OPTIMAL USE OF FLOCCULANTS ON THE MANUFACTURE OF FIBRE CEMENT MATERIALS BY THE HATSCHEK PROCESS

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ABSTRACT

In the Hatschek process used to produce fibre-cement products, it is necessary to use a suitable flocculant when asbestos is substituted by pulp fibres. The right selection of flocculant is crucial in the industrial process due to its effects on mineral fines retention, dewatering and formation and, as a consequence, on the overall efficiency of the machine. Therefore, the optimisation of the flocculation process during fibre cement production is a key issue for the fibre cement industry. Many companies face difficulties in optimising the flocculant dosage in real time, which leads to product strength losses.

The presentation will be focus in the description of a new methodology for flocculant selection in the fibre-cement manufacture. Results show that this methodology gives an in-depth knowledge of flocculation process. A real-time methodology has been used to study size, shape, strength and reversibility of formed flocks, based on a focused beam reflectance measurement (FBRM) system. The results have been corroborated by particle vision and measurement (PVM) analysis.

The influence of the molecular weight and the anionic charge of anionic polyacrylamides on the flocculation behaviour of fibre cement suspensions and on the bending strength of the final product will be reported.

Finally, will be reported the feasibility of using artificial neural networks (ANNs) to establish correlations between flocculation data, in-line measured in a Hatschek machine by a focused beam reflectance measurement (FBRM) sensor, and mechanical properties of final composites. The results show a clear relationship between the mechanical properties of fibre cement composites and the flocculation process and that these are determined in real time.

KEYWORDS:

Fibre-cement; Hatschek process; flocculation; fibre/matrix bond, retention.

INTRODUCTION

Over the last few years, many research studies related to the substitution of asbestos for others raw materials have been published (Daniel, 1996). These mainly focus on natural cellulose fibres from wood (virgin or recycled (Souroushian, 2000)) or non-wood raw materials (Savastano, 1993 and 2003) and synthetic fibres, alone or as a mixture (Bohnemann, 1998; Hannant, 1995). Out of all these sources the softwood un-bleached Kraft fibres are the most widely used due to their strength characteristics, the high availability and the price.

Asbestos is a naturally occurring fibrous silicate and the fibre's size together with its chemical structure, make asbestos very compatible with cement. However, the different density, chemical composition and hygroscopic character of pulp fibres make the compatibility between cellulose fibres and cement much more complex and, therefore, new aspects need to be considered. In the Hatschek process, the behaviour of these fibres is different and therefore, a suitable flocculant is needed when using pulp fibres. The machine type determines the addition points for the flocculants. The right selection of flocculant is crucial in the industrial process due to its effect on mineral fines retention, dewatering and formation and, as a consequence, on the overall efficiency of the machine. Most work in this field has been carried out at mill sites and no public information is available in the literature. This paper addresses this issue, providing a methodology for optimal flocculant selection.

MATERIALS AND METHOD

Methodology

The methodology to monitor flocculation is based on using a focused beam reflectance measurement system FBRM M500LF manufactured by Lasentec. The focused beam reflectance measurement offers the possibility of particle characterization in a wide concentration range. The FBRM instrument operates by scanning a highly focused laser beam, at a fixed speed, across the particles in the suspension and measuring the time duration of the reflected light from these particles (Figure 1). The temporal duration of the reflection from each particle or flock multiplied by the velocity of the scanning laser, which is known, results in a characteristic measurement of the particle known as the chord length. Thousands of chord length measurements are collected per second, producing a histogram in which the number of the observed counts is sorted in several chord length bins over the range of 0.2 to 2000 µm. From the data, total counts, counts in specific size regions (population), mean chord length, and other statistical parameters can be easily calculated. The evolution of these various statistics under varying process conditions allows us to interpret the evolution of the flocculation process.

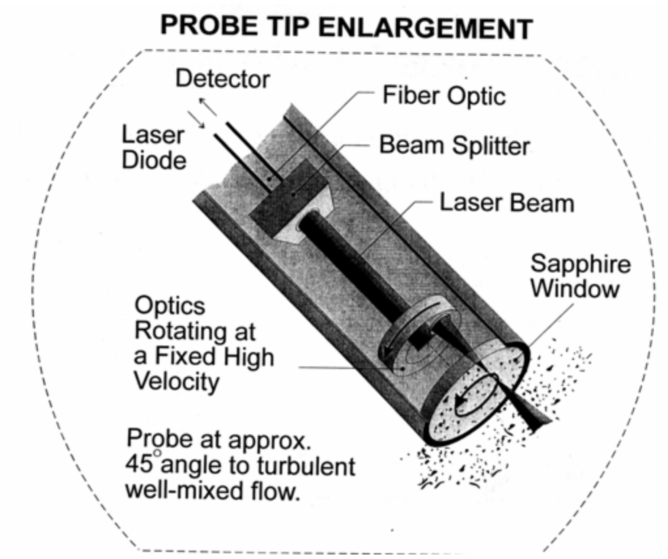

Figure 1 – FBRM probe.

RESULTS AND DISCUSSION

Influence of type of PAM charge on flocculation

The influence of type of polyacrylamide on the size and floc properties was studied with a 5%w cement suspension stirred at 300 rpm for 10 minutes before the flocculant was added, to simulate the residence time in a fibre cement mill. A dose of PAM was added and the evolution of the formed flocs was recorded for 5 minutes to study the floc strength at low shear intensity. Then the stirring intensity was increased to 800 rpm for 5 minutes, to break down the flocs . Finally, the agitation was reduced to 300 rpm for 5 minutes, to study the reflocculation process.

Figure 2 shows the evolution of the mean chord length when 100 ppm of a non-ionic (N-PAM), cationic (C-PAM) or anionic polyacrylamide (A-PAM) is added to a cement suspension. This dosage is expressed as milligrams of flocculant per milligram of solids in suspension. The three PAM's induced a fast flocculation at 300 rpm, reaching a maximum floc size in a few seconds, before the flocculation equilibrium was reached. Formed flocs were unstable and their size decreased. The flocculant is rapidly adsorbed on 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 fracturing process, because flocs become larger than the Kolmogorov microscale. The polymer conformation tends to evolve towards a flat conformation on the cement particles, which does not allow any further bridge formation. Figure 2 shows important differences between the three polyacrylamides. Ionic forms allow higher maximum chord sizes to be achieved than the non-ionic one because of the higher electrostatic polymer adsorption. As expected, the longest chord length is achieved with C-PAM because Portland cement particles have a negative surface charge. However, a high maximum size was also reached with the A-PAM. One possible reason is the electrostatic interaction with C_3A and C_4AF particles because they have a positive surface charge, but the most important one is the strong adsorption of Ca^{2+} ions in the Stern layer. It is known that calcium or other divalent cations enhance the action of anionic flocculants providing ionic links to fix the carboxylic groups of the polyacrylamide on to the silicate surfaces. Furthermore, the high ionic strength of the medium reduces the thickness of the electric double layer and the electrostatic repulsion between the polymer and the particles.

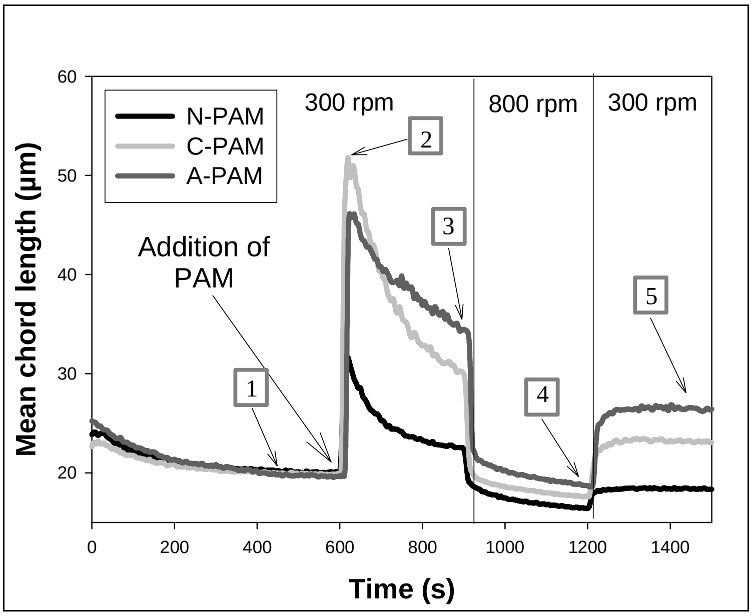

Figure 2 – Mean chord length evolution with time for 100 ppm dosage of different types of PAM.

Figure 2 also shows important differences in floc strength between the three types of polyacrylamides. Quantitative floc strength indexes have been calculated:

$$\text{Low shear floc strength index (\%)} = 100 \times (A_3-A_1)/(A_2-A_1)$$

$$\text{High shear floc strength index (\%)} = 100 \times (A_4-A_1)/(A_3-A_1)$$

where: A_1 is the mean chord length of cement suspension before polyacrylamide addition at 300 rpm, A_2 is the maximum mean chord length of formed flocs at 300 rpm, A_3 is the mean chord size at 300 rpm, 5 minutes after adding the flocculant, and A_4 is the mean chord size after stirring the flocculated suspension at 800 rpm for 5 minutes. The results are summarised in table 1.

The value of the low shear strength index of flocs induced by A-PAM is the highest due, probably, to the interaction with the calcium ions. Cation interaction with the anionic carboxylic groups of the polymer increases the stiffness of the chains reducing the relaxation of the attached polymer into flattened adsorbed conformation.

Table 1 – Calculated indexes for different types of polyacrylamide addition.

Type of PAM	Low shear floc strength index (%)	High shear floc strength index (%)	Reversibility index (%)
N-PAM	20	-151	-14
C-PAM	32	-19	11
A-PAM	55	-7.5	25

The high shear floc strength indices results are negative because the mean chord lengths at 800 rpm are smaller than the initial values at 300 rpm. When stirring intensity increases to 800 rpm, shearing forces are high enough to break down the elastic bridge bonds, and stronger than the electrostatic and Van der Waals balancing forces that formed the cement coagula before adding the flocculant. Furthermore, the mean chord size value at 800 rpm is higher than the value shown in figure 1 for the cement suspension without flocculant. This indicates the PAM bridges are stronger than the cement coagula, formed by the neutralisation. The highest shear floc strength from A-PAM shows that it induces the strongest flocs again because of the higher stiffness of the chains.
Reflocculation behaviour of formed flocs was studied with the reversibility index obtained with the following Eq., where A_5 is the final value of the mean chord size after decreasing the stirring intensity to 300 rpm.

$$\text{Reversibility index (\%)} = 100 \times (A_5 - A_1)/(A_2 - A_1)$$

The values of the reversibility index are given in table 1. As expected, broken flocs did not reflocculate to their original size because the shear could partially break down some polymer chains and the polymer-particle junctions, thus the remaining chains could evolve towards a flatter configuration forming patches. This could explain why the anionic polymer shows the best behaviour with regard to changed shear stress conditions again. A flattened configuration would favour a patching mechanism, where even anionic patches could be linked together through Ca^{2+} ions.

To facilitate the interpretation of the data, images of formed flocs have been continuously captured using a PVM device. The five most characteristic experiment-time images (corresponding to the 5 moments indicated in Figure 2) are given in Figure 3. No significant differences are observed in the floc shapes. The most important facts obtained with FBRM are corroborated with the qualitative analysis of PVM images. Ionic polyacrylamides induce larger flocs than the nonionic. Furthermore flocs induced by A-PAM are, in general, larger, stronger and more reversible than the ones obtained with the C-PAM. Therefore, A-PAM is the most suitable flocculant, among the three studied, to induce cement flocculation for wood fibre cement manufacture using the Hatschek process. (Negro, 2006b)

Influence of molecular weight and anionic charge

Experiments were performed using a fibre cement suspension typical of the main process technologies for the production of fibre cement sheets in the air cured process. It is a mixture of highly refined *Pinus Radiata* unbleached Kraft pulp, poly-vinyl-alcohol (PVA) fibres and silica fume on a matrix of ASTM Type II cement.

A wide selection of anionic polyacrylamides (A-PAM), with different charges and molecular weights supplied by Sachtleben Chemie (Germany), were chosen as flocculants. Figure 4 shows their molecular weights and anionic charges. (Negro, 2005a).

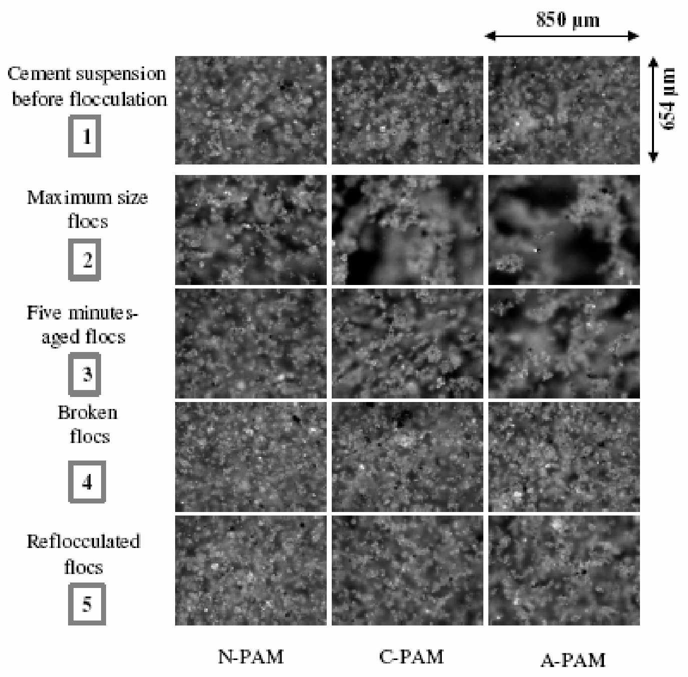

Figure 3 – PVM images evolution with time for 100 ppm dosage of different types of PAM.

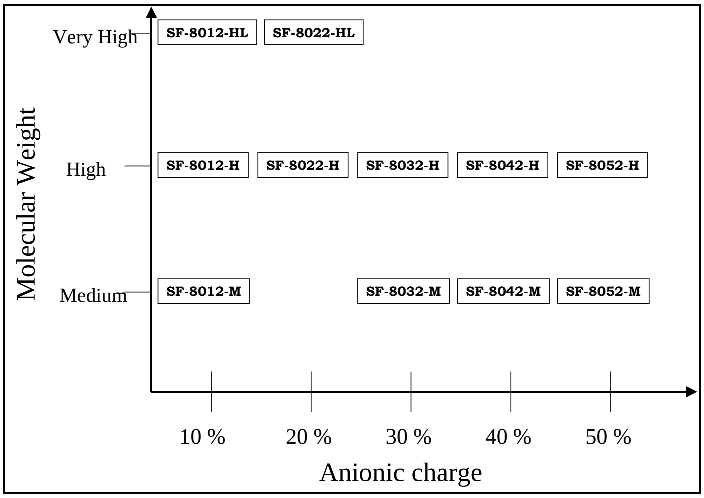

Figure 4 – Anionic charge density and molecular weigth of different PAMs.

Figure 5 shows the bending strength when 100ppm of A-PAM was used in fibre cement preparation; both flocculant properties (molecular weight and anionic charge) affect the product bending strength. A flocculant molecular weight increase reduces both the density and in-turn the bending strength of the product significantly. This effect is more important for the lowest anionic charge. The influence of molecular weight can be explained because bigger flocks are formed when flocculant molecular weight increases. As a consequence, the water content inside the flock increases. Therefore, the air content in the sheet will be higher after curing and thus the density will be lower and hence a reduction in strength properties is expected. Another explanation could be proposed considering that a high molecular weight flocculant induces the production of big flocks and, therefore, the sheet formation in the sieve is poorer and that is why a strength reduction could be expected.

An increase in anionic charge increases the bending strength and the density. The explanation could be that when flocculant anionicity increases, more compact (denser) flocks are obtained because of there being more bonding groups to interact with the cement particles. As a consequence, the water in the flocks is lower and after the curing process the air content of the sheet is lower, the density is higher and it leads to increases in the strength properties of such a product. The improvement in strength properties can also be explained as a consequence of the better formation obtained if smaller, flocks are formed when the flocculant anionicity increases, and these flocs are able to interact each other strong enough to form a sheet with high strength.

Figure 6 shows that the reversibility of the flocks increases with the anionic charge which makes the flocculation process easier to control. The molecular weight has a negative effect on flock reversibility when the anionic charge is low.

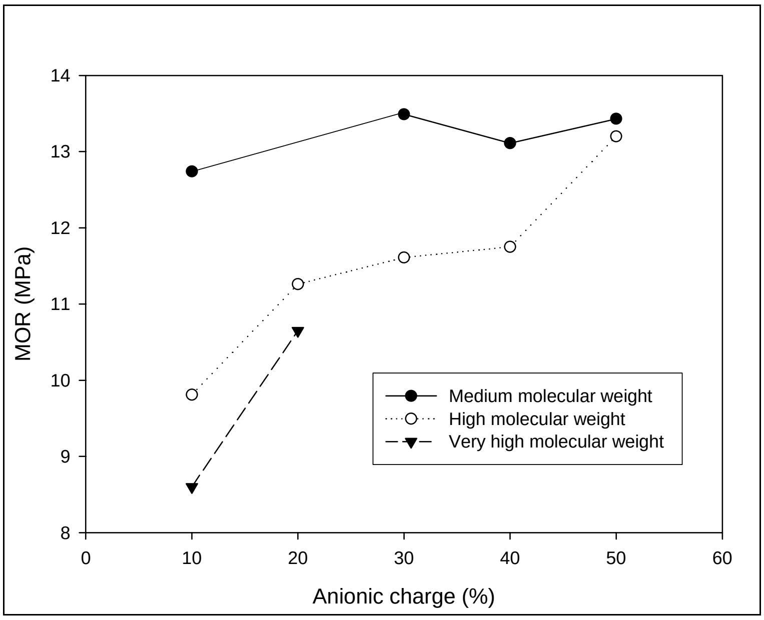

Figure 5 – Effect of molecular weight and charge density of the flocculant on bending strength.

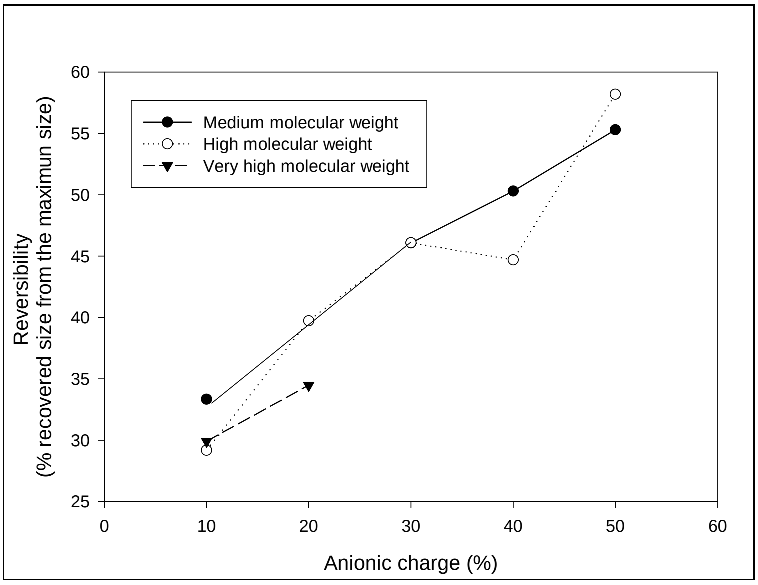

Figure 6 – Effect of molecular weight and charge density on the flock reversibility.

Effect of PAM on bending strength.

The use of A-PAMS is suitable for improving the productivity due to retention, dewatering and formation improvements. However, mill experiences show that problems in flocculant dosage could lead to a reduction in bending strength properties. The loss in bending strength was first attributed to variability of fiber supply and the inhibiting characteristics of the fiber extractives and composition. However, a more detailed study has shown that the flocculant also affects bending strength properties, as can be observed in table 2. A significant bending strength reduction is observed for the three different A-PAMs tested.

According to the references hydroxy-carboxylic groups appear to be particularly active in producing retardation. A further analysis of the results obtained for the three tested flocculants justifies this fact, since the lower bending strength reduction is in correspondence with the use of A-PAM 2, being the one with lower charge density and, therefore, with less carboxylic groups in its structure and consequently with less retardation effect.(Negro, 2005b; Miller, 1991).

Table 2. Influence of several A-PAM at different dosages

	Flocculant dosage (ppm)	Density[1] (g/cm^3)	MOR[1] (MPa)	COD (ppm)
A-PAM 1	0	1.45±0.02	13.1±0.8	122
	100	1.52±0.03	11.2±0.9	214
	200	1.51±0.01	9.4±1.3	99
	300	1.47±0.03	9.3±0.6	140
	400	1.47±0.02	9.3±0.6	99
	500	1.54±0.03	9.5±1.0	129
A-PAM 2	0	1.45±0.02	13.1±0.8	122
	100	1.54±0.03	13.1±0.7	233
	200	1.51±0.01	10.5±0.5	194
	300	1.52±0.02	10.1±0.7	131
	400	1.47±0.02	8.4±0.5	168
	500	1.47±0.01	8.6±0.6	159
A-PAM 3	0	1.45±0.02	13.1±0.8	122
	100	1.49±0.01	11.2±1.1	218
	200	1.48±0.02	9.8±1.5	151
	400	1.47±0.03	10.3±0.9	190

[1]Results obtained from the average of 6 test specimens

However, in order to improve Hatschek machine productivity (retention, dewatering and formation) at industrial level, flocculants are needed but these negative effects should be minimized, avoiding flocculant over dosage through a good flocculation process control. Another alternative is to use new flocculant chemicals in order to overcome the drawback of the actual A-PAM used in the industry or to develop new methods to improve bending strength, e.g. fiber surface treatment. A high strength is required, but product must be also yielding enough to avoid failure.

A patent describing the improvement of fiber cement composites using sizing agents has been recently published (Merkley, 2002). It focused on the improvement of the fiber cement materials performance against humidity. However, there are no technical or scientific papers in the literature confirming this improvement (Negro, 2005b) our research group it is working on that.

In-line flocculation monitoring

The objective of this part was to prove the suitability of using an FBRM probe for in-line flocculation monitoring in a Hatschek machine. In order to obtain results that could be applied to a wide range of industrial installations, the trials were performed in three different Hatschek machines using two different technologies (air cured and autoclave curing), with different mineral raw material compositions and using unbleached softwood pulp alone and in a mixture with PVA (Poly-Vinyl-Alcohol) as reinforcing fibres.

A set of preliminary tests was performed to check the adequacy of the probe location and its sensitivity to process changes. Figure 7 shows the FBRM probe location. The best location in the process is the inlet of the vat, where the primary thin fibre cement layer is formed on the Hatschek machine, because this is the place where the flocculant has just been added and, therefore, the effects will be seen quickly. Moreover, since the critical step for the retention of solids is this primary sheet formation, the selected probe location could allow the correlation to be made between flock size and final product properties.

Results obtained during these trials shows that it has been possible to quantify the flocculation changes produced by both flocculant dosage and type of flocculant changes, for different furnish formulations. (Negro, 2006c) Furthermore, a good correlation between the sensor data and the density of the final product was obtained as can be observed in figure 8. This will allow the mill to predict product quality based on floc properties and to detect out of specification production in real time instead of waiting 7 days to get the product data. Thus, FBRM data may be used to control the flocculation process and as an alarm sensor to predict quality problems related to low density values.

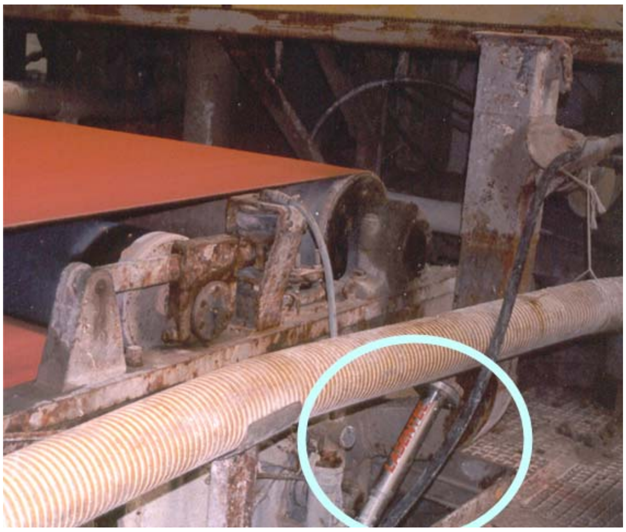

Figure 7 – Location of the FBRM probe.

Based on these results the next step was to study the feasibility of using artificial neural networks (ANNs) to establish correlations between the focused beam reflectance measurements in-line in a Hatschek machine and the mechanical properties of the final fibre cement composite. ANNs could be used to simulate the relationships between process parameters and the product performance and thus be used as the basis for computer-based process optimisation.

An artificial neural network (ANN) can be defined as a data processing system consisting of a large number of simple, highly interconnected processing elements (artificial neurons) in an architecture inspired by the structure of the cerebral cortex of the brain (Zhang, 2003).

In this study, three neural networks have been made to predict three important fibre cement properties: breaking load for 48 hours (F_s^{48h} N/m, ANN-1), breaking load for 7 days (F_s^{7d} N/m, ANN-2), and bending strength for 7 days (M N·m/m, ANN-3). These properties represent the mechanical resistance of the products and they were measured according to EN 494.A man controlled property was added as predictable to validate the robustness of the ANNs responses with properties that cannot be influenced by measured process variables.

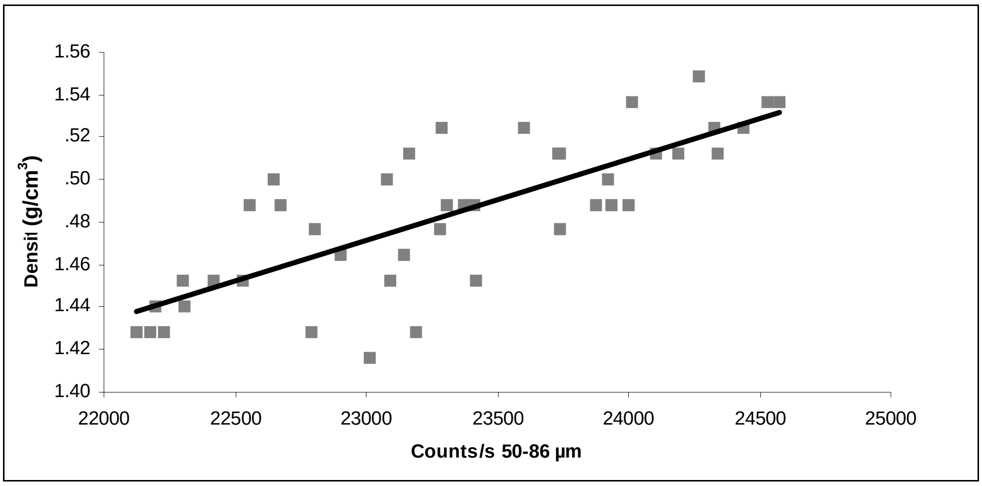

Figure 8 – Air cured product density versus counts/s of particles between 5 and 86 µm size range.

As an example results obtained for the prediction of breaking load at 7 days gave an average error of 8.5%. Correlations and comparisons between predictions and mill values are analysed in figure 9, in which the good performance of the network can be observed. The correlation index (0.85) shows the great prediction capabilities of this ANN. (Negro, 2005c).

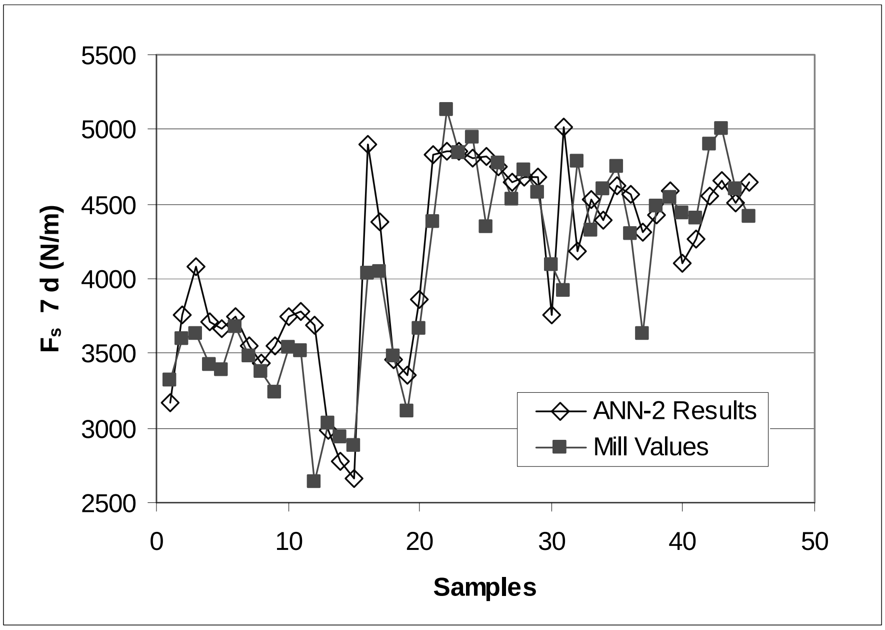

Figure 9 – Comparsion between production data and network results in validation samples for F_s after 7 days air curing.

Once was proved the good relationship between sensor data and final mechanical properties a complete optimization study was carried out. Three different ANN have been developed and analysed: (A)First, an ANN was created in order to select the best sensor statistical data to be used in further optimisation. In this case, 7 different sensor statistical parameters were used as input variables and 7 different product properties were used as output variables. (B) Once the main sensor data were selected it is possible to establish a second ANN with these main variables. (C) Finally, a third ANN with the same variables as used in ANN-B, was established in order to validate the results for different product moulds during fibre cement manufacture. Figure 10 shows an overview of the work carried out. (Negro, 2006d).

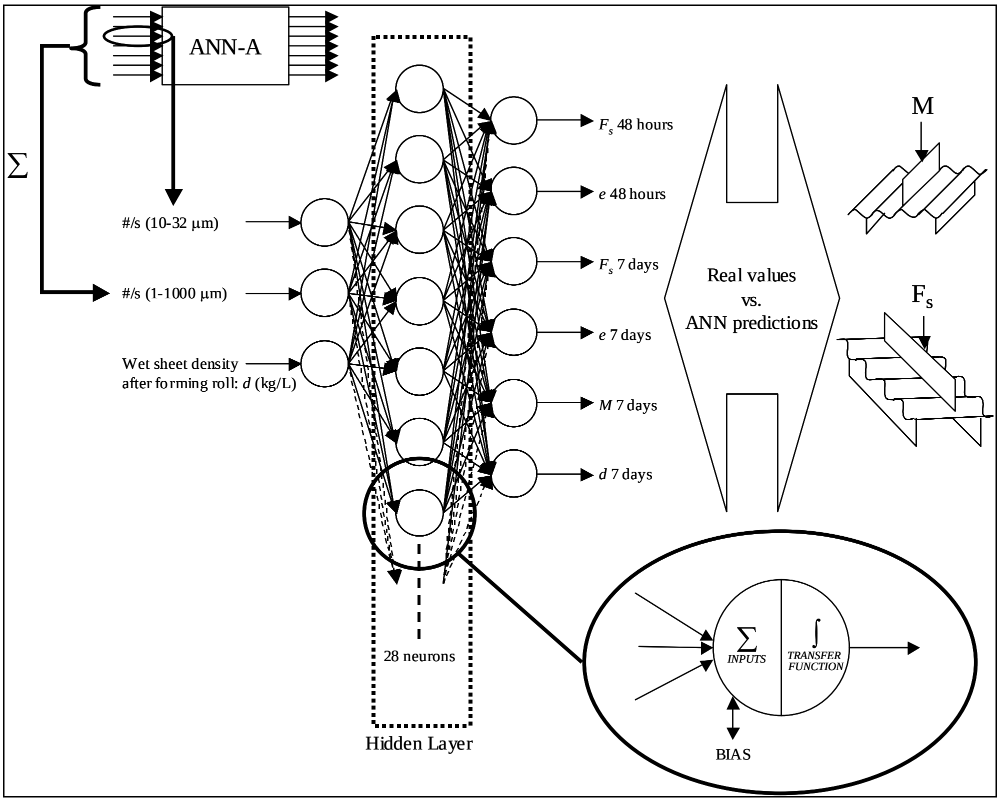

Figure 10 – Scheme for the carried out work. The main ANN of the scheme could be either ANN-B (one profile) or ANN-C (different profiles).

Results show that the total number of counts and the counts in the range between 10-32 µm are the most important statistic from the FBRM sensor to predict final product properties.

The developed neural networks are able to distinguish clearly between predictable and non-predictable outputs. Good correlations are obtained for predictable outputs like breaking loads (correlation coefficients are 0.82 and 0.88) and bending strength (R=0.68). Poor correlations are obtained for variables that could be affected by the operators like the thickness (correlation coefficients are 0.48 and 0.14) demonstrating the robustness of the developed neural network. ANN-C has shown good prediction capabilities even for the manufacture of different mould sheets.

CONCLUSION

Summarising anionic polyacrylamide (A-PAM) is the most suitable to induce cement flocculation because the interactions between Ca^{2+} ions and the anionic carboxylic groups of A-PAM are responsible for the interaction between polymer and cement coagula in water saturated in $Ca(OH)_2$. They also enhance the stiffness of the chain and reduce the flattening conformation increasing the floc strength. The reversibility of flocs induced by A-PAM was the highest because of the flocculation mechanism evolution from bridging towards a patching mechanism, which joins the broken flocs and even anionic patches could be linked together through Ca^{2+} ions. The medium molecular weight polyacrylamides with high anionic charge induce slower flocculation, forming smaller, more compact, stable and reversible flocks. This leads to a better formation (higher strength of the product) and easier flocculation control. According to the results obtained with the FBRM probe can be considered as a good soft sensor for predicting online fibre cement resistance, without modifying the process.

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