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Chemical stability of cementitious materials based on metakaolin

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Abstract

The alkali activation of metakaolin is a way of producing high strength cementitious materials. The processing of these materials has been the subject of numerous investigations. The present paper describes the results of a research project initiated to study the stability of these materials when exposed to aggressive solutions. Prisms of mortar made of sand and alkali-activated metakaolin were immersed in deionized water, ASTM sea water, sodium sulfate solution (4.4% wt), and sulfuric acid solution (0.001 M). The prisms were removed from the solutions at 7, 28, 56, 90, 180, and 270 days. Their microstructure was characterized and their physical, mechanical, and microstructural properties were measured. It was observed that the nature of the aggressive solution had little negative effect on the evolution of microstructure and the strength of these materials. It was also found that the 90-day and older samples experienced a slight increase in their flexural strengths with time. This tendency was most pronounced in those samples cured in sodium sulfate solutions. This behavior may be related to the change in microstructure of the cementitious matrix of the mortars cured longer than 90 days. Some of the amorphous material present had crystallized to a zeolite-like material belonging to the faujasite family of zeolites.

Keywords: Thermal analysis; X-ray diffraction; Physical properties; Alkali-activated cement; Metakaolin

The use of calcined clays as a pozzolanic additive for cement has been known since the time of the Romans. However, in spite of its historical significance, the use of metakaolin as a pozzolanic additive for modern cement and concrete has not been very popular. This may be due to the relatively high cost of metakaolin compared to that of other pozzolanic materials such as fly ash and finely divided silica.

Nevertheless, the utilization of metakaolin as a mineral admixture for cement and concrete is a well documented practice; numerous references can be found in the literature [1,2]. One is also able to find papers dealing with metakaolin's influence on the microstructural development of concrete and consequently on some of the properties directly related to its durability. For example, metakaolin improves mechanical strength [3], reduces the transport of water and salts through the sample [4,5] and prevents the alkali-aggregate reaction from occurring [6].

Metakaolin has also been used for other very different purposes. For example, it has been found that alkali activation of metakaolin is a way of making new cementitious materials (hydroceramics—ceramic-like materials synthesized from a solid aluminosilicate and an alkali-rich solution at low temperatures, $<100°C$). Metakaolin is essentially an anhydrous aluminosilicate that is produced by the thermal decomposition of kaolin, a naturally occurring clay basically containing kaolinite [$Al_2Si_2O_5(OH)_4$] and trace amounts of silica and other minerals. The hydroxyl ions are strongly bonded to the aluminosilicate framework structure; thus only temperatures in excess of 550°C are capable of eliminating them. During the dehydroxylation process, a considerable atomic readjustment is produced. The final result is a partially ordered structure that cannot rehydrate in the presence of water (or does so very slowly). Due to its disorder and X-ray amorphous nature, it possesses a huge reactive potential when in the presence of an alkali/alkaline earth containing solution.

It is clear that the products that form are complex alkali aluminosilicates. Davidovits [7] described the alkali activation of metakaolin using a polymerization model similar to that proposed to describe the formation of zeolites or zeolite precursors from alkali aluminosilicate solutions. More recently, the authors have focused on the identification of the fundamental factors that control the synthesis of metakaolin-based hydroceramics (alkali activation at temperatures between 35 and 85°C), their characterization, and the evaluation of their usefulness in a commercial setting [8–11]. The current work is an extension of this earlier work. It deals with the performance of these materials when exposed to

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Table 1
Chemical composition of the starting materials

Composition of kaolinite (%wt)				Composition of sodium silicate (%WT)
SiO_2	49.8	Na_2O	Not determined	SiO_2, 28.01 Na_2O, 8.53 H_2O, 62.99 Density, 1.40 g/cm^3
Al_2O_3	36.34	K_2O	Not determined	
Fe_2O_3	0.57	TiO_2	Not determined	
MgO	0.15	L.O.I.	12.65	
CaO	0.00	Total	99.51	

various aggressive solutions. It has been found that these materials are remarkably durable.

1. Methods

1.1. Materials

The chemical composition of the kaolin together with the analysis of the water glass used in the present investigation are given in Table 1. Other constituents used for making samples consisted of a very pure sand (>99% wt quartz) and reagent grade NaOH pellets.

1.2. Preparation of prisms of activated metakaolin

A sodium hydroxide solution was prepared (44.738 g of NaOH plus 51.387 cc of deionized water). When the solution had cooled slightly, it was mixed with 102.568 g of water glass. The hot liquid was then mixed with 133.897 g of metakaolin using a planetary mixer. The paste was typically mixed for 3 min to ensure that the mixture was homogeneous. During this period, 167 g of sand were added to the mixture in small increments. The paste was then poured into prismatic molds (1 × 1 × 6 cm) and allowed to cure in a laboratory convection oven at 85°C for 2 h. After curing, the prisms were extracted from the molds, visually examined for soundness, and then subjected to the following series of "aggressive" solution testing.

1.3. Immersion of prisms in aggressive solutions

Groups of prisms were placed in glass jars containing deionized water (reference test), sodium sulfate solution (4.4% wt), sea water (ASTM D 1141-90), and sulfuric acid solution (0.001 M). Bottles were maintained at room temperature throughout the test. After 7, 28, 56, 90, 180, and 270 days, the prisms were extracted from the different solutions and characterized (see Fig. 1 for an example of prisms immersed in solution).

1.4. Characterization of materials

The prisms were analyzed using X-ray powder diffraction analysis (Philips PW 1700 diffractometer, The Netherlands), infrared spectroscopy (FTIR) (ATI-Genesis, USA), DTA/TGA (Netzsch STA 409, Germany), three-point flexural strength testing (European Standard EN 196-1 press, Netzsch 6111.2, Germany), and porosity accessible to water [12].

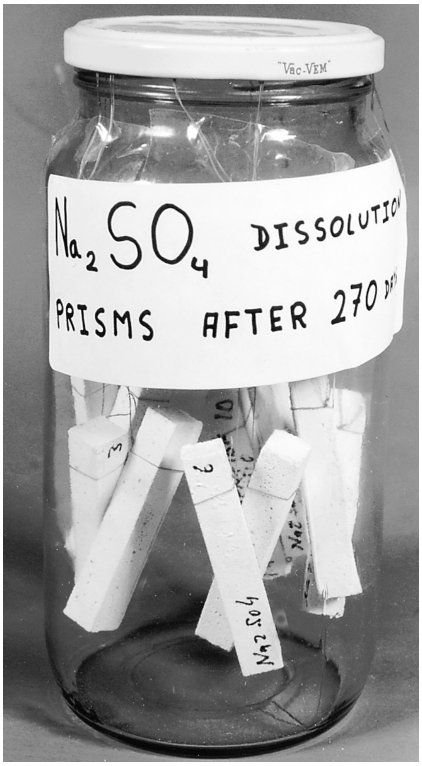

Fig. 1. Photograph of prisms after 270 days in Na_2SO_4 solution.

1.5. Flexural strengths and porosity

Fig. 2 shows the evolution of the flexural strengths of the prisms as a function of time and aggressive medium. Each point was determined using six prisms. As a general rule (independent of the nature of the solution in contact with the prisms), it is observed that during the first three months of

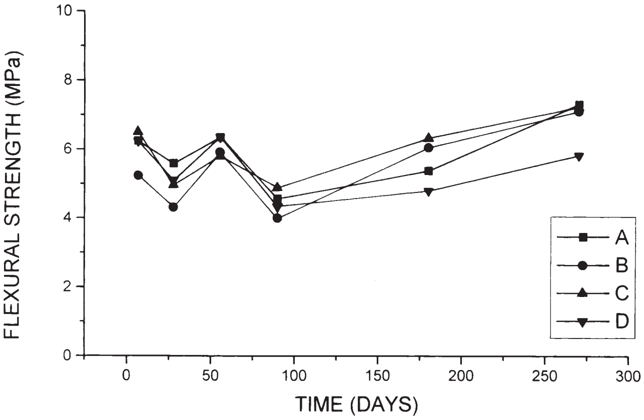

Fig. 2. Evolution of the flexural strengths as a function of time and aggressive solution. A = deionized water; B = acid dissolution; C = Na_2SO_4 dissolution; D = seawater. Pastes precured for 2 h at 85°C, followed by room temperature immersion.

Table 2
Development of porosity (volume %) as a function of time (days)

Sample	7 days	28 days	56 days	90 days	180 days	270 days
Deionized water	26.97	31.18	26.16	32.33	30.25	27.56
Na_2SO_4	26.60	28.83	24.98	29.52	25.19	24.99
Seawater	26.43	28.93	25.61	30.85	29.10	27.26
H_2SO_4	27.40	31.25	27.17	32.41	29.54	27.98

immersion, the strengths of the prisms fluctuate with time—values range from 4.0 to 7.5 MPa. This fluctuation is similar regardless of the nature of the aggressive solution. Between 7 and 28 days, the strengths of the prisms decrease; between 28 and 56 days, they recover their strengths; and between 56 and 90 days, strengths fall once again. After that, from 90 days until the samples are 270 days old, all of the prisms acquire mechanical strength continuously.

In the fluctuation stage, between 1 week and 3 months, the prisms submerged in acid consistently had the lowest flexural strengths of the group. However, after 3 months of attack and until the conclusion of the trial (9 months), the prisms submerged in seawater became the ones that most commonly exhibited inferior strengths relative to their peers. Interestingly, the flexural strengths of the prisms submerged in deionized water, in sodium sulfate solution, and in the acid solutions maintained very similar values.

Table 2 shows the porosity values of the prisms before they were mechanically tested. Each number represents a single sample. Note that the evolution of porosity with time of immersion is opposite to that of strength development.

1.6. X-ray diffraction

Before being analyzed by X-ray diffraction (XRD), the samples were ground and sieved to remove most of the quartz sand from the sample; therefore the diffraction lines representing quartz turned out to vary quite a bit from sample to sample. This is an artifact that does not influence interpretation of the results of the present paper and therefore it will be ignored. An example of the evolution of the diffraction lines of some samples immersed in Na_2SO_4 solution is shown in Fig. 3.

Table 3 presents the most relevant results obtained using XRD to analyze the samples of activated metakaolin extracted from the aggressive media at the previously established ages. The most important aspects to be emphasized from the XRD data in the table are listed below:

1. A percentage of the product of all of the samples studied consists of an amorphous fraction and consequently it is difficult to characterize using XRD.
2. After 180 days of immersion of the prisms in the seawater and acidic solutions, it was observed that small amounts of a crystalline zeolite belonging to the faujasite family began to form. The phase is represented by the main diffraction lines located at $°2\theta = 6.22$, 23.49, and 31.17.
3. In the case of the samples that were immersed in deionized water and in sodium sulfate solution, some traces of faujasite-type zeolitic phase were also detected in these samples after 56 days of attack.

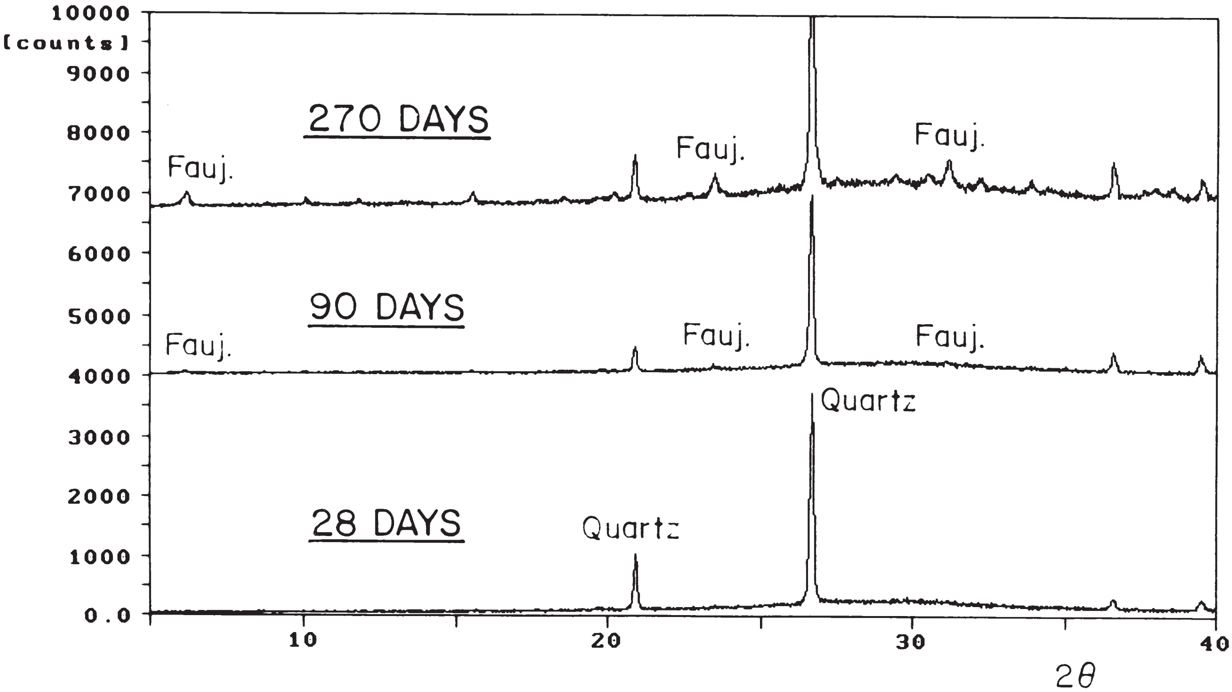

Fig. 3. XRD patterns of samples immersed in Na_2SO_4 solution.

Table 3
Results obtained using XRD

	Aggressive media							
	Deionized water		Acidic dissolution		Seawater		Na_2SO_4 dissolution	
Immersion time of prisms	Amorphous	Faujasite	Amorphous	Faujasite	Amorphous	Faujasite	Amorphous	Faujasite
7 days	A	–	A	–	A	–	A	–
28 days	A	–	A	–	A	–	A	–
56 days	A	T	A	–	A	–	A	T
90 days	A	T	A	–	A	–	A	T
180 days	A	T	A	T	A	T	A	L
270 days	A	L	A	L	A	L	A	L

A = abundant; L = little; T = traces.

1.7. IR

From the analyses of the IR spectra corresponding to the samples selected for study using this technique, it cannot be deduced that the aggressive solutions used (deionized water, seawater, H_2SO_4, and Na_2SO_4) induce relevant changes in the samples' chemical structure that are reflected by changes in their respective IR spectra (i.e., through the appearance of differences in the position or in the intensity of the bands of the spectra). Examples of spectra can be seen in Fig. 4.

The band assignments are as follows: The absorption at 3470–3450 cm^{-1} and 1655–1650 cm^{-1} are respectively due to stretching and deformation vibrations of OH and H-O-H groups from the water molecules. The sharp band, though of small intensity at 1390 cm^{-1}, is due to an absorption that also represents the IR spectrum of the starting material (metakaolin). Its presence, together with the band at 565 cm^{-1} (also belonging to the metakaolin), is an indication that a small quantity of raw material still exists in the sample. Some authors [13] assign a band between 560 and 570

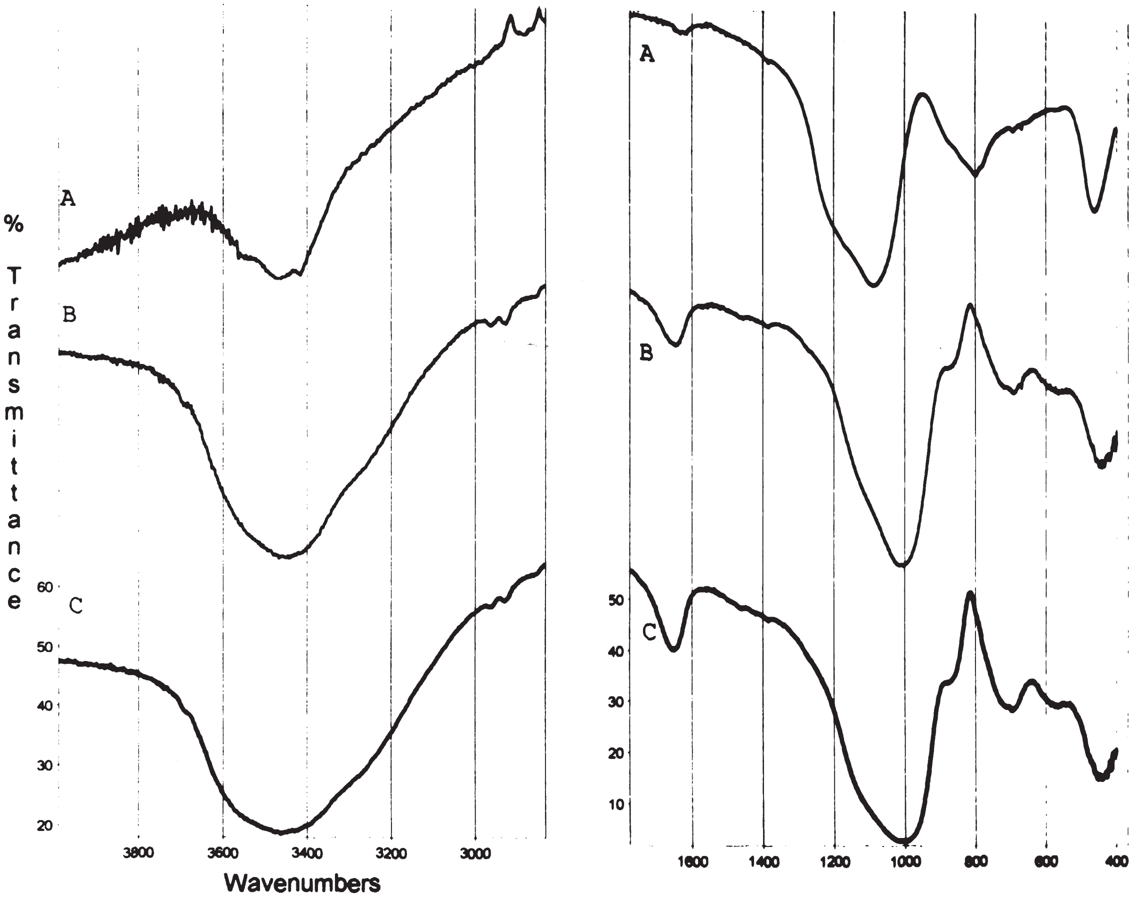

Fig. 4. Typical IR spectrum for the starting metakaolin (A) and the hydroceramic soaked in seawater solution for (B) 28 days and (C) 270 days.

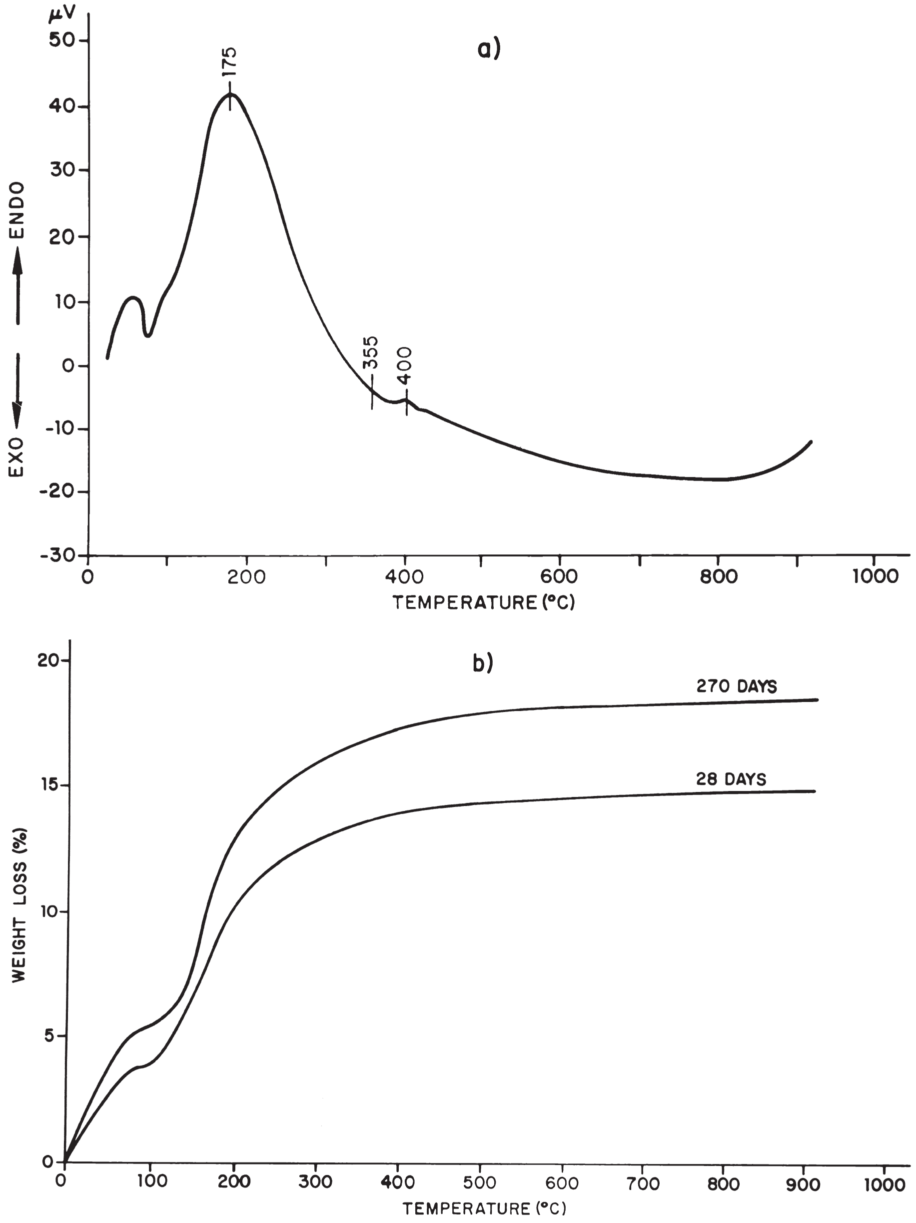

Fig. 5. (a) Typical DTA curve for hydroceramic. (b) Loss of weight of the 28 and 270 day cured hydroceramic samples as a function of the temperature.

cm^{-1}, together with a band at 375–380 cm^{-1} to a faujasite type of zeolite. Such bands, according to the cited authors, correspond to a double-ring linkage and to the pore openings in the zeolite, respectively. The bands in the 1009, 870, 693, and 445 cm^{-1} regions are indicative of the presence of a zeolitic precursor (amorphous aluminosilicate network structure) in the samples. The absorption at 1009 cm^{-1} is interpreted as a tension vibration of Si-O and joint Si-O-Al. The absorption located at 870 cm^{-1} is due to vibrations of Si-OH; that at 693 cm^{-1} is assigned to tetrahedral groups AlO_4 (condensed) and SiO_4 (rings). Finally, the band at 445 cm^{-1} is considered due to deformation vibrations of Si-O-Si. In the region of 720–650 cm^{-1}, some absorptions appear together with those already indicated at 693 cm^{-1}. These bands are thought to be due to symmetrical vibrations of tetrahedral groups (TO4) of some zeolites. However, it is practically impossible to differentiate the zeolite or zeolites present using these peaks. On analyzing this zone of the spectrum in all the obtained spectra, considerable modifications are not observed. Therefore it can be deduced that the existing amorphous matrix and crystalline zeolite have a similar nature in all the samples.

1.8. Differential thermal analysis and thermogravimetric analysis

This portion of the study was carried out using the same set of samples as above (specifically those extracted at 28 and 270 days) (Fig. 5). The form of the DTA curves (Fig.

5a) is very similar in all the samples: Initially an endothermic signal is always detected before reaching 100°C. This peak is basically related with the moisture absorbed by the sample from the environment. After that the appearance of a large endothermic peak having a maximum between 160 and 165°C (for the case of the samples submerged during 28 days in the aggressive solutions) or between 170–175°C in the case of the samples cured for 270 days can be observed. This peak, a broad one, is attributed to the process of dehydroxylation of the amorphous zeolitic precursor and to the dehydroxylation of any zeolitic crystals of the faujasite type in those samples that contain them. It has not been possible to characterize the small peak that occurs at about 400°C.

The curves in Fig. 5 are representative of all of the 28 and 270 day old samples, independent of the aggressive media in which they were soaked. With respect to the TGA curves, representing the loss of weight of samples taken to 900°C, it is of interest to note the difference observed between the samples immersed for 28 days and those immersed for 270 days (see Fig. 5b). This difference is not influenced by the type of aggressive medium. The 28-day immersed samples lose 9.5% of their weight between 70 and 300°C, while those that have been submerged a longer time (270 days) lose (in the same temperature interval) 11.5% of their weight. This may suggest not only that the samples are taking up water as the zeolitic character of the samples increase with time, but also that increasing amounts of amorphous reaction product are formed with increasing exposure time.

2. Discussion

When highly layer structured materials such as kaolinite are subjected to an intensive thermal treatment (850°C), the material undergoes a series of transformations that enhance its subsequent reactivity with given chemical agents. At approximately 600°C, kaolinite loses most of its crystallinity. This implies that the hexagonal layer structure in the kaolinite is partially destroyed at this temperature. The original mineral structure becomes disorganized, forming the material referred to as metakaolin. The exothermal dehydroxylation reaction is represented by Eq. (1):

$$2Al_2Si_2O_5(OH)_4 \rightarrow 2Al_2Si_2O_7 + 4H_2O \qquad (1)$$

If metakaolin is mixed with specific amounts of NaOH solution or NaOH + sodium silicate solution (concentrations ranging from approximately 7 to 12 M) and then cured at temperatures below 100°C, it is possible to produce a solid having an aluminosilicate network structure resembling a zeolitic material. And, as such, the solid possesses some interesting mechanical properties [7,9,14]. According to data obtained by the authors of this paper using nuclear magnetic resonance [14], the network structure consists of a series of SiO_4 and AlO_4 tetrahedra linked by their corners and sharing all oxygen ions. The alkali ions from the activating solution are present in the structure balancing the negative charge of the tetra-coordinated aluminium ions.

In terms of cementing properties, the hydroceramic can be compared to C-S-H gel formed during the hydration of portland cement. The strength/stiffness that the pseudozeolitic matrix confers to the three-dimensional structure of the material gives it some excellent mechanical properties [9,14].

In the current work, the mechanical strength of the hydroceramic was evaluated vs. time of immersion in various solutions containing aggressive agents. The initial fluctuations in flexural strength observed between 7 days and 3 months of immersion (independent of the type of aggressive agent) were considered to be due to a dissolution-precipitation phenomenon that occurs during this period. Clearly this process has a negative influence on the development of mechanical strength.

On the one hand, a dissolution of the soluble part of the material occurs [10]. This demonstrates that during the activation process of metakaolin with NaOH solution or NaOH + sodium silicate solution, with concentrations like the one used in this investigation, most of alkalis are fixed into the structure of the hydroceramic but some alkalis can remain in soluble form. Naturally the free alkalis (that part not fixed by the zeolitic precursor) are easily dissolved, which generates an increase in the porosity of the specimen and consequently a decrease of its mechanical strength (data in Table 2 and Fig. 2 confirm this hypothesis). In this case, the experimental results show that the acidic medium was the most aggressive of all the tested liquids (having the greatest capacity to dissolve the sample). On the other hand, the sample continues to react with time, which partially offsets the effect of the dissolution process. Between 28 and 56 days, the samples seem to undergo a slight recovery in strength. This could well be attributed to the precipitation of a small quantity of zeolitic product (the first trace of faujasite that is detected by XRD occurred in some of the samples at 56 days, and according to the IR spectra, some zeolitic material could have already been formed as early as 28 days). This product could fill a part of the porous space in the sample and account for the strength gain.

The situation observed in the evolution of the strengths of the prisms immersed 90 days and longer is quite different. All the experimental results obtained through XRD seem to indicate the partial but limited transformation of the amorphous structure of the hydroceramic to a crystalline material having a faujasite structure. This could be related to the continuous gain in strength after 90 days. The effect is apparently independent of the solutions the prisms were stored in. The mechanical effect may be similar to that produced by a structural reinforcement, as in the case of fibers when they are mixed with a cementing matrix. The most important aspect to be emphasized in this particular case is that the reinforcement agent (the faujasite crystal) is self-generating with time. Research dealing with this subject can be found in the literature [15]. It is suggested that the continuing improvement in the mechanical strength of the hydroceramic can be attributed to a continuation of the network-forming reaction with time at ambient temperatures. This is based on the observation that the reaction was not 100% complete (as demonstrated by the fact that characteristic bands of the metakaolin were still present in the IR spectra of samples with ages of 270 days). Although the activation of metakaolin is rapid when it is thermally stimulated [11], it seems to continue at a much slower rate at ambient temperatures. A prolonged contact of the hydroceramic with different aqueous media has been shown to have a positive effect on the mechanical strength. It is considered of interest to discuss some details in connection with the different phases that are observed (i.e., faujasite and its amorphous precursor):

1. Faujasite can be formed under a wide range of pH conditions (acidic and neutral as has been demonstrated for the tested prisms, whatever the aggressive media was: acidic solution pH = 3, distilled water pH = 7, seawater pH = 7, and sodium sulfate solution pH = 6).
2. One must emphasize the high water content of the crystallized zeolite; it has more than its precursor, as is deduced from the TGA analyses. Complementary studies support such a deduction: the atomic ratio of the amorphous precursor is $Na_2Si_3Al_2O_{10} \cdot 3H_2O$ [14]; however, in the case of faujasite, this is $Na_2Al_2Si_{2.4}O_{8.8} \cdot 6.7H_2O$. Then crystallization of faujasite from the precursor involves an additional crystallization of combined water, which could justify the differences observed in the curves of Fig. 5*(b)*. This high water content indicates the capacity of faujasite for adsorbing and desorbing water in a reversible way. In the case of the amorphous precursor, the loss of weight that is produced during the thermal treatment is probably due to the dehydration of the terminal OH groups. At the temperature of 300°C, the hydroceramic has finished its structural dehydration and in that moment, no longer contains structural spaces that allow it to readsorb water. The terminal Si-OH group was present in the materials analyzed according to the IR spectra (band at 870 cm^{-1}).
3. The results of Shigemoto et al. [13] are confirmed. These authors say that the differences and similarities between the IR spectra of zeolites and of their amorphous precursors can be interpreted as due to the existence of identical structural units with T-OH terminals.

3. Conclusions

The alkaline activation of metakaolin with concentrated NaOH solutions produces an amorphous material—a zeolitic precursor with excellent cementing properties in terms of mechanical strength. The resultant hydroceramic demonstrates good stability for up to 270 days when submerged in aggressive liquids of various types.

The time that the sample spends in solution is responsible for a certain degree of transformation of the amorphous aluminosilicate network structure into a crystalline one. Small amounts of these crystals having the faujasite structure account for the continuing development of the mechanical strength of the material after 90 days of immersion.

Faujasite crystals appear to act as reinforcement of the cement matrix.

Naturally, long-term experiments are needed to clarify whether or not the transformation of the noncrystalline precursor gel into a crystalline zeolite continues with time, and if it does, whether or not the conversion process has a positive or negative impact on performance-related properties of the hydroceramic. Another positive aspect related to the in situ growth of zeolites in a cement matrix is the ability of zeolites to adsorb/desorb water vapor from the air. This characteristic might allow one to design new building materials that can interact with their surroundings.

Acknowledgments

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