Colloids and Surfaces A: Physicochem. Eng. Aspects 449 (2014) 157–169

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Wall effects during settling in cylinders

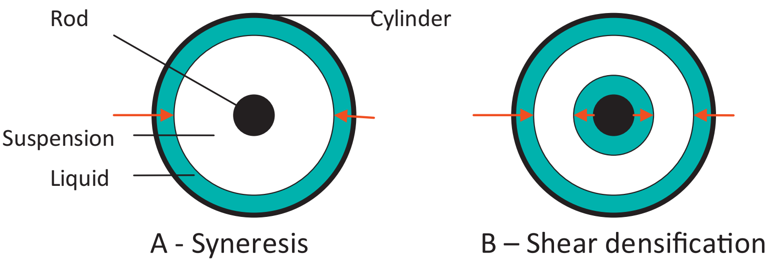
Benjamin Buratto, Shane P. Usher*, David Parris, Peter J. Scales

Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

HIGHLIGHTS

- Compared settling of alumina slurries in cylinders and cylinders with vertical rods.
- Polymer flocculated solids shrank from rod and settled faster: Shear densification.
- Salt coagulated solids clung to the rod and settled slower: Syneresis.
- Aggregation state influences settling rate changes in presence of vertical rods.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 September 2013
Received in revised form 16 February 2014
Accepted 17 February 2014
Available online 28 February 2014

Keywords:
Densification
flocculation
settling tests
syneresis
wall effects

ABSTRACT

The phenomena of syneresis and shear densification were analysed through the sedimentation of alumina suspensions. Experiments compared cylinder settling tests with a rod inserted in a cylinder against free settling without a rod for the cases of polymer flocculated and salt coagulated suspensions. Additionally, dye intrusion was used to visualise the final bed structure to identify the influence of cylinder walls and the potential presence of aggregate arching structures.

It was found that, for various cylinder diameters, polymer flocculated alumina suspensions settled more quickly when a rod was placed in the centre of the settling cylinder. This is attributed to shear induced densification of the flocculated aggregates during the settling process, as it was observed that the solids shrank away from the rod, creating a channel which allowed water to escape more easily than when the rod was absent. The reverse result was observed when a rod was placed in an unflocculated/coagulated alumina suspension; the solids stuck to the rod, resembling the syneresis mechanism of isotropic shrinkage towards the rod. Industrially these results are significant since inserting rods into sedimentation devices such as a thickener can result in a flocculated suspension settling further and at a faster rate, such that rods can provide an alternative to mechanical devices such as rakes.

Dye intrusion tests indicated that there was arching in the network bed, resulting in small pockets of water being trapped in the structure. An equation was derived to predict the maximum diameter arch that could be supported, taking into account the shear yield stress of the suspension. The solution to this equation was supported by observed cavities at the cylinder wall of up to 3 mm. These results suggest that cylinder walls may have a negative effect on the extent to which a suspension dewaters.

1. Introduction

Solid-liquid separation techniques are used extensively in industry in a variety of applications. There are two main mechanisms through which separation occurs; filtration and sedimentation. Filtration is based on separation by a physical barrier, as the liquid moves through the filter the solids are impeded. Sedimentation is the movement of solids due to a density difference under the influence of a body force such as gravity or centrifugal acceleration. The focus herein is on sedimentation as it occurs in thickeners and clarifiers typical of the minerals industry with the addition of flocculants to aggregate fine particles and achieve

---

* Corresponding author: Tel.: +61 3 8344 5592; fax: +61 3 8344 4153.
E-mail address: spusher@unimelb.edu.au (S.P. Usher).

http://dx.doi.org/10.1016/j.colsurfa.2014.02.045

significant increases in solids volume fraction. Through the process of thickening, slurry is separated into an underflow of a higher solids concentration along with an overflow liquor (supernatant) that is effectively free from solids. Ideally, optimised gravity thickener operation involves stable performance that consistently achieves high underflow solids concentrations with minimal solids in the liquor overflow.

In order to improve understanding of the continuous sedimentation process used in industry, batch bench-top sedimentation experiments are often performed in the laboratory [1]. A suspension of known solids concentration is allowed to settle under gravity in a cylinder and the height of the suspension-supernatant interface is recorded as it varies with time. Plotting and analysing the height versus time data can reveal information about the settling characteristics of the slurry [2,3]. These tests have been used widely to study aspects such as the effects of different flocculants [4–6] and the improvement of dewatering using rakes [7].

One aspect of dewatering performance which has not been extensively considered is the influence of surfaces and walls. Surfaces in the form of walls, sloped bases, lamellas, pickets, rods and rakes play important roles in improving dewatering performance [8]. Wall effects, including wall friction and adhesion to the wall, might be expected to make testing in relatively small diameter cylinders an unreliable guide to the behaviour of large bodies of sediment, but careful work using cylinders of different diameters can identify when wall effects are negligible for practical purposes. In this study we intend to focus on the settling region next to the wall and attempt to understand the underlying mechanisms at work.

It is well known that once beds settle beyond their gel point, a gap forms between the solids and the wall at the top of the bed. This has been shown to be due at least in part to the wall supporting the bed adjacent to the wall; the centre of the bed then settles faster and draws the edges inwards, giving the characteristic ring shape on the top of the bed. What is not clear from this is the relative contribution of gravity and syneresis.

Syneresis does not appear to have a single agreed definition. It actually defines a phenomenon rather than a mechanism, namely the shrinkage of gels over time with the expulsion of water. For the purposes of this paper it is defined as the shrinkage of a reticulated gel over time driven by the reduction in internal solid surface area and surface energy. Shrinkage due to applied pressure, such as the weight of the overhead portion of the bed, is excluded. Vliet et al. (1991) [9] refers to the former as *endogenous* syneresis. A review of a spectrum of work carried out on syneresis is included below.

In a fully reticulated, uniform bed, such as one formed by fine coagulated alumina, the effects of syneresis can be predicted with some confidence. The bed will shrink *isotropically*, and the rate of shrinkage will depend on the size and the shape of the bed. The first effect is self-evident. The size and shape have an impact because the water has to percolate through the bed to be expelled, and the distance that water has to travel and the flux both depend on the size and shape of the bed.

In a flocculated bed, syneresis, as defined here, will occur within the flocs, but not between flocs. Isotropic shrinkage over large distances is not expected. Without gravity they would shrink into themselves, and away from their neighbours. Under gravity they will densify and settle without significant lateral movement.

Some shear is generally required to cause densification and syneresis or at least accelerate these processes. Even in the absence of an applied shear through raking, hydrodynamic shear flow is induced by the settling of particles and aggregates of particles while the liquid flowrate is zero on surfaces such as walls and rods. Consequently there is a shear gradient or effective shear rate in the region of these surfaces. This shear rate, though much lower than in the presence of raking, does contribute to densification and syneresis.

Both shear densification and syneresis would generate a gap between the settling bed and the cylinder wall. However, if a smooth rod is placed within the bed, the effects should be diametrically opposed. Shear will cause the top of the bed to move away from the rod just as it does at the wall. Syneresis will cause the “hole” generated by the rod to shrink isotropically, as shown in Fig. 1. The gel around the rod will be under compaction due to this shrinkage, and will be pressed against the rod with some force.

The second topic to be addressed is the distance to which wall effects extend into the settled bed. If the wall is supporting the bed in contact with it, the bed adjacent to the wall will in turn support the bed further in and so on. In the extreme case an arch would form across the cylinder between opposite walls, and no sedimentation would occur. This is analogous to the arch formed in hard rock tunnels, or the Gothic arch in cathedrals, Fig. 3. A formula has been developed to describe this arching which has a characteristic diameter that depends on the ratio between the shear yield stress and the effective density of the solids.

A review is presented on the concepts of syneresis, shear densification and techniques that seek to improve the dewatering process. By considering the cases of flocculated and unflocculated alumina suspensions (AKP-30), these phenomena are investigated in this work by performing settling tests with rods inserted in cylinders. The settling data is analysed to confirm that these phenomena produce significant effects for settling around rods and determine the conditions under which this could have an industrial application. Additionally, dye techniques are used to examine if arching occurs due to wall effects in the settled bed.

1.1. Syneresis

Syneresis is based on the isotropic shrinking of a solid to decrease its energy state [10], while shear densification is aggregate contraction or shrinkage due to a shear force [1]. Research on syneresis has been predominantly on organic gels, in particular polymer gels or natural gelled products as are often utilised in the dairy industry. Syneresis is often defined as the expulsion of a liquid as a gel contracts resulting in uniform shrinkage due to the immobilisation of particles [9,11]. Vliet et al. (1991) observed syneresis in suspensions of colloidal particles formed from casein protein molecules [9]. They divided syneresis into two components, one due to external pressure (gravity in this instance) and another termed endogenous syneresis. They focus on the latter and state that large pores in the gel facilitate syneresis and that the extent of syneresis depends on the rate at which the polymer strands yield. Brinker and Scherer (1990) proposed that it occurs because the repulsive double layer that stabilises the sol collapses [10]. They also found that the addition of electrolyte causes additional shrinkage.

Scherer (1989) defines syneresis as the contraction of gel spontaneously without solvent evaporation [10]. Scherer studied the syneresis of silica gels, which expel water through the following condensation reaction: Si-OH + HO-Si → Si-O-Si + H_2O. Vysotskii and Strazhesko (1973), along with Raman et al. (1996) found that for silica gels, condensation is the slowest at the isoelectric point and hence syneresis is at a minimum [12,13]. This occurs because, at the isoelectric point, silica gels have the smallest pores making it difficult for the solvent to escape. However, Scherer states that vastly different microstructures can form at other pH values, resulting in varying rates of syneresis due to differences in pore permeability [10]. Scherer suggests it could be caused by the reduction in surface energy and that it can be the result of both the chemical structure and also microstructure of the gel. Raman et al. support this definition, finding that in inorganic gel condensation, reaction rates increase until the interfacial free energies between the