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A Review of Flocculation Strength and Breakage

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1 **Abstract**

2 The main focus of the paper is to review current understanding of floc structure and
3 strength. This has been done by reviewing current theoretical understanding of floc
4 growth and breakage and an analysis of different techniques used for measuring floc
5 strength. An overview has also been made of the general trends seen in floc strength
6 analysis. The rate of floc formation is a balance between breakage and aggregation
7 with flocs eventually reaching a steady state size for a given shear rate. The steady
8 state floc size for a particular shear rate can therefore be a good indicator of floc
9 strength. This has resulted in the development of a range of techniques to measure
10 floc size at different applied shear levels using a combination of one or more of the
11 following tools: light scattering and transmission; microscopy; photography; video
12 and image analysis software. Floc strength may be simply quantified using the initial
13 floc size for a given shear rate and the floc strength factor. More complex techniques
14 have used theoretical modelling to determine whether flocs break by large scale
15 fragmentation or smaller scale surface erosion effects, although this interpretation is
16 open to debate. Impeller based mixing, ultrasound and vibrating columns have all
17 been used to provide a uniform, accurate and controllable dissipation of energy onto a
18 floc suspension to determine floc strength. Other more recent techniques have used
19 sensitive micromanipulators to measure the force required to break or compress
20 individual flocs, although these techniques have been limited to the measurement of
21 only a few hundred flocs. General trends emerge showing that smaller flocs tend to
22 have greater strength than larger flocs, whilst the use of polymer seems to give
23 increased strength to only some types of floc. Finally, a comparison of the strength of
24 different types of floc (activated sludge flocs, organic matter flocs, sweep flocs and

1 charge neutralised flocs) has been made highlighting differences in relative flocculation
2 strength.

3

4 *Key words:*

5 Floc, breakage, growth, re-growth, shear, strength

6

1 **1. Introduction**

2 Floc strength is a particularly important operational parameter in solid/liquid
3 separation techniques for the efficient removal of aggregated particles. Unit processes
4 at water treatment works (WTW) are generally designed to minimise floc breakage,
5 however in reality often this is not the case, with regions of high shear being
6 prevalent (McCurdy *et al.*, 2004). This may include regions around the impeller zone
7 of flocculating tanks, processes such as dissolved air flotation (DAF) or transfer over
8 weirs and ledges and through pumps. Flocs are therefore exposed to a range of
9 stresses. Flocs must resist these stresses if they are to prevent being broken into
10 smaller particles. In an operational sense, this is important because small particles
11 generally have lower removal efficiencies (Boller and Blaser, 1998). Smaller particles
12 will generally settle more slowly than larger particles of similar density. Flocs formed
13 for removal in dissolved air flotation that subsequently break up into many smaller
14 parts may be captured less efficiently by air bubbles. In addition, flocs that are
15 removed using membrane filtration will foul membranes if small pieces of floc break
16 off and plug membrane pores.

17

18 Floc strength is dependent upon the interparticle bonds between the components of
19 the aggregate (Parker *et al.*, 1972; Bache *et al.*, 1997). This includes the strength and
20 number of individual bonds within the floc. Therefore a floc will break if the stress
21 applied at its surface is larger than the bonding strength within the floc (Boller and
22 Blaser, 1998). Increased floc compaction is considered to increase floc strength due to
23 an increase in the number of bonds holding the aggregate together. Leentvaar and
24 Rebhun (1983) also list the size and shape of floc microparticles as being an
25 important consideration for floc strength.

1 However, the development of a satisfactory technique to quantify floc strength has
2 proven to be difficult. This is partly due to the inherent complexity, fragility and
3 variation in floc size, shape and composition and also due to a generally accepted
4 view that there are two modes of floc rupture (Parker *et al.*, 1972; Francois, 1987;
5 Yeung and Pelton, 1996; Mikkelsen and Keiding, 2002). These have been classified
6 as **surface erosion** and **large-scale fragmentation**. Surface erosion is the removal of
7 small particles from the floc surface resulting in an increase in the small particle size
8 ranges. Large scale fragmentation is the cleavage of flocs into pieces of a similar size
9 without an increase in primary particle concentration. The problem of describing
10 strength arises from the fact that these two rupture modes are thought to be caused by
11 different stresses (Yeung and Pelton, 1996). Fragmentation is thought to occur from
12 tensile stress acting normally across the whole floc, whilst erosion is due to the
13 shearing stress acting tangentially to the floc surface (Figure 1). In addition there are
14 complex interpretations of floc strength data arising from relative eddy size which
15 will be discussed in later sections.

16

17 A review of the literature shows there to be no established standardised floc strength
18 test, although a number of techniques have been evaluated. Floc strength may be
19 broadly considered in terms of the energy required to break flocs under tension,
20 compression or shear (Zhang *et al.*, 1999). However, finding ways of quantifying the
21 energy input for floc breakage has not been easy. There is therefore a need for a more
22 thorough understanding of how floc strength can be measured and what information
23 can be found from floc strength tests. This paper aims to review current knowledge
24 on floc formation and breakage, the different techniques used to measure strength for
25 a range of flocs including activated sludge flocs, inorganic metal flocs, natural

1 organic matter flocs and flocs formed from ionic salts. Particular emphasis has been
2 placed on the applied shear rate, since most previous research has been concerned
3 with this aspect of floc strength. Finally, the review looks at the interpretation of floc
4 strength information.

5

6 **2. Floc formation and breakage**

7 Floc strength is directly related to floc structure and is therefore highly dependent
8 upon the floc formation process. The combined processes of coagulation and
9 flocculation aim to increase particle size for increased removal efficiency of very
10 small particles, colloids and micro-pollutants. Coagulation is the process of
11 chemically changing colloids so that they are able to form bigger particles by coming
12 close to one another. This may be achieved by particle destabilisation by double layer
13 compression or physical enmeshment of colloids within coagulant precipitates or
14 chemical reaction or chemical sorption (Cornwell and Bishop, 1983). Flocculation is
15 the process of transferring coagulated colloids into contact with each other to form
16 larger aggregates (Klimpel and Hogg, 1991; Gregor *et al.*, 1997). The exact process
17 of particle destabilisation and the subsequent colloid aggregation is complex. It is
18 generally considered to be a two stage process of particle transport and particle
19 attachment (Armirtharajah and O'Melia, 1990). Agglomerating particles must firstly
20 collide with each other and secondly must adhere upon collision. Gregory (1989)
21 treats these steps as being independent and separate from one another. However, flocs
22 do not continue growing and reach a steady state size for a given shear condition. It
23 has been generally accepted that floc growth is held in check by floc breakage so that
24 the rate of aggregation is considered a balance between floc formation and floc
25 breakage (Parker *et al.*, 1972; Francois, 1987; Spicer and Pratsinis, 1996; Ducoste and

1 Clark, 1998; Biggs and Lant, 2000). The stability of flocs in suspension is therefore
2 dependent upon how easy they are to break with aggregate breakage being directly
3 related to the strength and number of the bonds holding the floc together. During the
4 rapid initial formation of microflocs aggregation dominates over floc breakage,
5 however the importance of breakage increases as floc size increases until a steady
6 state floc size distribution is reached. Thus the steady state floc size is governed by
7 the prevailing shear/stress conditions within the containing vessel. The rate of particle
8 collision and the nature of the particle interactions are fundamental to the rate of floc
9 growth (R_{floc}) and may be summarised as in Equation 1 as the difference between the
10 the rate of aggregation and the rate of floc breakage (R_{br}). The former can be written
11 as the rate of particle collision, R_{col} and a collision efficiency factor, α . The factor α is
12 the fraction of collisions which result in attachment. Thus the overall rate of floc
13 growth may be written as:

$$14 \quad R_{floc} = \alpha R_{col} - R_{br} \quad \text{Equation 1}$$

15 When the two terms on the right hand side of equation 1 are equal, the net rate of floc
16 growth is zero and the floc size attains a limiting value. The collision efficiency is not
17 constant, but depends on the effective shear rate and particle size. For given shear
18 conditions αR_{col} decreases as the particle (floc) size increases as the number of
19 particles in the system is reduced. This is another reason why flocs reach a limiting
20 size (Brakalov, 1987). Another important consideration is that floc breakage may be
21 irreversible to some extent, so that broken fragments do not readily re-form (Francois,
22 1987; Spicer *et al.*, 1998; Gregory and Dupont, 2001). For irreversible breakage the
23 collision efficiency will be reduced and, for completely irreversible breakage $\alpha = 0$.

24

1 To summarise floc formation and breakage, flocculating suspensions are governed by
2 the prevailing shear conditions and will reach a steady state. When the shear rate
3 increases above a critical level flocs will break until a new steady state is reached. In
4 some cases, because of the irreversible nature of floc breakage, flocs are unable to re-
5 grow if broken at a higher shear rate. Measuring the shear energy required to break
6 individual flocs or those in a suspension is therefore of high operational importance.

7

8 **3. Measuring floc strength**

9 Two fundamental approaches have been taken in measuring floc strength; a
10 **macroscopic** measure of the energy required in a system for floc breakage and a
11 **microscopic** approach that measures the inter-particle forces within individual flocs.
12 A brief summary of these techniques is shown in Table 1. Due to the fact that the
13 applied shear rate determines floc size, most work on floc strength has been in the
14 macroscopic field, using applied shear techniques.

15

16 ***3.1 Macroscopic floc strength tests***

17 Macroscopic floc strength tests have arisen from the relationship between the applied
18 hydrodynamic shear rate and the resulting floc size. Under low shear rate conditions,
19 particles may be encouraged to aggregate, but, under increased shear rate, aggregate
20 break-up is observed (Mikkelsen and Keiding 2002). Floc size is therefore a dynamic
21 equilibrium between floc break-up and aggregation. Gregory (2003) states that when
22 comparing different flocs, the size (or flocculation index) for a given shear rate
23 indicates floc strength. Whilst this is the case for the given shear condition under
24 which the flocs were formed, it does not give an indication of how flocs will behave
25 upon exposure to an increased shear rate, as could occur at a WTW when flocs are

1 transferred from flocculators or to higher shear treatment processes such as DAF or
2 high rate filtration. For this reason, floc strength can be measured by applying an
3 increased shear rate or a normal stress to the formed aggregates and relating the
4 energy dissipation or velocity gradient applied to the maximum or average floc size
5 remaining (Yeung *et al.*, 1997, Boller and Blaser, 1998 and Lee and Liu, 2001). The
6 major problem to overcome with these techniques is the fact that the energy
7 dissipation is never homogenously distributed in the test vessel.

8

9 The majority of macroscopic floc strength tests have used impeller-based systems
10 whereby a known shear rate is applied to a grown floc suspension within a vessel of
11 between 1-4 L volume. However the geometry of the vessel and impeller type varies
12 between the techniques (Table 2). The breakage behaviour of flocs is monitored by
13 following at changes in floc size over a range of shear rates. As can be seen, the range
14 of shear rates investigated varies from study to study. The method of floc size
15 determination is crucial and varies between techniques. It is important to ensure that
16 the technique used to measure floc size does not act to damage the aggregates due to
17 their highly fragile nature. Most of the techniques listed aim to be as non-destructive
18 as possible, although some rely upon taking flocs from the containing vessel and
19 observation using microscopy and image analysis (Wu *et al.*, 2003). However it is
20 difficult to imagine that removing flocs in this manner cannot damage and break the
21 floc particles. The remaining methods have been with commercial particle size
22 instruments that use light scattering to determine particle size (Francois, 1987; Spicer
23 *et al.*, 1998; Biggs and Lant, 2000) or from analysis of video frames or photographs
24 using image analysis (Leentvaar and Rebhun, 1983; Bache *et al.*, 1999; Bouyer *et al.*,
25 2001; Bache and Rasool, 2001).

1 The light scattering instruments measure particle size by passing a laser beam through
2 a suspension of particles. These techniques rely upon a constant flow of the
3 suspension through the instrument during the measurement cycle (Farrow and
4 Warren, 1993). This feature has been harnessed to allow the development of a less
5 destructive methodology for measuring floc size (Spicer *et al.*, 1998; Biggs and Lant,
6 2000). These methods have a stirred vessel containing the aggregate suspension and
7 are connected to the particle sizing device by plastic tubing. Intrinsic to this type of
8 system is a requirement to pump the suspension through the optical unit of the size
9 analyser. Spicer *et al.* (1998) compared 3 types of pumping techniques for delivery to
10 the optical cell: a peristaltic pump, a syringe pump and a hand pipette. They
11 concluded that a continuous recycle using a peristaltic pump on the return side of the
12 measuring cell was the least severe technique on the flocs and allowed easy
13 continuous monitoring of the suspension. However, the problems of pumping can be
14 removed by sending the suspension to waste after making a measurement to
15 overcome any issues involved in a continuous recycle system (Francois, 1987). This
16 in itself is problematic as the volume of the suspension is continuously decreasing
17 and will affect the velocity gradients within the containing vessel, which will
18 therefore not be constant over the duration of the experiment, so most workers have
19 favoured a continuous loop.

20

21 Similar dynamic systems have been employed using the PDA to give an indication of
22 floc size (Burgess *et al.*, 2000; Gregory and Dupont, 2001; Yukselen and Gregory,
23 2004; McCurdy *et al.*, 2004). In this technique, a narrow light beam is passed through
24 a flowing suspension. The transmitted light intensity (dc value) is measured along
25 with the root mean square value of the fluctuating component (rms). A ratio of the

1 rms:dc gives a very sensitive indication of particle aggregation and is known as the
2 previously mentioned flocculation index. The PDA is reported to be a very good and
3 easy to use comparative tool showing qualitative changes in floc aggregation
4 (Gregory and Nelson, 1986). However, the instrument is unable to give an absolute
5 particle size for comparison with other techniques. In addition, the FI is an indicator
6 of both particle size and particle number (McCurdy *et al.*, 2004). As such there is no
7 way of knowing the precise contribution of each of these components in the final FI
8 value. However, aggregate size is probably the over-riding factor as previous work
9 has shown that when flocs grow larger the FI value always increases.

10

11 A combination of photography/video and image analysis has also been widely used to
12 monitor floc suspensions, such that a flocculated suspension can be observed by
13 capturing images of a stirred suspension by focusing on a plane a short distance (0.3 –
14 1 cm) behind the wall of vessel containing the suspension (Leentvaar and Rebhun;
15 1983; Ducoste and Clark, 1998; Chakraborti *et al.*, 2000; Bache and Rasool, 2001).
16 Calibration is achieved by focusing on a graticule suspended into the tank prior to
17 flocculation experiments. The advent of powerful digital and CCD cameras and
18 comprehensive image analysis software has allowed much quicker measurements of
19 an almost inexhaustible number of different floc size measurements to be made from
20 floc samples (Wang *et al.*, 2002).

21

22 For measuring floc size, no particle size method can be considered ideal. Aggregates
23 are highly irregular and porous and so their scattering patterns are likely to be very
24 different than for equivalent solid spheres of the same material in light scattering
25 devices. Although the light scattering properties of aggregates have yet to be fully

1 quantified, Farrow and Warren (1993) conclude that, similar to the PDA device,
2 light/laser scattering and transmission techniques are good for showing qualitative
3 (rather than absolute) changes in floc size for aggregation systems. In addition their
4 capability for measuring a very wide range of floc sizes (20 nm to 2 mm) makes them
5 very suitable for monitoring flocs and colloidal systems, although the expense of
6 these instruments limits their wide-scale application. In the previously mentioned set-
7 ups, the inclusion of the measuring instrument will undoubtedly change the shear
8 profile in the containing vessel and as such may inadvertently affect the floc size.
9 Photographic techniques are good in this respect, because the flocs are only exposed
10 to the shear rate of the impeller in the containing vessel and do not have to pass
11 through a pumped system. The limitations of photography are the time and care that
12 must be taken in preparing complex background lighting arrangements to allow for
13 suitable contrast between floc and background. Furthermore, very small flocs may be
14 missed that are beyond the detection limits of the camera being used thus biasing
15 towards the detection of large particles (Leentvaar and Rebhun, 1983). Bache *et al.*
16 (1999) concluded that floc sizes below 30 μm could not be reliably measured using
17 their camera system. This limitation may prevent the detection of floc erosion
18 mechanisms as the small eroded particles may be missed by the technique. Masking
19 effects can also occur in very concentrated floc suspensions. Given these constraints,
20 care must be taken when comparing floc size data obtained from different
21 methodologies.

22

23 *3.1.1. Floc strength factor*

24 One of the simplest evaluations of floc strength is the calculation of a floc strength
25 factor (Francois, 1987 and Govereau, 1987). This is effectively the ratio of floc size

1 after and before breakage at a particular shear rate and may be calculated as shown in
2 Equation 2 in Table 1.

3

4 The higher the value of the strength factor, the less sensitive the flocs are to breakage
5 as a result of increased shear rate and are therefore considered stronger. The strength
6 factor is not a constant and changes depending upon the applied shear rate during
7 rupture and so strength factors can only be compared for similar breakage conditions.

8 Francois (1987) noted an increase in the strength factor from 23.9 to 29.3 for kaolin
9 flocs formed with longer rapid mix times between 0-360 s and an increase in strength
10 factor from 17.5 to 26.5 for flocs formed with increased slow stir shear rate between
11 21-54 s⁻¹. A breakage shear rate of 1396 s⁻¹ for 1.5 minutes was applied in these

12 experiments. Fitzpatrick *et al.* (2003) compared the strength factor of kaolin flocs
13 and observed the impact of temperature (6-29° C) on floc strength using a PDA and a
14 breakage shear rate of 520 s⁻¹ for 10 seconds. Whilst the PDA does not give an
15 absolute floc size, the FI value before and after breakage can be used as a surrogate

16 for $d(1)$ and $d(2)$. Floc strength has been seen to decrease with increasing
17 temperature. For example, the floc strength factor decreased from 21 to 14 for alum-
18 kaolin flocs dosed at 3.4 mg L⁻¹ Al over the experimental temperature range
19 (Fitzpatrick *et al.*, 2003). A general trend was seen that showed floc strength

20 decreased with increasing floc size, such that flocs formed at the original slow stir
21 that had a high FI value had lower floc strength factors than those of lower FI value.

22

23 A comparison of kaolin floc strength factors for a range of different coagulants has
24 shown that hydrolysing coagulants such as alum and polyaluminium chloride (PAX

1 XL-9) give lower floc strength than cationic polyelectrolytes (polyDADMAC and
2 Zetag 64) (Yukselen and Gregory, 2004).

3

4 The floc strength factor allows a relatively quick and easy method of determining a
5 floc strength value and indicates how small a floc will become relative to its previous
6 size for a given increase in shear rate. However, as the breakage shear rate and mixer
7 characteristics are invariably different between different studies it is hard to directly
8 compare the results other than for general trends. There has been little work showing
9 how the relationship between the floc strength factor changes with increasing
10 breakage shear rate. More work needs to be done in this area to give a better
11 comparison of floc strength using the strength factor and on a wider range of
12 suspensions other than kaolin in order to compare strength values between different
13 coagulated systems for a standardised breakage shear rate.

14

15 *3.1.2. Shear based floc strength and breakage models*

16 Shear based floc strength models have evolved from strong empirical evidence
17 showing that the final floc size distribution is related to the applied shear rate (Parker
18 *et al.*, 1972; Spicer *et al.*, 1998). Shear has usually been characterised by the average
19 velocity gradient as shown in Equation 9 for homogenous and isotropic turbulence
20 (Camp and Stein, 1943).

$$21 \quad G = \sqrt{\frac{\varepsilon}{\nu}} \quad \text{Equation 9}$$

22 G is the average velocity gradient (s^{-1}); ε is the rate of energy dissipation per unit mass of fluid (N m s^{-1}
23 kg^{-1}) and ν is the kinematic viscosity ($\text{m}^2 \text{s}^{-1}$).

24

25 The energy dissipation term is given by Equation 10.

1
$$\varepsilon = \frac{P_0 N^3 D^5}{V}$$
 Equation 10

2 ε is the energy dissipation per unit mass of fluid ($\text{N m s}^{-1} \text{kg}^{-1}$); P_0 is the impeller power number; N is
3 the impeller speed (rps); V is the stirred tank volume (m^3) and D is the impeller diameter (m).

4

5 Due to the relationship between the velocity gradient in the flocculating vessel and
6 aggregate size, Parker *et al.* (1972) suggested an empirical expression for the stable
7 floc size (Equation 11).

8

9
$$d = CG^{-\gamma}$$
 Equation 11

10 d is the floc diameter (m); C is the floc strength co-efficient; G is the average velocity gradient (s^{-1}) and
11 γ is the stable floc size exponent.

12

13 Linearization of the equation allows values of γ and $\log C$ to be found from a log-log
14 plot of floc size measurement against the average velocity gradient (Equation 12).

15

16
$$\log d = \log C - \gamma \log G$$
 Equation 12

17

18 There is some argument in the literature as to whether the maximum floc size
19 remaining in the system should be measured or the average floc size. The initial
20 empirical observations relate the shear rate to the maximum particle size (d_{max}), as in
21 Equation 3 (Table 1). Bache *et al.* (1999) used the 95 % floc diameter obtained using
22 an external video camera. This was done to remove problems associated with
23 resolution when measuring smaller floc sizes using this technique. However, both
24 Leentvaar and Rebhun, (1983) and Francois (1987) concur that the same relationship

1 is seen when using average floc diameters. When the values of γ have been compared
2 for the mean, median and maximum floc size for the same coagulation conditions γ
3 remained fairly constant – between 0.43 and 0.49 – for all three floc sizes (Leentvaar
4 and Rebhun, 1983).

5

6 The value of $\log C$ strongly depends upon the method used for particle size
7 measurement and which characteristic value of d has been used. As there has been
8 wide variation between different studies, $\log C$ can only be used to compare of floc
9 strength within specific experimental systems. However, as the value of γ remains
10 relatively constant whichever value of d has been used it is a useful value for
11 comparing floc strength and break-up.

12

13 The steeper the slope γ , the greater the reduction in floc size is seen with increasing
14 G . The curves shown in Figure 2 are three theoretical examples of different floc
15 suspensions formed at a slow stir of G_{init} showing different resistance to floc break-
16 up. One interpretation of the data is to consider the steepness of the slope as an
17 indicator of floc strength. For example, considering line (a) the slope of the line is 0
18 and floc size is independent of the applied shear rate. The flocs do not break upon
19 exposure to shear and as such must be considered strong flocs. If the slope of the line
20 is shallow as in line (b) then these flocs are better able to resist shear than the
21 example in (c). Therefore flocs (b) should be considered stronger than flocs (c) as the
22 average/maximum floc size does not decrease so rapidly. However, this is likely to be
23 an over-simplification of the situation. Many workers ascribe the value of γ to the
24 dominant mode of floc degradation from both theoretical and experimental analysis
25 and increasing values of $\log C$ as an indicator of increased floc strength (Parker *et al.*,

1 1972; Leentvaar and Rebhun, 1983; Francois, 1987). Solving complex equations to
2 describe floc break-up and turbulence patterns, Parker *et al.* (1972) were the first to
3 theoretically describe the impact shear has on floc size. These types of models assume
4 flocs are composed of mono-disperse primary particles and characterise eddy
5 frequency and breakage capacity.

6

7 The theoretical basis of the value γ may be explained by turbulent shear patterns
8 relative to eddy size (Biggs and Lant, 2000; Bache 2004). In most flocculation
9 processes, conditions are generally considered to be turbulent (Francois, 1987; Boller
10 and Blaser, 1998). Eddy viscosity is the proportionality factor describing the turbulent
11 transfer of energy as a result of moving eddies, giving rise to tangential stresses. This
12 is analogous to molecular viscosity in laminar flow where liquids resist flow as a
13 result of intermolecular friction, therefore, when a liquid moves, energy is dissipated
14 in a tangential direction to the moving viscous fluid. This energy is commonly
15 referred to as viscous dissipation. Inertial convection is the release of energy in an
16 outward direction, normal to the rotational eddy flow. Levich (1962) described
17 turbulence using a scale whereby turbulent flow is described by the velocity and size
18 of eddies. Very large eddies are responsible for the mixing of the system with little
19 energy dissipation and therefore do not rupture or break flocs, whilst smaller eddies
20 are responsible for most of the energy dissipation. The Kolmogoroff microscale
21 describes the length scale (η) of the energy-dissipating eddies (Equation 13).

22
$$\eta = \left(\frac{\mu^3}{\varepsilon} \right)^{\frac{1}{4}} \quad \text{Equation 13}$$

23 η is Kolmogoroff's microscale of turbulence (m); μ is viscosity ($\text{kg m}^{-2} \text{s}^{-1}$) and ε is the energy
24 dissipation ($\text{N m s}^{-1} \text{kg}^{-1}$).

1 Inertial convection is responsible for energy dissipation of the larger eddies within the
2 microscale range, whilst viscous energy is responsible for the energy dissipation of
3 the smaller eddies in this range (Figure 3).

4

5 At high energy inputs, the value of the micro-scale η is of a similar order of
6 magnitude to the floc sizes whilst at low velocity gradients it is much larger, which
7 helps to explain why flocs become more prone to breakage at high velocity gradients.

8 However, it is difficult to say which eddies are responsible for floc breakage as it the
9 floc break-up is highly dependent on the eddy size relative to the floc size. Under
10 normal flocculator conditions, viscous effects dominate (Boller and Blaser, 1998).

11 Some authors suggest that when flocs are smaller than the micro-scale they become
12 prone to breakage by surface erosion, whilst above the microscale flocs are thought to
13 be more exposed to breakage by fracture (Thomas *et al.*, 1999). Other theoretical

14 analysis suggests that when flocs are in the viscous energy region (i.e. below the
15 critical microscale eddy size) values of γ of 0.5 have been calculated to indicate floc
16 fragmentation, whilst erosion mechanisms are dominant if $\gamma = 1$. In the inertial

17 convection zone a value of $\gamma = 0.5$ suggests large scale fragmentation events and $\gamma =$
18 2 suggests surface erosion (Parker *et al.*, 1972). The values of some of the previous
19 experimental work for the calculation of floc strength co-efficient (Log C) and

20 constant (γ) obtained for a variety of flocs are shown in Table 3. Good linearity is
21 always seen between floc size and shear rate on a log-log scale for all of the
22 experimental studies shown in the table. For example, both Bache *et al.* (1999) and

23 Biggs and Lant (2000) had an R^2 correlation co-efficient in excess of 0.99.

24

25

1 *Floc strength coefficient*

2 For a fixed shear rate the larger the value of $\log C$ the stronger the floc (Bache, 2004).
3 As has been explained, comparing values of $\log C$ between studies is not possible due
4 to the different impeller/tank geometries and different floc sizing protocols employed,
5 however a number of trends can be seen from within individual research. Wu *et al.*
6 (2003) saw that an increase in the polymer dose lead to an increase in the floc
7 strength coefficient for alum sludge flocs. A comparison of ferric hydroxide flocs in
8 tap water and sewage sludge showed an increase in $\log C$ from 1.5 to 1.9 with the
9 authors stating that floc strength was higher in tap water than sewage (Leentvaar and
10 Rebhun, 1983). For sewage flocs, it has been shown that adding polymeric flocculant
11 doubled the floc strength co-efficient. Bache *et al.*, (1999) and Bache and Rasool
12 (2001) have investigated alumino-humic flocs. In the latter case, a useful comparison
13 of flocs obtained from flocculators at 7 water treatment plants treating water of high
14 colour (50-140° Hazen) has been made. The value of $\log C$ was highest for flocs
15 where polymer was used and in the instance of water that was initially of high
16 alkalinity.

17

18 *Floc strength constant*

19 Whilst the value of $\log C$ provides a good indication of how strong flocs are when
20 they are formed at a given shear rate, it does not provide information on how flocs
21 will respond to subsequent increases in shear rate. This information can be provided
22 by the previously mentioned floc strength factor but also by the floc strength constant
23 (γ). The higher the value of γ the more prone the flocs are to breakage into smaller
24 sizes with increasing shear rate.

25

1 For alumino-humic flocs under low alkalinity conditions, the value of the slope varied
2 between 0.44 and 0.64 (Bache and Rasool, 2001). Looking at the data for comparable
3 Al doses (2.4-2.7 mg L⁻¹), the humic floc degradation was reduced from 0.63 to 0.44
4 when polymer aid had been added. The value of γ was seen to increase when the
5 water alkalinity was high suggesting that these flocs were less able to withstand
6 increases in shear rate than the low alkalinity flocs. Coagulant dose also has an
7 impact on γ , for kaolin flocs, increasing coagulant dose from 4.02 to 5.02 mg L⁻¹ Al
8 increased the floc strength constant, whilst above this coagulant dose there was a
9 decrease in γ (Francois, 1987). This suggests that there is an optimum coagulant dose
10 in terms of floc strength.

11

12 For all types of floc the values of γ were around 0.5 (the exception being alumino-
13 humic flocs formed in high alkalinity water were $\gamma = 0.81$). Whilst these values of γ
14 do not highlight major differences in degradation rate for different types of floc (e.g.
15 sewage, kaolin and humic), the mode of breakage can be theoretically determined
16 from the floc strength constant. If it is assumed that viscous effects are responsible for
17 most of the energy dissipation in flocculating systems and the models of floc
18 breakage are correct, then it appears that floc breakage is generally dominated by floc
19 fragmentation as the value of γ remains around the theoretical value of 0.5 as derived
20 by Parker *et al.* (1972). However, this strict theoretical interpretation is open to
21 debate. For example fragmentation and erosion could occur simultaneously in a
22 containing vessel. This may explain the result seen for the high alkalinity water, where
23 the value of γ was half way between the theoretical values for fragmentation and
24 surface erosion. In addition, large flocs in an aggregated system may be larger than
25 the microscale (η) whilst the smaller flocs may be smaller than η . This has been

1 shown experimentally for activated sludge flocs with the $d_{95} > \eta > d_{50}$. This again
2 suggests that erosion and fragmentation can occur at the same time, perhaps as a
3 result of the larger flocs in the system fragmenting and the smaller flocs eroding
4 (Biggs and Lant, 2000).

5

6 Hydrodynamic shear based techniques using impellers have been widely used
7 because of their similarity to operational flocculators and the likelihood that
8 hydrodynamic shear stress is probably of great importance when considering floc
9 breakage. In addition these techniques have highlighted differences in how a floc will
10 respond to different increased levels of shear rate as determined by the value of γ .
11 However, whilst the observation of an empirical relationship between shear rate and
12 floc size is widespread, the problem has been in the interpretation and application of
13 shear based models to the data. Whilst experimental work is fitted to these models
14 there is little direct evidence to suggest either erosion or fragmentation is definitively
15 taking place. Ideally, the particle size distribution of a ‘fragmenting’ floc system
16 needs to be compared to an ‘eroding’ system to show the differences in particle sizes
17 to confirm that the models are totally accurate. A final problem with these techniques
18 has been an accurate description of the shear energy dissipated into impeller systems.
19 G_{av} is probably not sufficient enough whilst critical threshold values of G_{max} have not
20 been sufficiently well modelled to directly relate to the resulting floc size. This has
21 lead to a number of workers tackling this problem by applying a reliable, accurate and
22 controllable measure of the energy input and the following section will review a
23 number of these techniques in turn.

24

25

1 3.1.3. *Ultrasound*

2 The use of ultrasound to condition sludge is a well known technique (Chu *et al.*,
3 2001). By applying a controlled ultrasonic field to a sludge suspension, flocs may be
4 effectively ‘exploded’ into smaller parts to improve biodegradability. During
5 ultrasonic treatment, pressure waves pass through a medium releasing large quantities
6 of energy. This induces the formation and collapse of gas bubbles. The result is a
7 release of energy in the form of temperature and turbulent eddies around the
8 collapsing bubble. There has been some limited application of this in determining floc
9 strength. Wen and Lee (1998) have developed a complex term for the calculation of a
10 floc strength value from an applied ultrasonic field (see Table 1). Above a critical
11 ultrasonic energy input it has been seen that kaolin flocs and activated sludge flocs
12 break-up and decrease in size (Wen and Lee, 1998; Chu *et al.*, 2001). A direct
13 measure of the ultrasonic energy per unit volume of sample can be made that reflects
14 the flocs internal binding strength as the flocs break up. The resulting floc size can
15 then be measured and compared to the original floc size using one of the previously
16 mentioned techniques. For activated sludge thickened with alum, the effect of
17 polymer addition on floc strength has been investigated (Lee and Liu, 2001). A non-
18 ionic polymer was compared with a cationic polymer and it was seen that floc
19 strength decreased with increasing polymer dose and that non-ionic polymer showed
20 greater floc strength than cationic polymer. The major problem associated with this
21 technique is the impact of temperature. At an applied ultrasonic rate of 44 Watts ml⁻¹
22 the temperature was seen to increase from 20 to 56° C in just over 1 minute.
23 Therefore considerable temperature control needs to be applied in order to better
24 stabilise the system conditions.

25

1 Wen and Lee (1998) investigated the strength of clay coagulated with cationic
2 polymer for different pH and polymer dose. They found that at higher pH and
3 polymer dose, the initial floc size was larger. The results were contradictory in that
4 the large flocs formed at pH 7 and 10 were observed to break down at a faster rate
5 than at pH 3 in terms of floc size. However, the binding strength based on Equation 4
6 was observed to increase with both polymer and pH. This is perhaps a reflection of
7 there being two approaches of considering floc strength. The first is a measure of the
8 maximum floc size attained at the end of the floc formation process such that larger
9 flocs should be considered stronger than smaller flocs because they have reached a
10 bigger size. The second considers the floc strength as a measure of the strength of floc
11 bonds to withstand increases in energy once formed.

12

13 For activated sludge flocs the use of ultrasound is confused due to the effect of
14 ultrasound on bacterial components of the floc. Ultrasound increases the formation of
15 free radicals which can impact on bacterial metabolism and also cause cell lysis
16 (Jorand *et al.*, 1995). Therefore, in these instances the applied energy may be causing
17 other effects other than breaking apart primary particles within the floc. For water
18 treatment flocs that are generally dominated by non-living chemical constituents,
19 ultrasonic methods may have potential for determining the forces required to break
20 flocs. From an operational sense it is difficult to relate the energy experienced by
21 flocs from an ultrasonic field to the hydrodynamic shear conditions that are important
22 in a flocculator. However, as inter-particle bonds are being broken in both techniques
23 a comparison of the results between the different methods would be of great interest.

24

25

1 3.1.4. Oscillating multigrid mixer

2 Bache and Al-Ani (1989) developed a technique whereby flocs are exposed to stress
3 in a vibrating settling column. An oscillating plunger was used to provide turbulent
4 energy dissipation in the column. In this manner relatively uniform energy dissipation
5 can be achieved in the horizontal plane with shear stress increasing as flocs pass
6 down the column, therefore the height at which a floc ruptures in the column is
7 proportional to a certain level of energy dissipation. A floc breaks when it passes
8 through a region where the hydrodynamic forces are greater than the binding force at
9 the point of rupture within the floc. The advantage of such a system is that the
10 hydrodynamic shear stress at each point in the column may be more accurately
11 modelled when compared to the more complex flow of impeller systems. In this
12 technique floc size before and after breakage has been monitored using closed circuit
13 television (CCTV) and image analysis. The underlying trend emerging from this
14 technique is for large flocs to rupture higher in the column than smaller floc
15 aggregates, showing the increased susceptibility of large flocs to increases in shear
16 rate. This has been shown for kaolin-alum flocs (Bache and Al-Ani, 1989) and for
17 humic-alum flocs (Bache *et al.*, 1991). The calculation of a value for floc strength
18 from these data is shown in Equation 5 (Table 1). This has been derived from a force
19 balance between accelerations across the floc at the plane of rupture where turbulent
20 energy acceleration have been defined as $\sqrt{3}\varepsilon^{3/4}\nu^{-1/4}$ from Levich (1962):

21
$$\frac{1}{4}\pi d^2\sigma = 2\frac{\pi}{6}\rho_w d^3\sqrt{3}\frac{\varepsilon^{3/4}}{\nu^{1/4}}$$
 Equation 14

22 d is the size of floc sub-units (m), σ is the floc strength per unit area (N m^{-2}), ρ_w is the density of water
23 (kg m^{-3}), ν is the kinematic viscosity ($\text{m}^2 \text{s}^{-1}$) and ε the energy dissipation ($\text{N m s}^{-1} \text{kg}^{-1}$).

24

1 Floc strength calculations have shown that flocs sheared at high G_{av} values were
2 smaller but had higher strength. For example, flocs sheared at 50 s^{-1} had a d_{95} of 238
3 μm and a strength of 0.08 N m^{-2} , whilst flocs sheared at 230 s^{-1} had a d_{95} of 120 μm
4 and a strength of 0.42 N m^{-2} . The relative floc strength of alumino-humic flocs was
5 found to change with coagulant dose. For doses of between 2-7 mg L^{-1} Al, an
6 optimum was seen at 4 mg L^{-1} .

7

8 **3.2 Microscopic Floc Strength Tests**

9 Whilst macroscopic techniques rely upon complex theory of turbulence, eddy size
10 and floc breakage models, recent work has been carried out to gain a more direct
11 measurement of floc strength by taking individual flocs and finding the force required
12 to pull or compress a floc until breakage (Yeung and Pelton, 1996 and Zhang *et al.*,
13 1999). The principal advantage of such a technique being that an understanding of the
14 mechanisms of how and where flocs break may be gleaned and a floc rupture force
15 may be directly measured to give floc strength. This may eventually lead to a more
16 thorough knowledge of the currently poorly-understood mechanisms of floc breakage.
17 The following section briefly reviews two microscopic techniques.

18

19 **3.2.1. Micromechanical approach**

20 In this method, floc strength is measured by the tensile force required to break single
21 flocs (Yeung and Pelton, 1996; Yeung *et al.*, 1997). A schematic overview of this
22 technique can be seen in Figure 4. Calcium carbonate flocs coagulated in NaCl with
23 polymeric floc aid were placed in a sample chamber consisting of two glass cover
24 slips separated by 2 mm. The force required to rupture the flocs was determined by
25 carefully attaching single flocs onto a glass rod cantilever beam and attaching and

1 translating an opposing pipette horizontally until the floc broke. The deflection of the
2 cantilever may be directly converted into a floc rupture force, provided the cantilever
3 stiffness is known, using sensitive micromanipulators. Floc size before and after
4 breakage was determined by averaging the major and minor axis of the aggregates of
5 the original floc and the broken floc pieces. In their first study (Yeung and Pelton,
6 1996) floc strength was reported as simply the force required to break apart the floc.
7 Initial floc sizes ranged from between 5-50 μm diameter. In this instance when this
8 force is plotted against floc size no correlation was seen between floc strength and
9 size. A change in floc strength was seen when two polymeric flocculants were
10 compared with the first system having an average floc strength of 64 nN and the
11 second was 110 nN. Boller and Blaser (1998) have transformed these data into a floc
12 rupture pressure so that floc strength is found from the ratio of the rupture force to the
13 cross sectional area of the smaller fractured aggregate (as shown in Equation 6 in
14 Table 1) giving floc strengths in the region of 100-1000 N m^{-2} . In this way, the size
15 dependency of floc strength was again seen, such that smaller flocs showed increased
16 strength. The application of this technique has been taken further to show the effect of
17 mixing speed on floc strength (Yeung *et al.*, 1997). A range of mixing speeds
18 between 50-2500 rpm were investigated for paper pulp with calcium carbonate
19 flocculated with polymeric flocculant. An optimum mixing speed was determined at
20 500 rpm that gave optimum floc strength of 1,500 N m^{-2} . However, it should be
21 stressed that the sampling technique may lead to significant floc breakage or
22 aggregation, such that the original floc size, and therefore strength, may not be
23 measured.

24

1 The technique provides an interesting insight into floc breakage in the tensile mode. It
2 was observed that not all flocs breakages resulted in large scale fragmentation. This
3 contradicts hydrodynamic shear models that suggest tensile stress is responsible for
4 large scale fragmentation. It was hypothesised that flocs were breaking at their
5 narrowest point because it is here that there are fewer attachment sites. The size ratio
6 of floc fragments (d_1) after breakage with the initial floc (d_0) were compared with floc
7 compaction (as determined by fractal dimension analysis). Values of d_1/d_0
8 approaching 0.5 indicate that the floc has been split into two similar sized pieces
9 whilst near 0 and 1 a floc has been broken into a very small and large aggregate. The
10 authors argue that the mode of floc breakage is therefore more to do with floc
11 compaction than the differences in turbulence stresses and eddy size. Very compact
12 flocs have fewer bonds in their margins, so surface erosion is more likely to occur.
13 More loosely bound flocs are more likely to have weak points randomly located
14 anywhere across their cross-section and are therefore more susceptible to large scale
15 fragmentation. This questions one of the fundamental assumptions of the shear based
16 floc strength characterisations based upon Equation 12 that flocs are homogenous
17 structures composed of similar primary particle units.

18

19 The micromechanical technique has provided a useful addition to the field of floc
20 strength quantification. However, as yet the application has been limited to the
21 measurement of only a few hundred individual floc aggregates in total and across a
22 relatively narrow range of floc types. More work is required in this field in order to
23 assess its broad application to all types of floc. In addition, the importance of tensile
24 stress as a mechanism for floc breakage in flocculators and other WTW processes has
25 yet to have been fully quantified.

1 3.2.2. *Micromanipulation*

2 A further microscopic technique has measured the compression force required to
3 break flocs between a glass slide and a fibre optic probe (Zhang *et al.*, 1999). In this
4 technique, a sample of floc suspension was placed on a microscope slide, individual
5 flocs could then be selected using a microscope (Figure 5). A 50 μm probe with one
6 flattened end was mounted onto a force transducer and lowered just above a floc
7 aggregate using a micromanipulator. The transducer then lowered the probe at a set
8 speed until the aggregate broke from compression between the probe and slide. The
9 applied force was then measured as the breaking force (Equation 7). The flocs under
10 investigation were very small latex particles aggregated in a salt solution. The mean
11 size of flocs aggregated by vortexing was 2.5 μm and the mean floc strength was 5.3
12 μN . However, the experimental procedure did not measure the sizes of the residual
13 flocs once they had been broken. This meant the results could not be normalised to a
14 floc rupture force over the floc cross sectional area and so compared to the other
15 techniques. This method provides an alternative microscopic measure of floc size and
16 again needs to be assessed over a range of floc types in order to rigorously evaluate
17 the technique. However from an operational sense it is difficult to think of a situation
18 where flocs would be exposed to such a compression stress under normal solid/liquid
19 separation conditions and as such this value of floc strength may not be indicative of
20 the likelihood of floc breakage in industrial unit processes.

21

22 **4. Comparison of floc strength values**

23 Direct comparison of floc strength between the different techniques is made difficult
24 because each technique measures floc strength in a different way giving either floc
25 strength as a relative measure or an actual breakage force. However an attempt has

1 been made in Table 4 to highlight the general trends that the floc strength
2 measurements indicate. Table 5 emphasises some of these trends with a comparison
3 of absolute values of floc strength from a number of techniques where the force per
4 area of floc has been measured.

5
6 The most significant trend to emerge from these strength tests is the increase in floc
7 strength with a decrease in floc size. This can be clearly seen from data in Table 5 for
8 alumino-humic flocs with an increased floc strength of over five times with a halving
9 of the initial floc size. This is further supported by polymer-calcium carbonate flocs.
10 Polymer A produced flocs with an average diameter of 25 μm and an average floc
11 strength of 100 N m^{-2} , whilst polymer B produced smaller flocs of 10 μm with an
12 increase in average floc strength to 1000 N m^{-2} . A mechanistic explanation for this
13 relationship has not yet been fully described. However, the reasons are likely to relate
14 to floc compaction and the number of internal bonds. In much of the strength work,
15 flocs are grown and then exposed to an increased shear rate. This acts to break flocs
16 and therefore reduce the average floc size in the suspension. The breakage procedure
17 breaks flocs at their weakest points, which results in smaller pieces that are smaller
18 and more compact. This has been shown by fractal dimension analysis of
19 polystyrene-alum flocs. There is a large amount of evidence suggesting that flocs are
20 examples of fractal structures (Gregory, 1998, Gorczyca and Ganczarczyk, 1999,
21 Thomas *et al.*, 1999; Bushell *et al.*, 2002). The floc fractal dimension (D_f) can
22 indicate the openness of the internal floc structure with a higher fractal dimension
23 indicating a more compact structure. Flocs formed at a high shear rate ($G_{av} = 300 \text{ s}^{-1}$)
24 were small and had a fractal dimension of 2.65 whilst floc size increased and the
25 fractal dimension was reduced to 2.4 when the flocs were formed at a much lower

1 shear rate ($G_{av} = 50 \text{ s}^{-1}$) (Spicer *et al.*, 1998). More compact structures indicate that
2 primary particles may have more attachments with one another or repulsive forces
3 between these particles is at a minimum. Floc restructuring during breakage is one
4 mechanism for allowing primary particles to become closer to one another so that floc
5 internal bonds break and re-form at more favourable points within the floc where the
6 attractive force is greater or the repulsive force lower.

7

8 Similarly, compaction is thought to explain why an optimum coagulant dose exists in
9 terms of floc strength. For charge neutralisation coagulation mechanisms, the
10 optimum floc characteristics should be seen when the repulsion forces between
11 primary particles are low. However, a slight amount of charge repulsion allows
12 attached particles to re-arrange into more compact structures rather than attaching at
13 the first contact (Waite *et al.*, 2001). In water and wastewater operations, charge
14 neutralisation is generally achieved by the addition of charged metal ions of an
15 opposite charge. Increasing or decreasing the ratio of the charged coagulant will
16 therefore reduce or increase the balance of the charge within the floc above or
17 below an optimum (Bache *et al.*, 1991).

18

19 A generally held conception within the water and wastewater industry is that the
20 addition of polymer acts to increase floc structural characteristics by aiming to
21 increase floc size, strength, settleability and filterability (Bratby, 1980). From the
22 limited data presented in this review, this statement appears to be at least partially
23 true in terms of floc strength and size. Sewage flocs and alumino-humic flocs were
24 seen to increase in size with the addition of a polymeric floc aid. However, only the
25 alumino-humic flocs showed improved resistance to shear rates, implying an increase

1 in floc strength. The difference in floc strength with and without polymer is likely to
2 be some reflection of the binding mechanisms of the polymer to the primary particles
3 of the floc. For a range of polymers (anionic, cationic and non-ionic), floc strength
4 was seen to decline for biological flocs in their response to increases in shear rate
5 (Lee and Liu, 2001; Leentvaar and Rebhun, 1983). No mechanistic explanations were
6 given although one possible hypothesis was a toxicity effect from the polymer on the
7 biological component of the floc. The polymer may act to kill bacteria or prevent
8 bacterial adhesion mechanisms within the floc, thus reducing the overall bonding
9 capacity in the floc through changes in concentration and character or extracellular
10 polymeric substances. However, some of this previous research goes against intuitive
11 and practical experience of polymers used in water and wastewater treatment. Much
12 more work is required in this field to more adequately quantify the effects of
13 polymeric flocculants.

14

15 During the removal of solid particles, enmeshment and bridging of particles within
16 the precipitated coagulant matrix are thought to be the principal binding forces
17 holding the floc together. These types of bond are considered much stronger than van
18 der Waals attractive forces formed during charge neutralisation (Bache *et al.*, 1997).
19 This is supported by the experimental data shown in Table 5. From the available data,
20 there are considerable differences in floc strength for different types of aggregate.
21 Flocs composed of coagulant and particles were one to two orders of magnitude
22 stronger than charge neutralisation flocs.

23

24 Flocs formed from waters of high colour and high natural organic matter (NOM)
25 content are widely recognised as being fragile structures when compared to other

1 flocs (Bache *et al.*, 1997). The floc strength data available confirm this, with these
2 flocs being weaker than flocs formed by charge neutralisation at their isoelectric point
3 (IEP). The weakness of humic flocs is explained by Bache *et al.* (1999) to be due to
4 the fact that charge neutralisation is the main removal route NOM removal preventing
5 stronger bridging bonds from forming. This in part explains the weakness of organic
6 flocs but does not help explain why IEP flocs are considerably stronger than humic
7 flocs. If both flocs are formed by charge neutralisation, then van der Waals forces
8 between primary particles will dominate. The reduced floc strength of humic flocs
9 therefore suggests an increased degree of repulsion within the floc matrix. This makes
10 sense because organic matter is a complex mixture of different organic compounds
11 (Goslan *et al.*, 2002). These organic molecules have differing degrees of charge and
12 hydrophobicity (O'Melia *et al.*, 1999). Therefore, whilst some molecules and parts of
13 molecules may be effectively charge neutralised by coagulants, regions of similarly
14 charge will exist that increase repulsion within the floc.

15

16 **5. Conclusions**

17 There have been a number of different approaches taken in measuring floc strength.
18 Some workers consider that floc strength is indicated by the size a floc reaches at the
19 end of its growth phase, whilst others consider the force required to break already
20 formed flocs.

21

22 Most research has concentrated on exposing flocs to increased shear rate in a
23 containing vessel by the application of stirring, ultrasonification and oscillation. More
24 recently microscopic techniques have been developed that relate the energy required
25 to pull apart or compress individual flocs until breakage.

1 Whilst there is strong evidence showing an empirical relationship between the applied
2 shear rate and the final floc size distribution, there are a number of problems
3 associated with comparing the data from one study to another. The interpretations of
4 floc breakage models need to be further analysed. These models ascribe floc breakage
5 as either erosion or fragmentation based upon the rate of floc breakage with
6 increasing shear rate relative to the eddy size in the system. These interpretations are
7 open to debate given the incomplete understanding of how eddies interact with flocs
8 during floc breakage. Different impeller geometries and containing vessels give rise
9 to different shear patterns and maximum shear levels experienced by flocs that result
10 in different floc breakage behaviour. For this reason a simple consideration of how
11 floc size changes relative to its initial size may give the best global indication of how
12 strong flocs are.

13

14 Some general trends have emerged from floc strength tests that show that floc
15 strength increases with decreasing floc size. The addition of polymer decreased floc
16 strength for biological flocs and increased floc strength for chemical flocs.

17

18 Floc strength is a difficult parameter to measure accurately due to the inherent
19 fragility and complexity of floc structures. As yet, there is no detailed understanding
20 of the internal composition and bonding that occurs within a floc aggregate such as
21 the number of bonds, locations of points of attachment and internal attractive and
22 repulsive forces within the structure. Therefore many of the floc strength and
23 breakage models developed so far have not reached a thorough mechanistic level.

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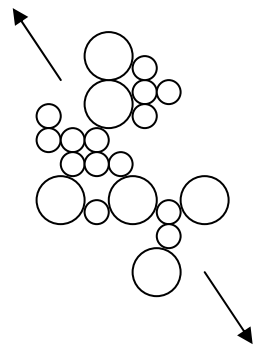
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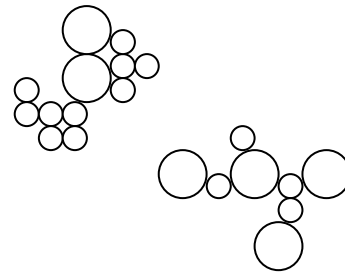
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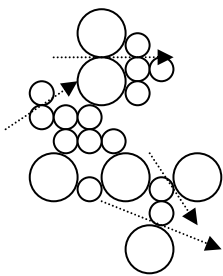
1) Large Scale Fragmentation



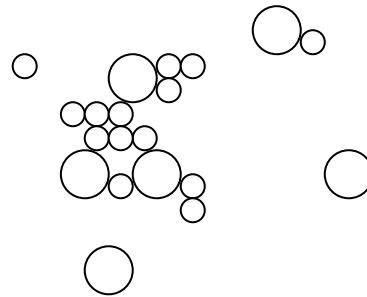
Tensile stress



2) Surface Erosion



Shear stress



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5 Figure 1. Two proposed mechanisms for the breakage of flocs under different shear

6 conditions.

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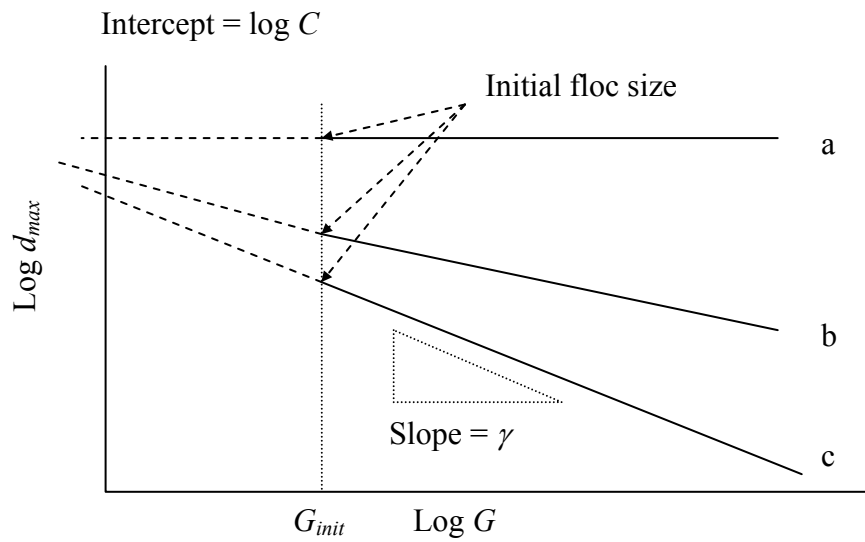
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2 Figure 2. The relationship between the change in particle size and an increase in
 3 velocity gradient for 3 types of floc. Floc (a) is resistant to breakage, floc (b) is
 4 thought to break due to large scale fragmentation and floc (c) is thought to break by
 5 surface erosion

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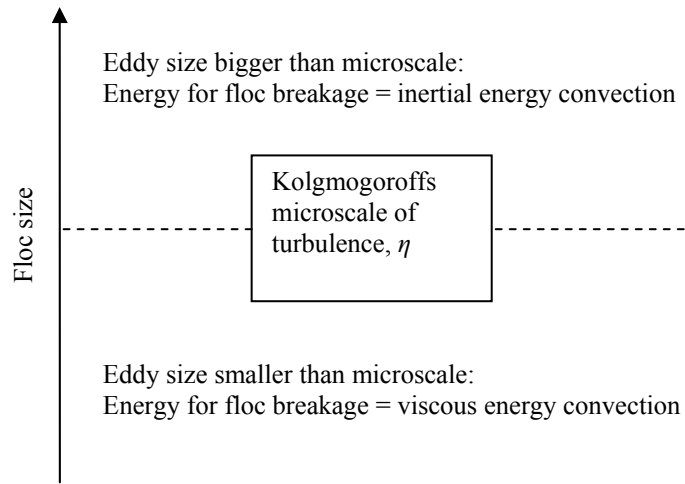
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2 Figure 3. The importance of eddy size on floc break-up mechanism.

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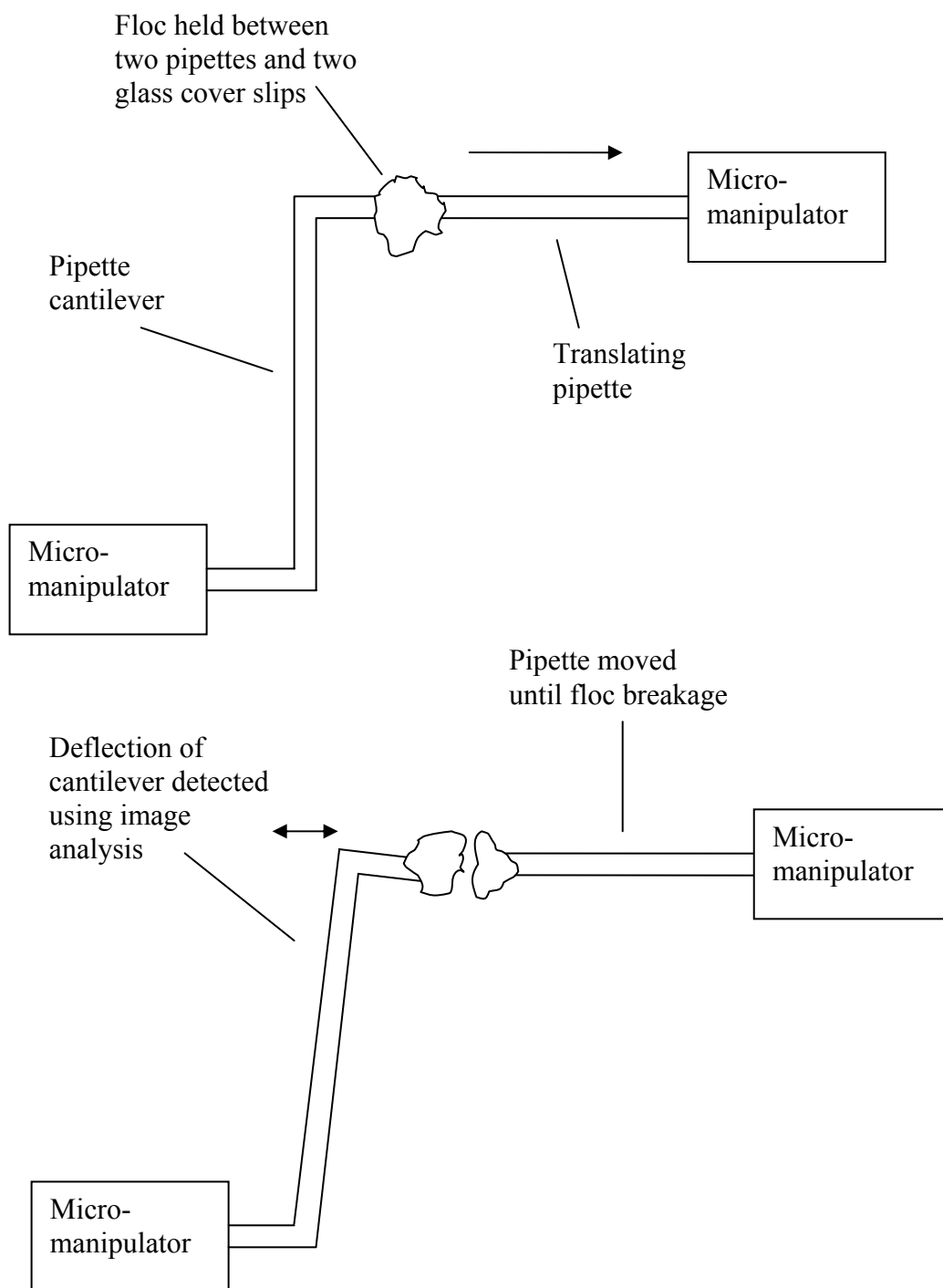
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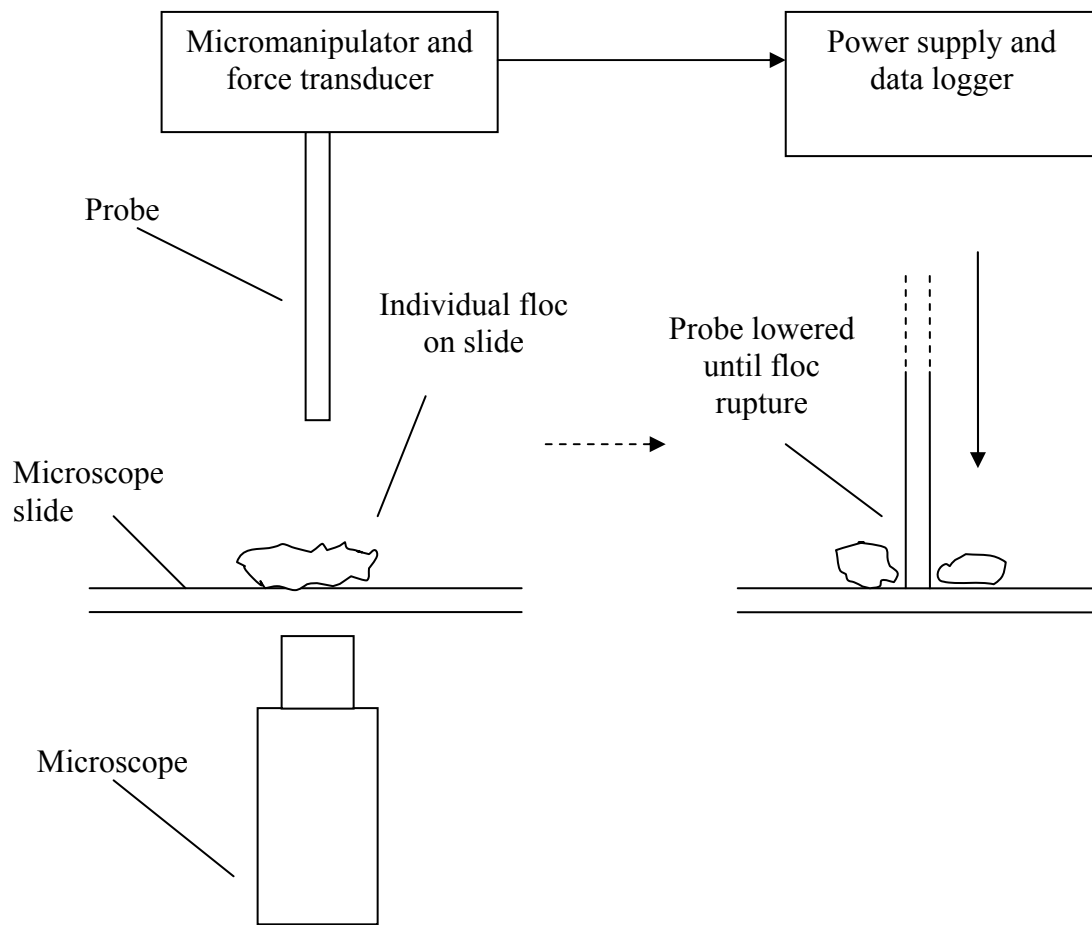
2 Figure 4. A schematic overview of the micromechanical floc strength technique.

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Figure 5. A schematic overview of the micromanipulation floc strength technique.

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2 Table 1. A review of the techniques used for determining floc strength.

Strength technique		Description	Strength calculation
<i>Macroscopic techniques</i>	Impeller	Exposure of floc to single level of increased shear within a containing vessel and compare the ratio of the floc size before and after breakage (Francois, 1987; Fitzpatrick <i>et al</i> , 2003)	$\text{Strength factor} = \frac{d(2)}{d(1)} \times 100$ <p style="text-align: right;">Equation 2</p> <p>where $d(1)$ is the average floc size of the plateau before breakage (m) and $d(2)$ is the floc size after the floc breakage period (m)</p>
		Exposure of the floc to increased levels of shear at a controllable rate within a containing vessel and measure the energy input for floc breakage (Leentvaar and Rebhun, 1983; Francois, 1987).	$\log d_{\max} = \log C - \gamma \log G$ <p style="text-align: right;">Equation 3</p> <p>d_{\max} is the maximum floc diameter (m); C is the floc strength co-efficient; G is the average velocity gradient (s^{-1}) and γ is the stable floc size constant, an exponent dependent upon floc break-up mode and the size of eddies that causes the breakage. A plot of the maximum floc size remaining against the average velocity gradient gives a line with a characteristic slope indicative of floc strength and break-up mode.</p>
	Ultrasonics	Application of a controllable ultrasonic field to a floc suspension and observe floc erosion (Wen and Lee, 1998; Chu <i>et al.</i> , 2001).	$\frac{\delta}{\phi} = \frac{-0.78k^{0.5} \Delta \tau}{d_{fo}^{-D/3} D \left. \frac{dy}{dj} \right _{j \rightarrow 0}}$ <p style="text-align: right;">Equation 4</p> <p>δ is the floc binding strength (J m^{-2}), ϕ is the power of the ultrasonic field per floc's volume and time ($\text{W m}^{-3} \text{s}$), $\Delta \tau$ is the ultrasonic time (s), d_{fo} is the floc size before sonification (m), d_o is the floc size after sonification (m), k is the proportionality constant (the ratio of the floc's cross-sectional area and $d_f^{2D/3}$), D_f is the floc fractal dimension and j is the time of ultrasonification (s).</p>

	Multigrid mixer	Flocs exposed to hydrodynamic stress from a controllable oscillatory mixer (Bache <i>et al.</i> , 1999). Flocs placed in a vibrating column and subjected to varying amounts of oscillation. The vibration is converted into an energy input for the system.	$\sigma \approx \frac{\rho_w \varepsilon^{3/4} d^{1/3}}{\nu^{1/4}}$ <p style="text-align: right;">Equation 5</p> <p>σ is the floc strength (N m⁻²), ρ_w is the density of water (kg m⁻³), ε is the energy dissipation at height of floc rupture (m² s⁻³), d is the floc diameter (m).</p>
<i>Microscopic techniques</i>	Micromechanics	The breaking force required to pull apart a single floc in the tensile mode (Yeung and Pelton, 1996).	$\sigma = \frac{F}{\frac{\pi}{4} d^2}$ <p style="text-align: right;">Equation 6</p> <p>σ is the floc strength (N m⁻²) and d is the floc diameter (m), where F is the floc rupture force (N):</p>
			$F = C_s D$ <p style="text-align: right;">Equation 7</p> <p>F is the floc rupture force (N), C_s is the cantilever stiffness (N m⁻¹) and H is the cantilever deflection (m).</p>
	Micromanipulation	The squeezing of a single aggregate in suspension between a glass slide and a fibre optic probe until floc breakage using a force transducer (Zhang <i>et al.</i> , 1999).	$F = K(W_0 - W)$ <p style="text-align: right;">Equation 8</p> <p>F is the floc breaking force (N), K is the sensitivity of the force transducer (N V⁻¹), W is the voltage output (V) and W_0 is the baseline voltage of the force transducer (V)</p>

- 1 Table 2. A review of the different methods employed in shear based techniques for
- 2 determining floc strength.

Type of flocs	Impeller system	Method of determining floc size	Shear levels investigated	Reference
Tap water + ferric chloride Tap water + ferric chloride	2 L glass tank with a turbine type impeller	Photography + image analysis Non-invasive	G_{av} 160-500 s ⁻¹	Leentvaar and Rebhun (1983)
Kaolin + alum	4 L stirred vessel (unknown impeller type)	Small angle light scattering (Malvern Mastersizer 2200) <i>in situ</i> measurement. Single pass to waste.	G_{av} 30-1000 s ⁻¹	Francois (1987)
Polystyrene + alum	2.8 L baffled tank with Rushton impeller	Small angle light scattering (Malvern Mastersizer E) <i>in situ</i> measurement. Continuous recycled pump loop.	100-460 rpm G_{av} 50-500 s ⁻¹ G_{max} 597-5969	Spicer <i>et al.</i> (1998)
Activated sludge	1.2 L baffled mixing tank with six flat blade impeller	Small angle light scattering (Malvern Mastersizer E) <i>in situ</i> measurement. Continuous recycled pump loop	100-700 rpm G_{av} 19.4-444 s ⁻¹	Biggs and Lant (2000)
Bentonite + alum	Jar tester (unknown volume and	Video camera + image analysis Non-invasive	30-150 rpm G_{av} 9-33 s ⁻¹	Bouyer <i>et al.</i> (2001)

	impeller type)	measurement	G_{max} 35-360	
Humic + alum	2 L square beaker with single flat blade impeller	Video camera + image analysis. Non-invasive measurement	G_{av} 10-400 s ⁻¹	Bache and Rasool (2001)
Sewage sludge + cationic polymer	Couette flocculator powered by variable speed motor	Image analysis with flocs removed <i>ex situ</i>	G_{av} 10-400 s ⁻¹	Wu <i>et al.</i> (2003)
Kaolin + alum/ polyaluminium chloride	1 L jar test beaker with single flat blade impeller	Photometric dispersion analyser (PDA). Continuous re-cycled pump loop	50-400 rpm G_{av} 23-520 s ⁻¹	Gregory and Dupont (2001) & Fitzpatrick <i>et al.</i> (2003).

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- 1 Table 3. The value of the floc strength constants and coefficients obtained from shear
- 2 based techniques.

Type of floc	Coagulant type and dose	Floc strength coefficient value, $\log C$	Floc strength constant, γ	Reference
Alum sludge	Cationic polymer (PL-320) 0 → 30 mg L ⁻¹	2.4 → 5.9	N/A	Wu <i>et al.</i> (2003)
Ferric hydroxide precipitate in sewage effluent	Ferric chloride 10 mg L ⁻¹ as Fe	1.9	0.29	Leentvaar and Rebhun (1983)
	Ferric chloride + anionic polymer 10 mg L ⁻¹ as Fe + 3 mg L ⁻¹ polymer	4.1	0.55	
Ferric hydroxide precipitate in tap water	Ferric chloride 10 mg L ⁻¹ as Fe	2.5	0.51	
Alumino-humic (commercial humic solution)	Al based coagulant	3.1	0.44	Bache <i>et al.</i> (1999)
Alumino-humic in low alkalinity and high colour water	Al based coagulant 2.4 mg L ⁻¹ as Al 2.7 mg L ⁻¹ as Al 4.7 mg L ⁻¹ as Al 5.4 mg L ⁻¹ as Al 2.5 mg L ⁻¹ as Al +	3.8 3.4 3.6 3.6 3.8	0.61 0.63 0.57 0.52 0.44	Bache and Rasool (2001)

Alumino-humic in high alkalinity and high colour water	0.1 mg L ⁻¹ polymer 3.7 mg L ⁻¹ as Al + 0.1 mg L ⁻¹ polymer	4.0	0.64	
	Al based coagulant 5.0 mg L ⁻¹ as Al	4.1	0.81	
Alumino-kaolin in de-ionised water	Aluminium sulphate	-		Francois (1987)
	4.02 mg L ⁻¹ as Al		0.44	
	4.52 mg L ⁻¹ as Al		0.48	
	5.02 mg L ⁻¹ as Al		0.61	
	5.52 mg L ⁻¹ as Al		0.50	
	6.02 mg L ⁻¹ as Al		0.43	
Activated sludge flocs	No coagulant dosed	2.9	0.35	Biggs and Lant (2000)

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1 Table 4. The general trends observed in floc strength tests*.

Floc characteristic	Trend observed
Floc size	Floc size increases → floc strength decreases
Coagulant dose	Optimum coagulant dose for floc strength
Polymer addition	Biological flocs: Addition of polymer → floc strength decreases Chemical flocs: Addition of polymer → floc strength increases
Type of floc	Bridging particle flocs > charge neutralised particle flocs > complexation flocs (e.g. NOM/coagulant)

2 * for this table, the symbol '>' indicates where flocs were stronger than another type of floc.

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1 Table 5. Floc strength estimates using a variety of different methods.

Method	Type of Floc	Floc Size, μm	Floc Strength Estimate, N m^{-2}	Reference
Oscillating multigrid mixer	Alumino-humic flocs	238	0.08	Bache <i>et al.</i> (1999)
		182	0.16	
		143	0.29	
		120	0.42	
Oscillating multigrid mixer	Rice starch aggregated at isoelectric point (IEP)	1100	1.0	Bache <i>et al.</i> (1997)
	Latex aggregated at IEP	600	0.9	
Micromechanics	Polymer A – calcium carbonate flocs	25	100	Yeung and Pelton (1996)
	Polymer B – calcium carbonate flocs	10	1000	
Micromanipulation	Latex aggregated at IEP	2.5	5.3 μN^*	Zhang <i>et al.</i> (1999)
	Latex aggregated by Brownian motion	1.7	3.1 μN^*	

2 * data unavailable to normalise to N m^{-2}

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