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Orthokinetic heteroaggregation with nanoparticles: Effect of particle size ratio on aggregate properties

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ABSTRACT

Three different aggregation methods were employed in this work: the addition of HMW polymer, the addition of silica particles (4.3, 105 and 285 nm diameter) and adjustment of suspension pH to 9. Stable alumina dispersions (310 nm) were flocculated using these three methods and each method was found to aggregate the alumina causing equilibrium between formation and destruction of aggregates. The equilibrium size of the aggregates (from largest to smallest) was found to follow the order: HMW Polymer, MP3040, STZL, STXS (285 nm, 105 nm, 4.3 nm) and pH 9. The use of light scattering simulations showed the effect of a second particle species (silica) on the scattering intensity versus wave vector relationship (I versus Q). It was still feasible to obtain a fractal relationship from the light scattering data, even with the complications arising from a two particle asymmetrical system. The fractal dimension increased slightly (2.04, 2.06, 2.19) with an increase in particle size ratio (0.014, 0.339, 0.92) suggesting stronger particle interactions between particles of similar size. The strength of the aggregates was rated from strongest to weakest: HMW Polymer, 285 nm, 105 nm, 4.3 nm and pH 9. Particle–particle interaction energy calculations showed the strongest interaction potential for the larger silica. The particle–particle interaction energy was found to be weaker the smaller the silica particles become.

1. Introduction

There are a number of different methods available to destabilise a particle suspension. Depending on the outcome required, most dewatering operations use high molecular weight polymers to bridge suspension particles together forming large aggregates. Other methods include increasing the electrolyte concentration, addition of ionic species, polymer depletion flocculation and changing the pH of a suspension to neutralise the particle charge. In this work, small particles of opposite charge are examined and compared to regular flocculation techniques. This process of particle aggregation using small particles of opposite charge is known as heteroaggregation.

Heteroaggregation is mainly applied to toner aggregation processes [1]. Other instances can be observed in natural waters [2], flotation [3,4] and pharmaceutical processing [5]. Particle flocculants are not commonly observed in mainstream flocculation processes as they tend to increase the solids or ash content of the dewatered product. However, recent research has shown possible benefits of heteroaggregation over polymer bridging flocculation. Filtration experiments were conducted by Glover [6] as well as Yates [7] on alumina particles aggregated using nano-sized silica particles of opposite charge. After filtration of the heteroaggregates it was found that the moisture content of the filtration cake was 2–4% less in moisture content than the polymer bridging case. Due to the paucity of research in this field it is still undetermined what other benefits this type of aggregation may have for industry, especially when considering waste waters where extra solids content is not so important.

Recent research into heteroaggregation has investigated the fractal structure of heteroaggregates produced by oppositely charged particles [8–10] and most of these studies only deal with symmetrical particle systems (size ratio of 1:1). Having two different particle species of different size can cause light scattering analysis to become much more complex. Understanding the effect of a secondary particle species on the light scattering behaviour is extremely important in structure analysis of the aggregates produced. Thus, the first aim of this paper is to show how a second particle species affects the light scattering behaviour of the heteroaggregate mixture.

One of the key measurements in this field is that of aggregate structure. The aggregate structure produced in any aggregation

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process is important in further processing, such as in filtration and sedimentation operations [11]. The number of contacts between particles in an aggregate and the strength of those contacts will be directly related to the strength of the aggregate [12]. Therefore accurately characterising the aggregate structure is important in the prediction of filtration behaviour.

Obtaining information about aggregate structure has been difficult in the past. Aggregates could only be characterised by size and weight measurements. Since the introduction of the fractal concept [13], an exponent can be obtained which describes the space filling capacity of an object. Many types of objects are fractal in nature including clouds, trees, coastlines, snowflakes and soot particles. It is important to note that the range of scale over which the objects are self similar is limited usually by the size of the object itself. Over the appropriate range of scale the objects structure will appear to be the same irrespective of what magnification is used to view the object.

The tool frequently used to measure the structural properties of aggregates in these studies is low angle laser light scattering (LALLS). The difficulty with examining heteroparticle mixtures with LALLS is that the different properties (such as RI and size) of the materials complicate the analysis. Most of the work dealing with the structure of aggregates produced by oppositely charged particles only considers particles of similar size [8,9]. This is mainly due to the unknown effects on the light scattering results if unsymmetrical particle systems are studied. One type of particle is said to dilute the other [14], especially in the case of small size ratios where the smaller particles are almost invisible and the larger particles are spread further apart. Thus, the effect of dilution will need to be investigated before any fractal analysis can be applied. The way in which the particle size ratio affects the scattering intensity/wave vector relationship will determine the accuracy of the fractal analysis. Currently, the use of light scattering to obtain aggregate structural information is commonly observed in the literature and the reader is referred to the following articles [8,15–24] for a more detailed explanation of the theory.

The mass of solid particles contained within a sphere of radius R, from the centre of the aggregate $m(R)$, of a mass fractal aggregate is proportional to its radius R, raised to power D_f, i.e.,

$$m(R) \propto R^{D_f} \tag{3}$$

D_f is not limited to integer values and can have any value between 1 and 3. Tence et al. [25] have shown that the number fractal dimension and the mass fractal dimension are the same even for polydisperse systems. Thus, Eq. (3) can be rewritten in more specific terms changing the mass to particle number:

$$N = k_g \left(\frac{R_g}{r_o} \right)^{D_f} \tag{4}$$

where k_g is the structure prefactor [26]. The size of the aggregates and R_g are measured by scattering experiments in the RGD (Rayleigh–Gans–Debye) limit.

In this work three different types of destabilisation methods are investigated: particle, polymer and pH adjustment. The main aim of this work is to investigate the effect particle size has on the properties of heteroaggregates produced. Also, a comparison with other more common flocculation methods such as polymer addition and pH adjustment is included. When using the term "flocculant" in this study, the authors refer to the use of silica particles or polymer.

2. Materials and methods

A detailed characterisation of all particle suspensions used in this work can be found in Yates et al. [27] and Yates [7]. It should be noted that the alumina particle concentration in this work is 0.01% (w/w) (light scattering concentration) whereas in the previous work it was 2.5% (w/w). A brief overview of the materials and methods will be described here.

Table 1
Size and zeta potential of particles

Code name	Size (diameter nm) $D_{(50)}$	Size ratio (d/D) (silica/alumina)	Zeta potential (mV) @ pH 5 (±5 mV)
STXS	4.3	0.014	−38
STZL	105	0.339	−38
MP3040	285	0.920	−39
AKP30 (alumina)	310		+40

All particle suspensions were pH adjusted with KOH and HNO_3 (BDH chemicals) and the background electrolyte concentration was 10^{-3} M KNO_3 (analytical grade, Ajax chemicals). Alumina and silica particles were dispersed with Milli-Q ultrapure water with a resistivity of 18.2 MΩ cm^{-1}. The model suspension particles (AKP-30 alumina) were obtained from the Sumitomo Chemical Company, Japan ($D_{(50)}$ 310 nm diameter, $\rho \sim 3.98$ g cm^{-3}). These particles have been well characterised by a number of researches over the past decade including [6,28–35].

The alumina was prepared at a concentration of 10% (w/w) and adjusted to pH 5, followed by ultrasonication (Misonix Inc.). At pH 5 the alumina is positively charged [31]. The three types of silica, ($\rho \sim 2.2$ g cm^{-3}, STXS, STZL and MP304) were obtained from Nissan Chemicals America and have a negative charge at pH 5. Further information on the properties of the particles is shown in Table 1.

The polyacrylamide copolymer was supplied by SNF Floerger, approximately 30% of monomer units are negatively charged acrylic acid. The molecular weight of the AN934SH polymer was obtained from SNF charts as 14–16.5 million grams per mole. The concentration of polymer stock solution used in experiments was 0.01% (w/w). The polymer crystals were mixed with pH 5 Milli-Q water according to the method of Owen et al. [36], leaving the sample for 24 h to attain equilibrium conformation before use.

The flocculant concentration range for optimum aggregation was determined from jar tests and zeta potential measurements as the range of doses that produce clear supernatants and low absolute zeta potential values. The method of obtaining the optimum flocculant concentration range has been shown previously in Yates et al. [27]. Fig. 1 shows a typical jar test experiment used in finding the optimum. The results of the jar testing is shown in Table 2 for all three silica particle types as well as the polymer. The resultant optimum concentration range for polymer flocculation was 0.1–0.4 ppm. The zeta potential of each test sample within the clear supernatant range was also measured (Zetasizer Nano, Malvern Instruments, UK). The median concentration in this range usually coincided with a zero zeta potential value and it is this optimum concentration that is shown in Table 2.

2.1. Light scattering experiments

The main method employed to determine the properties of particles and aggregates in this study was LALLS(Mastersizer S, Malvern Instruments, UK). Light scattering experiments were carried out using two 5000 scan sweeps of the sample and refractive indices of alumina (1.76) and water (1.33). Fig. 2 shows the configuration of the experimental setup. A peristaltic pump (Master flex console drive, model 7518-10, Cole-Palmer) was used with a flow rate through the tubes of 78 ml/min. The average shear rate of mixing was calculated using a similar method to that of Spicer et al. [19] with an impeller power number of six and a standard geometry cell [37,38]. The shear rate calculated is an average shear rate and does not fully characterise the localised velocity gradients occurring in the cell. However, a