through the other two apices and composition N° 7. The results are plotted on Fig. 9. It can be seen that by varying the CA percentage between 2.5 and 95%, it gives V_L values ranging between 1970 and 2570 $m \cdot s^{-1}$. If we examine the case of C_3AH_6 or AH_3, we notice that compositions containing either low amounts of C_3AH_6 or AH_3 present small velocities values, of the order of 1500 and 1670 $m \cdot s^{-1}$ (compositions N°4 and N°5). However, C_3AH_6 contributes to high V_L values compared to AH_3 when its content is high (comparison between compositions N°2 and 3 in Fig. 9). This behaviour can be due to dissimilarities in densities (2.42 $g \cdot cm^{-3}$ and 2.57 $g \cdot cm^{-3}$ for AH_3 and C_3AH_6, respectively), or to difference in the structural state (C_3AH_6 crystals are bigger than AH_3 ones [17]), or the difference in the type of chemical bonding in the two components.

4. Conclusion

C_3AH_6 has been prepared from the hydration of chemically synthesised C_3A. After mixing with water, the material is essentially amorphous and crystallises progressively into C_3AH_6. In order to reproduce a typical phase composition of an hydrated aluminous cement material, C_3AH_6 is mixed with CA and AH_3. Measurement and simulation of ultrasonic longitudinal wave velocities on mixtures of these three constituents give values that range between 1400 and 2500 $m \cdot s^{-1}$. Amongst the two hydrates, C_3AH_6 gives the highest contribution to the ultrasonic velocities. Nevertheless, these values are lower than in an hydrated aluminous cement. It shows that predicting the ultrasonic properties of a cementitous system from the behaviour of a porous material where the different constituents do not present chemical interfaces is too simplistic and that the role of interfaces should be taken into account.

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Received 19 November 2001
and accepted 14 May 2002