SELECTION AND PERFORMANCE OF FLOCCULANTS FOR HATSCHEK MADE AIR CURED FIBRE CEMENT

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ABSTRACT

The manufacture of fibre cement by the Hatschek process involves the filtration of dilute slurries of finely divided particles on screens with relatively large openings. Agglomeration of fine particles into larger particles by the use of flocculants reduces the amount of materials passing through the filter screens .Nevertheless, the large quantities of water passing these screens still contain significant amounts of very fine chemically active solids (particularly cement and fine silica) that must be promptly recovered and reused. Prompt recovery of these solids in the water clarification and solids recovery system associated with the Hatschek system requires the use of chemical flocculants which agglomerate these fine solids into hydraulically coarser particles that settle rapidly to a position from which they are returned to the feed of the machine.

Effective flocculants for cement based materials are anionic in nature and their chemistry is surprisingly similar to effective dispersents and super-plasticisers used in concrete. This paper discusses the chemistry and the properties required of suitable flocculants contrasting these with those required of super-plasticisers. Critical factors within the Hatschek machine itself including the delivery system for slurry to the Hatschek machine vats and delivery of flocculant to the system are also discussed and recommendations are made.

The results disclosed here were obtained during the optimisation of the operation of a recently commissioned 4-vat Hatschek machine installed. Several flocculants were evaluated before and after changes were made to the feed system with various molecular weights (MWt's) and charge densities.

Several practical methods for the selection of flocculants were evaluated but it was found that these did not reliably predict their performance and that the best method of evaluation was through limited trials on the Hatschek machine itself.

KEYWORDS:

flocculants; fibre cement; manufacture;

INTRODUCTION

The manufacture of fibre cement by the Hatschek process involves the filtration of dilute slurries of finely divided particles on screens with relatively large openings (Cooke 2002). The particles consist of finely divided mineral materials such as Portland Cement, Silica, Calcium Carbonate and others as well as fibres that may include refined cellulose and synthetic materials such as Polyvinyl Alcohol (PVA), Polypropylene (PP) or other similar fibres. The operation of the process requires that the fibrous components, which are for the most part longer than the screen openings, form a filtration layer which traps the fine mineral material. Where extremely fine particles such as Silica Fume are used, then the use of flocculants can reduce the amount of material passing the screens by attaching them to the fibres, however the formation of filtration layer still takes time and until the layer has been built to sufficient thickness large quantities of the mineral

materials pass through the screen with the process water. These materials must be recovered partly for economy of operation and partly because materials such as cement and silica (in the conditions of process) are chemically active and their loss or inactivation could seriously diminish the properties of the resulting fibre cement. Prompt recovery of these solids in the water clarification and solids recovery system associated with the Hatschek system is therefore necessary and it has been found that this requires the use of chemical flocculants which agglomerate these fine solids into hydraulically coarser particles that settle rapidly to a position from which they are returned to the feed of the machine.

The majority of solid particles suspended in water develop an electrical charge (Gregory 2006) which becomes positive in the case of the minerals used in fibre cement manufacture. Thus it is found that effective flocculants for cement based materials are anionic or negative in nature and they bind quite strongly to the minerals. It is also found that effective flocculants are of high molecular weight which allows a molecule of the flocculant to attach itself to two or more mineral or fibre particles thus binding them together. There are however other factors in the molecular structure of the flocculant molecules and the mineral particles that are relevant to their performance in this situation. Cement is not a simple material but is a combination of several distinct mineral moieties which develop different surface charges when suspended in water. The composition of the cement affects the proportions of each mineral that will be present in the cement particle and this affects its interaction with the flocculant. The proportion of soluble materials such as Alkaline Earth metals within the cement also affect the ionic environment in which the particles are suspended because these determine the composition of the process water. This in turn affects the charge developed on the surface of the particles and their interaction with the specific flocculant being used. Thus a flocculant being used effectively with one specific cement or mineral composition may function quite differently with another set of raw materials.

The chemistry of flocculants is surprisingly similar to that of effective dispersents and super-plasticisers used in concrete and it would seem that a material that is used in one circumstance to agglomerate fine particles should not be able to disperse the same particles. However this is quite explicable in terms of the chemistry and physics of the situation and can be shown to explain what often happens in situations where the flocculants are overdosed or incorrectly used. We later discuss the chemistry and the properties required of suitable flocculants contrasting these with those required of super-plasticisers and show that foam generation and indeed lack of flocculation may be the result of overdosing and improper use of flocculants.

Finally we show that operating parameters within the Hatschek machine itself, including its slurry delivery system and introduction of flocculant to the system are critical to the performance of the flocculant. Preparation of flocculant solutions is also important but space prevents us discussing this factor in this paper.

We may conclude that the performance of flocculants in the manufacture of fibre cement is determined by many factors as is illustrated in Figure 1 on the following page.

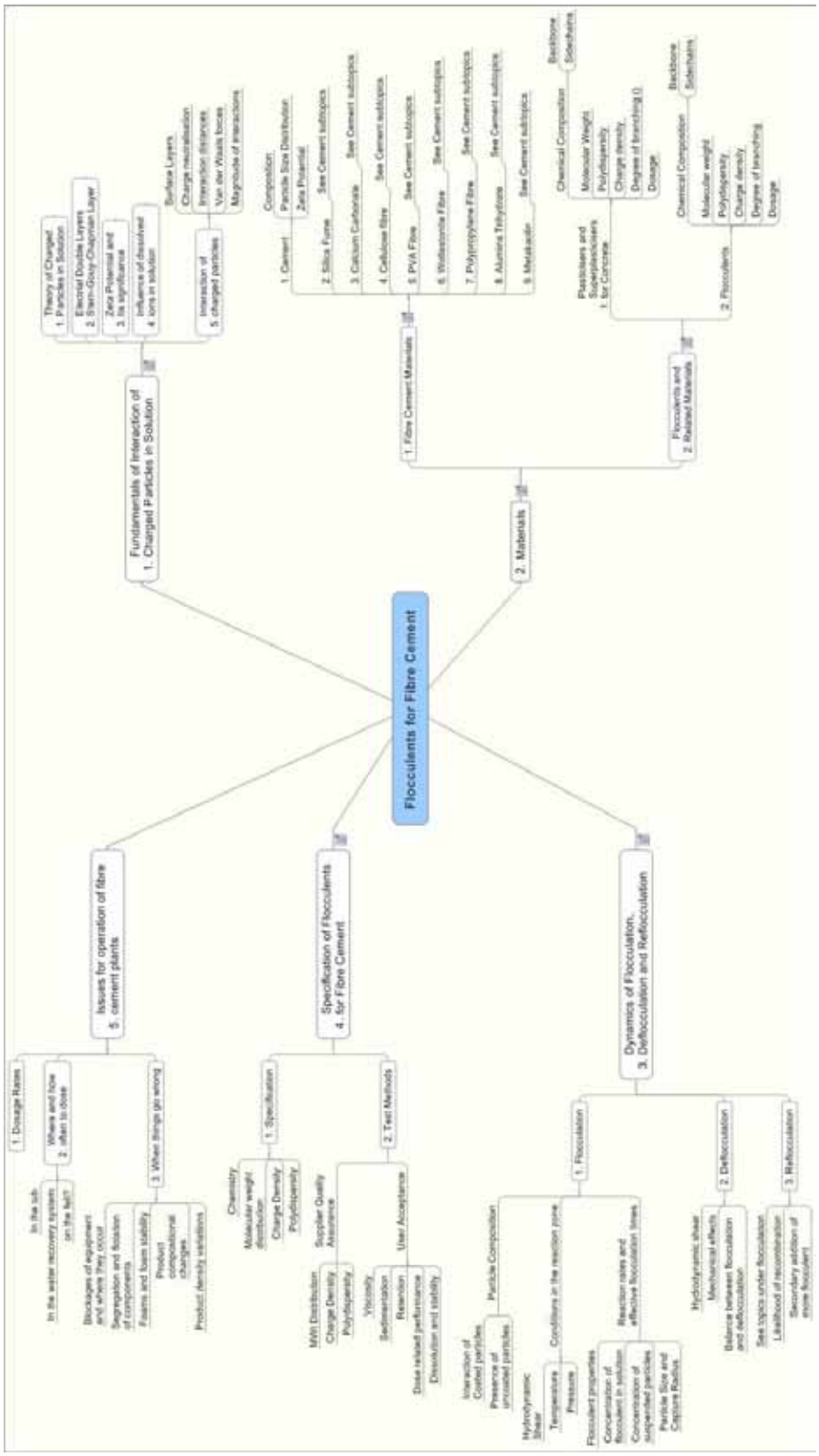


Figure1: Factors relevant for the performance of flocculants in fibre cement manufacture.

Brief Introduction to Interaction of Charged Particles in Solution[1]

In this section we will briefly discuss topics relevant to flocculation of fibre cement materials.

Origin of Charge on particles in solution (Gregory),(Pashley)

There are various sources of surface charge which may be grouped according to their origin

1. Ionisable surface groups leaving a residual charge e.g. acidic or basic groups at which H^+ groups can be released or acquired depending on pH of the solution
2. Dissolution of constituent atoms of low solubility compounds Ions within a compound have different tendencies to dissolve into the liquid e.g. Ca^{2+} ions may escape from $CaCO_3$ leaving a negative charge behind
3. Isomorphous substitution of one ion for another - in complex layered materials such as clays Al^{3+} ions and Si^{4+} ions may be interchanged leaving a charge imbalance at the surface – important for certain cement minerals
4. Specific Adsorption of Ions - Ions can be adsorbed from solution where there is a "specific" interaction between the surface and dissolved materials e.g. soaps consisting of a hydrocarbon tail combined with an ionic head adsorbed on the surface of oil and other materials compatible with the hydrocarbon tail leaving the charged head on the outside of the oil surface.

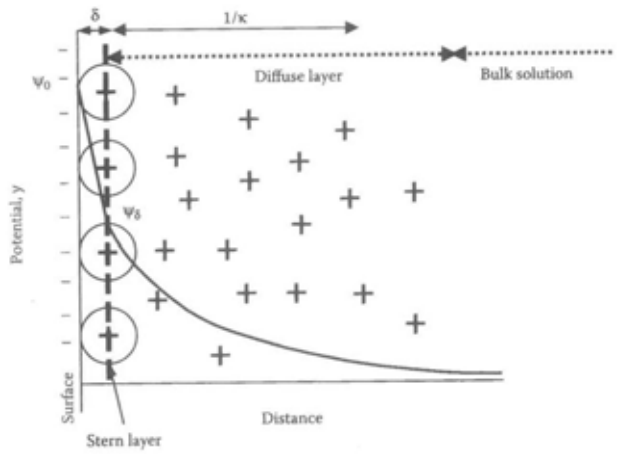


Figure 2: Stern-Gouy-Chapman model of the electrical doublelayer adjacent to a negatively charged surface (Gregory, Figure 3.5 p54)

The ionic environment in which these charged particles are suspended is also important. In a Hatschek manufacturing process the carrier water is essentially a saturated solution of Calcium Hydroxide (Ca^{2+} and OH^- ions) which is modified by the presence of the alkaline earth ions Sodium and Potassium as well as anions such as Sulphate (SO_4^{2-}). These ions in solution are mobile and the surface charged solids attract oppositely charged ions and repel same charged ions. The result is the formation of the so called electrical double layer (Stern-Gouy-Chapman or SGC layer, sometimes abbreviated to just Stern Layer) as illustrated in Figure 2.

In Figure 2 the solid surface is negatively charged. Thus positive ions absorbed on to the negative surface from solution initially forming a compact layer of positive charge that shields the negatively charged surface. The number of ions absorbed depends on the attractive force between the surface and the ions i.e. the initial negative charge of the surface derived by one of the means above and the charge on the positive ion. The

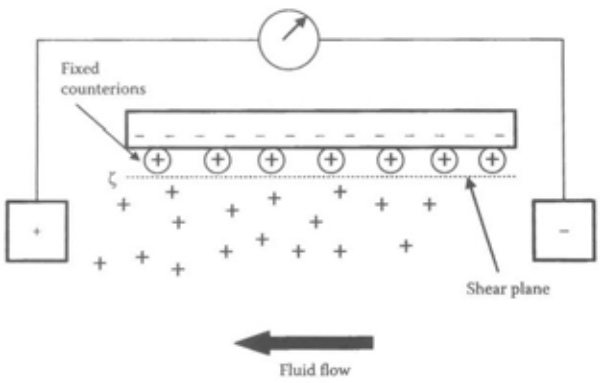
[1] For more detailed discussion of topics of this section see references Gregory and Pashley.

compactness of the layer of adsorbed ions is also determined by thermal agitation and the concentration of positive charge. Thus the solid surface becomes covered with a positive charge with a layer of solution depleted in positive ions surrounded by a diffuse layer of ions whose concentration eventually reaches that of the bulk solution. An electrical field develops whose potential (Ψ) can be described by the following equation

$$\Psi = \Psi_{\delta} \exp^{(-Kx)}$$

δ = distance of Stern layer ~ depth of hydrated ion

K = Debye-Huckel parameter determined by the ions present in solution



Development of a streaming potential as a result of fluid flow past a charged surface. The movement of counterions in the mobile part of the double layer, outside the shear plane, causes the left-hand electrode to acquire a positive potential relative to the right-hand electrode. The potential at the shear plane is the *zeta potential*, ζ, which can be derived from such measurements.

The Stern layer is the layer of essentially fixed adsorbed charge on the surface of the particle. If the particle is subjected to the shear that commonly occurs in fluid systems then the loosely attracted ions in the diffuse layer are stripped away from the particle (Figure 3). This results in a streaming potential being developed which can be measured and the electrical potential of the surface at the Stern layer can be calculated. This is named the Zeta Potential and is the effective potential either positive or negative of the surface of the charged particle. Zeta Potentials depend on the environment in which the particle is found and are not material parameters.

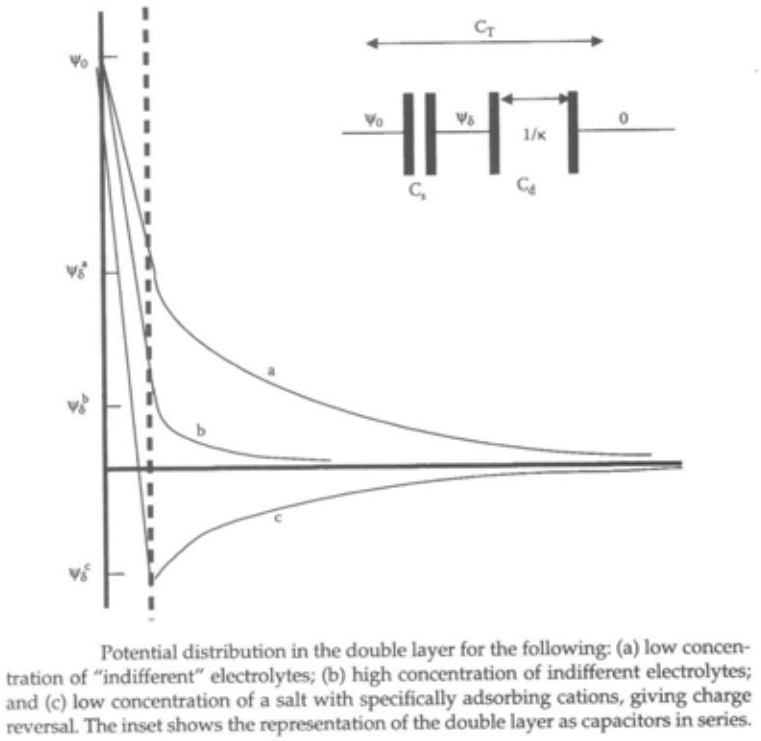
Figure 3: Determination of Zeta potential (Gregory, Figure 3.8 p59)

The potential within the SGC layer also depends on the environment in which the particle is suspended and the potential distribution depends on the type and concentration of ions present in solution. Increasing ionic strength decreases the Stern potential and decreases the thickness of the diffuse layer i.e. the charge density of ions in solution compresses the diffuse layer. Both of these effects occur with any added salt and are quite important for dissolved ions other than Ca^{2+} and SO_4^{2-}derived from the cement.

Variations in the potential distribution with the SGC layer are illustrated in Figure 4 for several situations. It is important to note that increasing ionic strength of the suspending solution decreases the apparent potential within the SGC layer. It is also possible with certain combinations ions and high ionic solution strength to reverse the Zeta potential of the particles. The Zeta Potential is shown in Figure 4 as the potential at the dotted line.

This situation is most important in systems containing Portland Cement because ions such as Ca^{2+}, SO_4^{2-}, K^+, Na^+ etc having dissolved from the cement are normally present in the process water. These alter the apparent charge on the particles and are thus important to their coalescence and settling. It has been found (Nagele 1989)(Andersen 1986) that cement naturally exhibits negative Zeta potential when suspended in pure water at low dilution. However it has also been found(Nachbaur 1998) that when cement is suspended in solutions of increasing concentration of Ca^{2+} ions its Zeta potential rises and becomes positive beyond a concentration of 8 mmol/litre. Nachbaur also found that the presence of SO_4^{2-} ions in solutions containing Ca^{2+}depressed the Zeta potential but that it still becomes positive above 10 mmol/litre. Nachbaur also found that Na^+ and K^+ ions were indifferent in these circumstances i.e. they had only a small effect on Zeta potential and this is in proportion to their concentration. These observations show that the Zeta potential of cements is due to the absorption of Ca^{2+} ions on their surfaces and that these ions can be stripped off in dilute solution.

It is important to note the ingredients for fibre cement manufacture are usually dispersed in process water that is saturated with Ca^{2+} and other ions mentioned above. Shin et al (Shin 1997) report that cellulose has a negative Zeta potential in low pH water but herecellulose is dispersed and refined in process water and silica may be ground in process water. Thus they are already in equilibrium with the soluble cement materials before they are added to the mix. Process water is also used to dilute the mix so the dry materials such as cement and other minerals are dropped into a high pH medium and can be assumed to quickly come to equilibrium thus all of the materials in the mix will exhibit positive Zeta potential.



Potential distribution in the double layer for the following: (a) low concentration of "indifferent" electrolytes; (b) high concentration of indifferent electrolytes; and (c) low concentration of a salt with specifically adsorbing cations, giving charge reversal. The inset shows the representation of the double layer as capacitors in series.

Figure 4: Variations of potential distribution within the SGC layer(Gregory, Figure 3.6 p57).

Flocculation

It is clear from the above that particles in a fibre cement suspension are identically charged,will repel one another and will not coagulate unless the repulsion force between them is overcome. It is equally clear that oppositely charged particles will be likely to coagulate because they are attracted to each other. However the propensity for particles to coagulate or separate will depend on the magnitude of the forces between them and the influence of the fluid environment in which they are suspended. Thus even in a quiet environment oppositely charged particles will coagulate while identically charged particles will tend not to coagulate. It should also be noted that the magnitude of the attractive or repulsive forces between particles is relatively small and not comparable even to Van Der Waals forces let alone chemical bonding forces. Therefore in an environment of high shear or high agitation the propensity of oppositely charged particles to coagulate will be quite small due to the dynamic forces involved and indeed previously formed agglomerates may be disrupted.

Flocculation or agglomeration of particles is also dependent on their being brought sufficiently close enough together that bonds can be formed. This requires sufficient agitation of the fluid to bring the particles randomly together. While there is agitation there will be some disaggregation of the particle agglomerates, so flocculation is a balance between agglomeration and disagglomeration and the rate of flocculation will depend on the differential rates of each of these processes.

In order to apply the principles of what has been said above it is clear that we need know the mechanical and electrical properties of the various particles that are used to manufacture fibre cement. Table 1 below shows **estimates** for some of these properties.

Table 1: Estimates of Properties of Materials used in the Manufacture of Fibre Cement

Material	Composition	Particle Size	ζ Potential*	Comment
Portland Cement	C_3A, C_4AF C_3S, C_2S	10 – 50 µm	~+5 to30 mV ~0 to 10 mV	Only the Al containing minerals are significantly charged Strongly –ve at high pH but switches to +ve in presence of Ca^{2+}
Ground Silica	→SiOH groups on surface	10 – 50 µm	~+5 to 30 mV	
Silica Fume	→SiOH groups on surface	<0.1 – 1 µm	~+5 to20 mV	Strongly –ve at high pH but switches to +ve in presence of Ca^{2+}
Alumina Trihydrate	Surface OH^-	10 – 50 µm	~+5 to20 mV	+ve over wide pH range
Calcium Carbonate	$CaCO_3$	10 – 50 µm	~-10 to -40 mV	Depends on $[Ca^{2+}]$
Cellulose fibre	Surface OH^-	~2.5mm x 20 µm	~+5 to20 mV	Strongly –ve at low pH but switches to +ve in presence of Ca^{2+}
PVA Fibre	Surface OH^-	~4mm x 20 µm	~+5 to 20 mV	Strongly –ve at low pH but switches to +ve in presence of Ca^{2+}
Polypropylene Fibre	Hydrophilic Coating for fibre cement use	~4mm x 20 µm	Probably 0	Unlikely to adsorb ions

The literature on Zetapotential is not definitive for the materials above because as we have seen the Zeta potential is dependent on the ionic environment in which the particles are suspended. We can however be sure that the process water of operating Hatschek machines is highly alkaline and saturated in Ca^{2+} ions to that all of the immersed particles will develop a positive charge or Zetapotential.

It is also possible that some self flocculation could occur between say the cellulose and the mineral materials providing that the pH of the water remained low and if there were no Ca^{2+} ions present. However this will rarely happen in an operating plant because the cellulose is usually dispersed and refined in process water and the cellulose fibre rapidly becomes positively charged.

The predominantly positive Zetapotential of the fibre cement materials explains why anionic flocculants are effective with fibre cement – they bind strongly to the particles of the fibre cement materials. However there are other factors related to their composition and MWt and structure that affect their performance and we will now discuss these.

Anionic Flocculants for Fibre Cement Manufacture

Effective anionic flocculants for this environment are copolymers of acrylamide and acrylic acid. The acrylamide provides the backbone of the copolymer and the acrylic acid provides the negative or anionic charge to the molecule that produces the flocculation effect.

As will be demonstrated later, the most effective flocculants have molecular weights around 10-27*10^6 Daltons and are thus long chain in nature. The main forms of supply of polymers are powders and emulsions. Whatever their form flocculants are diluted in potable water as a solution prior to use.

Flocculants are characterised by their MWt and charge density. The charge density is expressed as a percentage and is the ratio of molecules of acrylic acid monomer to the molecules of acrylic acid plus acrylamide in the original batch formulation. Although manufacturers are reluctant to disclose the details of their manufacturing processes, flocculants containing only acrylamide and acrylic acid can only be linear molecules, as their component monomers (Acrylamide and Acrylic Acid) contain only one double bond which is broken during polymerisation. However, given the often considerable difference in the performance of apparently similar flocculants from the different manufacturers and even with different batches of the same specified flocculant from the same manufacturer, additional explanations must be sought for this behaviour.

This may be due to branching but while it could also be due to the distribution of molecular weights. While the above implies that each polymer molecule in a batch will be of equal MWt the probabilistic nature of the reaction process means that there will be a distribution of MWt for the polymer molecules around the mean value. The range of MWt's also affects their performance as a flocculant in addition to their degree of branching, average MWt and charge density.

Interactions of Charged Particles in Ionic Solution[2]

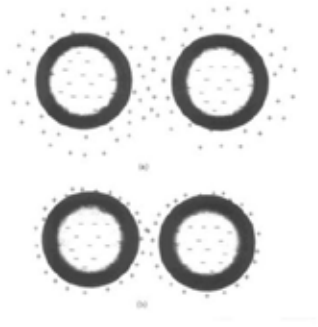
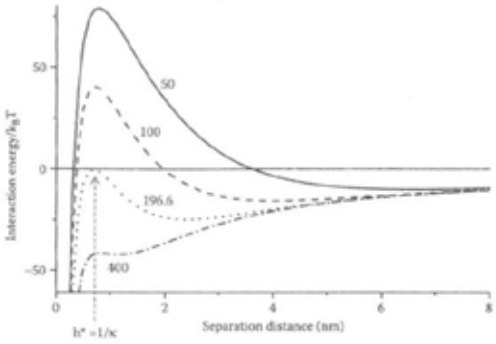


Figure 5 – negatively charged particles in ionic solution(Gregory, Figure 4.7 p81)



The effect of 1-1 electrolyte concentration on the total interaction energy. The electrolyte concentrations (mM) are shown on the curves.

Figure 6 - Interaction energy of charged particles in solution with different electrolyte concentrations(Gregory, Figure 4.6 p79)

Like charged particles repel one another due to electrical forces however if they are forced to approach closely enough they may spontaneously coalesce due to Van der Waals attraction forces. In solutions of low

[2] The material in this and the following sections is derived largely from reference Gregory

ionic concentration there is usually a large energy barrier that must be overcome before the particles can coalesce which means that small (i.e. colloidal sized) charged particles stay stably in suspension. Non colloidal charged particles may not stay in suspension but their electrical charge may be sufficient to prevent their easy further coalescence and they will stay in suspension for longer than otherwise.

Figure 5 shows negatively charged particles in ionic solution which as we have already seen, attracts a layer of positive counter-ions that partially or fully neutralises their electrical charge. The degree to which their electrical charge is neutralised depends on the concentration of counter-ions in solution and higher concentrations reduce their apparent charge to a greater extent. The presence of counter-ions in solution reduces the energy barrier between the charged particles and it becomes easier for them to coalesce.

As shown in Figure 6, at sufficiently high ionic concentrations the energy barrier is eliminated or even becomes positive and a colloidal suspension then becomes unstable and coalesces spontaneously. This is useful for some situations such as salting out butter but it is not useful with cement containing materials because many salts interfere with or alter cement hydration. Furthermore we are usually dealing with relatively large particles that will spontaneously settle out at least in the longer term. The concentration of ions such as K^+ and Na^+ differs from cement to cement and thus the apparent charge on the suspended cement minerals will be different in different environments and will affect the performance of various flocculants.

Mechanisms of Flocculation and Dispersion of Particles in Solution

We first consider the behaviour of flocculant molecules in solution.

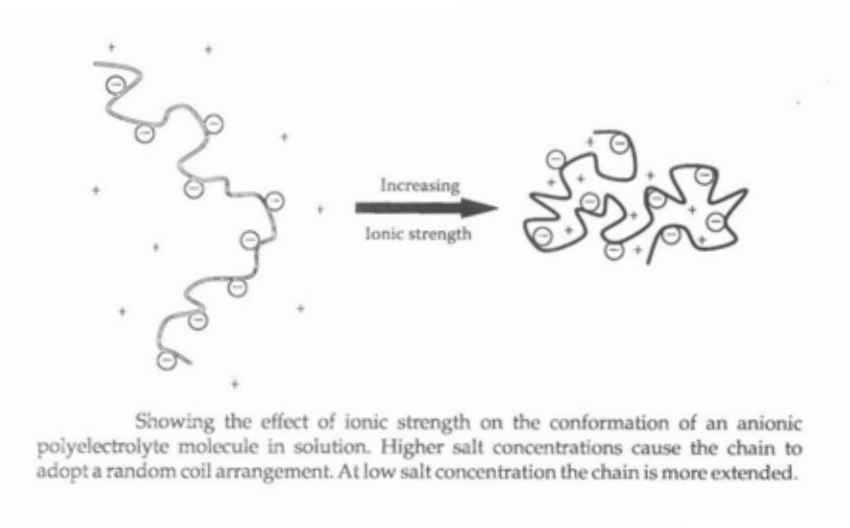


Figure 7 - a linear polymer in solution.(Gregory, Figure 6.7 p134)

Figure 7 shows the conformation of a linear polymer in an ionic solution. As has been previously remarked the acrylate disassociates in solution and the acrylate portion of the polymer becomes negatively charged. The charges along the polymer chain repel each and the molecules uncoil and straighten out. However, the polymer molecule attracts opposing charges from solution which neutralise or shield the charges on the molecule and this effect becomes greater with increasing concentration of ions in solution.. Furthermore, the increase in ionic strength reduces all the electrostatic forces because it affects the dielectric constant of the medium. Thus the repulsive forces among the acrylate groups decreased. Thus as the solution becomes more concentrated in soluble ions the thermal agitation of the polymer molecules makes them adopt a less extended shape.

The same is generally true with branched polymers but is slightly different because the repulsion between adjacent branches extends the molecules. In this situation the volumetric concentration of charged moieties is greater between these branches because each branch contributes to the charge and is constrained from

moving away from the adjacent branch by being bonded in the molecule. There is also steric hindrance between those portions of the branches close to the branching point that reduces access to counter-ions between the chains and reduces their effective concentration. Thus, a degree of branching is probably beneficial to the performance of flocculants.

We now consider the interaction of anionic flocculant molecules with charged particles in general and the components of fibre cement in particular.

Figure 8:1 - Low MWt linear polymer patches on spherical surface(Gregory, Figure 6.10 p141)

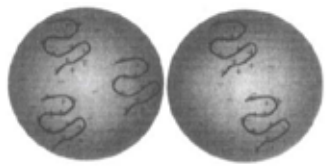


Figure 8:2 – High MWt linear polymer on flat surface(Gregory, Figure 6.9 p138)

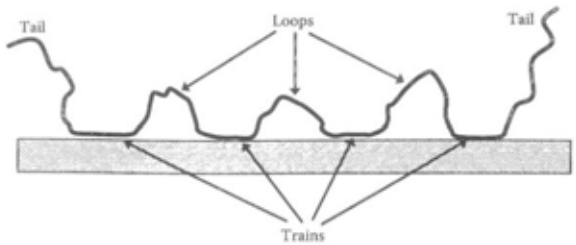
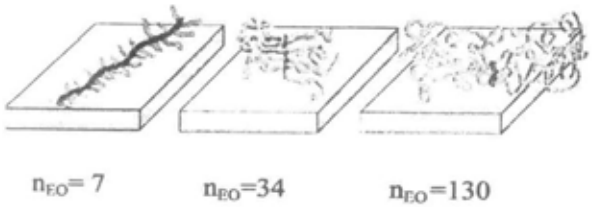


Figure 8:3 – High MWt branched polymer on flat surface. n_{eo} refers to relative length of ethylene oxide side chains on differing length backbone(Plank and Sachsenhauser)



The charged anionic polymer molecules are attracted to and attach themselves to positively charged surfaces of the particles in suspension. Figure 8 illustrates three possible conformations of polymer attaching to charged surfaces.

Figure 8:1 shows low MWt linear polymer absorbed on a spherical (i.e. idealised 3 dimensional) surface. In this situation the polymer forms patches on the surface. If sufficient polymer is present in the solution then patch formation can bring about charge neutralisation and the particles may agglomerate or passively flocculate as a result. However, if additional polymer is present then charge reversal may result and the particles will redisperse. Dispersion of cement in fresh concrete can be achieved by this method and plasticisers and super-plasticisers for concrete are low MWt anionic polymers and are used at high concentrations to achieve this dispersion.

Figure 8:2 shows the more common conformation of anionic polymer resulting in flocculation. Because the high MWt polymer molecule is extended in solution it initially touches the surface of the charged particle at only a few positions and may bind to the surface. Thermal and hydraulic agitation bends the molecule and may allow it to reattach at several further positions along its length. As a result the molecule forms a series of loops and trains with trailing tails. These effectively increase the size of the particle, increase its collision cross-section which results in an increased likelihood of a collision. The loops and tails are also electrically charged and the collision of two coated particles is therefore likely to result in the particles becoming bound together i.e. active flocculation occurs and the combined particles are more likely to settle out.

Figure 8:3 shows the situation with several different branched polymer structures. In the first two illustrations the polymer sub-chains are similar in length to the low MWt polymer in the Figure 8:1 so

patches of polymer form on the surface. The third illustration is however similar to Figure 8:2 where the sub-chains are relatively long and thus tend to form loops and trains. Thus a branched polymer of this structure is more likely to be an active rather than a passive flocculant.

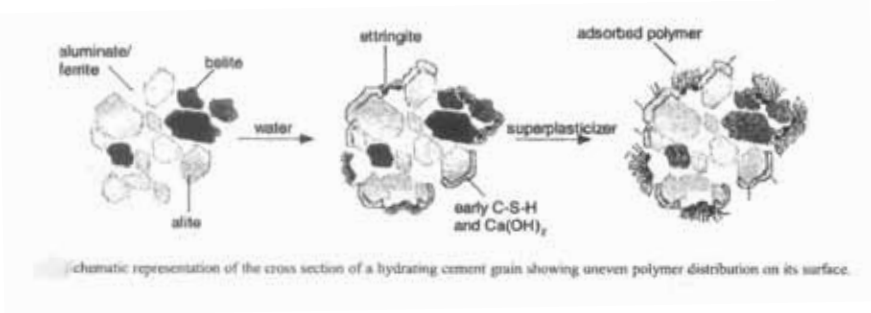


Figure 9 – Polymer distribution on a cement grain (Plank and Hirsch)

We have assumed that the surface on which the polymer adheres is uniform and this is generally true where a mineral material consists of one species or type e.g. Silica or Limestone. However cement clinker comprises of 4 major minerals (i.e. C_3S, C_2S, C_3A and C_4AF) and several minor minerals Gypsum is also present as a cement hydration inhibitor. The clinker minerals do not separate during crushing and cement grains consist of aggregates of different minerals. In addition the cement grains are chemically active in water and are hydrating as well as forming compounds such as Ettringite (Calcium Alumino Sulphate hydrate formed in place from the C_3A on the surface of the cement grain and Gypsum) with different electrical properties. These compounds have different inherent surface charges so the polymer does not absorb uniformly on the surface of the cement grains but rather is found to attach preferentially to the Aluminates, the Alumino-Ferrites and the Ettringite. This is shown in the Figure 9 above.

This clearly complicates the situation further because not all cement particles are equally likely to bind to the flocculant and the behaviour of the other mineral particles and the fibres is different from those of the cement. Nevertheless it is observed that the cement/mineral slurries containing cellulose and synthetic fibre readily flocculate in the presence of suitable anionic flocculants. Flocculation is rapid but not instantaneous and flocculation occurs as follows.

When flocculant is introduced into slurries of cement, mineral and fibres, flocculant molecules bind to the particles by electrical attraction in the manner shown in Figures 8.2, 8.3 and 9. This induces a charge reduction and the flocculant molecules have tails that extend from the particle surfaces into solution.

Should two flocculant coated particles come close enough to collide then the free tails or loops of the flocculant molecule on one particle can interact with the other particle resulting in their becoming bound together. The possibility of two particles becoming bound together depends on the amount of polymer present and the properties of the polymer. The rate at which such binding occurs depends on the degree of agitation in the suspension which determines how frequently particles collide and the shear force that tends to separate connected particles. Overall rates of flocculation therefore depend on the rate of flocculation compared to the rate of deflocculation.

The possibility of deflocculation is high in highly agitated suspensions because the strength of the flocculant bond is small in relation to the inertial and shear forces that can be induced. Indeed these forces are sufficient to break the molecular chains of the flocculant molecules. If this occurs shortening the tails of these molecules, the ends of the molecules can reconnect to the surface of the particles resulting in a situation similar to that shown in Figure 8.1. The effectiveness of the remaining flocculant is therefore greatly reduced even though there may be some charge neutralisation which diminishes the electrical dispersion effect. Thus in extreme agitation it will be found that the flocs will be broken up and that flocs do not reform should the subsequent agitation be greatly reduced.

FLOCCULANT PERFORMANCE IN PRACTICE AND SELECTION OF FLOCCULANTS

The work reported in this paper arose from commissioning and tuning of the operation of a 4 vat Hatschek machine at Everite, Kliprivier South Africa, manufacturing air cured fibre cement corrugates. It also arose from attempts to determine the differences between apparently similar flocculants and because of the flocculant supply situation in South Africa where there was no local manufacture of flocculant which resulted in uncertainty of supplier and supply.

It should be noted that while equipment such as the focussed beam reflection measurement (FBRM) equipment for the evaluation of flocculants [Negro et al] may have been desirable, such equipment was not available. Therefore this paper focuses on methods for evaluation of flocculants that can be adapted and used in most fibre cement manufacturing facilities and their laboratories.

It was determined during tuning of the Hatschek machine that flocculant performance was a major factor determining its smooth and efficient operation. The performance of the machine was compared with an adjacent Mazza pipe machine using similar mix formulation and was found to be quite different in retention of film solids and in the behaviour of the flocculant in the water system. Thus the Hatschek machine compared to the Mazza machine using the same flocculant showed significantly lower retention and was subject to excessive foaming and a greater tendency for blockages in the water recuperation system.

Previous experience with both the Mazza and the Hatschek machines showed that if either machine is running stably then solids content of the water passing the sieve would be approximately 50% of the solids in the feed to the machine but that this was not consistently achieved. Experience with various flocculants showed great variations in the quality of flocculants being received and there was even a variation in the performance of flocculants drawn from the same batch or even from individual bags of the same batch.

A visit by one of the authors to a fibre cement plant in another country showed a very similar but more stable experience and this was attributed to different flocculants that this plant used. When flocculant of the same type were obtained reasonable performance was achieved and they gave good settling of the mud water tanks. However these materials were not readily available in South Africa and alternative supplies of flocculant having similar properties were sought from local importers as well as flocculants having specifications within the range found satisfactory from previous experience (i.e. medium molecular weight and ionic charge).

It was also Everite's experience that a particular flocculant (hereafter called the Preferred Floc) gave consistent performance and this flocculant was used whenever possible. However, experience with this flocculant was mixed and the importer had analysed "good" and "bad" batches of this material which showed significant differences in average and range of molecular weights.

It had also been realized that it was possible that the feed pump delivering feed from the mix box (or homogeniser) to the vats could be damaging the flocs and nullifying their effect so it was decided to modify raise the mix box and feed the machine by gravity. This was undertaken on the weekend between the first and second weeks of the trials.

In the first week of the trials several flocs were tested systematically and their performance was evaluated. These flocs were designated as 5230, 5618, 5230/5618 50:50 Blend, 5290, 62716, 9011, 63226, 9048, Preferred Floc 'Good', Preferred Floc 'Bad' and 6260.

The flocculants were first evaluated in laboratory tests for viscosity of 0.1% solutions and ease of dissolution in water.It was found that it was not possible in the lab to dissolve flocs 62716, 9011, 63226 and 9048 at 0.1% and achieve a reasonable viscosity. Similar difficulties were found when these flocculants were dissolved in the plant and one of the flocculants had previously caused considerable difficulties elsewhere in the plant. As a result none of these was used in subsequent trials.

Laboratory tests were then conducted using two types of sedimentation and two types of retention tests. Each test was performed by first flocculating slurry of known formulation and consistency with 150 ppm of flocculant relative to the solids in the slurry . The sedimentation effectiveness test is performed by following

the sedimentation of 100 ml of flocculated slurry in a standard cylinder and determining the time for the clear layer to reach volumesspecified in Table 2.

Retention is determined by pouring the flocculated slurry through 45# screen (i.e. identical to the sieve screens on the Hatschek machine), collecting the filtrate and filtering it on a No 41 Whatman filter. The retention was then determined from the weight retained on the screen divided by the sum of the weights retained on the screen and the Whatman filter.

The second retention test was done by performing a modified Canadian Standard Freeness drainage test on the flocculated slurry and determining the amount retained.

The rationale behind these tests is that the flocculants perform 2 functions – to improve the amount of solids contained in the film on the Hatschek machine thus reducing the recycling load and to improve the sedimentation of solids in the water recovery system thus reducing the time that solids are present in the water before being returned to be reused. Although the initial results of the tests were promising they proved to be difficult to reliably repeat and they were eventually abandoned.

Table 2 Results of tests from Week 1 – mix pumped to the vats

Flocculant Properties and Laboratory Tests											
Flocculant Properties					Effectiveness Test					Laboratory	
Floc	Viscosity				Secs to	50/50 *		80/10/10 **		Retention	
	Prod'n	Lab	Charge	M Wt	Volume	Prod'n	Lab	Prod'n	Lab		
					40	15	15	16	14	Passing	19.9
5230	13	22	10	12	35	18	18	20	19	Retained	47.8
					30	24	27	28	31	% ret'd	70.6%
					40		28		23	Passing	20
5618		49	40	12	35		39		34	Retained	43.3
					30		60		52	% ret'd	68.4%
					40	28	31	32	32	Passing	8.8
5290	52	107	55	16	35	39	45	47	50	Retained	60.8
					30	66	70	74	82	% ret'd	87.4%
5230					40	26	34	28	26	Passing	12.1
/5618	18	37	25	12	35	38	49	39	37	Retained	44.7
					30	66	76	59	55	% ret'd	78.7%
62716	38	37	26	17	40	27	27	38	33	Passing	19.9
					35	38	38	55	45	Retained	45.3
					30	58	58	91	68	% ret'd	69.5%
					40		15		14	Passing	9.5
Preferred		28	8	10.5	35		16		15	Retained	54.5
Floc					30		22		22	% ret'd	85.2%
					40	30	26	37	36	Passing	16
6260	34	67	45	15	35	39	35	44	52	Retained	59
					30	62	33	66	80	% ret'd	78.7%

* mix tested contains 50:50 cement:ground silica

** mix tested contains 80:10:10 cement:silica fume: ground limestone

Hatschek Machine Parameters									
	Water System			Average	Feed		Sieve Solids		Ret'n
Floc		Spray		Film	Consistency %				in
	Settling	Water	Foam	mm	Min	Max	Min	Max	film %
5230	Good	Clear	Little	0.25	6	6.6	4	4.6	32%
5618	Bad	Dirty		0.25	6	6.2	4	4.6	30%
5290	Bad	Dirty	High	0.25	6.5	7.1	4.3	4.5	35%
5230 /5618	Good	Clear	Some	0.25	6	7.5	4	4.9	34%
62716	Bad	Dirty		0.22	6.5	7.5	4	6	29%
Preferred Floc	Good	Clear	Some	0.27	5.5	6.7	2.8	3.6	48%
6260	Bad	Dirty	?	0.27	8	9	5	7	29%

With the exception of the Preferred Floc, the results of the first week trials showed very little difference in the laminar build or sieve solids for a given mix box consistency or for product density or retained moisture. The Preferred Floc although quite variable showed good settling in the mud water tanks, low mix box consistency and low sieve solids. Good settling was shown with 5230, 6260 and 5230/5618 blend.

There was no apparent correlation between the desired properties and the retention values and uncertain correlation between the settling effectiveness and the settling in the mud water tanks. The settling effectiveness values of the two different formulations were broadly correlated and there appears to be little point to performing two tests.

The other series of retention and drainage tests were also inconclusive or it proved to be difficult to duplicate results in subsequent iterations of the tests and these tests were abandoned.

Table 2 on the previous page and above summarises the results of week one.

During the weekend between the trials, the mix box was raised by about 2 metres and modified to direct gravity feed into the vats. The interior of the mix box was modified so that mud water (water from the bottom of the first cone tank) was introduced tangentially to the mix box wall with the feed just downstream and flocculant downstream of the feed. Flow was arranged to strike the baffle on the wall of the mix box and create an area of turbulence that facilitated the mixing of the ingredients. The stirrer in the mix box was set up to create a counter-rotating flow so that mixing of the ingredients was further facilitated. Gravity feed from the mix box proceeded to each vat through a single 150mm diameter flexible tube connecting to a steel manifold connected to two 100mm diameter feed pipes. Flow to each vat was controlled by a 200mm diameter air operated pinch valve.

The machine was started with the Preferred Flocculant which experience had shown gave good results and the effects of the mechanical changes were immediate. The retention sieve solids increased from their previous values of around 30% to between 40 and 53% and the film thickness had increased with an early exception to be consistently above its previous 0.27mm maximum. Foaming which had been a major problem reduced to almost zero although it was subsequently found to reoccur but at a lower level.

Following the early encouraging results extended tests were made for each of the flocculants selected from the earlier trials. The results of these trials are shown in Table 3 below.

Table 3 Results of tests from Week 2 – mix gravity fed to the vats

Week 2								
Floc		Effect's	Mix Box	Sieve solids		No	Film	Comments
Name	Viscosity	Test	Consist'	Mean	Ret %	Turns	Thickness	
5230								
								Not run
								No Sample
5618	16	32		4.7				
		47	8.2	5.2	40	7	0.29	fissuring
		73						
5290								
			5.6	2.9	48	7	0.3	Retest long term
5618			7.4	4				Moisture down,
2nd Run			6.1	3.7	47	7	0.29	density up, no foam
			6.3	3				gd settling,fissuring
Preferred								
Floc	20	17		3.8			0.25	
		20	7	4.4	47	7	0.29	
		30						
6260	13	21						
		23	8.4	5	40	7	0.28	
		30						

The results show the following

The Hatschek machine is relatively less sensitive to the type of flocculant and all the flocculants performed in a similar way. It was however necessary to adjust the film water content for each specific flocculant to allow corrugation without fissuring as was the case of the second run of 5618.

It proved easy to obtain a film build of around 0.3mm and produce a sheet in 7 turns at a felt speed of 60m/min. This had proved difficult in the previous week and since there was a corresponding reduction in solids passing the sieve to the backwater, it may be concluded that this is a result of better retention of solids in the film. All of the flocculants resulted in good settling in the mud water system and water overflowing to the dam was noticeably cleaner than in the first week.

Although foaming was reduced it was still evident in the latter parts of the week and was more prevalent with certain flocculants than with others.

Not all of the flocculants that had been tested during the first week were available during the second week and therefore some were not tested. It is however intended to test those which were not available and to conduct extended trials to ensure that other problems are not encountered and to optimise the selection of flocculants.

The settling test does not appear to offer much information in the selection of flocculants. It does not predict the retention of solids in the film and because the dwell time of water in the cone tanks is quite long the settling rate does not appear to be critical to their performance.

COMPARISONS OF FLOCCULANTS

In this investigation, a wide range of viscosities was observed in the recommended flocculants. On the basis that the viscosity is dependent on the chemistry, the molecular weight and the extension of the molecule in solution it seemed reasonable to attempt an experimental analysis of the viscosities obtained and the product of the reported molecular weights and charge density of the flocculants obtained. The following was the surprising result.

Table 4 Flocculant Charge, Molecular Weight and Ford Cup #4 Viscosities from Plant and Laboratory

Flocc't	Charge %	M Wt Million	Charge* M Wt	Lab Viscosity secs	Prod'n Viscosity secs
5230	10	12	120	22	13
Mag 10	8	10.5	84	28	
5230/5618	25	12	300	37	18
5618	40	12	480	49	
6260	45	15	675	67	34
5290	55	16	880	107	52

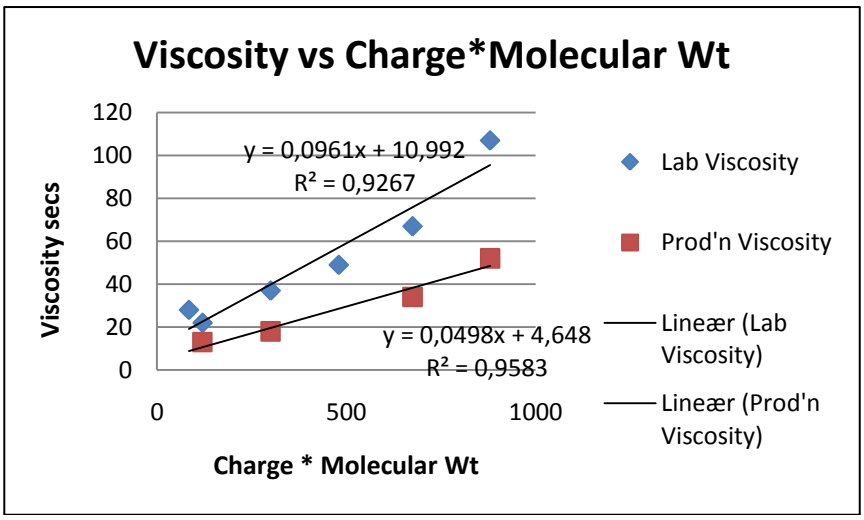


Figure 10: Viscosity of flocculant solutions compared to Charge*Molecular Wt

In the above table and figure flocculant 62716 has been eliminated because it was dissolved at 0.05% and thus its viscosity will be low in respect to its intrinsic properties. As can be seen there is a very strong correlation between the viscosities measured either in the laboratory or the plant with the product of the charge and the molecular weight. The chemistry of all of these polymers is similar being acrylamide/acrylate copolymers and while there is some doubt about their degree of branching and their molecular weight distributions around the mean molecular weight, it would seem that there is a strong relationship between [charge*molecular weight] and measured viscosity. Its practical significance is that it the [charge*molecular weight] provides an easy means to select flocculants having a known ease of dissolution and the above suggests that the maximum value of this parameter should be around 600-700. However, further investigation is needed to confirm this relationship.

It is interesting to note that 62716 which was eliminated has the highest reported molecular weight of all of the flocculants tested and this was eliminated because of its high viscosity although its charge was not the highest.

The information that has been provided for each of the flocculants is inadequate and given that large differences in performance have been previously observed at Everite between batches of flocculants there is reason to believe that there is a large scope for variation of flocculant molecular structure. It is possible therefore that these results are fortuitous rather than definitive although on first inspection there appears to be

a good relationship suggesting a chemically closely related series. It would therefore be interesting to have determined the true molecular weights, polydispersity and degree of branching of each of the flocculants.[3]

It is speculated that there is some optimum degree of branching for this or any other application and the big differences between apparently similar flocculants and different batches of the same flocculant suggest that degree of branching may be a contributing factor. Blanco et al (Blanco 2009) found that there is a change in the mechanism of flocculation from bridging to patch when the degree of branching is high.Since it appears that flocculation in fibre cement is largely of the bridging variety and that highly branched polymer molecules are structure differently in solution, it is likely that there is some optimum degree of branching for any particular molecular weight of polymer. It should also be noted that it is difficult to reconcile the mechanisms of polymerisation of acrylamide polymers with any degree of branching as such mechanisms produce linear molecules. Clearly this needs further investigation.

FURTHER TESTS

Following continuing difficulties with flocculant supplies and after a visit to another fibre cement facility in Brazil Ashland was contacted and Dr Leite visited the Everite and conducted a series of laboratory tests using the following test method.
Leite Sieve Method - The dewatering behaviour of flocculated fibre cement suspension is examined using the Sieve Method. The results are evaluated using

- The rate of water flow through the sieve
- The relative concentration of solids contained in the filtrate passing through the sieve compared to their concentration in the original unflocculated suspension.

The test therefore simulates the rate of filtration that may be expected in the Hatschek machine and the ability of the flocculant to retain the solids in the resulting film that forms on the sieve.

Because flocculation is a dynamic process and the formation of flocs takes time, dewatering behaviour is significantly influenced by the type of slurry conditioning and the procedure for mixing the flocculant solution with the slurry is critical and must be consistent. The method is explained below and the required apparatus is shown in Figure 11.

Two beakers (approx. 800 ml capacity) are required. The first is filled with 500 ml slurry, and the second contains a measured quantity of prepared flocculant solution (0,1% solution). The slurry is now poured into the beaker with the flocculant solution, the contents of this beaker is then poured back into the first, and so on, so that the slurry and flocculant solution are mixed by repeated pouring. Floc formation and growth are observed between pouring operations. The number of pouring operations is 10.

Immediately after mixing, the slurry is poured onto the 200 mesh sieve, (which has a similar mesh of the sieve cylinder of the vats). The filtrate is collected in a measuring cylinder and its volume is measured after a specified filtration time of 1 minute. The quantity of solids contained in the filtrate is determined and finally the retention of solids in the sieve is calculated as a percentage of the original solids in the slurry.

Results of Testing

A range of flocculants was tested with a variety of mixes with the following results being obtained for air cured mixtures. These mixtures contain large quantities of very fine Silica and Limestone and are thus quite demanding of flocculant performance.

[3] The same relationship has subsequently been confirmed by one of the authors with other flocculents not listed here.

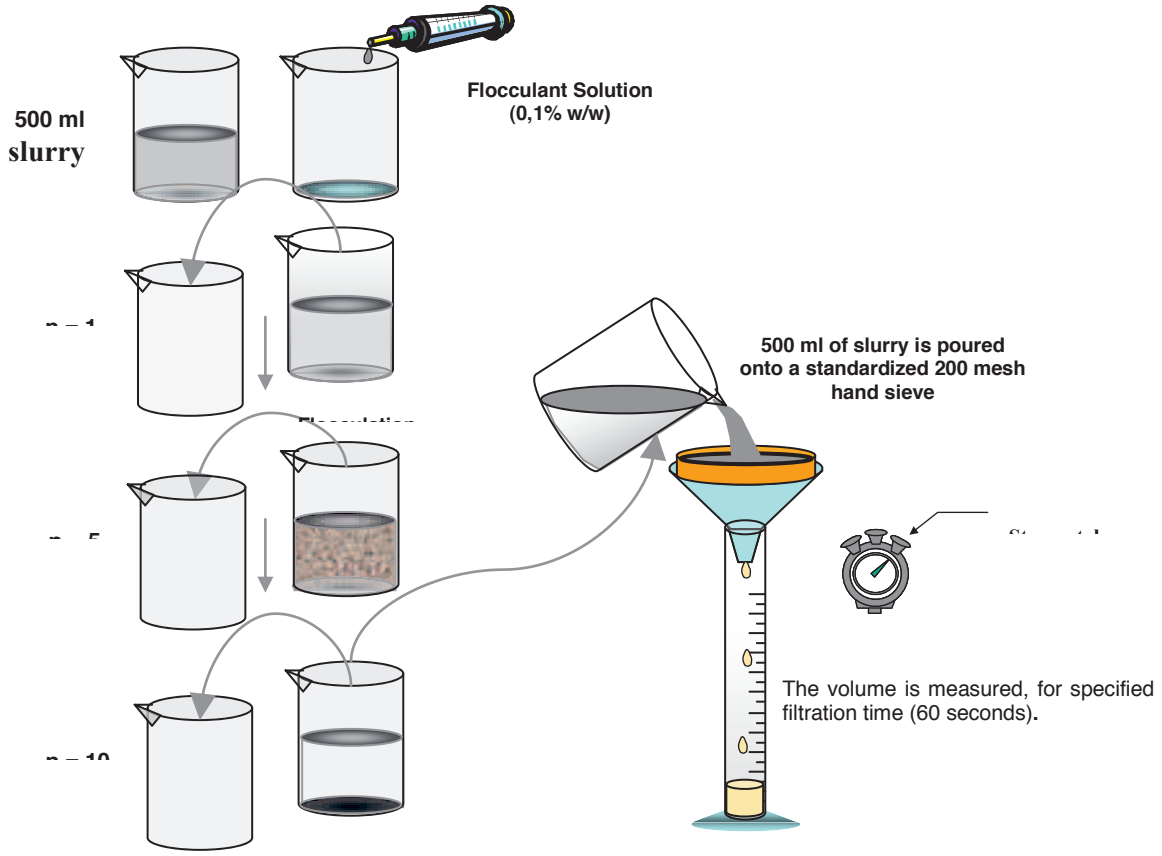


Figure 11 - The pouring method and the required apparatus.(Leite)

The following results were obtained with the flocculants designated by number or by "Preferred Floc". Flocculants were selected for plant evaluations on the basis of maximum flow rate through the sieve and maximum retention of solids through the sieve.

Table 5.1 Standard Natural Cured Mixes

Std Nat Cure	*Filtration Volume (ml)*				*Solids in the filtrate (g/L)*				*Retention %*			
Polymer g/tonne	90	100	110	120	90	100	110	120	90	100	110	120
Preferred Floc	350	390	380	380	3.31	5.23	6.1	4.03	96%	94%	93%	95%
5230 + 5618	385	385	425	400	12.78	8.55	5.2	10.77	85%	90%	93%	87%
2620	300	340	355	440	11.4	10.15	6.71	1.45	89%	89%	93%	98%
2640	320	300	390	340	14.84	14.32	9.86	14.43	85%	87%	88%	85%
2520	320	340	350	340	12.87	2.67	12.14	9.44	87%	97%	87%	90%
2540	250	280	350	300	18.22	14.73	7.18	11.26	86%	87%	92%	89%
5230	130	170	120	160	17.5	19.8	22.2	12.4	93%	89%	92%	94%
5618	340	310	230	190	8.18	9.94	7.3	2.62	91%	90%	95%	98%

Table 5.2 Modified Natural Cure Formulations

Modified Nat Cure	*Filtration Volume ml*				*Solids in the filtrate (g/L)*				*Retention (%)*			
Polymer g/tonne	**90**	**100**	**110**	**120**	**90**	**100**	**110**	**120**	**90**	**100**	**110**	**120**
Preferred Floc	395	390	410	420	2.63	9.33	1.15	1	96%	86%	98%	98%
5230 + 5618	380	400	380	390	15.55	12.57	9.87	4.59	78%	81%	86%	93%
2620	370	410	370	400	8.76	4.78	5.03	4.6	88%	93%	93%	93%
2640	360	405	350	340	10.83	11.42	8.03	9.23	85%	83%	89%	88%
2520	290	300	300	270	11.69	11.57	8.6	11.59	87%	87%	90%	88%
2540	240	213	215	300	14.67	6.39	10.37	8.79	87%	95%	92%	90%
5230	190	150	180	160	19.5	39.7	40.5	31.3	86%	78%	73%	81%
5618	110	125	130	180	54	45.9	33.92	28.5	78%	79%	84%	81%

Discussion of Laboratory Test Results

There are clear differences between the flocculants in either drainage rate or in solids retention. Analysis of the data shows that for the standard and the modified natural cured formulations, there is a negative correlation between the solids in the filtrate and the volume of filtrate after 1 minute of filtration. This means that the higher the volume of filtrate the lower the expected value of the solids that will pass through the sieve. It is reasonable to expect this as the drainage rate of the filtrate will depend on the viscosity of the suspension and if the suspension is largely colloidal then its viscosity will be high and the drainage rate will be low. However if the suspension has been broken by the flocculant and the solids are no longer colloidal then its viscosity will low and its drainage rate will be high.

Observations in the Factory and in the Hatschek Machine

Samples of flocculant were tested using the Leite method with virgin materials at a consistency of between 6 and 6.5% solids, the best performances were noted and selected flocculants were tested in the plant. Although one would typically select the best performers from the lab tests, not all these polymers were available at the time of the test so the best available polymers were used.

The following method was used to test polymers in the plant. The Hatschek machine was stabilized at a set consistency and the flocculant was turned off, until such a time as its effect could no longer be seen in the process. Thereafter the flocculant was incrementally introduced into the mix box (homogeniser) in stages of 10 sec/litre down to 2 sec/litre[4].

In between the increments the machine was stabilized and the Liete test done immediately on a sample drawn from the mix box and the vat simultaneously. These results were then tabulated and compared to the lab test results.

The following results were obtained.

[4] Dosage of flocculant into the mix box is controlled by increasing its flow rate. For convenience the factory measures the time to dose one litre of 0.1% flocculant solution. Thus reduced time is equivalent to increased dosage. The machine produces approximately 6 tonnes/hour, therefore 10 secs/litre flocculant is equivalent to approximately 60 g/tonne flocculant to solids in the vat and 2 secs/litre is equivalent to 300 g/tonne.

Table 6 Production and Laboratory Results Compared

5230	Filtration Volume (ml)				
dose rate sec/litre	2	4	6	8	10
MIXBOX	308	288	285	305	342
VAT	315	305	280	285	360
LIETE SIEVE TEST	463	515	503	525	500
	Solids in the filtrate (g/L)				
dose rate sec/litre	2	4	6	8	10
MIXBOX	41.17	44.59	48.85	55.34	39.43
VAT	39.57	37.83	33.76	38.74	36.3
LIETE SIEVE TEST	57.25	53.64	51.43	53.81	56.19
	Retention (%)				
dose rate sec/litre	2	4	6	8	10
MIXBOX	76%	76%	74%	68%	75%
VAT	77%	78%	82%	79%	75%
LIETE SIEVE TEST	50%	48%	51%	47%	47%

DISCUSSION OF THE RESULTS

The object of the exercise was to determine the influence of the mix box design, dwell time in the mix box, feed systems into the vat and the effect of mechanical agitation in the vats. It was theorised that if the design is incorrect or if there is a high shear action in the vats, the effectiveness of the flocculant would be less than predicted by the lab test.

It is clear that the results from the laboratory test differ from those in production. However there is a consistent relationship between the laboratory and the production test.

Initially, it was expected that the effectiveness of the flocculant would be less in the vat than the mix box. However it was found in several instances that the effectiveness of the flocculant in the vat was higher than in the mix box and in all other instances there was little difference between its performance in the mix box and vat.

This can be explained by the dynamics of flocculation. Flocculation occurs by collision and attachment of the molecules of the flocculant to the particles of solid in suspension and the subsequent collision and attachment of those coated particles with each other or uncoated particles. The time required for this to occur depends on the frequency of collisions which in turn depends on the concentration of flocculant and particles in suspension and the mixing conditions or turbulence in the vats. Thus equivalent performance in the mix box and the vat indicates that adequate mixing has occurred in the mix box while and improvement in performance in the vat relative to the mix box indicates that additional time is needed to adequately flocculate the suspension.

It would have been interesting to determine the effectiveness of the flocculant in the vats with the pumped system. However, based on the observations of the first set of tests it is clear that the effectiveness of the flocculant would have been significantly poorer in the vat compared to the mix box as passing the flocculated suspension through a centrifugal pump breaks up the flocs and may break the molecules of the flocculant.

This test method can also be used experimentally during design of a plant to determine if the design is suitable and to determine the influence of different designs and feed systems.

It was also observed that some flocculants produce changes to the product properties such as moisture, density and mouldability. Flocculants that work well on one formulation do not necessarily work well with another formulation.

Although it may be undesirable to lose solids into the backwater this cannot be prevented and it is usual practice to introduce additional flocculant into the backwater after the backwater pump. Some of the tests and practical observations suggest that it may also be necessary to use one type of flocculant for the drainage and retention of product in the vat and a second product to settle out the solids in the clarification tanks. This however has not been systematically investigated to date.

Although there are differences between the laboratory and production tests and there appears to a reasonable correlation between them, further work is required to improve the predictability of the laboratory tests.

CONCLUSIONS

Flocculant performance in the Hatschek Machine

1. The performance of the machine differed greatly between the first and the second stages of the trials and the flocculants behaved differently before and after the modification of the slurry delivery method. This meant that flocculants that performed poorly prior to modification were satisfactory after modification of the machine. This can entirely be attributed to the reduction in the severity of the treatment of the flocculated slurry which was not deflocculated before entering the vats.
2. After modification the Hatschek Machine could be more easily adjusted to accommodate the different flocculants and more subtle differences can be detected in the performances of the flocculants.
3. Despite some initial concerns about the time needed to develop adequate flocculation it was found that dosing of flocculant in the mix box gave sufficient time for the flocculant to react with the feed slurry and reduce the amount of solids carry-over through the sieve.
4. Foaming in the vats was much reduced after modification but not eliminated. This may be attributed to the reduction in damage to the flocculent molecules and their propensity to form patches rather than bridges on the other particles. Patches are water repellent and tend to disperse the particles and entrain air or bubbles so their reduction will reduce foaming.

Flocculant selection tests

1. The Leite test of flocculant performance provides two measures related to the desired results in the Hatschek machine – an indication of drainage rate and retention of fine solids in the finished Hatschek film. At this stage the test is useful for comparison of different flocculants but not absolutely predictive of their performance in a production environment. This is most likely due to the exigencies of the production machinery and the difficulty in accurately assessing flocculant dose rates in such a machine.
2. Further work is needed to develop selection teststhat better predict the performance of flocculants for Hatschek Machines.

Information on Flocculants

1. Further work needs to be done to develop understanding the performance of flocculants in the Hatschek process as it relates to the effect of polydispersity and degree of branching combined with molecular weight and charge density.
2. Other than average molecular weight and charge density little detailed information is provided by suppliers on the properties of their flocculants and it would be useful to routinely have this in order to establish the best flocculants for the Hatschek machine with optimal running conditions.

3. The apparent relationship between the viscosity of polymer/water solutions at constant concentration and the product of their Molecular Weight and Charge density needs investigation in the context of their polydispersity and degree of branching.

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