A short overview of the formation of aerated flocs and their applications in solid/liquid separation by flotation

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ABSTRACT

This review summarises the formation of aerated flocs or aeroflocs and describes their use in solid/liquid or liquid/oil/water separations during flocculation–flotation wastewater treatment. Here, the key future flocculation devices, techniques and trends are reviewed. Knowledge regarding the formation of aeroflocs and their current applications will be used for future applications and lead to the development of compact and high-throughput devices for rapid flocculation–flotation separations.

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1. Introduction

Flocculation–flotation processes have been widely used in water and wastewater treatment (urban and industrial), mineral processing, papermaking and hydrometallurgical treatments. Overall, the objective is to efficiently use solid/liquid, liquid/solid/oil or oil/water separations in various technical applications, which include the following: fine ore processing by selective flocculation; oily agglomeration of coal and gold particles; thickening of flotation concentrates; removing precipitated pollutant ions, suspended particles, organic matter, emulsified oils or residual organics reagents; separating precipitates from “neutralised” acid mine drainages; and thickening, filtration, settling and flotation in effluent treatment (Amato et al., 2000; Bolto et al., 1996; Dobiás and Stechemesser, 2005; Edzwald, 2010; Edzwald and Haarhoff, 2011; Finch and Hardie, 1999; Gregory, 1988; Gregory et al., 1999; Harbort et al., 1994; Hunter, 2002; Jameson, 1999; Kiuru, 2001; Laskowski, 1992; Letterman, 1999; Matis, 1995; Mavros and Matis, 1991; Metcalf and Eddy, 2003; Miller, 2001; Nguyen and Schulze, 2004; Parekh and Miller, 1999; Perry and Green, 2007; Rodrigues and Rubio, 2007; Rubio, 2003; Shibata and Fuerstenau, 2003; Svarovsky, 2000; Voronin and Dibrov, 1998; Warren, 1992; Yan and Jameson, 2004).

Rapid (aerated) floc–flotation is of great importance in effluent treatment with or without water reuse. In addition, the application
of floc–flotation in mineral processing may be possible, especially in mineral separation by selective flocculation at the solid/liquid stage (Atti and Driscoll, 1991; Chuangbing and Yuhua, 2008; Dogu and Arol, 2004; Forbes, 2011; Ma, 2012; Patra and Natarajan, 2008; Yuhua et al., 2011).

In this context, various important research studies have demonstrated significant improvements in the flocculation–flotation processes. These improvements were mainly from the generation of aerated flocs (also namely, aeroflocs), which are the central subjects of this short review.

Aerated flocs are structures composed of flocculated particles, polymers and air bubbles. These flocs (with trapped and attached bubbles) become light and rapidly rise (high-rate flotation) (Carissimi and Rubio, 2005a; Colic et al., 2001, 2007b; Da Rosa and Rubio, 2005; Kitchener and Gochin, 1981; Miller, 2001; Oliveira et al., 2010; Oliveira and Rubio, 2012; Owen et al., 1999; Rodrigues and Rubio, 2007; Rubio, 2003; Rulyov, 1999, 2001; Yan and Jameson, 2004).

The terms “aerated flocs” and “aeroflocs” come from an analogy to the aggregates generated in mineral processing flotation that are called aeroflocs (a cluster of mineralised bubbles) (Ata and Jameson, 2005; Gaudin, 1957; Glembotskii et al., 1963; Malysa et al., 1999a, 1999b; Schulze, 1984). These structures are composed of bubble-particles and were only recently applied to rapid contaminant removal from wastewater.

Herein, this work summarises the basic principles and applications of aeroflocs in water and wastewater treatment. Moreover, it is believed that rapid floc formation may create opportunities for additional applications and scientific studies. Fig. 1 summarises some of these contributions.

In the 2000s a number of articles (Carissimi and Rubio, 2005a; Colic et al., 2007a; Da Rosa and Rubio, 2005; Miller et al., 2010; Oliveira et al., 2008; Rodrigues and Rubio, 2007; Rulyov, 1999, 2001) regarding the formation and application of aerated flocs were reported. These articles reported that the floc structures had the following features:

i. a large size,

ii. an up-rising rate significantly higher than independent bubbles of gas (air),

iii. a high shear resistance during turbulent conditions, and

iv. a low moisture content.

However, although these studies provided useful information, additional investigation is needed. In this context, Oliveira et al. (2010) developed a new technique named Aerated Flocs Characterisation (AFC) for characterising the aerated flocs (multiphase systems) formed in flocculation–flotation studies. This technique used two cameras that were positioned orthogonal to each other. One camera (coupled to the optical microscope) was placed at the surface of the system to obtain qualitative data from the investigations. This qualitative data included the arrangement of the bubbles in the flocs, the bubble size distribution, and the stability of the bubbles inside the flocs and the attached and individual bubbles. Another camera placed in front of the tube was used to take video recordings of the flocs flow to obtain quantitative data. In this work, the techniques employed for image processing resulted in a detailed evaluation of the aerated flocs (Fig. 2). This evaluation included the size, shape factor, up-rising rate, fractal dimension and density of the flocs. In addition, the adhered, attached and entrapped bubbles in the flocs were characterised (Fig. 2) by quantitatively analysing the captured multiphase system images. Furthermore, the work showed that the presence (formation) of these large bubbles within the flocs increased their air volume and reduced their density.

According to some authors, the generation of the aerated floc structures might occur “in situ” after injection of air under pressure and turbulence.

In addition, further investigation showed that aeroflocs may form after injection of air or air-saturated water during the flocculation stage. In the first case, air bubbles are formed by introduction of air in a suspension at a high shearing rate by using flow constrictors as orifices and needle valves, venturi or static mixers. In this case, a wide size distribution of air bubbles is generated and the air bubble size range depends on the air/water interfacial tension.

Conversely, when the air-saturated water is depressurised in needle valves or orifice plates, consistent 30–70 μm microbubbles are produced (Rodrigues and Rubio, 2003).

Thus, aeroflocs are formed by either form of injection and the following mechanisms are held responsible for their generation.

i. Polymer precipitation at the air/liquid interface would occur in the presence of excess air. In this case, a fraction of macromolecules would precipitate by entrapping bubbles within the polymeric structure. Thus, the precipitation of a polymer may explain the observation of flocs with high shear strength.

ii. Elongated feature of the flocs can result from the uncoiling of polymeric chains. This process results from salting out at the water/air interface (under a high shear rate). In these conditions, the repulsive hydrophobic forces between the
polymer and the liquid phase are reduced by the presence of the hydrophobic phase (air). Consequently, fewer molecule interstices are available to be filled by water, which results in flocs that have higher solids content.

iii. Coalescence of fine bubbles inside and on the surface of the flocs may occur. In this case, the entrapped bubbles coalesce and the resulting large bubbles rise at a high speed.

iv. Bubble-particle collisions and attachment and detachment phenomena that are similar to what happens during the flotation of mineral ores also may occur.

v. Heterogeneous precipitation of pressurised gas may occur at the internal and external surfaces of the flocs. In this case, the precipitation of the dissolved gas that results in bubbles is known as “cavitation” or the formation of gas wells in a continuous liquid phase. The first stage of cavitation is the generation of the gas nuclei, also referred to as bubble nucleation or dissolved gas precipitation.

vi. Bubble nucleation, which occurs in the homogeneous phase (liquid) or on the solid surfaces (heterogeneous phase) may also occur. The cavitation process is enhanced in the presence of dust or mineral particles. These particles may act as nuclei for the bubbles that arise from small amounts of non-dissolved air in the particle pores. Moreover, the internal roughness of the containers may enhance the cavitation phenomenon (this process has been modelled by several researchers).

vii. The interactions between air bubbles and polymeric macromolecules (flocculants) have recently been revealed by Oliveira and Rubio (2011, 2012) that may also enhance the formation of aeroflocs. These authors showed a significant change in the air bubble surface charge in the presence of polymer flocculants, which indicated the adsorption of macromolecules at the air bubble/water interface. This finding results in a new mechanism for bubble and particle adhesion, which may play a key role in the formation of the aerated flocs.

2. Recent techniques and upcoming applications involving aerated flocs

The upcoming and efficient techniques and the patents and technologies associated with aerated flocs have been discussed by several authors (Beeby and Nicol, 1993; Carissimi and Rubio, 2005a; Colic et al., 2007a, 2001; Da Rosa and Rubio, 2005; Lelinski,
1993; Miller, 2001; Owen et al., 1999; Rubio et al., 2007; Rulyov, 1999, 2001; Ye et al., 1988). Applications have been reported in different areas that significantly improve pollutant removal and solid–liquid separation. Surprisingly, no research studies have been published regarding the use of aerated flocs in the selective flocculation of fine mineral particles.

Some of these techniques and applications have been developed in our research group, and a few are summarised as follows.

2.1. The Flocs Generator Reactor (FGR)

The FGR consists of an innovative helical mixing reactor for rapid aggregation followed by a solid–liquid separation. In this device, the flocculant is dispersed by the slurry flow through the helical tubes, which permits the occurrence of both polymer adsorption and flocculation within seconds. Additional details are described in the trademarked Flocs Generator Reactor (FGR) patent (Carissimi and Rubio, 2005b) and in Carissimi (2007) and Carissimi and Rubio (2005a).

The mixing regime has been characterised as a plug flow with small dispersion, which has ideal hydrodynamic conditions for the reagent and the growth of flocs.

However, FGR may be employed as a hydraulic flocculator or as a rapid flocculation flotation machine if microbubbles are injected (Carissimi and Rubio, 2005a; Rubio and Zaneti, 2009; Silveira et al., 2009). Thus, after air microbubbles are injected, they may become entrapped, occluded and coalesced inside of the flocs (in addition to the attachment of bubbles onto the particles). Thus, aeroflocs are readily formed and float quickly like they do in flotation processes (floc–flotation). Therefore, FGR has shown a high potential for use as an aggregation and flotation reactor for applications that require high solid–liquid separation rates (Rubio and Zaneti, 2009; Silva and Rubio, 2009; Silveira et al., 2009).

A schematic of aeroflocs generation in the FGR by introduction of air microbubbles is shown in Fig. 3.

Recently, several applications of the FGR have been reported, which include tap (potable) water clarification, treated wastewater reuse and acid mining drainage (AMD) treatment (Carissimi and Rubio, 2005a; Da Rosa and Rubio, 2005; Rubio et al., 2007; Rubio and Zaneti, 2009; Silva and Rubio, 2009).

In potable water clarification studies, Rubio et al. (2007) used three different coiled reactors (FGRs) (FGR1, FGR2 and FGR3) that were constructed for aggregate generation at the semi-pilot scale with flow rates of 0.3, 0.6 and 0.9 m$^3$/h, respectively. Coupled to a FGR, a flotation cell (high rate dissolved air flotation unit, HR-DAF) was designed for the solid/liquid separation studies (Fig. 4). Thus, raw water was pumped from the Guaiaba Statuary (Porto Alegre/Brazil) and transported to a water treatment plant (São João) that receives the chemical reagent. Next, the water was pumped before entering the plant settling tanks and an extra reagent was added to generate the flocs in the FGR and the solid–liquid separation in the HR-DAF.

This process yielded treated water with reduced turbidity (approximately 87%), which enabled the formation of flocs. The authors believed that the HR-DAF has a great potential for tap (potable) water clarification at high hydraulic loading capacities, shorter residence times (especially in the flocculation stage) and a smaller foot print.

In addition, this technique has been successful applied to the treatment of coal acid mining drainage (AMD) in Southern Brazil. Herein, some authors (Silva and Rubio, 2011a, 2011b; Silveira et al., 2009) described AMD techniques of neutralisation. These
techniques included the use of lime and the flocculation of the precipitates (by either flotation with microbubbles or lamellar settling (LS)) using a small pilot unit for flocs/liquid separation that treated approximately 1 m³/h–1.5 m³/h over 8 months. The authors showed that when microbubbles (generated by depressurisation of saturated air in water, as in dissolved air flotation-DAF) were injected, aerated flocs were formed (within seconds). These flocs were raised at >120 m/h, which allowed for a rapid solid–liquid separation by flotation (HR-DAF) at a loading capacity of approximately 13–15 m³/m²/h.

Therefore, these results showed that both flotation and lamellar settling (LS) had similar efficiencies (at pH 9) for the removal of flocs containing heavy metals (>90%). However, both units were compact and took advantage of the rapid flocculation in the FGR, which allowed for quality water treatment. In fact, the treated water was nearly free of heavy metal ions, had a low BOD (biological oxygen demand), low TOC (total organic content), a low solids content and could be easily reused for irrigation, industrial processes or wash water (among others, streets, vehicles, dust control).

2.2. Flocculation–flotation (FF)

The FF reactor is a special design (zigzag or static mixer type) for generating light flocs (aerated flocs) that are formed in the presence of polymers, air bubbles (injected air), high shearing force and a high head loss (or velocity gradient) (Da Rosa and Rubio, 2005; Rubio, 2003; Rubio et al., 2002). Fig. 5 shows the FF scheme. A version of this FF was patented for treatment and reuse of wastewater from washing vehicles (Rubio et al., 2003).

Applications of the FF technique include the separation of oil from oil-in-water emulsions, flocculation–flotation of suspended (dispersed) solids and water treatment and reuse from washing vehicles. Da Rosa and Rubio (2005) used a typical petroleum refinery effluent in a FF system coupled by columns, tanks or centrifugal three phases cavitation pump) are contacted and separated by flotation. Because of the low residence time, the rig has a high hydraulic-loading capacity (>13 m/h) and has a small foot-print area and reduced energy consumption.

Aerated flocs have also been formed in a Flocculation-Column Flotation technique (FCF). Fig. 6 shows the layout of this FCF, whose details have been described elsewhere (patent PI 0802871-0 by Rubio and Zaneti (2010)). This system consists of a hydraulic flocculant disperser (zigzag) coupled to a FGR (for generating the aerated flocs which feed the flotation column), where flocs and air bubbles (generated by a centrifugal for generating the aerated flocs which feed the flotation column), where flocs and air bubbles (generated by a centrifugal three phases cavitation pump) are contacted and separated by flotation. Because of the low residence time, the rig has a high hydraulic-loading capacity (>13 m/h) and has a small foot-print area and reduced energy consumption.

To achieve high quality treatment of water, full-scale car wash wastewater treatment and recycling using the FCF technique coupled to a sand filtration and final chlorination systems were reported by Zaneti et al. (2011). These authors studied (during 20 weeks of operation) the more than 200 car washings and showed that nearly 70% wastewater reclamation was attainable with <40 L of fresh water per wash. In addition, the reclaimed water quality was good in terms of chemical, physicochemical and biological parameters. These parameters include the aesthetic quality (water clarification and odour), health (pathological) and chemical (corrosion and scaling) risks (with almost 70% of odourless and clear water achieved) of the water. Additionally, the cost-benefit analysis showed that at least 8 months were needed for the FCF-SC equipment amortisation for a car wash wastewater reclamation system in Brazil for demands exceeding 30 washes per day.

A similar system was used by Rubio and Zaneti (2009) at the Metropolitan Transportation Bus Company (a 250 bus fleet site). The company installed a FCF unit followed by a sand filter for the treatment and recycling of fleet washdown wastewater.

In this case, the FCF system produced clear, high quality water (low turbidity and high colour reduction) for a high hydraulic reuse load. With regard to water reuse, the FCF treated water is suitable for washing busses. The aerated flocs were formed rapidly (10 s residence time) in the presence of a Tanin base flocculant and the microbubbles within an in-line rapid flocculator (retention...
Due to the rapid formation of these very light flocs with high up-rising rates (up to 150 m/h), the FCF system was able to handle a high hydraulic-load capacity (>15 m/h) with a small footprint (compact unit) and low energy consumption.

Other techniques, such as ASH flotation (Air Sparged Hydrocyclone), BAF flotation (Bubble Accelerated Flotation), ultraflocculation and microflocculation have also been reported (Beeby and Nicol, 1993; Colic et al., 2001; Lelinski, 1993; Miller, 2001; Owen et al., 1999; Rulyov, 1999, 2001; Ye et al., 1988). Although these authors do not use the term “aerated flocs” or “aeroflocs”, they described the formation of aggregates with rapid up-rising rates that improved the solid/liquid separation processes.

### 2.4. Turbulent microflocculation

The micro-flotation is characterised by the use of extremely small bubbles (diameter 5–50 μm) generated by electrolytic decomposition of water (so-called electro-flotation) or other techniques.

It has been hypothesised that both turbulent microflocculation and ultra-flocculation (Rulyov, 2001) occur simultaneously in generating flocs that rapidly float. To achieve this, flocculants and microbubbles are introduced into the effluent and then submitted to a vigorous shearing regime. The mixing flow rate is adjusted to maintain a turbulent stream flow, to avoid early phase separation, to ensure the aggregation (flocculation, coagulation) or heterocoagulation of the particles (and/or their aggregates) with bubbles and to ensure the aggregation of the bubbles with particles (Rulyov, 1999, 2001).

Moreover, by controlling the amount of microbubbles the selection of suitable reagents and their dosage points in the stream permitted an effective attachment of the particles to microbubbles. Thus, large foam aggregates with high buoyancy are generated at the channel outlet, which leads to an easy separation of the aggregates from the liquid.

Rulyov (1999) applied this technique for treating waste oil/water emulsion lubricants. In this study, Rulyov (1999) used turbulent microflocculation, which generated aggregates that had rising velocities that were hundreds of times higher than treatment systems that did not use microflocculation and easy to separate.

### 2.5. ASH flotation (Air Sparged Hydrocyclone) and BAF (Bubble Accelerated Flotation)

The ASH flotation (Air Sparged Hydrocyclone) and BAF (Bubble Accelerated Flotation) techniques have been reported that describe the rapid formation of flocs (Beeby and Nicol, 1993; Colic et al., 2001; Lelinski, 1993).

The ASH technique couples a porous cylindrical membrane with the design features of a hydrocyclone. In this system, gas is introduced through the membrane while wastewater is pumped through the hydrocyclone. Because the bubbles are sheared off the wall of the porous membrane (due to the high velocity and centrifugal forces inside the hydrocyclone) they are dispersed into very small bubbles that resemble those generated in DAF operations. Thus, the flocs float within seconds after leaving the downcomer cylinder and are removed by force through an overflow (vortex finder).

The BAF technique is similar to the ASH technique. For the BAF technique, the bubble/particle/polymer aggregates are formed in a bubble chamber (Fig. 7) before they reach the tank. Thus, the tank is used as an ancillary separator for the flocs. This feature (combined with the fact that the aggregates are already formed) allows for high hydraulic flow rates through the flotation tank. Fig. 7 depicts the air sparged bubble chamber, which is an important component of this device.

According to the authors, these technologies are particularly efficient for the removal of free and emulsified fats, oils, and grease (FOG). The BAF system has also been used to remove totally hydrophilic particles such as zeolites or quartz. In addition, the BAF system has a short response time (seconds) to changes in the solution chemistry (contrary to hours in clarifiers or DAF).

Conversely, Colic et al. (2001) observed that high molecular weight polymeric polymers can be added directly into the bubble chamber head, which results in the rapid formation of large flocs (aeroflocs) with diameters of <10 cm.

### 3. Future trends in the formation of aerated flocs

A full knowledge of aerated flocs or aeroflocs generation for different purposes and systems will further improve the techniques.
and technologies described above. The presence of rapid flocs in all of these investigations demonstrated that it is important to search for optimal conditions that favour the formation of aerated flocs. Accordingly, a full understanding of the mechanisms involved in the generation of these structures is needed.

Recently, Oliveira (2010) and Oliveira and Rubio (2011) showed that important interactions between polymers and bubbles-particles occur in activated carbon and kaolin aerated flocs systems. These aerated flocs had large bubbles inside their structures resulting from the interactions between the trains of bubbles, bridges of bubbles and/or clusters of bubbles. The microphotographs obtained in these investigations suggest the formation of polymer-coated bubbles that interact with particles, bubbles and/or other particle-coated bubbles. According to the author, these structures are highly interactive and facilitate the formation of light aerated flocs in suspension with improved rising rates.

This finding led to new investigations regarding the interactions between polymers and bubbles and to the improvement of these mechanisms in a continuous system for generating aerated flocs assisted by polymer-coated microbubbles. These findings were based on the images shown in Fig. 8, which verified the flocculation mechanisms involving polymer-coated bubbles that strongly interacted with particles, free bubbles, other polymer-coated bubbles and aerated flocs in suspension.

In addition to the existing data that indicated that interactions between polymers and air bubbles occurred, this work considered

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**Fig. 7.** A scheme of a bubble chamber with ASH technology. Source: Colic et al. (2001).

**Fig. 8.** Photomicrographs of polymer-coated bubbles interacting with flocs and/or other bubbles. Source: Oliveira (2010).
the occurrence of van der Waals and hydrophobic forces between the air bubbles and the hydrophobic moieties present in the polymeric chain backbones. The hydrophobicity of the polyacrylamides has been previously described (Ghannam, 1999; Oliveira, 2010). Such interactions, phenomena and investigations could be important for explaining some of the discovered phenomena, which include the following: (i) the presence of large bubbles in aerated flocs, and (ii) their growth assisted by the polymer-coated microbubbles. The improvements and knowledge of these phenomena will improve the existing techniques and upcoming technologies (with high loading capacities).

The rapid formation of aerated flocs is potentially useful in several operations, which include mining, metallurgical and physico-chemical separation. For example, the effective removal of adsorbed pollutants onto carrier flocs (not explored yet); the solid–liquid separation of slimes that are difficult-to-flocculate (clays) and sometimes pose settling problems in ore tailing thickeners and separation of organic and hydrometallurgical solvents (emulsified); and the rapid separation by flotation of rich protein bearing dispersions.

Moreover, the aerated flocs may be employed to improve oil enhanced production in the reuse of water in thickener overflows and the treatment of water for reuse in filtered mining pulps (flotation concentrates, for example).

4. Conclusions

The formation of aerated flocs (or aeroflocs) has been observed in several research studies, patents and technologies that promote and facilitate solid–liquid separation operations by flocculation–flotation. The mechanisms of aerated floc formation involve many phenomena that occur simultaneously, including the following: polymer precipitation at the air/liquid interface; uncoiling of the polymeric chains; bubbles, nucleation and/or coalescence inside and onto the surface of flocs; bubble-particle collisions, attachments and detachments; heterogeneous precipitation of the pressurised gas; and the interactions of air bubbles with polymeric macromolecules (floculants). Techniques and technologies for the formation of these aerated flocs have been described that show their high throughput. Future wastewater treatment trends emphasise the importance of understanding and using new phenomena (namely polymer-coated microbubbles or “floculant bubbles”) to improve rapid solid/liquid separation by advanced flocculation–flotation processes.

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References


