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Review Article

DAF–dissolved air flotation: Potential applications in the mining and mineral processing industry

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Abstract

Conventional and non-conventional flotation for mineral processing and for water (and wastewaters) treatment and reuse (or recycling) is rapidly broadening their applications in the mining field. Conventional flotation assisted with microbubbles (30–100 μm) finds application in the recovery of fine mineral particles (<13 μm) and flotation with these fine bubbles is being used as a solid/liquid separation to remove pollutants. The injection of small bubbles to conventional coarse bubbles flotation cells usually leads to general improvements of the separation parameters, especially for the ultrafines (<5 μm) ore particles. Results obtained are believed to occur by enhancing the capture of particles by bubbles, one of the main drawbacks in fine ore flotation. It is believed that by decreasing the bubble size distribution (through the injection of small bubbles), increases the bubble surface flux and the fines capture. DAF or dissolved air flotation with microbubbles, treating water, wastewater and domestic sewage is known for a number of years and is now gradually entering in the mining environmental area. This technology offers, in most cases, advantages over settling, filtration, precipitation, or adsorption onto natural and synthetic adsorbents. The targets are the removal of oils (emulsified or not), ions (heavy metals and anions) and the reuse or recirculation of the process waters. Advantages include better treated water quality, rapid start up, high rate operation, and a thicker sludge. New applications are found in the mining vehicles washing water treatment and reuse, AMD (acid mining drainage) neutralization and high rate solids/water separation by flotation with microbubbles. This work reviews some recent applications of the use of microbubbles to assist the recovery of very small mineral particles and for the removal of pollutants from mining wastewaters. Emphasis is given to the design features of innovative devices showing the potential of conventional and unconventional DAF flotation.

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Keywords: Environmental; Flotation; Flocculation

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1. Introduction and a short overview

Flotation technology is employed for more than a century in ore processing and its environmental applications are best known in the civil (sanitary), chemical and food engineering fields. DAF or dissolved air flotation, pressure flotation, or flotation with microbubbles (30–100 μm) is the most utilized process removing a number of pollutants, among others, colloids, fines and ultrafines particles, precipitates, ions, microorganisms, proteins, dispersed and emulsified oils in water (Rubio et al., 2002a,b; Ross et al., 2003; Carissimi and Rubio, 2005a; Matis and Lazaridis, 2002).

In the mineral processing area, all employed flotation devices do not generate these microbubbles but coarser bubbles, usually between 600 and 2500 μm. According to most researchers, the lack of "mid-sized" bubbles in the cells is the main reason why the capture of the very fine particles is inefficient leading to considerable losses, an old problem in mineral processing (Rubio et al., 2003; Sivamohan, 1990), especially for the fine (<13 μm) mineral particles. The losses are due to the intrinsic properties of these particles (mainly small mass and low inertia) and main flotation drawbacks are related to the low probability of bubble–particle capture phenomena (Reay and Ratcliff, 1973; Anfruns and Kitchener, 1977; Yoon and Luttrell, 1989; Yoon, 1999, 2000; Dai et al., 2003). Many authors have also found high efficiencies of bubble–particle detachment in fine particles–bubbles (coarse) interactions (Jameson et al., 1977; Crawford and Ralston, 1988; Dai et al., 1998).

Many different processes to reduce this problem have been proposed but most of them have not found practical applications yet (Collins and Read, 1971; Trahar and Warren, 1976; Fuerstenau, 1980; Subrahmanyan and Fossberg, 1990; Sivamohan, 1990; Rubio et al., 2003).

But, this is not the situation in effluents treatment whereby most particles are fine (even within the colloidal range) and are readily removed by flotation because of the use of fines bubbles. Accordingly, it may be concluded that for the recovery of fine minerals particles in ore flotation the cell machine should provide a wide bubbles size distribution, which must include micro or mid-sized bubbles (100–600 μm) plus the coarser bubbles generated in conventional flotation cells. This is a great challenge!

Column flotation cells generate, with their various commercial spargers, finer bubbles than conventional "rougher" cells machines, improving somewhat the recovery of the F–UF mineral particles (Finch, 1995). However, determination and report of bubble size distribution, in this kind of flotation cells are scarce and more; recoveries of the coarser particles, in columns, are usually very low and this is another reason to explain why they are used mostly in cleaner flotation circuits.

Main differences between these main flotation applications are related to the concentration of solids being separated, low in DAF processes (1–3% weight basis) compared 30–40% (weight basis) in mineral separation and the volume of air which is introduced in each process (Rubio et al., 2002a,b). In DAF system, the process is limited to the dissolution properties of air to water, following the Henry's law (Bratby and Marais, 1977). Dilute suspensions about 59–117 g air m^{-3} (3–6 atm pressure saturation, respectively) are dissolved in the treated water (recycle) and injected into flotation cell, at 0.3–0.5 recycle/feed ratio. This value is equivalent to about 20–30 L of air into 1 m^3 of water. Conversely, in mineral flotation or dispersed air flotation systems, about 10 m^3 of air are dispersed into 1 m^3 of water (pulp) or 500 times more than that used in DAF. Thus, DAF microbubbles are used to capture only the small, light solids and metal-ion hydroxide flocs, bacteria, etc., having specific weights close to that of water. Bubbles generated in the ore flotation machines (600–2500 μm bubbles diameters) are not suitable for the separation of those fine particles (Solari and Gochin, 1992; Rubio et al., 2002a,b).

Summarizing, DAF may be used and appears to have potential in many mining applications, namely:

- In solid–liquid separation and water recirculation (as in thickeners).
- Removal of ions from process waters which may activate gangue particles if fed to mineral flotation plants.
- Treatment of flotation liquid effluents removing pollutants anions, oil spills or emulsions, heavy metal ions, colloidal precipitates, residual organic collectors and frothers.
- Treatment of AMD-acid mining drainage removing solids generated after neutralization.
- In mining equipment, vehicles and big machinery washing water treatment and reuse.
- Treatment of filtered water from ore flotation concentrates.
- Recovery of valuable ions (Au, Pd, Ag, Pt).
- In fine mineral treatment, associated to coarser bubbles.

The aim of this work is to overview the actual applications of microbubbles in mining and mineral processing operations and to forecast future trends in both areas: the flotation of F–UF fractions and the removal of particles by flotation (treatment) from liquids effluents, acidic generated waters and reuse of wastewater.

1.1. The generation of the microbubbles, exploring the air dissolution under pressure

Bubbles are formed by a reduction in pressure of water (treated wastewater recycled) pre-saturated with air at pressures higher than atmospheric (3 to 6 atm). The supersaturated water is forced trough needle-valves or special orifices, and clouds of bubbles, 30–100 μm in diameter, are produced just down-stream of the constriction (Bratby and Marais, 1977; Lazaridis et al., 1992; Rodrigues and Rubio, 2003). Fig. 1 shows how these microbubbles look like and Fig. 2 illustrates a photomicrograph of mixed coarse and microbubbles.

Microbubbles rise under laminar flow under rigid-sphere conditions and obey Stokes' law. The rising rates are lower in cold water due to the increased viscosity of the water (example: 9.6 m h^{-1} at 20 °C for a 70 μm bubble diameter). Some nanobubbles or microbubbles are below visible size and reflect light in all directions, similar to snow. This explains why the bubbles are "seen" as a slowly rising white cloud in water, sometimes called whitewater.

The microbubbles, after having been attached or entrapped within the flocs, increases the rising rate of the composites dramatically (Carissimi and Rubio, 2005a,b). The rising rate of individual composites is related to their size, specific weight, mass (volume) of air attached, aggregates form, water temperature and flow conditions (see some values in Table 1).

1.2. Mechanisms involved in the interaction between particles and microbubbles

The question whether hydrophobicity is or not a prerequisite in dissolved air flotation (DAF) systems has been addressed by Gochin and Solari (1983a,b). These authors reckon that in the industry it is not a common practice to add surface-active reagents to the suspension

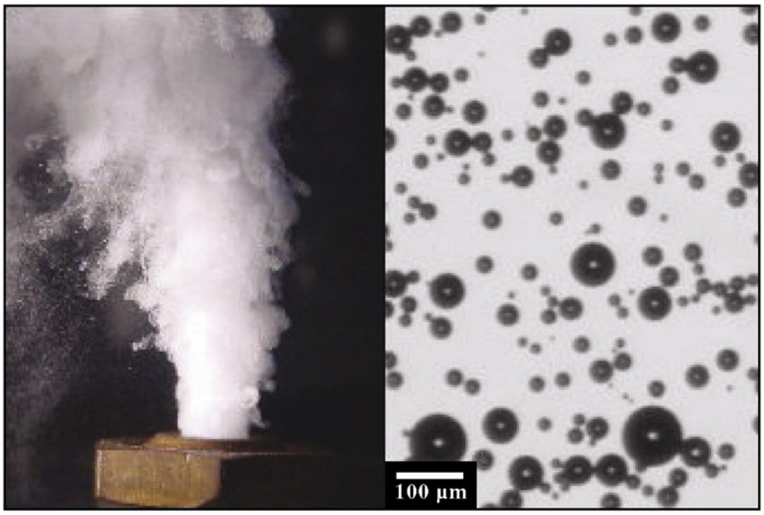

Fig. 1. Microbubbles rising in aqueous medium and a digital image of microbubbles measured with the LTM-BSizer, (Rodrigues, 2004).

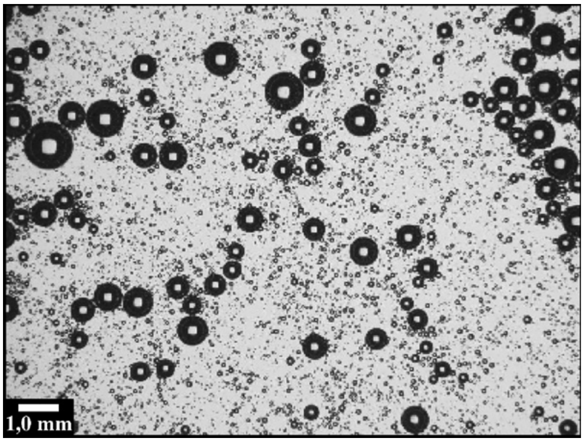

Fig. 2. Digital image of conventional coarse bubbles with injection of microbubbles measured with the LTM-BSizer (Rodrigues, 2004).

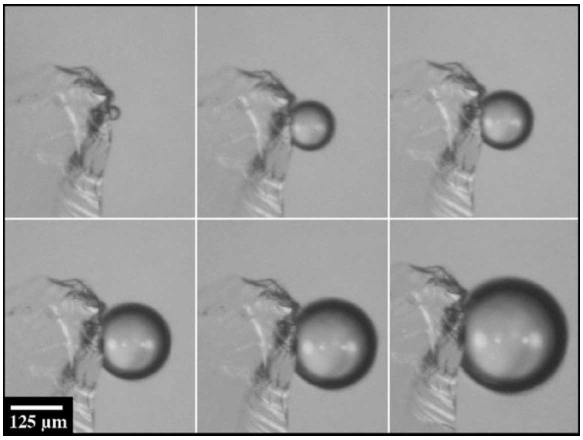

Fig. 3. Nucleation and growth of a microbubble at a quartz particle surface coated with dodecylamine (collector).

in order to increase the efficiency of flotation of solids from effluents or wastewater. This led some researchers to postulate that microbubbles flotation of hydrophilic solids was possible through bubbles physical entrapment in flocs structures and therefore that particle aggregation was the key factor in solid–liquid separation by DAF. Yet, studies conducted by Gochin and Solari (1983a,b), with quartz and silica in the presence of surfactants and various polymeric flocculants, indicated that flotation by microbubbles was possible only in the presence of surfactant adsorption at the quartz–solution interface.

However, in flotation with microbubbles, mechanisms of bubble/particle (aggregates) interactions, other than the common adhesion through hydrophobic forces, have been proposed, namely (Solari and Gochin, 1992; Rubio et al., 2002a,b, Rubio, 1998, 2003; Carissimi and Rubio, 2005b):

a) Nucleation phenomena at solid surfaces. Part of the dissolved air in water does not convert into bubbles in the nozzles, remains in solution and “nucleate” at particle surfaces (Solari and Gochin, 1992). In this case, bubbles nuclei and growth at the solid/liquid interface, as can be seen in Fig. 3. This mechanism is independent on surface hydrophobicity and might allow flotation of hydrophilic particles. Fig. 4 shows, for example, the flotation of hydrophilic ferric hydroxide by DAF or flotation with microbubbles without any collector.
b) Bubbles entrapment or physical trapping inside the flocs or aerated flocs formation. This phenomenon (Fig. 5) occurs for bubbles entering and remaining inside the iron hydroxide flocs. As a result, the density of the bubbles–particles aggregates drastically decreases. This phenomenon is quite known and has being recently very well explored (Owen et al., 1999; Rubio et al., 2002a,b; Carissimi and Rubio, 2005a,b; Rosa and Rubio, 2005).
c) Aggregates entrainment, by the rising bubbles (“cloud”) (see Fig. 6). This corresponds to a physical particles (aggregate) carryover by the bubbles (attached or not, to particles) and depends mainly on hydrodynamics and on bubbles size distribution

Table 1
Comparison between bubbles at different size ranges

Size, in μm	20	50	100
Number of bubbles in ml	1,250,000	100,000	14,000
Surface area, cm^2 in 1 cm^3	23	12	6.6
Rising rates, mh^{-1}	1	5	20

Fig. 4. Colloidal iron precipitates, Fe $(OH)_3$, floated by DAF, without collector.

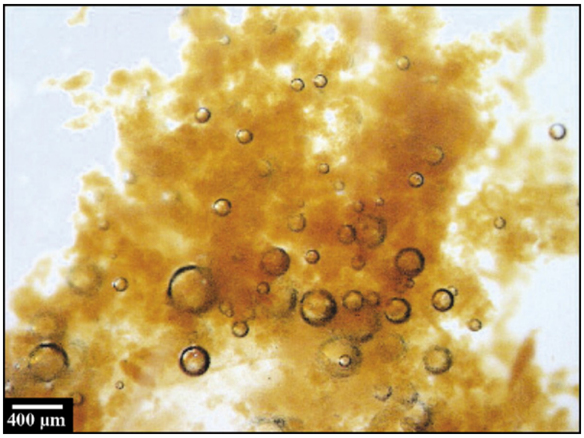

Fig. 5. Bubbles being entrapped inside flocs (colloidal iron precipitates, Fe $(OH)_3$).

(Solari and Gochin, 1992; Rubio et al., 2002a,b; Carissimi and Rubio, 2005a,b; Rosa and Rubio, 2005).

Mechanisms "a" and "b" occur only with the microbubbles and not with the coarser bubbles and explain why, in DAF, no collector or froth is required and a thick and stable float layer is formed at the flotation cell top. The rising velocity is highly dependent on particles (aggregates) density or on bubbles trapping inside the flocs. In mineral treatment, flotation of the F–UF particles by surface nucleation and entrainment may occur independently of the nature of the particles, whether hydrophobic or hydrophilic, and if gangue particles are very small this would lead to unselective flotation (Zhou et al., 1997). Yet, interactions between hydrophobic particles and the microbubbles are generally higher (stronger and faster) and therefore, more selective than those with the hydrophilic (Rubio et al., 2003).

2. The applications of flotation with microbubbles in mineral processing

Earlier applications of the use of microbubbles (alone) in mineral particles recovery were not successful due to problems with the low lifting power of these bubbles for the coarse or dense particles, even worse, at high solids concentrations (Solari, 1980). Yet, recent bench studies of flotation of different minerals; with injection of microbubbles (40 μm, mean diameter) to lab cells (in addition to the cell generated coarse bubbles) have improved separation parameters when compared to the mill standard (Yalcin et al., 2002; Rubio et al., 2003).

The potential use of dissolved gas bubbles in mineral flotation was investigated using a copper–nickel ore (Inco Ltd. in Sudbury, Canada) (Yalcin et al., 2002). Such bubbles were generated by pressurizing (during 1 min) the ore pulp in an air or argon atmosphere at 276 kPa gauge (40 psig), and then releasing the pressure by discharging the pulp into a column where flotation took place. Based on the conclusions of an earlier work, dissolved gas bubbles were employed together with conventional bubbles, the latter being produced by a gas sparger located inside the flotation column.

Yet, practical observations (plant) in column flotation have shown that the very fine bubbles are entrained off to the tailings! This phenomenon might be even worse using microbubbles.

2.1. Recent studies

An extensive work on fines flotation (Cu and Mo sulfides) using DAF with microbubbles in addition to conventional bubbles has been conducted in our laboratory (Table 2) (Project on flotation of fines and ultrafines—Codelco-Chuquicamata-IM2-LTM, Rubio et al., 2003). Here, the injection of the small bubbles led to slight general improvements in particles recovery

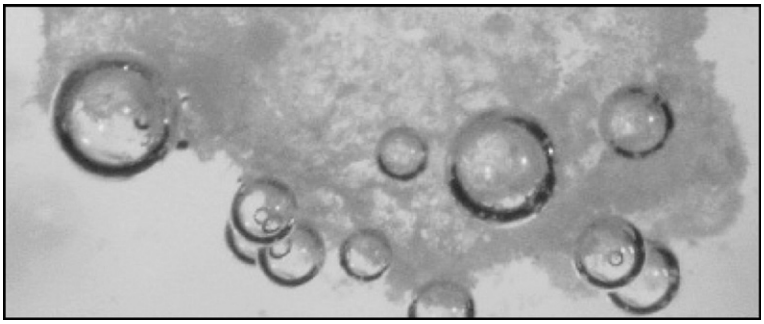

Fig. 6. Aggregate physical entrainment by the rising bubbles.

Table 2
Studies of flotation of different minerals, with presence of dissolved gas/microbubbles

Author	Mineral system	Comments
Solari (1980)	Cassiterite	Separation studies showed that cassiterite particles could be selectively recovered from quartz suspensions by DAF. Main factors influencing cassiterite recovery and selectivity were the surface chemical characteristics of both minerals in the presence of the collector (a degree of hydrophobicity was necessary) and operational parameters associated with DAF operation (stirring, solids content, saturation pressure, injection pressure, and lifting power).
Guerra et al. (1986)	Coal	The authors compared the performance of flotation of coal fines with DAF with conventional flotation, floc flotation and oil agglomeration for ultrafine coal.
Yalcin et al., 2002	Fine magnetite flotation	The presence of dissolved gas bubbles in the flotation pulp was found to have an important impact when argon was used as the flotation gas, resulting in substantially higher grades and recoveries in the concentrate. At the same time, mass recoveries by size showed a 20% increase across all sizes when air was used as the flotation gas, and 40% to 100% increase in the case of argon.
Zhou et al. (1994), Zhou et al. (1995)	Flotation of fine silica and zinc sulfide	The generations of fine bubbles in a cavitation tube and in columns have been reported, improving the flotation performance of mineral fines. Flotation of fine silica and zinc sulfide precipitates in a flotation device incorporating hydrodynamic cavitation showed significantly increased flotation kinetics. It is expected that this “bubbling” approach will be utilized for the design of future flotation devices.
Hart and Nicol (2001)	Coal	A simple device, called a cavitation tube generating extremely fine picobubbles, has been proposed to improve coal flotation. The picobubbles are generated from air naturally dissolved in water, by pumping flotation feed already conditioned with reagents through the cavitation tube. No extra air is added. The picobubbles are thought to nucleate on the surfaces of the coal particles and thus act as a secondary collector, enhancing particle attachment to the larger bubbles in the flotation cell.
Yoon (1993)	Coal, gold	Decreasing bubble size would be more effective for flotation rate than increasing gas rate. This would explain the upcoming of many new flotation machines, mostly in the form of columns, having various forms of microbubbles generators.

(2%) and in flotation kinetics, when compared to a standard (STD) (Fig. 7). Results obtained are believed to occur by enhancing the capture of particles by bubbles, one of the main drawbacks in fine ore flotation, see Table 3 (Yoon, 2000; Sivamohan, 1990).

It is believed that by decreasing the bubble size distribution (through the injection of small bubbles), increases the bubble surface flux and the fines capture. It is expected that this “bubbling” approach will be utilized for the design of future flotation devices.

Peng et al. (2005), Dziensiewicz and Pryor (1950), Klassen and Mokrousov (1963), Solari (1980) and Solari and Gochin (1992) have observed that fine bubbles alone were not able to improve mineral particles flotation while Peng et al. (2005), Dziensiewicz and Pryor (1950), Klassen and Mokrousov (1963) and Rubio et al. (2003), showed that a combination of fine and conventional bubbles increased overall flotation recoveries, especially that of fine particles.

Yet, Peng et al. (2005) noticed that a greater amount of water was recovered at the same time but contrary to Fuerstenau (1980) quartz particles were not entrained but were actually floated by the bubbles. Peng et al. (2005) believe that flotation with injection of dissolved air was probably due to the improvement in collision-attachment efficiency of fine quartz particles and fine bubbles rather than entrainment. However and strangely, with pyrochlore particles, Peng et al. (2005) (in the very same work), found a linear relationship between water and particle recoveries with microbubbles and believe that because the ore slimes were very fine, recovery would be due to entrainment only! These fine bubbles would even promote the entrainment phenomenon and might aggravate the problem of fine gangue entrainment due to the increased water recovery. The authors conclude that it is unlikely that microbubbles flotation can find any practical application unless measures can be taken to reduce fine gangue entrainment!

These controversies need further explanations but it is clear that microbubbles are able to capture small mineral particles with advantages over the coarser bubbles (Solari, 1980; Solari and Gochin, 1992; Rubio et al., 2003). Yet, problems of gangue entrainment, water recovery, fines valuable/gangue slimes concentration ratios, bubble coalescence and microbubbles entrainment to tailings certainly need further investigation.

3. Environmental applications of the flotation with microbubbles

Advantages of the DAF process are the high volume of the effluents being treated (100–20,000 m^3 h^{-1}), smaller footprint, yields excellent treated water quality, generates thicker sludge, rapid start up and operation

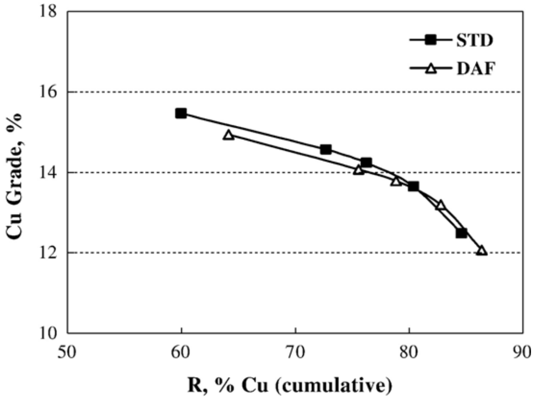

Fig. 7. Grade-recovery curves for Standard (STD) and with injection of microbubbles generated by depressurization of an air saturated water at 4 atm (as in DAF) (Proyecto Flotación de finos y ultrafinos-Codelco-Chuquicamata-IM2, 2002).

reliability (Feris et al., 2001; Rubio, 1998, 2003; Rubio et al., 2002a,b; Ross et al., 2003; Capponi et al., 2006).

The high development in the area and the new up-coming applications outside the Scandinavian countries, where this technology is commonly employed, resulted in the organization of more specific conferences and congresses. In parallel two strategic workshops took place in the last 5 years where the idea was to stress the exchange of flotation experience in mineral flotation and in water and effluent treatment. Yet, more and more events of such a nature appear to be required whereby a cross fertilization of flotation experience in mineral flotation and in wastewater treatment should lead to new and improved procedures in the mineral and metallurgical industry, the chemical and petroleum industries and domestic wastewater treatment. All these aim to an efficient reuse or recycling of water resources and wastewater.

Dissolved air flotation (DAF) has gained widespread usage for the removal of contaminants and the recovery of by-products from wastewater and other industrial process streams over the last 20 years. While considered a relatively simple technology, there have been significant improvements in the technology including operating parameters, bubble generation systems, and process design. There has also been an expansion of applications using DAF over the last several years in traditional and non-traditional areas of water and industrial effluent treatment (Capponi et al., 2006).

Mavros and Matis (1992), Matis (1995), Rubio (1998), Voronin and Dibrov (1999), Parekh and Miller (1999), Miller et al. (1988), Matis and Lazaridis (2002), Rubio et al. (2002a,b, 2003) and Costa and Rubio (2005), have reviewed the great potential of the use of flotation in environmental applications presenting novel separation concepts and emerging (unconventional) flotation devices.

More, many articles (Bahr, 1985; Harbort et al., 1994; Finch, 1995; Finch and Hardie, 1999; Feris et al., 2001; Rubio et al., 2002a,b; Rosa and Rubio, 2005; Capponi et al., 2006) reviewed fundamentals, techniques and general features of flotation (usually preceded by flocculation) for environmental applications, namely, flocculation–flotation, (FF process) induced air flotation, dissolved air flotation, nozzle flotation, column flotation, centrifugal flotation and Jet flotation (Jameson type cell, Jameson, 1988).

Due to the efficient reagents and separation schemes now available, flocculation and rapid flotation have great potential as unitary or ancillary processes in many areas (Voronin and Dibrov, 1999; Finch and Hardie, 1999; Rubio et al., 2001, 2002a,b, 2003; Capponi et al., 2006).

According to Haarhoff and Edzwald (2001), Kiuru (2001), Rubio et al. (2002a,b, 2003) and Capponi et al.,

Table 3
Flotation separation (bench) parameters of a copper sulfide ore

Time, min	STD			With injection of microbubbles (DAF)		
	Grade Cu, cumulative (%)	Cu recovery (%)	Water recovery (%)	Grade Cu, cumulative (%)	Cu recovery (%)	Water recovery (%)
1	15.5	60.0	5.7	14.9	64.2	6.7
2	14.6	72.7	8.4	14.1	75.6	9.7
3	14.2	76.2	9.4	13.8	78.8	11.0
5	13.6	80.4	11.6	13.2	82.8	13.5
9	12.5	84.6	16.8	12.1	86.4	19.2
Tailings	0.17	15.4	83.2	0.16	13.6	80.8

True flotation (%)	Cu entrainment	Rate constant, K (min^{-1})	True flotation (%)	Cu entrainment	Rate constant, K (min^{-1})
63.3	1.3	3.1	66.5	1.1	3.5

Comparison between Standard (STD) test and with injection of microbubbles (DAF). Microbubbles generated by depressurization of an air saturated water (4 atm) (Proyecto Flotación de finos y ultrafinos-Codelco-Chuquicamata-IM2, 2002).

2006, the big trend is to decrease flocculation times and to increase DAF loadings, developing compact (small "foot-print" areas) and efficient treatment units. Small aggregates can be easily removed at high DAF (modern design) rates, contradicting the conventional bias that large flocs units and bubbles are needed for successful separation.

In Brazil we find the most notable unconventional applications found namely, the treatment by flotation of sea polluted water to feed "sea pools" in beaches, treatment of contaminated parks lagoons and, even rivers waters! (Bio, 2002; Oliveira, 2004; Carissimi and Rubio, 2005a). DAF units removing mostly algae, solids and humic acids may reach up to 25,000 m^3 h^{-1} (Tessele et al., 2005).

Main conclusions of all these activities are that future technologies have to treat wastewater from mining and many other industries efficiently, not only to meet legislation standards but also to recycle or reuse water, considered a finite, vulnerable and costly (in the near future) resource.

3.1. Environmental DAF industrial applications

Environmental DAF industrial applications in mining and metallurgy are scarce but growing (Rubio et al., 2002a,b, 2003) and it is believed that this growth will be higher as a result of the combination of DAF (conventional or not) and flotation in upcoming high throughput devices (>40 m^3 m^{-2} h^{-1}) (Owen et al., 1999; Carissimi and Rubio, 2005a,b; Rosa and Rubio, 2005).

3.1.1. DAF applied to remove pollutants from filtration liquors

A DAF process to remove solids, metal ions, sulfide and molybdate anions from Cu–Mo concentrate "filtrates" is successful being employed in Chile since 2000 (Fig. 8). Reagents used are ferric chloride and sodium oleate, which is prepared in the same plant. The interesting feature is that the plant (Fig. 9) removes, in the first stage, sulfide and some molybdate anions, most of the suspended solids and Ca and Cu, (among others) ions, as insoluble metal-oleate (this would be a sort of a "rougher" stage). Then, the rest of the Mo ions in a "cleaner" stage at pH about 5 using colloidal $Fe(OH)_3$ precipitates (from iron chloride hydrolysis) as carrier (adsorbing colloid). Sodium oleate also enhances particle hydrophobicity and process kinetics.

3.1.2. DAF applied in AMD treatment

AMD-acid mining drainage from coal mines using neutralization and solid/liquid separation by DAF are now in progress in the USA (Ross et al., 2003) and Brazil (Menezes et al., 2004). AMD is a significant problem for coal and metal sulfides mining regions. Natural drainage or subterranean flows pass through surface and deep mine coal mining activities and are contaminated with metals ions and low pH. These flows eventually migrate into streams and rivers and negatively impact the quality of these bodies of water. The mining industry is required to mitigate these contaminants usually through the addition of lime in large sedimentation ponds. In many cases, this technology either does not work well, neither the systems are not optimized.

In 1999, in the USA (Ross et al., 2003) a DAF system was integrated to an AMD treatment system to provide an adequate stream prior to discharge to a local stream. The unit was preceded by a flash mix tank for pH control followed by a floc mix tank for polymer flocculation. This system has been in operation for over these years and has kept the site's owners in compliance with state regulations for their discharge. Thus, concentrations of iron, manganese, and aluminum were reduced by 87–89% by DAF and the discharged pH was raised from a pH of approximately 3 to a pH of 7–9, which was well within permit limits.

In South Brazil, at Carbonífera Metropolitana, the very same treatment was applied to an AMD generated from a coal stockpile successfully (Menezes et al., 2004). The only difference was the initial pH and that sodium oleate was employed instead of the polymer flocculants (see Table 4–conventional DAF). Thus, this "fresh" AMD, formed because of the water rain passing through the stockpile, is neutralized with lime and the resulting precipitates are hydrophobized with sodium

Fig. 8. Dissolved air flotation unit treating sulfides concentrates filtration water. The iron hydroxide is the adsorbing carrier for most of the ions (heavy metals and anions, sulfides and molybdates) in Chile (Rubio et al., 2002a,b).

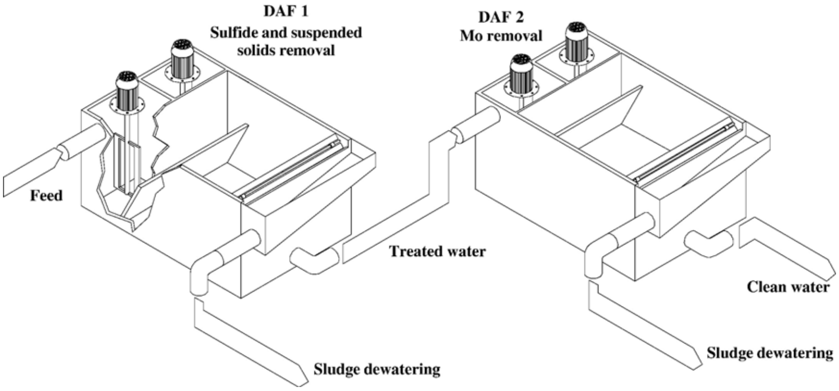

Fig. 9. Staged removal of solids and ions by dissolved air flotation. Filtration waters from sulfides concentrates in Chile (Rubio et al., 2002a,b).

oleate before flotation with microbubbles. When the solids content rises (acidic AMD) the recycling ratio has to increase over 40%; this "lifting power" problem appears to be the main drawback of this microbubbles flotation process.

3.1.3. Optimization of the coal AMD treatment unit

A new device, the Flocs Generator Reactor (FGR) has been used as an ancillary process before flotation and a new design DAF tank cell-column-like cell was employed. The FGR is a compact system whereby the flocculation of particles is assisted by the kinetic energy transfer from the hydraulic flow through a helical reactor (Carissimi and Rubio, 2005b).

The DAF unit was called FADAT or high throughput (loading capacity) flotation unit has incorporated inclined lamellae in the collection zone to enhance the aggregates floating "bed" stability and fluidization (Fig. 10). In the flotation tank (bottom), where the treated AMD abandons the cell a specially designed porous tube was introduced to allow the treated water to flow in a laminar hydrodynamic regime (higher flow rate).

Accordingly, a 2 m^3 h^{-1} FGR-FADAT unit was installed (Fig. 11) to treat the same AMD and results were compared to the conventional DAF unit in the same plant. The process included heavy metals precipitation (pH 9); aggregates formation in the FGR and separation by dissolved air flotation (DAF-FADAT). Comparative results showed that, FGR followed by flotation in the FADAT cell, had a much higher rate of loading capacity compared to the conventional DAF, for a similar residual turbidity (Table 4 and Figs. 12 and 13).

Table 4
FGR-FADAT applied to the treatment of an AMD from a coal mining (South Brazil)

	FGR-FADAT	Conventional DAF
Flow rate, m^3 h^{-1}	2	5
Throughput (hydraulic loading), m^3 m^{-2} h^{-1}	14	8
[Sodium oleate], g m^{-3}	18	23
Residual turbidity, NTU	8.5	8.0
pH	8.5–10.0	8.5–10.0

3.1.4. Manganese and sulfate ions removal by precipitation–DAF

In an AMD from a gold bearing sulfides ore, the treatment included two alternatives: the first with removal of the heavy metal (Mn included) ions exclusively and a second alternative to separate metal ions and the sulfate ions together. The latter is conducted following a novel process based on a chemical precipitation which entails the addition of lime to precipitate the metal hydroxides, and the subsequent formation (precipitation) of calcium sulphoaluminate or ettringite (Cadorin, 2006).

The removal of most metal ions (not the sulfate ions) is readily performed after precipitation of iron (>pH 3), copper, zinc, lead, nickel, chromium and Mn. The removal efficiency of Mn (included process kinetics) is highly dependent on pH or formation of the Mn $(OH)_2$ species (Figs. 14 and 15). Then, the removal of Mn begins at pH 6.5 (Fig. 14), when Mn $(OH)_2$ species begins to form (Fig. 14).

Regarding the "extra" removal of sulfate ions, the key of this new technique, developed in our laboratory (Cadorin, 2006) lies in the correct use and recycling of PAC (polyaluminum chloride) and derivatives (sodium aluminates) used to precipitate the ettringite. The water produced by this process is suitable for reuse in water-courses or for agricultural, domestic (but not drinking water) or industrial consumption and the ettringite should be recycled and used in the cement industry. No brines are produced as the salts are converted to solid hydroxides,

Fig. 10. The FADAT, high loading capacity flotation cell endowed with inclined lamellae and water drainage porous tube at the bottom. Figure at the right, is for the FADA in operation.

gypsum and calcium carbonate. The floated product bearing lime and PAC might be dissolved in acid and used back as normal coagulants or recycled as ettringite. Results obtained indicate that AMD treated water can be produced (containing less than 200 mg/L sulfate and no heavy metals) as long as the monovalent ions (Na^+, Cl^-, etc.) are within limits. It is believed that this precipitation technique coupled with rapid flotation have a great potential in the treatment of sulfate bearing AMD and water reuse.

4. Miscellaneous and the future

- DAF applied to water reuse from mining vehicles washing wastewaters is currently being performed in Brazil (CVRD, 2003). When oil or another organic

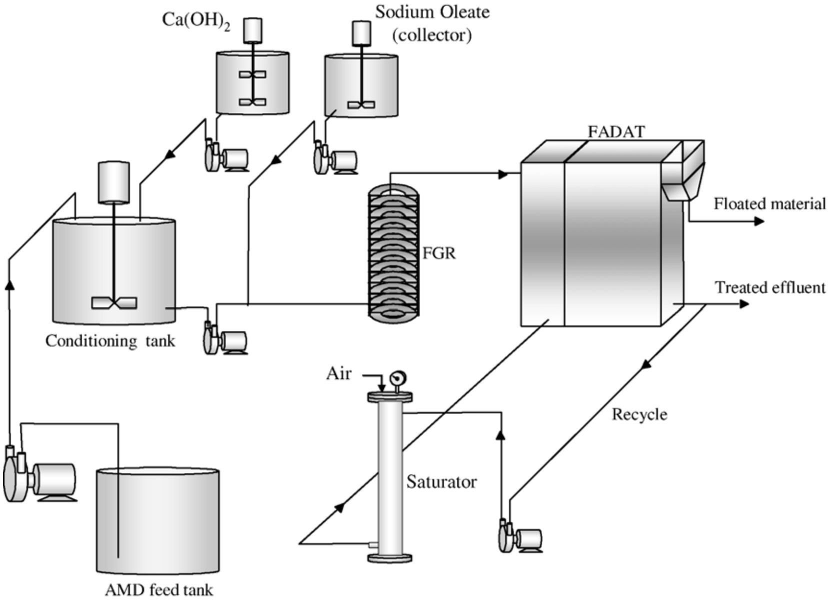

Fig. 11. FGR–FADAT flowsheet applied to the treatment of an AMD from a coal mining (South Brazil).

Fig. 12. Floated product in a FGR–FADAT pilot unit treating an Acid Mine Drainage (AMD) from a coal mining.

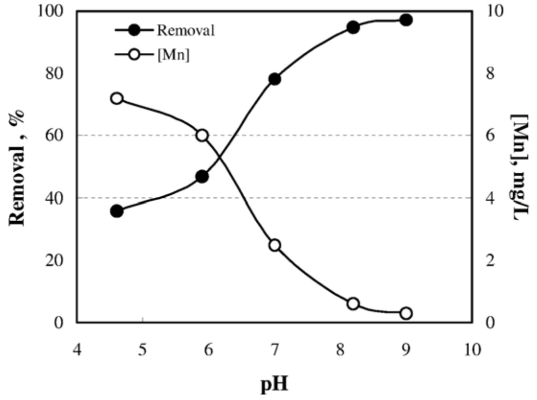

Fig. 14. Removal of Mn ions as a function of medium pH by precipitation and DAF (4 atm, saturation pressure).

fluid is discharged, the oil/water separation becomes difficult especially when the oil is emulsified and worse when the mean droplet size is small or if the emulsions are chemically stabilized (Rubio et al., 2003; Carissimi and Rubio, 2005a; Rodrigues, 1999). The separation of solids, oil in water (emulsified or not) by dissolved air flotation has been employed as an alternative to gravity separation as a process to improve the quality of the discarded effluent in truck washing systems, locomotive and equipment and parts cleaning (with water) in Brazil at Companhia do Vale do Rio Doce (CVRD, 2003).

- Water reuse or recycling. Water resource is getting expensive and scarce, especially in mining areas and for this reason the reuse or recycle (as process water) is important and sometimes fundamental. The potential of the so-called primary treatment is high in water reuse or recycling and DAF is considered as one of the most powerful tools to remove light and difficult-to-treat colloidal suspensions, precipitates or fine (haze) dispersions (oily or not). Thus, in any new plant addressed to water reuse, DAF process should be included in the plant design, especially those working at high hydraulic loadings. Yet, and because of the high volume of water and wastewater to treat, future DAF installations will have to change the design, incorporating new elements to enhance the hydraulic loadings. Rapid DAF is being claimed by modifying the cell design (taller tanks) and by placing lamellae inside the separation tank (Kiuru, 2001; Carissimi and Rubio, 2005b).
- Because of the need for new technologies to solve the problem of treating loaded and huge effluent streams, it is believed that a feasible solution is the use of "rapid", high throughput flotation units, based on a wide bubble size distribution and formation of "aerated" (entrapped

Fig. 13. Treated water in a FGR–FADAT pilot unit. Same AMD as in Fig. 12.

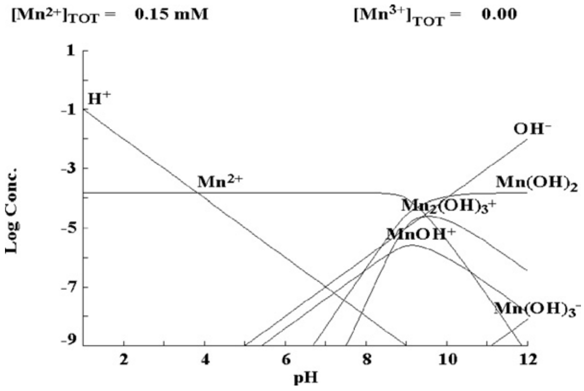

Fig. 15. Species diagram for Mn 0.15 mM concentration as a function of medium pH.

or entrained bubbles) flocs (Rubio et al., 2002a,b, 2003; Parekh and Miller, 1999).

Advances in the design, development and applications of innovative flocculation and flotation devices for successful solid–liquid separation processes have recently been reported (Feris et al., 2001; Carissimi and Rubio, 2005a,b; Rosa and Rubio, 2005; Owen et al., 1999; Capponi et al., 2006). “Rapid” flotation is attained by widening the bubble size distribution with mid-sized or coarse bubbles, well known in ore flotation but not in water and wastewater treatment. This approach would solve an old problem found in DAF, namely the low lifting power of the microbubbles which limits the process to only about 1–3% solids. Yet, another problem that may arise with bigger bubbles is that floc and coagula may not withstand shear and may not be separated in flotation devices operating with high turbulence (centrifugal, jet). Here, DAF with microbubbles is more amenable for the separation of coagula or precipitates.

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