EFFECT OF SEPIOLITE ON THE BEHAVIOUR OF FIBRE CEMENT SUSPENSIONS IN THE MANUFACTURE OF FIBRE-REINFORCED CEMENT

ELENA FUENTE[1]; ROCÍO JARABO[1]; ANA MORAL[1]; CARLOS NEGRO[1]; LAURA IZQUIERDO[2]

[1].*Chemical Engineering Department, University Complutense of Madrid.*
Avda. Complutense s/n, Madrid 28040. Spain
[2].*Industrial development R&D Department, TOLSA S.A.*
Rd. Vallecas-Mejorada del Campo, Km 1600, Madrid 28031, Spain

ABSTRACT

Sepiolite, an additive to modify rheological properties of cement, has been used during the last decade in fibre-reinforced cement manufacture to increase interlaminar bond between the films. However, the effect of Sepiolite on flocculation, retention and drainage of fibrecement is as yet unknown and the aim of this research, is to optimize its use in fibre-reinforced cement manufacture.

The effect of Sepiolite on flocculation of fibrecement and on floc properties induced by anionic polyacrylamide was studied by monitoring the chord size distribution in real time by means of a focused beam reflectance measurement probe. The effect of Sepiolite on retention and drainage was evaluated by using a vacuum drainage tester. The use of Sepiolite increased the flocculation of the fibrecement and floc stability. Solids retention obtained with all of the tested mixtures was increased, and those mixtures containing PVA showed increased drainage rate.

KEYWORDS

Sepiolite; flocculation; retention; drainage; fibre-reinforced cement.

INTRODUCTION

Sepiolite is a hydrated magnesium silicate mineral belonging to the group of phyllosilicate which includes other well known industrial minerals such as Montmorillonite, Kaolin, Mica and Vermiculite. The main differences between it and other members of the group are its acicular morphology (figure 1) and its high and active surface that reaches the biggest values for natural materials, in the range of 340 m^2/g. Other important characteristics are related to its thermal and chemical stability that allows it to maintain stable properties, at temperatures up to 300ºC and in a wide pH range (3-14). It also has very low electrolyte sensitivity which is very important in saturated cation media such as cement slurries. In addition to this, Sepiolite does not show any reactivity during the cement setting process.

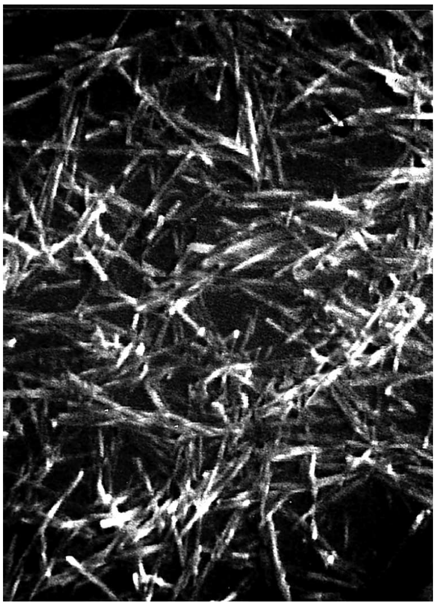


Figure 2 – Morphology of rheological grades of Sepiolite. Pangel gel network in water from a scanning electronic micrograph.

The small length of Sepiolite fibres (in the range of 2 µm) prevents direct effects on mechanical properties. However its great interaction with other fibres and components either organic or inorganic is responsible for an increase of homogeneity of the system which is due to the high density of hydroxyl groups that cover all if its highly irregular and porous microfibre surface (Figure 2).

The most important deposits in the world are found in the Tajo river basin in the vicinity of Madrid (Spain), the Eskisehir area in Turkey and the Amargosa Valley in the USA. Its main uses from an industrial point of view, are in the construction, coatings or bitumen industry, along with the applications as an absorbent, a carrier or binder in a great variety of industries.

PANGEL® is the name of a range of Sepiolite-based rheological additives agents for aqueous systems. They are produced from high purity Sepiolite whose bundles of particles are disagglomerated and separated without their acicular structure being affected. These particles are dispersed in the cement slurry to form an intermeshed network in which the main components of the system are homogeneously distributed. This network is stabilized by the weak forces provided by hydrogen bonds that can be re-configured as some shear is supplied to the system during mixing steps. This change allows the production of highly viscous gels that sharply reduce in consistency when some energy is supplied to the system, in other words, thixotropic and pseudoplastic behaviour. These physicochemical effects are responsible for the high degree of plasticity and consistency imparted to cement slurries, along with the observed process improvements.

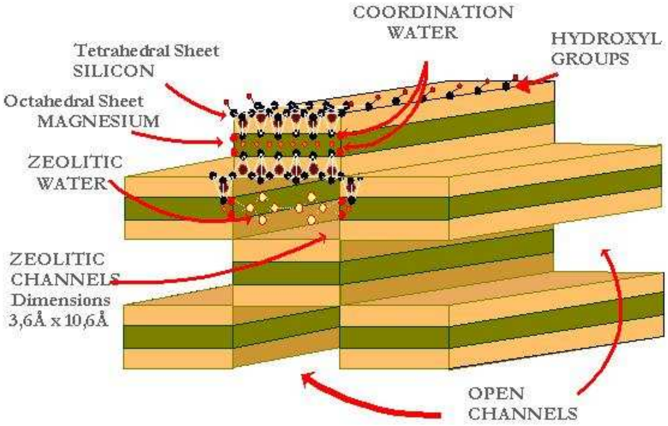


Figure 2 – Scheme of Sepiolite main structural characteristics.

The rheological properties of PANGEL® make it a valuable ingredient in non-asbestos fibre reinforced cement sheets manufactured on a Hatschek machine and similar (Perez et al., 1988; Kavas et al., 2004) and it has been used in this process for more than ten years. Sepiolite based products improve the required rheology necessary to make high quality product while simultaneously improving the manufacturing process and are particularly efficient in improving the interlaminar bonding, especially in corrugated sheets, while also improving process stability, surface finishing and VAT efficiency.

MATERIALS METHODS

The effect of Sepiolite on flocculation, retention and drainage of three different fibre-reinforced cement slurries (M1, M2 and M3), whose composition is summarised in table 1, was studied.

Table 3 – . Composition of studied fibre-cement mixes.

Raw materials	M1 (%)	M2 (%)	M3 (%)	M4 (%)
Cellulose	3,2	9	3,2	3,3
ASTM II Cement	91	44	92.4	92.9
Microsilica	4	0	2	2
PVA	1,8	0	1,8	1,8
Silica	0	39	0	0
Al_2O_3	0	4	0	0
Metakaolin	0	4	0.5	0

Each mixture was studied in absence of Sepiolite and with 1.25% of Sepiolite.

Two Sepiolites PANGEL®, HV and H45 were supplied by TOLSA S.A. Both products have been developed from a very high purity Sepiolite from the Madrid deposit and purified during the manufacturing process in order to show maximum particle disagglomeration. PANGEL® H45 is a product developed for improving mixing conditions of PANGEL® HV and cement The surface of PANGEL® H45 has a higher anionic charge density than the surface of PANGEL® HV.

The flocculant used was a commercial anionic polyacrylamide (APAM) commonly used in the industrial Hatschek process. A 1.5g/L solution was prepared in distilled water at least 12 h before its use.

METHODS

Flocculation, retention and drainage of the fibre-cement slurries were studied without Sepiolite, adding APAM to the slurries with Sepiolite and adding the Sepiolite to the slurries with APAM, to determine the effect of the Sepiolite and APAM addition order on the suspension behaviour.

Flocculation studies

A commercial Focused Beam Reflectance Measurement probe (FBRM) M500L manufactured by Mettler Toledo, Seattle, USA was used to monitor flocculation process and to determine floc properties. FBRM allows the in situ measurement of chord length distribution over a wide range of solid concentrations. This is especially relevant for flocculation processes where any change in the suspension will alter the structure of the flocks. The principle of the measurement and the details of the applied methodology have been described by the authors in previous references [Blanco et al., 2002; Negro et al., 2006a]. In a typical trial the probe was immersed in 400 mL of fibre-cement suspension, prepared with water saturated in $Ca(OH)_2$, stirred at 800 rpm. Sepiolite was added after 6 min of stirring and, 4 min after its addition, stirring intensity was reduced to 400 rpm. 100 ppm of APAM was added 5 min after that, and the evolution of the flocs was studied at 400 rpm during 4 min. Then, the stirring intensity was increased to 800 rpm to break down the formed flocs during 2 min and, finally, stirring intensity was reduced again to 400 rpm to induce the reflocculation of the system. A set of trials were carried out adding the Sepiolite 15 s after APAM addition instead of adding it at the beginning of the trial.

Retention and drainage studies

The equipment used for measuring retention and drainage was a vacuum drainage tester (VDT). It has two jars separated by a barrier: the upper jar is used to keep the fibre–cement suspensions stirred until the addition of the flocculant. In a typical trial, 400 mL of fibre-cement suspension, prepared with water saturated in $Ca(OH)_2$, was stirred at 600 rpm for 6 min before adding the Sepiolite and for a further 4 min after that. Then, the stirring intensity was decreased to 300 rpm and 100 ppm of APAM was added after 5 min. A set of trials were carried out adding the Sepiolite 5 sec after APAM addition instead of adding it at the beginning of the trial.

After 15 sec of contact time between flocculant and mixture, the stirring was stopped, the barrier was removed and the suspension was drained into the second jar in which an 18 mesh wire was located. The suspension was drained under a vacuum of 0,2 atm through the filter while a computerized balance recorded the mass of drained water over time (Negro et al., 2006b). The drainage curve was analysed in order to obtain the drainage rate for the different flocculants. Retention and cake moisture content were determined from the analysis of the formed cake.

RESULTS

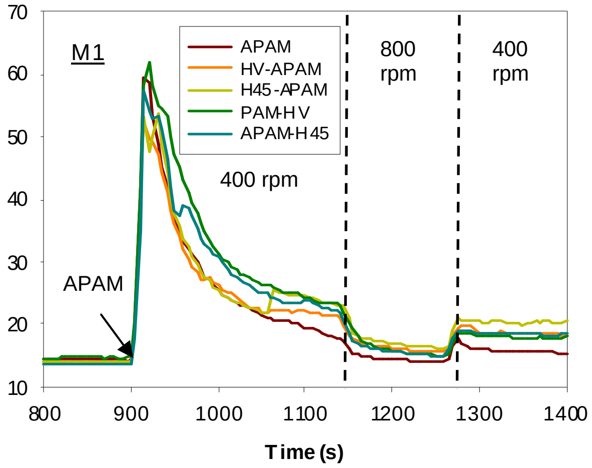
Effect of Sepiolite on flocculation and solids retention

Figure 3 shows the evolution of the mean chord size during the flocculation-deflocculation-reflocculation trials and the retention of solids obtained after dewatering the mixture in the VDT.

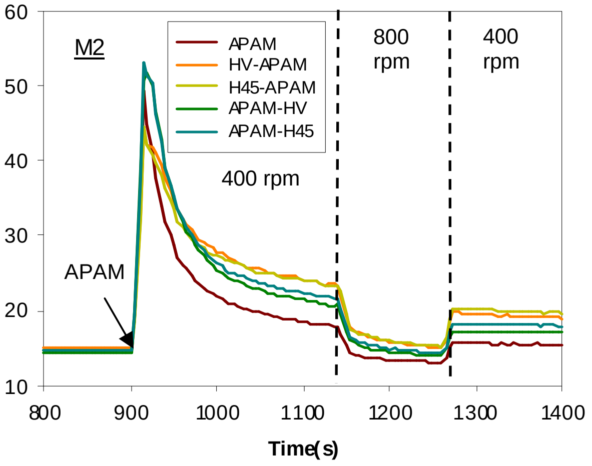
The addition of APAM to the fibre-cement suspensions induced a fast flocculation, as shown by the notable increase of the mean chord size in all cases due to the aggregation of the particles to form flocs. A maximum mean chord size was reached in a few seconds. Then, it decreased slowly towards equilibrium. This indicates that formed flocs were unstable. The flocculant is rapidly adsorbed onto the particles and forms bridges between them, leading to their aggregation. As the floc size grows, the probability of finding weak bonds in the agglomerated structure increases, which enhances the deflocculation process (Lu and Spielman, 1985). Furthermore, the polymer conformation tends to evolve towards a flat conformation on the cement particles, reducing its bridging ability (Selomulya et al., 2003; Negro et al., 2005; 2006a). When stirring intensity increased the remaining flocs were broken down by the high hydrodynamic forces. A partial reflocculation was observed when stirring intensity was reduced to 400 rpm.

The presence of Sepiolite in the suspension increased the mean chord size obtained after flocculation and evolution of the formed flocs. This indicates that the presence of Sepiolite increased the stability of flocs. This advantage is kept to the end of the trial, which indicates that the reflocculation ability of the flocs did not decrease.

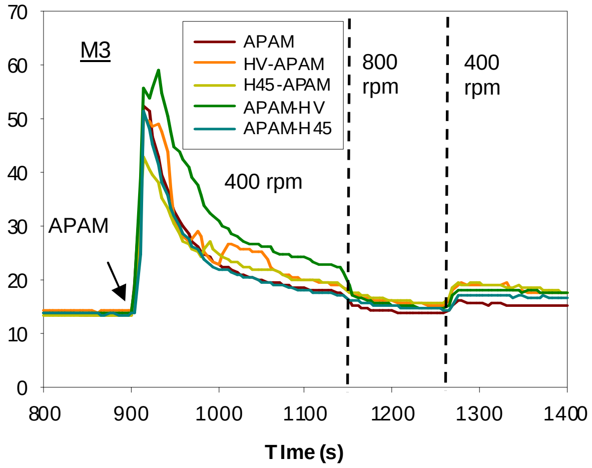
The use of APAM increased retention notably in all cases, because of the interaction among fibres and mineral particles to form flocs. The use of Sepiolite and APAM in fibre-cement suspensions increased the solids retention in all cases, as shown in Figure 3. This is due to the effect of Sepiolite in flocculation as shown by the close relationship between the increase in floc stability and the increase in retention. Sepiolite increased the amount and size of the flocs remaining when drainage started and, therefore, less material passed through the wire with the filtrate.



Additive	Retention (%)
APAM	88,7
HV-APAM	91,4
H45-APAM	93,4
APAM-HV	97.1
APAM-H45	96,2
No Additive	59,8
HV	56
H45	57



Additive	Retention (%)
APAM	87,9
HV-APAM	93,6
H45-APAM	93,7
No Additive	81,6
HV	82
H45	85



Additive	Retention (%)
APAM	75,5
HV-APAM	89,7
H45-APAM	84,2
APAM-HV	90,9
APAM-H45	76,7
No Additive	40
HV	60
H45	50

Figure 3 – Mean chord size evolution during flocculation, deflocculation and reflocculation with APAM and solids retention.

Solids retention in M1, with or without APAM was higher than the ones obtained with M3, although both mixtures are very similar. To analyse the cause of this difference, a fourth mixture M4 was prepared with the same composition as M3 except the metakaolin was omitted (see table 1). Retention of solids in M4 with APAM was 73.2%, which is similar to that obtained in M3. Furthermore, trials carried out in absence of flocculant shows that retention obtained in M1 was higher than retention of solids in M3 and M4 (table 2). Therefore, the cause of the low solids retention observed in M3 is its lower content in microsilica, because this is the only difference between M4 and M1.

Table 2 – . Effect of microsilica and metakaolin on retention.

		M1 (%)	M3 (%)	M4 (%)
Content in	**Microsilica**	4	2	2
	Metakaolin	0	1	0
Retention with the additive	**APAM**	89	75	73
	No Additive	60	40	52
	HV	56	60	51
	H45	57	50	51

Data in figure 3 show that even in absence of flocculant, the use of Sepiolite can increase retention of some fibre-cement mixtures, as M3. The surface properties of Sepiolite could facilitate its interaction with small particles such as metakaolin and improve its retention.

Effect of Sepiolite on drainage process

Drainage is carried out in two steps: first, the suspension is filtered and a cake is formed with fast water removal, which corresponds to the first part of the drainage curves (a linear part with high slope); secondly, the cake is compressed and thickened and the water removal rate decreases towards zero. The loss of most solids takes place during the first stage with the filtrate while the second stage determines the final moisture content and the properties of the cake. Drainage time was determined as the time required to reduce the drainage curve slope to zero.

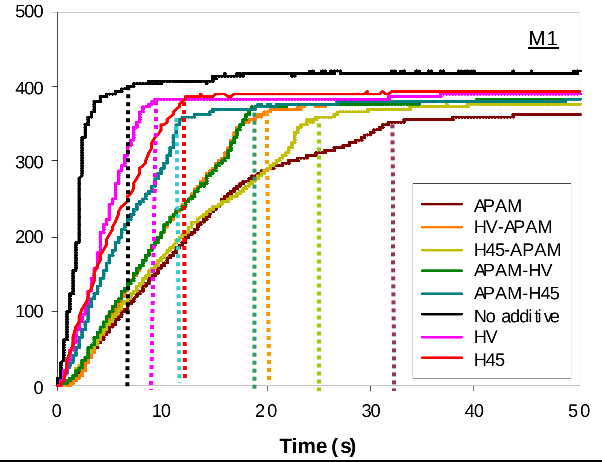
Figure 4 shows that the behaviour of M2 was completely different from the behaviour of the other mixtures. The compression of the cake was very short in the drainage of mixtures M1 and M3, but it was the largest in the M2 drainage process. Consequently, the drainage time of M2 was more than twice the drainage of the other mixtures.

Except in the case of M2, the use of APAM notably increased the drainage time. There are two explanations for this: firstly, the main effect of APAM on drainage is the reduction of the drainage rate during the first stage, as shown by the curves in Figure 4; secondly, M2 has a very high percentage of metakaolin, whose particle size is very small which can obstruct the pores if it is not flocculated with APAM. Data in Figure 5, which shows the normalised chord size distribution of all the components used to prepare the three mixtures, proves this explanation since the mode of the metakaolin particle chord size distribution is the smallest. Furthermore, in absence of APAM, solids retention of M2 was the highest. Despite the high content of metakaolin, which may indicate that many small particles are retained in the pores of the cake instead of passing with the filtrate, solids content retention was almost as high as it was with APAM.

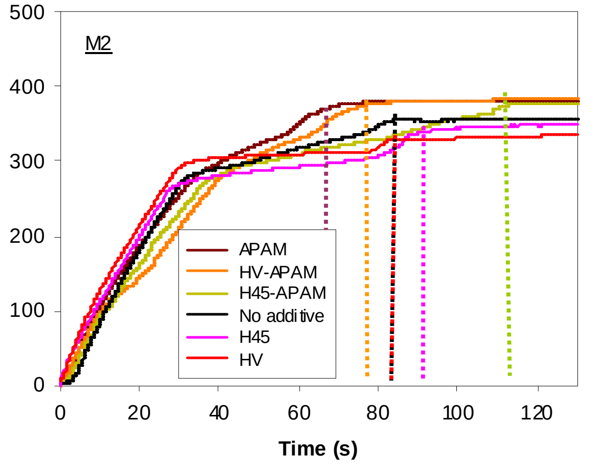
When Sepiolite was used in combination of APAM, in the mixtures M1 and M3, the drainage rate increased, which can be related to the increase in floc stability. The higher grade of flocculation during the drainage makes easier the flow of water through the spaces among the flocs.

The drainage time of M1 was much longer than the drainage time of M3 despite their similar composition. To determine the cause of this difference, the drainage curve of M4 was obtained. Figure 6 shows that, in presence of APAM, drainage curves of M3 and M4 were equal and the compression stage was almost negligible in both curves while the drainage of M1was much longer. Therefore, the cause of the longer drainage time of M1 is its higher content of microsilica. Figure 5 shows that part of the microsilica has a very small chord size. These particles are part of the flocs and they could reduce the porosity of flocs and cake. Therefore, the compression stage is increased, as shown in figure 6 and moisture content decreased because of the the higher presence of fine microsilica particles in the pore space.

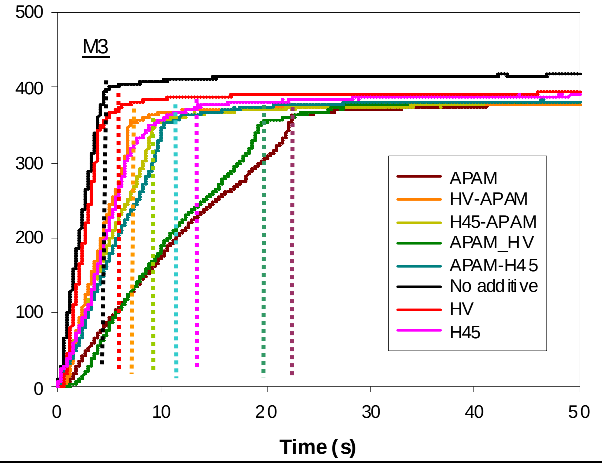
The addition of Sepiolite increased the moisture content of the cake obtained from M1 and M3 when APAM was used. However, this effect depended on the addition order of the Sepiolite and APAM and, furthermore, the use of Sepiolite in absence of flocculant did not have the same effect and it even decreased the moisture contentof the cake. Water retention in presence of Sepiolite and flocculant is due to the high hygroscopicity of the Sepiolite surface and to the increase in the bridging ability of APAM, caused by its interaction with the Sepiolite (this increases the space among particles in the floc and, therefore, flocs can retain more water). Because the dosage of Sepiolite in the mixtures is very low, the amount of water adsorbed on its surface would be too low to explain the observed effects and, furthermore, this does not explain the effect of Sepiolite on moisture content in absence of APAM. Therefore, the effect of Sepiolite on moisture content of the cake is mainly due to the increase in the bridging ability of APAM and on the final floc size.



Additive	Drainage time (s)	Moisture content of cake (%)
APAM	32	39,9
HV-APAM	20	66,3
H45-APAM	26	41,9
APAM-HV	19	58,5
APAM-H45	12	55,3
No additive	6	47
HV	12	49
H45	9	45



Additive	Drainage time (s)	Moisture content of cake (%)
APAM	71	47,9
HV-APAM	78	47,5
H45-APAM	111	37,6
No additive	82	56
HV	82	55
H45	90	46



Additive	Drainage time (s)	Moisture content of cake (%)
APAM	23	46,5
HV-APAM	7	50,8
H45-APAM	9,5	51,0
APAM-HV	20	69,8
APAM-H45	11	52,2
No additive	4	56,5
HV	6	43,2
H45	13	37

Figure 4 – Effect of APAM and Sepiolite on drainage process and the moisture content of the formed cake.

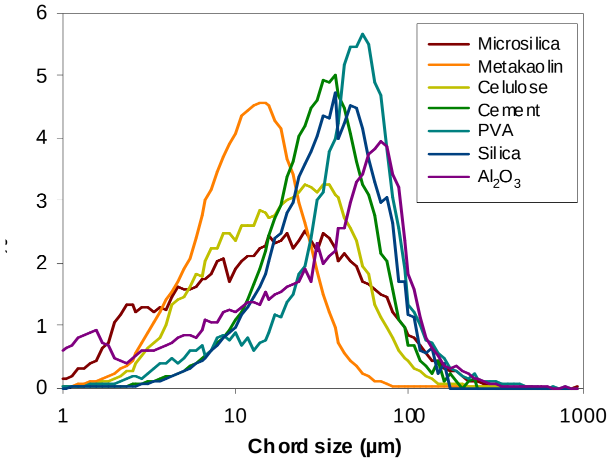
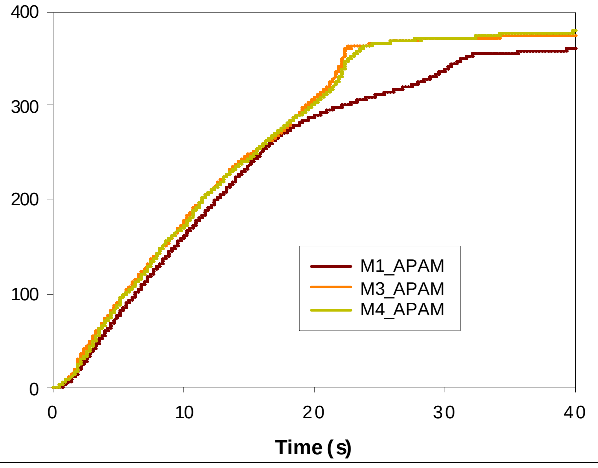


Figure 5 – Chord size distributions of the components of the mixtures.



Mixture	Drainage time (s)	Moisture content of cake (%)
M1	32	39,9
M3	23	46,5
M4	23	54,9

Figure 6 –Effect of microsilica and metakaolin on drainage with APAM and without Sepiolite.

Table 3 shows the moisture content obtained with M4 in absence of flocculant, with and without Sepiolite.

Table 3 – . Effect of microsilica and metakaolin on moisture content of the cake.

		M1 (%)	M3 (%)	M4 (%)
Content in	**Microsilica**	4	2	2
	Metakaolin	0	0.5	0
Moisture content obtained with the additive	**APAM**	40	47	55
	Nothing	47	57	48
	HV	49	43	46
	H45	45	37	48

The moisture content of cake was very similar to the one obtained with M1 and the effect of Sepiolite on the moisture content of the cake of M1 and M4, in absence of flocculant, was very low. Therefore, Sepiolite did not affect the moisture content of the cakes from mixtures without Metakaolin and APAM, but in presence of Metakaolin it reduced the moisture content of the cake. This can be related to the effect on retention in absence of APAM (figure 3 and table 2), retention increased only when Sepiolite was added to the mixture with metakaolin (M3). These facts indicate that there could be an interaction between Sepiolite and metakaolin that allows the retention of metakaolin and other small particles and reduces their interaction with water, decreasing water retention.

CONCLUSIONS

The addition of a very high purity Sepiolite to the fibre-cement slurries improves the stability of the flocs induced by APAM when it was added before or after the APAM.

The use of Sepiolite in the manufacture of fibre-reinforced cement increases the solids retention improving the economy of the process, reducing the accumulation of solids in recycled process water and allowing a better use of raw materials and additives. In slurries containing metakaolin, Sepiolite could be used to improve retention even without APAM.

Addition of Sepiolite to the fibre-cement suspension increases drainage rate improving the productivity in processes where APAM is used as retention aid, because it reduces the slowing down effect of APAM on drainage (TOLSA, 2002).

The use of APAM reduced the moisture content of the cake obtained after drainage. Sepiolite can reduce the effect of APAM on the moisture content of the sheets obtained from M1 and M3 and this could improve the interlaminar bonding in the process in the cases when the use of APAM leads to a too dry sheet.

REFERENCES

Blanco, A., Fuente, E., Negro, C., Tijero, J. 2002. “Flocculation monitoring: focused beam reflectance measurement as a measurement tool”. The Canadian Journal of Chemical Engineering 80 734–740.

Kavas, T., Sabahb, E., Çelikc, M.S. 2004. “Structural properties of Sepiolite-reinforced cement composite”. Cement and Concrete Research 34 2135–2139.

Lu, C.F., Spielman, L.A. 1985. “Kinetics of floc breakage and aggregation in agitated liquid suspensions”. Journal of Colloid and Interface Science 103 95–105.

Negro, C., Blanco, A., Fuente, H., Sánchez, L.M., Tijero, J. 2005. “Influence of flocculant molecular weight and anionic charge on flocculation behaviour and on the manufacture of fibre cement composites by the hatschek process”. Cement and Concrete Research 35 2095–2103.

Negro, C., Sánchez, L.M., Fuente, E., Blanco, A. 2006a. Tijero, J. Polyacrylamide induced flocculation of a cement suspension. Chemical Engineering Science 61 2522 – 2532.

Negro, C., Blanco, A., San Pío, I., Tijero, J. 2006b. “Methodology for flocculant selection in fibre–cement manufacture”. Cement & Concrete Composites 28 90–96.

Pérez, R., Álvarez, A. 1988. “Process for manufacture of fibre reinforced concrete articles”. European Patent ES2002268.

Selomulya, C., Amal, R., Bushell, G., Waite, T.D. 2003. “Understanding the role of restructuring in flocculation: the application of a population balance model”. Chemical Engineering Science 58 327–338.

TOLSA. 2002. “PANGEL HV. Rheologycal additive for the manufacture of non-asbestos fibre reinforced cement product”. Technical Information Report, Madrid, Spain.