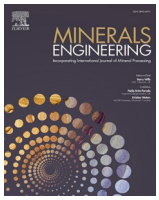
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Stibnite froth flotation: A critical review

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ABSTRACT

Antimony has a long and diverse history of applications, and concerns about its future supply have emerged in recent years. Stibnite-bearing ores continue to be the main source of this critical element, although its sourcing from secondary resources (e.g. mine tailings) is becoming increasingly relevant yet technically challenging. In this sense, froth flotation plays a key role in the recovery of stibnite from both sources. In view of this, a comprehensive review of technical and environmental aspects related to the flotation of stibnite across scales (microflotation, bench-scale and industrial-scale) has been carried out. One of the major topics reviewed is stibnite flotation reagents; while the overall practice has been mostly conservative, relying on the use of xanthate collectors and lead nitrate as an activator, less common (bio)reagents for the flotation of stibnite ores of varying complexity have been shown to be a promising alternative. Other challenges identified from the literature are discussed, highlighting areas of opportunities for further research to enhance stibnite flotation, minimise antimony losses throughout the mine life cycle and thus make antimony more available for future generations.

1. Introduction

Antimony (Sb) has a long and diverse history of applications, from a marginal use in cosmetics, pigments and pharmacology in ancient times to a drastic increase in its demand over the 20th century, especially for the fabrication of military artefacts and munitions during war periods, and as the main compound in lead-acid batteries for mass production in the automotive industry. More recently, antimony has been increasingly employed in the fabrication of flame retardants (heavy textiles, plastics, rubber, paints, etc.) and also as a catalyst for polyethylene terephthalate (PET) production and as a lead alloy component, among several other applications (Anderson, 2019, 2001; European Commission, 2017a; Schwarz-Schampera, 2014).

As environmental and supply risk concerns have increased compared to much earlier decades, there has also been a growing interest in the supply of antimony from secondary sources, including used lead-acid batteries (Anderson, 2019, 2001; Schwarz-Schampera, 2014; USGS, 2020a) and residues generated during the processing and refining of economically valuable metals such as copper, lead and gold (Anderson, 2019, 2001; Schwarz-Schampera, 2014).

A number of factors, however, might affect the supply of this valuable resource for future generations. These include geopolitical, economic, social, environmental, and technological aspects, such as:

- China continues to be the major supplier of antimony worldwide, and current production is still limited to a few countries (Anderson, 2019; European Commission, 2017b, 2014, 2010; USGS, 2020a). More than 60–70% of the antimony production is supplied by China, although there are some other countries (e.g. Bolivia, Russia, Australia, Serbia, Slovakia, Bulgaria, Greenland, Turkey, Thailand, Kyrgyzstan, South Africa, Tajikistan) which might be relevant exporters of antimony (e.g. ore concentrate, refined metal) in the future, based on their estimated reserves (Anderson, 2019; European Commission, 2017a; Grund et al., 2011; Lauri, 2018; Schwarz-Schampera, 2014; USGS, 2020a);
- The recycling rates of this metal are still low (below 30%) and mainly restricted to used lead-acid batteries (European Commission, 2017a; Grund et al., 2011; Sundqvist Ökvist et al., 2018; USGS, 2020a), whose availability could decrease over time due to the use of alternative technologies;
- The substitution of antimony trioxide for its main application in flame retardants might be challenging when high performance is required (European Commission, 2017a, 2010; Schwarz-Schampera, 2014), although some estimates suggest that this measure could be feasible in the medium term (Henckens et al., 2016); and
- Antimony is becoming more relevant for emerging applications including micro-capacitors (European Commission, 2010; Sinding-Larsen and Wellmer, 2012), the semiconductor industry (Multani

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et al., 2016; Schwarz-Schampera, 2014), emerging thin film photovoltaic cells (Kondrotas et al., 2018; Nair et al., 2018; Yang et al., 2019), and as an anode material for sodium-ion storage batteries (Li et al., 2019); this may give a potential rise to its demand in the future.

The vulnerability of Europe, in particular, to the antimony supply risks has influenced the European Commission to seriously consider this matter. In that sense, the European Commission has carried out a series of assessments (European Commission, 2020, 2017b, 2014, 2010) where a selected group of raw materials has been considered as "critical", and antimony has persistently been positioned on the criticality list so far.

Antimony is considered to be found in the Earth's crust at an abundance of approximately 0.2 ppm (Anderson, 2001; Schwarz-Schampera, 2014), requiring an enrichment of about 150000 times its crustal content to achieve a concentration that can be considered as potentially economic (about 3% antimony by weight) (Schwarz-Schampera, 2014). Although this metalloid has been found in more than two hundred antimony-bearing mineral phases (Multani et al., 2016; Schwarz-Schampera, 2014), its sourcing from mining activities has been largely from stibnite or antimonite (Sb_2S_3) (Anderson, 2019, 2001; European Commission, 2017a; Lager and Forssberg, 1989a; Morizot and Ollivier, 1993; Richards, 1977; Schwarz-Schampera, 2014). Some of the major stibnite-bearing deposits known are the Xikuangshan deposit in Hunan, China, and the Antimony Line, Murchison Belt in South Africa (Schwarz-Schampera, 2014).

Stibnite frequently occurs in greenstone-hosted deposits comprising quartz-carbonate veins and carbonate replacements (1.5–25% Sb_2S_3; lacking significant base or precious metals). It also occurs, in minor proportion, in epithermal gold-antimony veins (0.1–3.5% Sb_2S_3; low-sulfidation subtype enriched in As, Hg, Au, Ag, Te), reduced-magmatic systems (approximately 0.1–1.5% Sb_2S_3; associated to metals such as Au, Bi, Te, W, As, Ag, Pb, Zn), polymetallic base metal veins (0.1–0.5% Sb_2S_3; enriched in Ag), and hot springs (0.1–0.2% Sb_2S_3; co-enrichment with As and Hg; might occur along with Te, Se, Au, Ag) (European Commission, 2017a; Schwarz-Schampera, 2014). When stibnite has been exposed to the surface it is usually weathered to oxides including bindheimite, kermesite, stibiconite and valentinite. For a comprehensive description of antimony-bearing deposits, the reader is referred to Schwarz-Schampera (2014).

The exploitation and processing of stibnite-bearing ores involve the use of conventional stages of mining (open-pit or underground), comminution (crushing and grinding) and concentration techniques including gravity separation and froth flotation (Anderson, 2019, 2012; European Commission, 2017a; Schwarz-Schampera, 2014). This allows an antimony-enriched concentrate to be obtained, the recovery of which will depend on the efficiency along the mining and processing chain. Considerable research efforts have been devoted in recent years to cover mineralogical and mineral processing aspects of antimony ores, with a greater emphasis on hydro- and pyrometallurgical processing of antimony concentrates (Anderson, 2019; Grund et al., 2011; Rohner and Millard, 2016; Schwarz-Schampera, 2014; Solozhenkin and Alekseev, 2010a; Yang et al., 2018), and to a lesser extent on stibnite froth flotation.

While relevant yet outdated reviews on stibnite froth flotation were carried out in the 1970s and 1980s, there has been no attempt in the literature to provide a critical review on progress over the last three decades. Richards' pioneering work in the 1970s (Richards, 1977), for example, combined a general overview of previous literature (i.e. patents, journal articles, reports, etc.) related to stibnite froth flotation with experimental work at laboratory-scale to establish optimal conditions for obtaining a stibnite concentrate from an ore deposit in New Zealand. Just over a decade later, Lager and Forssberg (1989a, 1989b) carried out an extensive analysis of published studies (including Richards' work (Richards, 1977)) concerning the flotation of stibnite and other antimony minerals. The authors summarised relevant findings regarding the effect of key process variables (e.g. pulp pH, collector type) and approached a selected number of case studies in mine locations around the world.

Other work for specific locations includes, for instance, a study of physicochemical and technical aspects related to the flotation of complex antimony ore deposits in Russia (Solozhenkin and Alekseev, 2010b; Solozhenkin and Kovalev, 2018); a discussion on flotation techniques employed at the Consolidated Murchison mine in South Africa (Grund et al., 2011; Davis et al., 1986); and the description of technological aspects of froth flotation for a stibnite ore from Xikuangshan and some other locations in China (Hu, 1988; Anderson 2012).

On the basis of the aforementioned considerations and to the best of the authors' knowledge, a comprehensive and updated assessment focusing on key aspects of the froth flotation of stibnite ores is still lacking in the literature. This is particularly relevant considering the increasing concerns in the supply of antimony from primary sources in the medium- and long-term. The present work aims to fill this gap by exhaustively revising the literature regarding the technological and environmental aspects related to froth flotation of stibnite-bearing ores. These include: surface chemistry and flotation reagents (Section 2), particle and mineralogical effects (Section 3), flowsheet design (Section 4), and topics related to antimony speciation in the environment, as well as a broader utilisation of antimony resources via froth flotation (Section 5). Finally, some concluding remarks are highlighted in Section 6. Through this approach, the authors aim to contribute to the dissemination of best practices towards a more sustainable supply of antimony (ore concentrate) from primary, and potentially secondary sources.

2. Surface chemistry and reagents in stibnite froth flotation

The first part of this section (Subsection 2.1) is concerned with a brief review of selected studies that have aimed to deepen the fundamental understanding of the interactions between the aqueous medium (i.e. water and flotation reagents/bioreagents) and the stibnite surface and how these affect the floatability of stibnite and its selectivity with respect to certain gangue minerals. Such studies have been carried out at the microscale, usually relying on a few grams of medium-to-high-purity, carefully prepared ore sample. In subsequent sections (Subsections 2.2 to 2.6, Sections 3 and 4) the review is mainly focused on discussing the research progress in stibnite froth flotation at both bench- and industrial-scale.

2.1. Floatability, electrokinetic behaviour and surface properties of stibnite at the microscale

According to Kelebek (1984), the study carried out by Derjaguin and Shukakidse (1961) was the first to report the remarkable effect of pH on the floatability and electrokinetic (zeta) potential of stibnite. A few years later, Arbiter et al. (1964) extended the scope of Derjaguin and Shukakidse's work to other "hydrophobic" minerals in addition to stibnite and complemented the microflotation and electrokinetic measurements with the estimation of the contact angle at various pH values. Unlike the previous study, Arbiter et al. (1964) did not use a frother in the microflotation tests, which certainly led to a much lower stibnite recovery over the entire pH range (Figure 1); however, the purity of their samples was not reported. On the other hand, Popov et al. (1987) showed a relatively good natural floatability of nearly pure stibnite at a pH less than 6.5 (Figure 1).

Several other authors have also studied the floatability behaviour of stibnite as a function of pH at the microscale by introducing a series of variations in their tests: ore type (Derjaguin and Shukakidse, 1961), addition of reagents (frother, collector, activator, depressant) (Kaigua and Dianzua, 1985; Popov et al., 1987; Richards, 1977), or flotation time (Laskowski, 1986). What has become evident from all these results (Figure 1) is that:

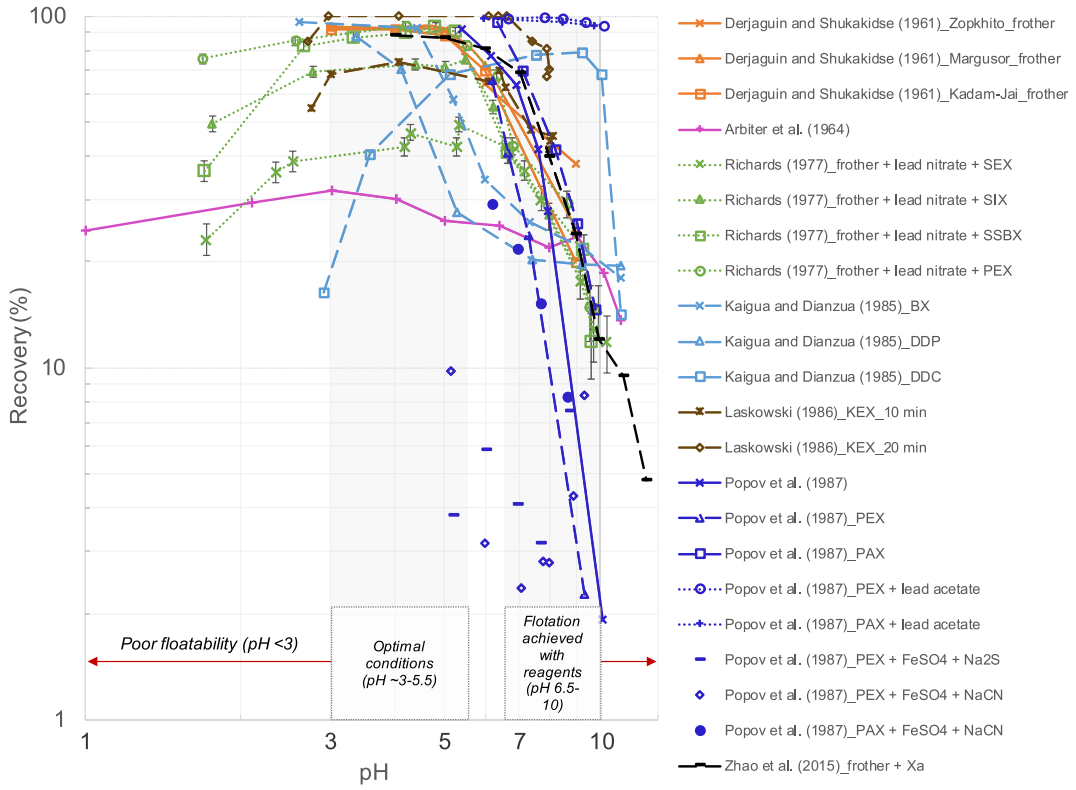


Fig. 1. Recovery of antimony (Richards, 1977) or stibnite (other authors) as a function of pH and a range of experimental conditions in microflotation studies.

- Extremely acidic or alkaline pH ranges (<3 or >10, respectively) are not favourable for the recovery of stibnite;
- An acidic pH (~3–5.5) seems the most favourable for the floatability of stibnite, especially with conventional reagents (e.g. xanthate collector, lead nitrate as an activator);
- It is possible to extend the floatability range of stibnite at slightly alkaline values (<10) with the use of certain reagents (lead acetate as an activator, diethyl dithiocarbamate as collector);
- It is also possible to inhibit the floatability of stibnite in a slightly acidic to slightly alkaline pH range (~6–9) with the use of some depressants ($FeSO_4$ in combination with Na_2S or NaCN).

On the other hand, Arbiter et al. (1964) explained the zeta potential and contact angle behaviour of stibnite at different pH values on the basis of the crystal structure of stibnite. It was, in fact, presumed that the existence of weak Sb-S bonds may lead to the development of ionic sites in the stibnite surface at alkaline pH (formation of SbO^- and S^- sites depending on the pH). The reversible proportion of these ionic sites could have explained the decrease in the contact angle of stibnite as pH was increased (Arbiter et al., 1964), as observed in Figure 2a. Overall, most of the contact angle measurements reported by different authors showed a similar trend; that is, contact angle remains relatively stable within a range between 30° and 44° at acidic pH (1< pH <7), while it tends to decrease as pH turns alkaline (Figure 2a). Moreover, the addition of collector and activator sharply increased the contact angle of stibnite (up to approximately 86°) and enhanced its floatability at a pH range from slightly acidic to alkaline (6< pH <11), on the basis of the work conducted by Vijayakumar and Majumdar (1972) *apud* Lager and Forssberg (1989a) (Figure 2a).

Nevertheless, there was some variability in the data reported (Figure 2a) that can be explained by the variation in materials and experimental procedures. In fact, the adoption of different methods for sample preparation clearly influenced the contact angle measurements in the results reported by Kelebek (1984), as observed in Figure 2a. Starting from the point that there is no contamination in the liquid or on

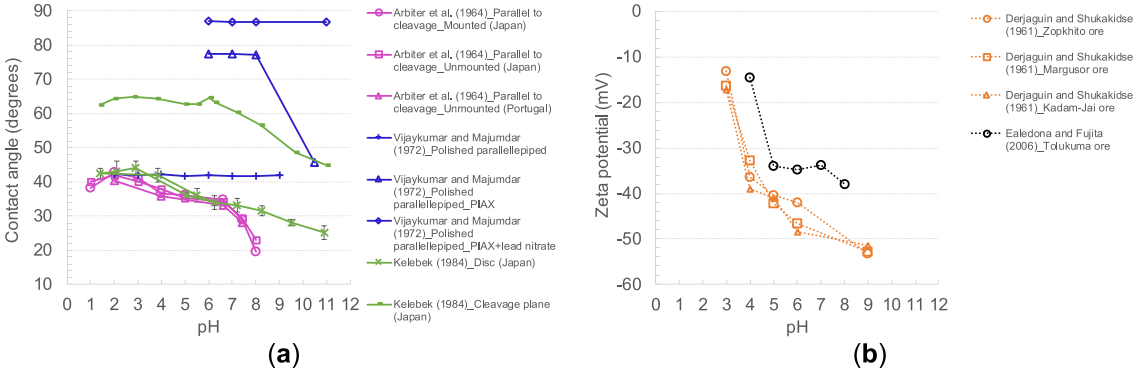


Fig. 2. (a) Contact angle and (b) electrokinetic (zeta) potential of stibnite as a function of pH.

the solid surface, physical and chemical aspects of the surface such as surface roughness (Arbiter et al., 1964; Chau et al., 2009; Ozcan, 1992), surface heterogeneity and surface geometry (Chau et al., 2009; Ozcan, 1992) have been highlighted as determining factors in the estimation of contact angles. Zeta potential measurements of stibnite (Figure 2b) have, on the other hand, indicated that its surface is negatively charged within a wide pH range, allowing positive ions in solution to be attracted to the surface (Ealedona and Fujita, 2006).

A detailed analysis of the Pourbaix diagram allows gathering insights into the predominance of antimony compounds on aqueous media as a function of potential (Eh) and pH. As observed in Figure 3, the ionic species $SbO_3^-{}_{(aq)}$ predominates over a wide Eh and pH range, particularly in more oxidising conditions. On the contrary, stibnite is more stable at reducing conditions and in an acidic to slightly alkaline pH. It is also clear that, at an alkaline (pH > 8) and reducing environment, stibnite dissolves and is transformed into the ionic species $Sb_2S_4^{2-}{}_{(aq)}$ (Vink, 1996). These observations indicate stibnite amenability to float more effectively at acidic pH, with its floatability diminishing at alkaline pH, as will be discussed in Section 2.5. This diagram (Figure 3) is, however, not considering the effect of flotation reagent addition.

While the Pourbaix diagram will vary depending on the thermodynamic data available, the assumptions made regarding the activity of the species, and the number of species considered, it provides useful information on the occurrence of species at either oxidising or reducing environments over the entire pH range. Notably, to the best of the authors' knowledge, there are no reported studies in the literature on the use of Pourbaix diagrams to support the interpretation of Eh and pH measurements for stibnite flotation. However, Eh-pH diagrams have been published for a wide range of species that typically are of interest in the context of stibnite flotation (e.g. the As-O-H-S-Fe system, as shown by Lu and Zhu (2011) and Vink (1996)).

Cao et al. (2018a) evaluated the effect of lead nitrate addition on the conditioning of stibnite at a pH of 6.5 and found that more than 89% of

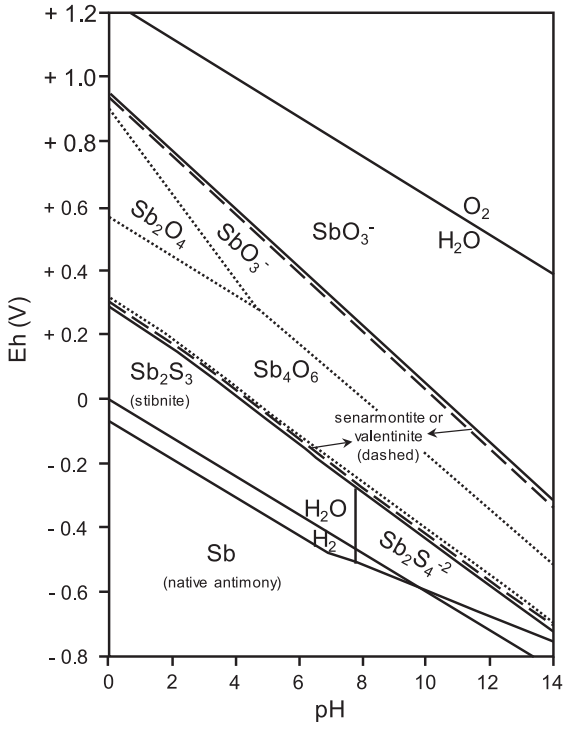


Fig. 3. Pourbaix diagram for the system Sb-O-H-S. Activities of $\sum Sb = 10^{-6}$ *m* and of $\sum S = 10^{-3}$ *m*. The dashed lines show the stability field of the polymorph valentinite. The dotted lines show the diagram, if $\Delta G^{\circ}_{298}(Sb_4O_6)$ as −320.0 kcal/g. Adapted from Vink (1996).

the lead added was adsorbed on the stibnite surface, mainly as Pb^{2+} ions. Interestingly, their results showed an intermediate dosage of activator for which the adsorption of lead was optimal (99.8% of Pb adsorbed on stibnite for an activator dosage of 5×10^{-5} mol/L). Additionally, they reported a slight increase of Sb in solution (up to 3.42×10^{-5} mol/L of Sb) as the activator dosage was increased, in relation to the initial concentration of Sb in deionised water (1.77×10^{-5} mol/L of Sb). This was believed to occur, according to the authors, due to the substitution of Sb ions by Pb ions on the stibnite surface. Furthermore, Cao et al. (2018b) showed that both copper sulphate and lead nitrate can modify the zeta potential of stibnite in deionized water at a pH of 6.5 (from −22.1 mV to nearly 0 mV), as the concentration of any of these reagents is increased (from 0 to 1×10^{-4} mol/L). The adsorption of Pb^{2+} or Cu^{2+}on the negatively charged stibnite surface was attributed as the reason for the increase in zeta potential of stibnite. The authors, however, did not carry out zeta potential measurements at higher activator dosages. Such a study would have been interesting in the context of stibnite stability (Figure 3) with metal ions (Pb^{2+} or Cu^{2+}) in solution in a less reducing, activator-induced environment. Furthermore, the effect of the collector-activator system on stibnite flotation could also be examined and supported by zeta potential measurements and Pourbaix diagram interpretation.

Some microflotation studies have also aimed to understand the effect of the reagent dosage on the recovery of stibnite. It has been shown that lead nitrate has a somewhat superior performance compared to copper sulphate in the activation of the stibnite surface, according to the comparative tests carried out by Richards (1977) and Cao et al. (2018b) at acidic pH (5.0 and 6.5, respectively). On the other hand, in the study by Qing and Ai (1988), copper sulphate achieved a good activation performance (slightly higher recovery of stibnite than the one obtained with lead nitrate in the aforementioned studies) in the flotation of a stibnite-bearing ore containing arsenopyrite at natural pH (no pH regulator added) and in combination with an organic depressant. The results of those tests have been summarised in Figure 4a.

The role of collector dosage on the microflotation of stibnite has also received some attention (Cao et al., 2018a; Richards, 1977). It has been demonstrated that short-chain xanthates such as sodium ethyl xanthate require a much higher concentration to achieve the performance obtained with long-chain xanthates at acidic pH. The aforementioned studies also confirmed that the activation of the mineral surface is essential for the adequate recovery of stibnite, at least when xanthate collectors are employed (Figure 4b).

A few researchers have also attempted to elucidate the possible mechanisms responsible for the alteration of the surface properties of stibnite when it comes into contact with reagents. For this purpose, a series of qualitative and quantitative techniques have been used to characterise the products formed at the liquid–solid interface, as well as the compounds in the solution (Table 1). Popov et al. (1987) analysed the infrared spectra of stibnite surface products and concluded that potassium amyl xanthate alone slightly improves the floatability of stibnite at acidic pH due to the formation of antimony xanthate on the mineral surface. On the other hand, they found that potassium ethyl xanthate (PEX) alone did not improve the floatability of this mineral as it was not adsorbed without activator. In the latter case, stibnite recovery in the concentrate was more likely attributed to the natural floatability of the nearly pure stibnite sample (Table 1), rather than to the addition of collector (i.e. PEX). Moreover, the addition of lead acetate allowed the formation of lead xanthate on the stibnite surface, which is responsible for the flotation of stibnite even at alkaline pH (Figure 1). Richards (1977) attributed the chain-length effect of xanthate collector on stibnite flotation performance to increased adsorption of the collector species on the mineral (at the mineral surface-liquid interface), due to lateral interaction between the adsorbed species. Richards also highlighted that the increase in carbon chain length of xanthates may affect the selectivity and, consequently, the antimony grade of the final concentrate in more complex stibnite-bearing ores, although this was

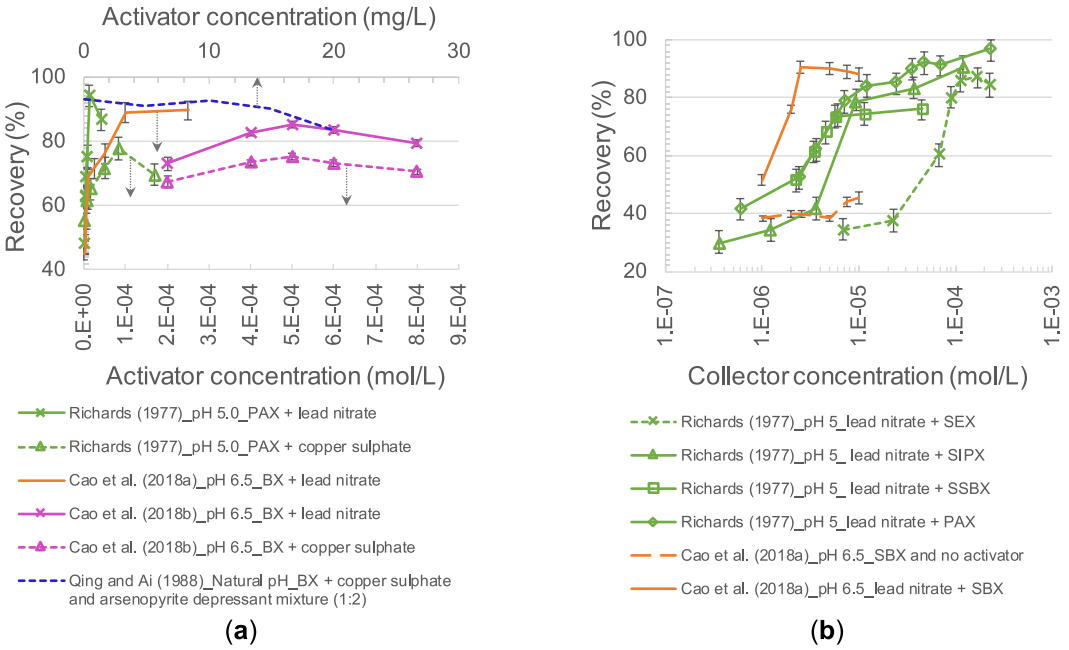


Fig. 4. Effect of reagent concentration on the recovery of antimony (Richards, 1977) or stibnite (other authors) in microflotation studies: (a) Effect of activator concentration; (b) Effect of collector concentration.

not tested in the experiments reported by the author.

Leming et al. (1998), on the other hand, combined microflotation and electrokinetic potential measurements with UV spectrophotometry. Pulp potential measurements on pure mineral samples at pH 9.2 and with the addition of butyl xanthate (5×10^{-4} mol/L) revealed that arsenopyrite floats in the range −200 to 200 mV, while stibnite is heavily depressed below 0 mV due to the reduction of butyl dixanthogen on its surface. Accordingly, the authors concluded that stibnite and arsenopyrite could be, in theory, separated at alkaline pH and in the potential region of −200 to 0 mV. Further microflotation tests carried out with artificial mixtures of both minerals and with a natural stibnite-arsenopyrite bulk concentrate sample confirmed that stibnite and arsenopyrite can be effectively separated at pH 9–10. The separation was achieved by controlling the pulp potential within a negative range (from −150 to −120 mV) and using $Na_2S_2O_4$ as the reducing agent of the hydrophobic compound (butyl dixanthogen) on the stibnite surface. Key experimental details regarding the electrode system (e.g. reference electrode type) were, however, not reported in their study.

More recent studies (Cao et al., 2018a; Zhao et al., 2015) have attempted to explain the surface properties of stibnite on the basis of its crystal structure and with the aid of first-principles calculations supported by Density Functional Theory (DFT). Zhao et al. (2015) postulated that the floatability differences between stibnite and jamesonite at high pH may be related to the coordination structures of Sb atoms and that the presence of metal atoms in the Highest Occupied Molecular Orbital (HOMO) favours the depression of both minerals with lime. Cao et al. (2018a) established that Pb^{2+} is the dominant species that is adsorbed on five possible sites on the stibnite surface and provides a stronger interaction of the xanthate with the activated stibnite surface, in contrast to the adsorption of butyl xanthate at Sb sites on a non-activated surface.

2.2. Frother effect

The most frequently used frothers in stibnite froth flotation according to literature are pine oil (natural oil-type frother, also referred to as 2# oil by Wang (2016)) and a polyglycol-type frother commercially known as DowFroth 250® (usually abbreviated as DF250 or similar). Although less commonly used, other frothers such as methyl isobutyl carbinol (4-Methyl-2-pentanol) or MIBC (alcohol frother) and cresylic acid (phenol-type frother) have also been reported for this application (Table 2). It should be noted that both pine oil and cresylic acid have gradually fallen into disuse in the minerals industry in general, the latter being more environmentally concerning (Khoshdast and Sam, 2011; Fuerstenau et al., 2007). On the other hand, MIBC has become more popular in recent decades despite its potential health risks and strong odour (Fuerstenau et al., 2007). Most of the aforementioned frothers perform well in both acidic and alkaline environments; notably, cresylic acid only has optimal frothing properties in the acidic pH spectrum (Bulatovic, 2007; Khoshdast and Sam, 2011). Frother dosage, in general, has typically been lower relative to that of other flotation reagents, usually ranging from 10 to 100 g/t. In some instances, staged frother addition has been required, with heavier dosage in the rougher stage (Table 2).

It has been reported that pine oil has good frothing properties and tends to form a more stable froth compared to terpene oil and polypropylene glycol (Bhatti et al., 2014). From the exhaustive flotation testwork carried out by Richards (1977) with various frothers (e.g. pine oil, cresylic acid, Aerofroth 65/71/73) at micro- and bench-scale, it was concluded that the best recovery was obtained with pine oil (88.9% of Sb recovery in the concentrate at bench-scale), in the presence of lead nitrate (activator) and a long-chain xanthate collector. Richards (1977) also highlighted that there may be an optimal frother dosage for the flotation of stibnite beyond which detrimental effects for the recovery of stibnite in the concentrate may occur, as the frother might interfere with the function of the collector. It is noteworthy that Richards' work was the only one to address the performance of different stibnite frothers on a systematic basis.

Another study (Wang et al., 1992) contradicted Richards' work, suggesting that collectorless stibnite flotation is a feasible option. Wang et al. (1992) reported that there were notable differences in stibnite recovery when using frothers such as pine oil, MIBC or butyl ether alcohol (stibnite recovery of 74%, 85%, and 94%, respectively). A detailed description of the experimental conditions used by these authors was, however, not disclosed. Most of the evidence obtained from bench- and industrial-scale studies on stibnite flotation reviewed herein

Table 1
Summary of the research techniques used in studies related to the characterisation of the floatability, electrokinetic behaviour and surface properties of stibnite at the microscale, with an emphasis on microflotation tests.

Source	Reported research methods [1]	Microflotation test conditions									
		Cell type/ volume (mL) [2]	Ore sample			Reagents					Max. recovery, % [5]
			Mass, g	Size range, μm	Purity,%	Frother	Collector [3]	Activator	pH Regulator	Depressant	
Derjaguin and Shukakidse (1961)	MF; EP	(70)	–	150 – 43	–	n-hexyl alcohol	–	–	H_2SO_4; NaOH	–	92 – 93 (pH 3, 2 min)
Arbiter et al. (1964)	MF; CA	B	–	150 – 44	–	–	–	–	–	–	31.8 (pH 3, 8 min)
Vijayakumar and Majumdar (1972) *apud* Lager and Forssberg (1989a)	CA	–	–	–	–	–	PIAX	$Pb(NO_3)_2$	–	–	–
Richards (1977)	MF; XRD; MA; AAS; UVS	A (120); D (250)	25 (cyl.)	500 – 50; 150 – 63 (Hall.); 147 – 74 (cyl.)	~28.5 (Sb)	Aerofroth 65/70/ 71/73/77; pine oil; cresylic acid	SEX; SIPX; SSBX; PEX; PAX	$Pb(NO_3)_2$; $CuSO_4$	H_2SO_4, Na_2CO_3	–	~94.4 (pH 5, PAX, Pb $(NO_3)_2$, 5 min)
Kelebek (1984)	CA; AASP	–	–	–	–	–	–	–	–	–	–
Kaigua and Dianzua (1985) *apud* Lager and Forssberg (1989b)	MF	A	–	–	–	–	BX; DDP; DDC	–	–	–	~96 (pH ~ 2.6, BX); ~87 (pH ~ 3.4, DDP); ~79 (pH ~ 9.3, DDC) [6]
Laskowski (1986)	MF	B	–	200 – 75	–	–	PEX	–	H_2SO_4; KOH	–	~74 (pH ~ 4, 10 min); ~100 (pH ~ 3.0 – 6.6, 20 min)
Popov et al. (1987)	MF; IRS	B (100)	1	100 – 75	70.27 (Sb)	–	PEX; PAX	Pb $(C_2H_3O_2)_2$	H_2SO_4; NaOH	$FeSO_4 + Na_2S$; $FeSO_4$ + NaCN	~99.9 (pH ~ 5.2, PAX, Na_2S, 5 min)
Qing and Ai (1988)	MF	–	2	< 75	95.2 (Sb_2S_3)	Pine oil	BX +"SN No. 9"	$CuSO_4$	–	"Organic depressant B"	~90 (natural pH)
Leming et al. (1998)	MF; EP; UVS	–	–	–	35.34; 54.31; 32.89 (Sb) [4]	–	BX	–	NaOH or Na_2CO_3	$Na_2S_2O_4$ (reducing agent)	~97 (pH 9.8, AM); ~88 (pH 9, NBC) [4]
Ealedona and Fujita (2006)	EP	–	–	–	–	–	–	–	–	–	–
Zhao et al. (2015)	MF; DFT	(50)	2	–	96.5 (Sb_2S_3)	Pine oil	Xa	–	NaOH	–	~88 (pH ~ 4, 5 min)
Matveeva et al. (2017)	MF; LSM; UVS	C (20)	1	100–63	48.4 (Sb)	Pine oil	DDC + OPDTC	–	–	Tannin	~68–70
Cao et al. (2018a)	MF; ICP-MS; DFT	C (100)	3	150–104	> 99 (Sb_2S_3); 71.6	Pine oil	BX	$Pb(NO_3)_2$	HCl; NaOH	–	~90 (pH 6.5, 2 min)
Cao et al. (2018b)	MF; EP; XPS; ToF-SIMS	C (40)	2	75–63	(Sb)			$Pb(NO_3)_2$; $CuSO_4$			~85.3 (pH 6.5, Pb $(NO_3)_2$, 1 min)

[1] MF = Microflotation; EP = Electrokinetic (zeta) potential; CA = Contact Angle; XRD = X-ray Powder Diffraction; MA = Microscopy Analysis; LSM = Laser Scanning Microscopy; AAS = Atomic Absorption Spectrometry; ICP-MS = Inductively Coupled Plasma Mass Spectrometry; ToF-SIMS = Time-of-Flight Secondary Ion Mass Spectrometry; AASP = Atomic Absorption Spectrophotometry; UVS = Ultraviolet–visible Spectrophotometry; IRS = Infrared Spectrophotometry; XPS = X-ray Photoelectron Spectroscopy; DFT = First-principles calculations based on Density Functional Theory.

[2] A = Hallimond cell; B = Modified Hallimond cell; C = Mechanical cell; D = Measuring cylinder, used by Richards (1977) in frother tests.

[3] PIAX = Potassium isoamyl xanthate; SEX = Sodium ethyl xanthate; SIPX = Sodium isopropyl xanthate; SSBX = Sodium *sec*-butyl xanthate; PEX = Potassium ethyl xanthate; PAX = Potassium amyl xanthate; BX = Sodium or potassium butyl xanthate; Xa = Unspecified ethyl xanthate; DDP = Dibutyl dithiophosphate; DDC = Diethyl dithiocarbamate; OPDTC = Oxypropyl diethyldithiocarbamate ester.

[4] MF tests carried out on artificial mixtures (AM) of high-purity minerals (stibnite and arsenopyrite) and on a natural stibnite-arsenopyrite bulk concentrate sample (NBC).

[5] The concentrate grade is not consistently reported in most of the studies. Flotation time corresponding to the maximum recovery of stibnite (or antimony) has also been included when available.

[6] Low selectivity of stibnite in relation to arsenopyrite when using BX or DDP and no activation. The best selectivity was achieved with DDC (<15% arsenopyrite in the concentrate).

Table 2
List of frothers reported in stibnite flotation literature. [1]

Source	Frother[2]	Dosage [g/t] [3]	Source	Frother[2]	Dosage [g/t] [3]
Brinker (1935)	Cresylic acid	–	Zhang et al. (2006)	730A	70 (R); 50 (S1); 20–30 (S2)
Engel (1949)	B-23 or cresylic acid	22.7	Ozkan (2007)	DowFroth 250	100
Erspamer and Wells (1956)	"Frother 63"	36.3 (R)	Bhatti et al. (2008)	Polypropylene glycol	50 (R)
	DowFroth 250	36.3 (R); 18 (C; S)	Celep et al. (2010); Güven et al. (2012)	MIBC	20
Wells et al. (1958)	D-250	22.7–81.6	Anderson (2019, 2012)	Pine oil	100
	Pine oil	45.4–59			
	Coal-tar creosote	45.4	Kanarskii et al. (2012)	Pine oil	10
Thom (1962)	Pine oil	22.7–68	Town and Stickney (1964)	DowFroth 250	45.4 (R)
Pierre (1977)	NCP 41G	50 (R)	Abdusalyamova et al. (2013)	Frother T-80	–
Richards (1977)	Pine oil	–	Senchenko et al. (2016)	Frother T-92	54 (R)
Lepetic (1978)	DowFroth 250	50			
Hu (1988)	Pine oil	8–13	Bhatti et al. (2014)	Pine oil	40 (R); 20 (C)
Davis et al. (1986)	Pine oil	–	Chen et al. (2014)	#2 oil (Terpineol or pine oil)	110
	Ethyl/*sec*-butyl dithiophosphate (Aerofloat 208)	50 [4]	Wei et al. (2017)		80–100 (R); 40–50 (S)
			Ai et al. (2018); Xu et al. (2018)		–
Ealedona and Fujita (2006); Lager and Forssberg (1989b)	MIBC	–	Gülcan et al. (2019)	D250	15–100
Krstev et al. (2003)	DOW-250	–	Wu et al. (2019)	No frother added (frothing effect of 5# oil collector)	

[1] Details on antimony grade and recovery in the flotation concentrate can be found in Table 6.
[2] For the purpose of this review, the names of the reagents are reported as indicated in the references.
[3] Capital letters in round brackets indicate the stage of reagent addition when reported: (G) = Grinding; (R) = Roughing or Conditioning; (S) = Scavenging; (C) = Cleaning.
[4] Personal communication.

(Section 2) advocates the use of collector(s) in combination with a metal salt (activator) to obtain a satisfactory stibnite recovery in the concentrate. As a wide variety of frothers has been employed in stibnite flotation (Table 2), the choice of frother does not seem critical in this context, in aspects other than the environmental and health risks that its use might entail. Nonetheless, there is still room for comparative assessments of frothers; for instance, on the basis of the determination of the critical coalescence concentration (CCC).

Davis et al. (1986), on the other hand, pointed out that a dithiophosphate collector (discussed in Section 2.3.) may act as a frother due to its alcohol base, although the occasional addition of small amounts of an alcohol-type frother may still be necessary. Similarly, Wu et al. (2019) reported that the addition of a collector, only referred to as 5# oil, can make the addition of pine oil unnecessary, leading to a reduction in entrainment of some gangue minerals (e.g. those that tend to form slimes such as clays) into the mineralised froth, consequently improving the antimony grade in the concentrate.

2.3. Collector effect

Certain metal sulphides such as stibnite have been reported as naturally floatable or naturally hydrophobic in the presence of air (Popov et al., 1987; Herrera-Urbina et al., 1990; Fuerstenau et al., 2007), or as partially hydrophobic (or partially floatable) on the basis of the critical surface tension of wetting (Ozcan, 1992). However, in practice, the conditions of the surfaces of minerals to be floated (that is, rough, heterogeneous, unclean surfaces in ore particles of varying sizes and shapes) are far from those employed in microscale experiments (Section 2.1), which has an impact on how the results can be extrapolated (Chau et al., 2009). In that sense, it has been a frequent practice to add collectors in order to improve the flotation rate of those minerals (Fuerstenau et al., 2007).

The most common collectors for stibnite flotation have been alkyl xanthates, preferably those of long chain (4 or more carbon atoms). Such collectors allow improved stibnite recovery compared to those whose hydrocarbon chains are shorter, even when the dosage is increased in the latter. This was experimentally demonstrated by Oberbillig (1964) *apud* Lager and Forssberg (1989a) and Richards (1977) at bench and microflotation scale, respectively. These studies may have established a reference for the selection of xanthates in later stibnite flotation studies, where a clear preference is observed towards long chain xanthates (Table 3), such as potassium amyl xanthate, potassium or sodium butyl xanthate, among others. Moreover, there seems to be a consistency in the superior performance of long-chain xanthates over short-chain xanthates for different pH values, at least in terms of antimony grade in the concentrate (Ealedona and Fujita, 2006; Richards, 1977).

Xanthates in general are considered as cost-effective and stable in an alkaline environment and have good solubility in water, although it is necessary to improve their selectivity towards target sulphide minerals by adding regulating agents. Additionally, their decomposition to CS_2 and an excess of these reagents in the discarded water may represent risks to health and aquatic life (Wills and Finch, 2016). Longer-chain alkyl xanthates (i.e. with ten or more carbon atoms) have not found wide application in flotation due to their poor solubility (Wang, 2016).

Bhatti et al. (2014, 2008) studied the flotation behaviour of stibnite ore samples from different regions of Pakistan. They found that an excessive dosage of xanthate collector may affect the recovery of stibnite, possibly owing to the reduction in selectivity caused by the formation of multi-layers of the collector on the surface of the particles. They also observed that the addition of collector becomes less necessary in a cleaning flotation stage when the particles are already coated by the collector.

The interest in improving the selectivity in stibnite recovery from more complex raw materials and developing more (eco)-efficient concentration routes led some authors to explore alternative reagent systems. In the case of collectors, dithiophosphates and dithiocarbamates

Table 3
Typical collector and activator dosage for various stibnite-bearing ores. [1]

Source	Other target specie(s)	Collector [g/t] [2]	Activator [g/t] [2]
Brinker (1935)	Au-bearing pyrite and arsenopyrite	(K) amyl xanthate (R, S)	$CuSO_4$ (G,C) [907.2]; $PbCl_2$ (S) [907.2] $PbCl_2$ (R) [907]; $CuSO_4$ (S) [907]
Engel (1949)	–	Potassium ethyl xanthate [18.1]	$CuSO_4$ [567–680]
Erspamer and Wells (1956)	Cinnabar	Potassium butyl xanthate (R) [181.4] Potassium butyl xanthate (S) [68]; Minerec 27 (G) [54.4]	$Pb(C_2H_3O_2)_2$ (R) [680.4] $Pb(C_2H_3O_2)_2$ (S) [136]
Wells et al. (1958)	Cinnabar	Potassium ethyl xanthate (R) [45.4–145.1] Potassium pentasol xanthate (R) [13.6–36.3]	$Pb(C_2H_3O_2)_2$ (R) [635–771]
Thom (1962)	Metal-bearing pyrite	(K) amyl xanthate [45.4–226.8]	$Pb(NO_3)_2$ [226.8–680.4]
Town and Stickney (1964)	Cinnabar	Aero-Xanthate 301 (R) [108.9]	$Pb(C_2H_3O_2)_2$ (G) [1329]
Oberbillig (1964) *apud* Lager and Forssberg (1989a)	–	(K/Na) butyl xanthate [450.0]	$CuSO_4$ or Pb $(C_2H_3O_2)_2$ [450]
		Long-chain xanthate (≥4 C atoms) [453.6–907.2]	No activator
Richards (1977)	–	Potassium amyl xanthate	$Pb(NO_3)_2$
Lepetic (1978)	–	Potassium amyl xanthate [100]	$Pb(NO_3)_2$ [300]
Davis et al. (1986)	Au-bearing arsenopyrite	Sodium isobutyl xanthate	$Pb(NO_3)_2$
		Sodium isobutyl xanthate [100] [3]; ethyl/*sec*-butyl dithiophosphate (Aerofloat 208)	$Pb(NO_3)_2$ [200] [3]
Hu (1988)	–	Butyl ammonium Aerofloat [250]	$Pb(NO_3)_2$ [120]
	Cinnabar	(K/Na) butyl xanthate	$CuSO_4$
	Au-bearing pyrite, scheelite	(K/Na) butyl xanthate	$Pb(NO_3)_2$
Kaigua and Dianzua (1985) *apud* Lager and Forssberg (1989b)	–	(K/Na) butyl xanthate or dibutyl dithiophosphate or diethyl dithiocarbamate	No activator
Lager and Forssberg (1989b); Pierre (1977)	Native Sb	Sodium diisobutyl dithiophosphate (R) [50]	$Pb(NO_3)_2$ (R, C) [800]
Lager and Forssberg (1989b)	–	(K) amyl xanthate	$Pb(NO_3)_2$ [300]
	–	Xanthate type	$CuSO_4$
	Au-bearing arsenopyrite	Sodium isobutyl xanthate; Sodium butyl dithiophosphate	$Pb(NO_3)_2$
	Au-bearing minerals	Sodium diisobutyl dithiophosphate [170]	$Pb(NO_3)_2$ [850]
		Sodium ethyl xanthate [107]	$Pb(NO_3)_2$ [1600]
Krstev et al. (2003)	–	Sodium isopropyl xanthate [20–25] or Potassium amyl xanthate [20–25]	$CuSO_4$ [100–150]
	–		
Zhang et al. (2006)	(tailings)		

Table 3 (*continued*)

Source	Other target specie(s)	Collector [g/t] [2]	Activator [g/t] [2]
		Sodium butyl xanthate (R, S1, S2) [100; 50; 30]	$Pb(NO_3)_2$ (R, S1, S2) [200; 100; 50]
Ealedona and Fujita (2006)	Au-bearing arsenopyrite	Potassium amyl xanthate (R) [200]	$CuSO_4$ (R) [100]
Ozkan (2007)	–	Sodium diisopropyl dithiophosphate [50–150]	$Pb(NO_3)_2$ [400–1200]
Bhatti et al. (2008)	–	Potassium amyl xanthate (R) [150]	$Pb(C_2H_3O_2)_2$ (R) [1500]
Celep et al. (2010)	Au/Ag-bearing sulphides	Potassium ethyl xanthate [200]	$CuSO_4$ [1000]
Anderson (2019, 2012)	–	Sodium diethyl dithiocarbamate [75]; Kerosene [65]; (K/Na) butyl xanthate [100]; Shale oil [300]	$Pb(NO_3)_2$ [150]
Güven et al. (2012)	Sb oxides (tailings)	Potassium amyl xanthate (R) [200]	–
		Potassium amyl xanthate (R1–R3, C1, C2) [600]	Na_2S/ No activator
Kanarskii et al. (2012)	Au-bearing arsenopyrite	Potassium butyl xanthate (R) [100]	$CuSO_4$ (R) [50–200] or Pb $(NO_3)_2$ (R) [50–200]
Abdusalyamova et al. (2013)	Cinnabar, Au/Tl/Se/Te-bearing arsenopyrite and pyrite	(K/Na) butyl xanthate [300]; Oksafor-1107 (O-1107)	No activator
		(K/Na) butyl xanthate [300]; Pemisol (kumilfenol: 1.5%–15%) [400]	No activator
Bhatti et al. (2014)	–	Potassium amyl xanthate (R, C) [300; 100]	$Pb(C_2H_3O_2)_2$ (R, C) [1250; 300]
Chen et al. (2014)	–	Composite MA-1 + butyl xanthate [220–350]	$Pb(NO_3)_2$ [80–100]
		(K/Na) butyl xanthate [480]	$Pb(NO_3)_2$ [130]
		MA-1 [150–350]; (K/Na) butyl xanthate [100]	$Pb(NO_3)_2$ [100]
Senchenko et al. (2016)	Au/Ag-bearing pyrite and arsenopyrite	Sodium dialkyl dithiophosphate [20] (R)	$Pb(NO_3)_2$ [500] (R)
Wei et al. (2017)	–	Sodium diethyl dithiocarbamate (R, S) [80–100; 30–50] Sodium butyl xanthate (R, S) [60–80; 30–50]	$Pb(NO_3)_2$ (R, S) [200–250; 100–150]
Ai et al. (2018); Xu et al. (2018)	Au-bearing minerals	Xanthate type	$CuSO_4$ or Pb $(NO_3)_2$
Solozhenkin and Kovalev (2018)	Au-bearing minerals	Potassium butyl xanthate and/or Sodium dimethyl dithiocarbamate	–
Gülcan et al. (2019)	Sb oxides	Potassium amyl xanthate [100]	$Pb(NO_3)_2$ [1000]; NaHS [0–500]
		Potassium amyl xanthate [50–100]; Aero 6493 (hydroxamate) [10–100]; Na-oleate [0–50]	$Pb(NO_3)_2$ [500–1000]
		Potassium amyl xanthate [50];Aero 6493 (hydroxamate) [50]	$CuSO_4$ [500]; $MnCl_2$ [500]
			NaHS [2000]

(*continued on next page*)

Table 3 (*continued*)

Source	Other target specie(s)	Collector [g/t] [2]	Activator [g/t] [2]
Wu et al. (2019)	–	Potassium amyl xanthate [100]; Na-oleate [25];Amin collector [25] Self-prepared 5# oil (R, S) [50; 10]	$Pb(NO_3)_2$ (R) [1000]

[1] Details on antimony grade and recovery in the flotation concentrate can be found in Table 6.

[2] Reagent dosage expressed in g/t (square brackets) when available. Capital letters in round brackets indicate the stage of reagent addition when reported: (G) = Grinding; (R) = Roughing or Conditioning; (S) = Scavenging; (C) = Cleaning.

[3] Personal communication.

have also been evaluated (Table 3); the latter, however, can be highly toxic to aquatic life. According to Davis et al. (1986), a dithiophosphate type (commercially known as Aerofloat 208) works not only as a secondary collector for stibnite (in conjunction with a primary xanthate collector) but also as a promoter for gold flotation and as a secondary frother due to its alcohol base. In a comparative microflotation study by Kaigua and Dianzua (1985) *apud* Lager and Forssberg (1989b), it was evidenced that dithiophosphates or dithiocarbamates might be advantageous compared to long-chain xanthates (potassium or sodium butyl xanthate in this case) for the selective recovery of stibnite from complex ores containing gangue sulphide minerals such as arsenopyrite. Diethyl dithiocarbamate was particularly efficient for stibnite recovery in a wide pH range. Such experiments were also verified in a laboratory flotation cell, but only for the case of dithiophosphate (Lager and Forssberg, 1989b).

Hu (1988), on the other hand, reported the replacement of conventional butyl xanthate with butyl ammonium Aerofloat as a collector for the selective recovery of stibnite at the complex Banxi deposit in Hunan province (China). Major minerals in the deposit included stibnite, arsenopyrite and pyrite, and minor proportions of scheelite, chalcopyrite and native gold were also found, besides quartz and other gangue minerals. The need to reduce the high content of arsenic (2.5–2.7% As) in the concentrate and the high reagent consumption led to the change of collector type, together with changes in the flotation circuit configuration (Hu, 1988). Butyl ammonium Aerofloat, in particular, has been reported as the most widely used reagent among the Aerofloat types in China due to its selectivity and collecting ability (Chen et al., 2020).

Aerofloat reagents or alkyl/aryl dithiophosphates (sometimes known as black powder due to the black colour of most dithiophosphates (Wang, 2016)) have found application as collectors in the flotation of native gold, copper and sulphides (Bulatovic, 2007; Yarar, 2000). These can be used alone or combined with xanthates and, as in the case of xanthates, form metal compounds (i.e. metal dithiophosphates) (Bulatovic, 2007). Their solubility is stronger when compared to xanthates with an equivalent hydrocarbon chain length; their selectivity is also higher, but at the expense of smaller collecting capability with regard to xanthates (Wang, 2016). The usefulness of dithiophosphates as collectors for stibnite flotation has also been demonstrated by other authors. Lager and Forssberg (1989b) for instance, reported the use of dithiophosphates either as the only collector or in combination with xanthates for the flotation of complex stibnite-bearing ores (e.g. containing also arsenic sulphides and/or gold-bearing sulphides) at various mine sites worldwide. One of these examples is an operation in Canada, where a dithiophosphate has been used as the only collector in the flotation of an ore containing stibnite and arsenic-bearing minerals, the latter being effectively depressed (Lager and Forssberg, 1989b; Pierre, 1977). Similarly, Ozkan (2007) used a combination of a dithiophosphate collector (commercially known as Hostaflot-LIP) and lead nitrate to study the flotation behaviour of a stibnite-bearing ore sample from the Odemis region (Turkey) at laboratory-scale. Besides stibnite, this sample also contained arsenic sulphides (arsenopyrite, realgar, orpiment), pyrite and quartz as the main gangue minerals. According to the author (Ozkan, 2007), a good balance between antimony grade and recovery in the final concentrate can be achieved from this ore with an optimal dosage of the selected reagents.

A more recent study (Senchenko et al., 2016) showed that it is possible to selectively recover stibnite and refractory gold (associated to pyrite/arsenopyrite) as separate concentrates from a very low-grade ore (0.42% Sb) at bench-scale, when a dithiophosphate collector is used (instead of xanthate) in combination with lead nitrate. In contrast, Ealedona and Fujita (2006) preferred the use of potassium amyl xanthate over a dithiophosphate collector (Aerofloat 208) on the basis of recovery and selectivity of stibnite towards gold-bearing sulphides; however, this comparison was done at different pH values (pH 6 for the xanthate and pH 8.5 for the dithiophosphate collector). In our view, the alkaline pH might have influenced the performance achieved with dithiophosphate in this study (Ealedona and Fujita, 2006). This is inferred from the microflotation results reported by Kaigua and Dianzua (1985) *apud* Lager and Forssberg (1989b), which are partially shown in Figure 1 and suggest that dialkyl dithiophosphates (DDP) perform better at acidic pH. Although Ealedona and Fujita (2006) showed that dithiophosphate (Aerofloat 208) did not allow a good selectivity of stibnite over gold-bearing sulphides at alkaline pH, it should be noted that this collector achieved a relatively good recovery of stibnite (approximately 70–75% Sb recovered in the concentrate for collector dosages between 200 and 300 g/t). This implies that dithiophosphates could also be used in combination with copper sulphate as an activator for the recovery of antimony from less complex stibnite-bearing ores (e.g. not containing recoverable amounts of gold or other valuable metals).

Alkyl dithiocarbamates (also called alkyl dithiocarbamic acids or amidosulfonic acid) have ranked third in preference as collectors for stibnite flotation after xanthates and dithiophosphates (Table 3). Although they originated several decades ago (as well as xanthates and dithiophosphates (Fuerstenau et al., 2007)), they appear to have drawn attention for practical application at laboratory-scale or industrial-scale flotation of stibnite only in more recent years, and mainly in combination with xanthates (Anderson, 2019, 2012; Solozhenkin, 2016; Solozhenkin and Kovalev, 2018; Wei et al., 2017). Dithiocarbamates are generally considered more selective than xanthates; sodium diethyl dithiocarbamate, in particular, has shown good selectivity in relation to pyrite (Wang, 2016), a gangue mineral that frequently occurs in stibnite-bearing deposits and may interfere in the recovery of stibnite. Nevertheless, the effectiveness of dithiocarbamates either alone or in combination with other collector species (e.g. xanthates) compared to conventional flotation of antimony ores of varying complexity at industrial-scale is something that requires further investigation.

Wu et al. (2019) recently reported the successful development of a collector referred to only as 5# oil to be used as the only collector along with lead nitrate (activator) for stibnite flotation. The collector was tested in a refractory stibnite ore from Shaanxi (China), which contained quartz, ankerite and illite as the major gangue constituents, besides minor amounts of pyrite, arsenopyrite, kaolinite and other gangue minerals. The authors argued that this special collector not only enhances the selective floatability of stibnite with regard to pyrite and arsenopyrite, but also improves froth stability by reducing the surface energy of clay minerals (illite, kaolinite) and, thus, preventing slime coating. Additionally, 5# oil was reported to exhibit frothing properties, so the dosage should not be excessive. While the functional group of this reagent was not disclosed, it may contain a S-N-dialkyl dithiocarbamate due to its yellow colour and insolubility in water ("oil-like liquid"), as is characteristic of such compounds (Bulatovic, 2007).

A few authors have also reported the use of other secondary collectors in combination with xanthates (Table 3), including Minerec 27 (Erspamer and Wells, 1956), kerosene and/or shale oil (Anderson, 2019,

2012), Oksafor-1107 and Pemisol (Abdusalyamova et al., 2013; Solozhenkin and Alekseev, 2010b), and MA-1 (Chen et al., 2014).

2.4. Activator effect

The addition of a lead compound (e.g. lead nitrate, lead chloride, lead acetate) as an activator either at the grinding or at the flotation stage for the selective recovery of antimony sulphides from simple or complex ores was patented by Brinker in 1935 (Brinker, 1935). Brinker's invention had also established using a copper compound (e.g. copper sulphate, copper nitrate, copper chloride) in an alkaline environment (i.e. by adding potassium or sodium hydroxide) to inhibit the flotation of antimony sulphide while favouring the recovery of gold associated to pyrite and/or arsenopyrite in the concentrate when the separation of antimony sulphides from complex ores through froth flotation is required. Moreover, the use of copper sulphate as an alternative activator for stibnite ores in an acidic or nearly neutral pH also became popular in the following decades (Engel, 1949; Lager and Forssberg, 1989a; Richards, 1977). Currently, the most common activator for stibnite froth flotation is lead nitrate, followed by copper sulphate and lead acetate, as observed in Table 3.

Several authors have attempted to get rid of lead salts as activators as the use of these substances may cause serious and irreversible toxicological effects. The way to explore this has been either by testing activation-free stibnite flotation or by replacing these salts with alternative activators. The first approach has been uncommon, yet not unexplored. Indeed, a couple of studies in the 60s and 80s (Kaigua and Dianzua (1985) and Oberbillig (1964) *apud* Lager and Forssberg (1989a, 1989b)) showed that a relatively good recovery (>80%) may be achieved at laboratory-scale when using long-chain xanthates (four or more carbon atoms) without the need of an activator if proper dosage of the collector is ensured. The effect of activator-free flotation on the antimony grade of the concentrate was, however, not reported. Furthermore, the positive effect of activator addition (copper or lead salt) on stibnite recovery was also highlighted by Lager and Forssberg (1989a, 1989b) and Oberbillig (1964).

Other studies, on the other hand, have made it clear that only a negligible amount of stibnite does float solely with the addition of a xanthate collector and, therefore, the use of a metal salt becomes mandatory. Abdusalyamova et al. (2013) have shown that it is possible to avoid using metal salts and still recover stibnite from a complex antimony-mercury-gold ore in an efficient manner by the combination of a xanthate collector with a new set of reagents, namely Oksafor-1107 and Pemisol (aromatic hydrocarbon-based compounds), which also seem to have good selectivity in stibnite-bearing ores containing arsenopyrite. In the search for alternative activators of stibnite (i.e. other than lead salts), copper sulphate has remained as the main choice over the last few decades (Table 3). This reagent certainly poses a lower health and environmental risk than lead activators, and also has proved to be efficient even in the flotation of complex stibnite-bearing ores, as can be noted in Table 3 (see, for example, Hu, 1988; Kanarskii et al., 2012).

Stibnite activation with metal salts has been conceived to occur, according to some authors (Pen'kov (2001) *apud* Bhatti et al. (2014, 2008)), by the adsorption of metal ions (e.g. lead or copper ions) on the crystal lattice of this mineral, which is followed by the formation of more stable molecules of metal sulphide at the solid–liquid interface. This facilitates the interaction between the collector (e.g. xanthate) and the metal sulphide, allowing the formation of a hydrophobic complex layer (Lager and Forssberg, 1989a; Solozhenkin and Alekseev, 2010b) consisting of lead/copper xanthate and antimony xanthate (Lager and Forssberg, 1989a) when a xanthate type collector is used. Complexes of this type can more easily attach to bubbles and facilitate the recovery of stibnite in the flotation concentrate.

Solozhenkin and Alekseev (2010b) argued that the solubility of copper xanthate is much lower than that of lead xanthate and this should be expected to create a more favourable activating capability for the former. Nevertheless, the authors (Solozhenkin and Alekseev, 2010b) considered lead salts to be better activators of stibnite when using xanthate collectors, which might be related to a possible reaction mechanism that can take place at the activation layer, that is, the migration of the metal ions (Cu^{2+} or Pb^{2+}) into a relatively deeper layer of the stibnite surface (Cao et al., 2018b; Solozhenkin and Alekseev, 2010b).

Solozhenkin and Kovalev (2018), on the other hand, used molecular simulations to study the interaction between flotation reagents and mineral clusters. For the case of stibnite, they affirmed that the charges are much greater on lead atoms than on copper atoms, which might explain a more widespread use of a lead salt over a copper salt as stibnite activator; this is because the total energy for copper-activated stibnite is lower than that of lead-activated stibnite. It has been suggested (Solozhenkin and Alekseev, 2010b) that a combination of Zn^{2+} and Cu^{2+} cations (optimal ratio 1:1) used to float antimony ores could eliminate the need for Pb^{2+} and improve environmental performance. This cation combination (from a mixture of copper sulphate and zinc sulphate) was confirmed to be successful in practice by Solozhenkin and Alekseev (2010b), while reducing activator consumption by 20% and obtaining performance results identical to those for lead nitrate. However, it must be noted that there are no further studies in the literature to support the use of zinc sulphate as a complementary activator for stibnite froth flotation.

A recent study carried out by Cao et al. (2018b) evaluated the characteristics of a stibnite surface activated with copper sulphate and lead nitrate in terms of the activation products and the depth profile of metal ions on the activated surface through techniques such as X-ray Photoelectron Spectroscopy and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), respectively (Table 1). It was found that both activators improve the floatability of stibnite and their metal ions are reduced at the stibnite surface to form a layer of either Cu_2S or PbS; this is in agreement with the results of previous experimental studies carried out by Solozhenkin and collaborators (Nefedov et al., 1980; Solozhenkin and Alekseev, 2010b). Furthermore, Cao et al. (2018b) found that the thickness of the Cu_2S layer was approximately 2.7–2.8 nm, while the thickness of the PbS layer was about 1.8 nm for the same concentration of reagents (5×10^{-5} mol/dm^3 of $CuSO_4$ or $Pb(NO_3)_2$, respectively). By reconstructing 3D images from depth profile data (TOF-SIMS), the authors noticed that lead ions tend to migrate into the bulk of stibnite while only a limited amount of copper ions was detected in the deeper layer. The authors (Cao et al., 2018b), then, suggested that this migration of lead ions into the bulk phase of stibnite may favour binding with sulphur atoms. The mechanisms responsible for the deeper migration of lead ions were, however, not explained. These features of the activated layer with different activators, as well as their possible relationship with the slight differences in the flotation performance of stibnite observed in microscale experiments (Figure 4a) require further investigation.

A few studies have systematically compared and reported the performance between lead and copper activators in stibnite flotation. For instance, bench-scale tests performed by Oberbillig (1964) *apud* Lager and Forssberg (1989a), showed that recovery of stibnite with copper sulphate is higher than when using lead acetate at various pH values and at high activator dosage (450 g/t). On the other hand, the performance of lead acetate was slightly superior compared to that of copper sulphate at lower activator dosage (below 450 g/t). Microflotation studies carried out by Richards (1977) on a simple stibnite ore indicated that, although lead nitrate allowed a much higher recovery of antimony (up to 93%) than copper sulphate (up to 78%) at lower activator dosage, the antimony grade in the final concentrate at maximum recovery was by far superior when using copper sulphate (51% Sb) rather than lead nitrate (40% Sb).

Richards (1977) also pointed out the fact that excess in the dosage of activator may cause the "pseudo-depression" of stibnite, as collector ions may be precipitated by the excess activator ions. Flotation

experiments carried out by Zhang et al. (2006) with a tailings sample containing stibnite and other antimony minerals showed a performance somewhat higher in terms of antimony recovery and grade in the concentrate when using lead nitrate instead of copper sulphate. Ealedona and Fujita (2006) found that while a similar recovery was achieved when using either copper sulphate or lead nitrate as activators (74% and 73% Sb, respectively), lead nitrate improved the antimony grade in the concentrate (45.9% Sb) compared to copper sulphate (35% Sb) at low activator dosage (100 g/t); further addition of copper sulphate (up to 300 g/t) increased the antimony grade but at the expense of a considerably lower recovery. Nevertheless, the authors (Ealedona and Fujita, 2006) prioritised the choice of activator on the basis of potential environmental effects and performance in terms of antimony recovery and finally recommended using copper sulphate in the conceptual flowsheet for the flotation of a complex stibnite-bearing ore from Tolukuma Gold Mines in Papua New Guinea.

Some authors have attempted to use sulphidising agents such as sodium sulphide (Na_2S) (Güven et al., 2012) and sodium hydrosulphide (NaHS) (Ealedona and Fujita, 2006; Gülcan et al., 2019) in combination with long-chain xanthate collectors (Table 3) as potential secondary activators for the recovery of oxidised antimony minerals. A more detailed discussion on aspects related to the recovery of antimony oxides by froth flotation is provided in Section 5.2.

2.5. pH regulator effect

Undoubtedly, pH is a critical and controversial variable in stibnite flotation. While several authors suggest that the optimal pH should be slightly acidic, others have worked with a neutral or natural pH (Table 4). A few studies report stibnite flotation at a slightly alkaline pH (Table 4) and usually in a reagent system involving lead salts and xanthates. Indeed, an alkaline pH seems to be the most favourable for xanthate collectors (Bhatti et al. (2014, 2008)). On the contrary, the use of copper or lead salts has been frequently reported in flotation studies at slightly acidic to neutral pH.

Plaksin (1960) *apud* Lager and Forssberg (1989a) compared the effect of salts and acids with equivalent anions (e.g. H_2SO_4 vs. Na_2SO_4, HCl vs. KCl, HNO_3 vs. KNO_3) and concluded that it is not the presence of anions or the type of acid that impacts stibnite recovery, but the concentration of hydrogen ions in solution (i.e. an acidic pH). Sulfuric acid and sodium carbonate have been used as the main pH regulators in stibnite flotation studies.

Many of the studies that report a slightly acidic pH (5.0–6.5) as the optimal condition for the floatability of stibnite have in common the fact that the mineralogy of the ore to be treated is relatively simple, i.e. when stibnite is the only target mineral and the use of depressant is unnecessary or only required for gangue minerals such as clay and silicates (Table 4). For more complex stibnite-bearing ores, such as those where

Table 4
pH regulation and reagent environment, as well as mineralogical characteristics for stibnite flotation. [1]

Source	pH	pH regulator		Reagent system		Ore type [4]
		Type	[g/t]	Collector type [2]	Activator type	
Hu (1988)	4.8–5.0	H_2SO_4	1450	DTP	$Pb(NO_3)_2$	I
Richards (1977)	5.0		–	Xa		
Chen et al. (2014)	5.0–6.5		500–1500	Xa; O		
	~5.5		1500	Xa		
Lager and Forssberg (1989b)	~ 6		–	Xa		
Engel (1949)	5.5–6.0	–	–	Xa	$CuSO_4$	II
Lepetic (1978)	< 6	Untreated acid, mine-type water	–	Xa	$Pb(NO_3)_2$	IIIb
Ealedona and Fujita (2006)	6	Na_2CO_3 (R)	–	Xa	$CuSO_4$	IIIa
Erspamer and Wells (1956)	6–6.5	–	–	Xa	$CuSO_4$ or Pb	IV
Oberbillig (1964) *apud* Lager and Forssberg (1989a)					$(C_2H_3O_2)_2$	I
Krstev et al. (2003)	6.5	Na_2CO_3 (G)	885	Xa	$CuSO_4$	IIIb
Ozkan (2007)	6.5	Na_2CO_3	4000	DTP	$Pb(NO_3)_2$	II
Davis et al. (1986)	6.8–7; 6.5–6.8; 6–6.5	H_2SO_4 (R, S, C)	2660 [3]	Xa; DTP	$Pb(NO_3)_2$	IIIa
Ai et al. (2018); Xu et al. (2018)	< 7	H_2SO_4	200–600	Xa	$CuSO_4$ or $Pb(NO_3)_2$	
Town and Stickney (1964)	7.1 (R1); 6.0 (R2)	–	–	Xa	$Pb(C_2H_3O_2)_2$	IV
Oberbillig (1964) *apud* Lager and Forssberg (1989a)	7.0	–	–	Xa	–	I
Celep et al. (2010)	7 ± 0.3	–	–	Xa	$CuSO_4$	IIIa
Brinker (1935)	> 7	NaOH (G, C)	680.4–907.2	Xa	$CuSO_4$; $PbCl_2$	IIIa
Kanarskii et al. (2012)	7.5	–	–	Xa	$CuSO_4$ or $Pb(NO_3)_2$	
Thom (1962)	8	NaOH or lime	–	Xa	$Pb(NO_3)_2$	IIIb
Erspamer and Wells (1956)	8.5 (R); 4.9 (S)	H_2SO_4 (S)	907.2	Xa; O	$Pb(C_2H_3O_2)_2$	IV
Hu (1988)	9	–	–	Xa	$CuSO_4$	
	7–8	–	–	Xa	$Pb(NO_3)_2$	IIIa
Bhatti et al. (2008)	8.0	Na_2CO_3 (R, C)	–	Xa	$Pb(C_2H_3O_2)_2$	II
Lager and Forssberg (1989b)	~8.5	H_2SO_4	–	DTP	$Pb(NO_3)_2$	IIIa
Bhatti et al. (2014)	9	Na_2CO_3 (R, C)	–	Xa	$Pb(C_2H_3O_2)_2$	IIIb
Brinker (1935)	–	NaOH (S)	907.2	Xa	$CuSO_4$; $PbCl_2$	IIIb
Lager and Forssberg (1989b); Davis et al. (1986)	–	None or H_2SO_4	–	Xa and/or DTP	$Pb(NO_3)_2$	II

[1] Details on antimony grade and recovery in the flotation concentrate can be found in Table 6.

[2] Xa = Xanthate type; DTP = Dithiophosphate type; DTC = Dithiocarbamate type; O = Other (unknown type or not classified as Xa, DTP or DTC). Capital letters in round brackets indicate the stage of reagent addition when reported: (G) = Grinding; (R) = Roughing or Conditioning; (S) = Scavenging; (C) = Cleaning.

[3] Personal communication.

[4] Type I: Simple stibnite-bearing ore (i.e. no other target minerals; may contain amounts of gangue minerals and toxic elements such as arsenic; it does not, however, demand the use of depressant or the use of such reagents is not reported); Type II: Stibnite as the main target mineral, potentially containing antimony oxides, depressant for the dispersion of some gangue minerals (e.g. quartz, clay, silicates) is reported; Type III: Stibnite-bearing ores containing other sulphides (e.g. pyrite, arsenopyrite) that are chemically depressed either as target (a) (i.e. containing recoverable amounts of gold and/or other valuable metals) or gangue minerals (b) (i.e. barren); Type IV: Stibnite-bearing ores containing also cinnabar as target mineral.

other target minerals also need to be recovered (e.g. stibnite-bearing ores containing gold-bearing pyrite/arsenopyrite or cinnabar), there are usually two options for the selective recovery of the minerals of interest. The first one consists in conducting a bulk rougher flotation of the target minerals followed by cleaning and/or scavenging stages where the separation of these minerals is usually assisted by the addition of depressants. Another alternative is to conduct a differential flotation from the beginning, that is, establishing the conditions for the depression of one of the minerals of interest in the rougher flotation stage. The latter is usually achieved by promoting the depression of stibnite at alkaline pH.

In summary, simple stibnite ores float more effectively at a slightly or moderately acidic pH, which is usually regulated with sulfuric acid. However, it is also feasible to use a natural pH and/or a pH within the range between 6 and 8 (Table 4), especially when the presence of certain gangue minerals (e.g. dolomite) can make it difficult to maintain the pH within an acidic range. In contrast, a more alkaline pH (above ~ 9–10) drastically impairs the floatability of this mineral, which may be favourable for some complex ores. In line with the findings from microflotation studies (Figure 1), a highly acidic or highly alkaline pH (pH <3 or >9, respectively) is not recommended for direct flotation of stibnite. There are also other key considerations on the effect of pH on stibnite flotation with regard to the presence of other minerals, the dosage of reagents, and others, as outlined in Table 5.

2.6. Depressant effect

The need for depressants depends on the liberated gangue minerals occurring in the stibnite ore. Sodium cyanide has been usually employed to depress gangue minerals such as pyrite (Bhatti et al., 2014; Brinker, 1935) and arsenic-bearing minerals including arsenopyrite and gersdorffite (Davis et al., 1986; Lager and Forssberg, 1989b). Cyanide as a pyrite depressant was, in fact, patented in the 1920s and represented a major innovation in froth flotation at that time. This reagent allows optimal depression of pyrite at lower pH (usually in the range 6.5–7.0) (Fuerstenau et al., 2007), which lies within the optimal pH range for stibnite flotation. The less alkaline the pulp, however, the higher the concentration of free HCN, a hazardous compound (Wills and Finch, 2016).

Cyanide consumption, on the other hand, increases at acid pH (Davis et al., 1986). An excess in the dosage of cyanide may also have detrimental effects in the recovery of stibnite due to the formation of soluble complexes with metal xanthates (especially when using short-chain xanthates) (Wills and Finch, 2016), and may also increase the losses of gold as this metal could be partially dissolved during flotation (Davis et al., 1986). Given the high toxicological risks of cyanide, its use demands special care, being more suitable for plants that recover gold from flotation concentrates by cyanidation and incorporate treatments for cyanide management (Wills and Finch, 2016; Yannopoulos, 1991).

Pyrite depression with cyanide has been presumably attributed to the formation of a ferric ferrocyanide complex on the surface of pyrite, which facilitates the formation of a hydrophilic site and interferes with a possible adsorption of collector (Fuerstenau et al., 2007; Wills and Finch, 2016). The use of a water-soluble sodium zinc cyanide complex (ZnO + NaCN) as a depressant for iron sulphides such as pyrite in a stibnite-bearing ore or bulk stibnite concentrate at acidic pH was, on the other hand, patented by Lepetic in the late 1970s (Lepetic, 1978). Potassium permanganate has also been reported to aid in the depression of pyrite and arsenic sulphides (Krstev et al., 2003; Wu et al., 2019), and has been recognized to have a depressing effect on various sulphide minerals (Bulatovic, 2007).

Some authors have attempted to seek alternative reagents that can assist or substitute the use of some hazardous depressants such as cyanides. Kanarskii et al. (2012), for instance, have proposed to separate arsenopyrite and stibnite from a stibnite pre-concentrate by the addition of an oxidising agent such as hydrogen peroxide. This method has allowed the authors to take advantage of the differences in oxidability of the minerals and thus favour the recovery of stibnite in the concentrate, and arsenic and iron oxides (As_2O_3 and Fe_2O_3, respectively) derived from the oxidation reaction of arsenopyrite in the tailings, without

Table 5
Effect of pH on froth flotation of stibnite and some other antimony minerals.

pH	Positive effect	Negative effect
Acidic	Maximum stibnite recovery at: pH ~ 3.5–5.8 (Lepetic, 1978) pH ~ 4.0–5.0 (Lager and Forssberg, 1989a) pH ~ 4.5–5.0 (Richards, 1977) pH ~ 6 (Ealedona and Fujita, 2006) pH ~ 6.0–7.0 (Davis et al., 1986) natural, slightly acidic pH (Engel, 1949)	Reducing pH in scavengers increases the floatability of Au-bearing arsenopyrite, thus, this concentrate requires regrinding before returning to roughing for further As suppression and Sb recovery (Davis et al., 1986)
	Acid pH favours the floatability of other Sb minerals such as berthierite, gudmundite, and oxidised Sb minerals (Davis et al., 1986)	The precipitation of lead as insoluble $PbSO_4$ may increase activator dosage and inhibit the flotation of oxidised Sb minerals (Davis et al., 1986)
	Dithiophosphates allow better selectivity between stibnite and arsenopyrite than xanthate collectors at acidic pH (~2–4) (Kaigua and Dianzua (1985) *apud* Lager and Forssberg, (1989b))	
	Consumption of collectors and activators may be considerably reduced (Lager and Forssberg, 1989b)	Consumption of cyanide (depressant) increases (Davis et al., 1986)
Neutral	Jamesonite has a good floatability at pH close to neutral and without activator (Lager and Forssberg, 1989a)	Activation with a metal salt is required to attain good stibnite recovery (Lager and Forssberg, 1989a)
Alkaline	Stibnite grade and recovery are optimal in slightly alkaline pH when using xanthate and lead acetate, probably due to the stability of the mineral-xanthate complex in such condition (Bhatti et al., 2014, 2008)	Alkali addition causes a sharp decline in the floatability and recovery of stibnite (Richards, 1977; Engel, 1949; Oberbillig (1964) *apud* Lager and Forssberg (1989a)). Floatability of stibnite worsens at pH ≥ 8 and is very poor at: pH above ~ 9–10 (Kanarskii et al., 2012; Lager and Forssberg, 1989a)
	Dithiocarbamates allow good selectivity between stibnite and arsenopyrite even at alkaline pH at microflotation scale, differently to xanthates and dithiophosphates (Kaigua and Dianzua (1985) *apud* Lager and Forssberg (1989b))	Possible solubilisation of gold-bearing sulphides, reducing their recovery in the concentrate (*reverse flotation*) (Brinker, 1935)
	Stibnite can be successfully separated from cinnabar by depression at pH 9 (*reverse flotation*) from a bulk stibnite-cinnabar concentrate using depressants such as ACMC and Na_2SiO_3 (Hu, 1988)	Sharp decline in the contact angle of stibnite. Addition of xanthate and $Pb(NO_3)_2$ expressively improves this parameter up to a pH < 11. Possible formation of hydrophilic $Pb(OH)_2$ at high pH (Vijayakumar and Majumdar (1972) *apud* Lager and Forssberg (1989a))
	Stibnite is depressed (*reverse flotation*) while Au-bearing pyrite is floated (Brinker, 1935) Collective rougher flotation of stibnite and arsenopyrite at pH slightly alkaline (7.5) (Kanarskii et al., 2012)	Presence of carbonate minerals (e.g. dolomite) may turn the pulp alkaline and increase the consumption of pH regulator (e.g. sulphuric acid) (Davis et al., 1986; Lager and Forssberg, 1989b)

requiring further addition of other reagents such as metal salts or collectors. A recent microflotation study (Matveeva et al., 2017) showed that the addition of a phytogenous reagent (tannin-containing modifier) to a pulp conditioned with a compound collector (sodium diethyl dithiocarbamate and oxypropyl diethyl dithiocarbamate ester) could aid the selective separation of stibnite and arsenopyrite by suppressing the floatability of the latter, particularly at a dosage of 200 g/t. On the basis of microscopic analysis of polished sections, the study concluded that tannin does not desorb copper dithiocarbamate from the stibnite surface if copper sulphate was used as an activator.

A study by Ealedona and Fujita (2006) revealed an important reduction in the arsenic content of the flotation concentrate (from 0.61% to 0.12% As), an increased recovery of gold in the tailings and a slight improvement in antimony recovery in the flotation concentrate when a small dosage of soluble starch (25 g/t) was added before the activation of stibnite with copper sulphate. This study also reported that the depression of arsenic (from arsenopyrite) was less effective (i.e. higher starch addition was required) if starch was added after the stibnite activator (copper sulphate). Moreover, Ealedona and Fujita (2006) stated that the depression effect of starch was higher compared to that of tannin, although no experimental data were shown for the latter. An innovative approach has also been recently patented for the separation of stibnite and arsenic sulphides such as realgar through the addition of cassava starch and ferric citrate (Wei et al., 2017).

Dextrin, an intermediate product of starch breakdown, has been employed in stibnite froth flotation. The description on its use has been limited and explicitly reported by some authors for the depression of talc (Davis et al., 1986; Lager and Forssberg, 1989b). Dextrin increases the hydrophilicity of talc by adsorbing at its surface, which favours the hydrogen bonding of water molecules to the polymer at the solid–liquid interface (Fuerstenau et al., 2007). On the other hand, the fact that dextrin has been employed in conjunction with sodium cyanide in the flotation of stibnite-bearing ores containing arsenic sulphides might not be fortuitous. In the authors' opinion, dextrin might also have assisted the depression of arsenic sulphides in those studies (Table 6). Similar to starch and other cationic polymers, dextrin could also act as sulphide depressant (Dunne, 2016). Indeed, dextrin has been reported as a depressant for pyrite in the flotation of an antimony oxide ore (Qin et al., 2017). According to Lager and Forssberg (1989b), moderate dosages of dextrin should not affect the flotation of stibnite. Dextrin dosages between 150 and 500 g/t have been reported in some stibnite flotation studies (Table 6).

Sodium silicate, on the other hand, is a frequently added depressant in stibnite flotation (Table 6). It inhibits the flotation of silicate gangue minerals (Bhatti et al., 2014, 2008; Celep et al., 2010) and aids the dispersion and depression of the clayey, colloidal material that can cause viscosity and slime coating problems in flotation (Bhatti et al., 2008; Engel, 1949; Gülcan et al., 2019). Sodium silicate forms a colloidal complex that adsorbs on the mineral surface of the gangue mineral and reduces its floatability (Fuerstenau et al., 2007). When added to the flotation pulp, sodium silicate undergoes a complex hydrolysis process that originates a series of ionic and colloidal compounds. The type of compounds formed depends on sodium silicate dosage and the pH of the pulp (Silva et al., 2012). The optimal depressant action of this reagent has been observed in a pH range between 7 and 10 for silicates. However, microflotation studies with amine collectors have suggested that the optimal depression of quartz may occur at high dosage (above 1000 g/t of sodium silicate) and within the pH range 5 to 8, with $SiO(OH)_3^-$ and $Si(OH)_4$ being the dominant silica species in this range (Silva et al., 2012). Stibnite froth flotation studies have usually reported a medium to high dosage of sodium silicate (up to 1000 g/t) and a pH range between 5.5 and 9 (Table 6). Some studies have shown that adding sodium silicate above a certain concentration may slightly affect the recovery and grade of stibnite in the concentrate, presumably due to the fact that some partially liberated particles may be subject to depression when coated by the excess of depressant (Bhatti et al. (2014, 2008)).

Stibnite has, in some instances, been separated from other target minerals such as gold-bearing pyrite/arsenopyrite (Brinker, 1935) and cinnabar (Erspamer and Wells, 1956; Hu, 1988; Lager and Forssberg, 1989b) by reverse flotation. For the latter, it has been suggested to condition the ore with sodium cyanide during grinding (pyrite depressant) and then perform a conventional stibnite-cinnabar bulk flotation (Erspamer and Wells, 1956). Stibnite can then be separated from the bulk concentrate by depression with conventional reagents including sodium or potassium dichromate (Erspamer and Wells, 1956; Hu, 1988). Selectivity of dichromate salts towards stibnite has been favoured at high reagent dosage (around 2000 g/t $K_2Cr_2O_7$ according to Lager and Forssberg, 1989b; above 500 g/t for $Na_2Cr_2O_7$ according to Table 6); such inorganic compounds are also very toxic and hazardous for the environment. Hu (1988), on the other hand, recommended to replace the dichromate salts with carboxymethylcellulose ammonium salt (ACMC); ACMC was reported to selectively adsorb on the stibnite surface previously conditioned with copper sulphate (activator) and a xanthate collector (Hu, 1988), which does not occur on the surface of cinnabar.

The use of more environmentally sustainable methods for the selective flotation of sulphide minerals through the modification of the mineral surface by microorganisms (or bioflotation) has also attracted research interest in more recent decades (Dwyer et al., 2012; Otsuki, 2016). Khoshdast and Sam (2011) and Sharma (2001) cited a study (Lyalikova and Lyubavina, 1986) where *Acidithiobacillus (At.) ferrooxidans* (formerly known as *Thiobacillus ferrooxidans* (Kelly and Wood, 2000)) was employed to selectively separate cinnabar and stibnite by flotation. Effective separation of both sulphides was achieved after about 90 min of pretreatment. Further microflotation studies of a stibnite-cinnabar ore subjected to bacterial preconditioning (*At. ferrooxidans*) confirmed that it is possible to selectively biooxidise stibnite and inhibit its floatability within 90 min without requiring the addition of inorganic depressants (Solozhenkin and Lyalikova-Medvedeva, 2001). Stibnite biooxidation has also been suggested prior to cyanidation as it may assist in liberating the finely disseminated or occluded gold in stibnite concentrates; it can also transform stibnite to a more stable and saleable form as antimony trioxide (Sb_2O_3) (Solozhenkin and Lyalikova-Medvedeva, 2001). *At. ferrooxidans* can oxidise various types of sulphide minerals through mechanisms that take place at the mineral surface either directly (i.e. adhesion of bacteria on the mineral surface and enzymatic attack that leads to the oxidation of the sulphide mineral) or indirectly (i.e. oxidation due to the interaction of the mineral surface with ferric ions produced by biooxidation) (Das et al., 1999; Lawrence et al., 1997).

3. Mineralogy and particle size effects in stibnite froth flotation

Pyrite and arsenopyrite commonly occur in stibnite deposits, either as gangue or target minerals; for the latter, it usually hosts finely disseminated gold and other valuable metals (Celep et al., 2010; Davis et al., 1986; Hu, 1988; Kanarskii et al., 2012). Arsenic-bearing sulphides such as arsenopyrite, gersdorffite, and realgar are the most frequent sources of arsenic, which is perhaps the most troublesome (Lager and Forssberg, 1989a) and frequently encountered impurity in stibnite froth flotation (Table 6). The presence of arsenic can affect the quality of the final concentrate, depending on its content which, in turn, determines the need for an arsenic depressant (as discussed in Section 2.6). In fact, European policy regulations regarding hazardous products have limited the content of arsenic in antimony trioxide (main antimony source for flame retardants) to 0.1% (Morizot and Ollivier, 1993; Swedish Chemicals Agency, 2008). In addition, it is desirable to reduce the amount of arsenic in a flotation concentrate to minimise the environmental pollution risks during the smelting process (Wu et al., 2019). It is observed that, in the flotation of some medium-to-high-grade stibnite ores (~4–13% Sb) containing arsenic up to approximately 0.7% with no appreciable gold, the use of depressants has not been reported (Table 6).

Table 6
Relationship between ore feed characteristics, depressant addition requirements and the grade and recovery of the stibnite concentrate for various mineral deposits worldwide.

Region/Country of the mineral deposit and source	Ore feed characteristics			Collector Type [1]	Depressed mineral(s)	Depressant [g/t] [2]	pH	Grade (g) and recovery (r) in final Sb conc.	
	Elements (%)		Particle size specification						
	Sb	Other						g (%)	r (%)
Marlborough Sounds, N. Z. (Richards, 1977)	13.3	As (0.5)	<150 μm	Xa	–	–	5.0	>60	>90
Hunan, China (Hu, 1988)	6.47	As (0.43)	–	DTP	–	–	4.8–5.0	64.4	93.5
China (Lager and Forssberg, 1989b)	–	–	60% < 74 μm	Xa	–	–	~ 6	50	80
New Brunswick, Canada (Lager and Forssberg, 1989b; Pierre, 1977)	4.4	As (0.63); Pb (0.018)	63% < 74 μm	DTP	–	–	–	65.43	93.1
Tailings from Yunnan (China) (Zhang et al., 2006)	*1.55*	–	*65.0% < 74 μm* *42.76% < 74 μm*	*Xa*	–	–	–	*40.94* *29.87*	*42.86* *39.45*
Hunan, China (Anderson, 2019, 2012)	3.19	–	60% < 74 μm	Xa/DTC/O	–	–	–	47.58	93.97
Not reported (Chinese patent) (Chen et al., 2014)	~ 3.6 ~4.2–5.3	– –	77% < 74 μm	Xa/O Xa or Xa/O	– –	– –	5.0–5.5 ~5.5–6.5	47.06 48.6–52	> 95 81.2–82.9
California, USA (Engel, 1949)	9.7	–	100% < 105 μm	Xa	Clay	Na_2SiO_3 [453.6]	5.5–6.0	57.4–64.1	96.8 (R)
Turkey (Lager and Forssberg, 1989b)	–	–	–	Xa	–	Na_2SiO_3 (dispersant) (C)	–	65	–
Odemis, Turkey (Ozkan, 2007)	8–9	As (0.8–1.0)	< 106 μm	DTP	Quartz	Na_2SiO_3 [100]	6.5	56–64.7	41.6–85.8
Chitral, Pakistan (Bhatti et al., 2008)	19.05	Pb (1.55)	95% < 150 μm	Xa	Quartz, clay, silicates	Na_2SiO_3 (R, C) [300; 50]	8.0	62.02	95.05
Tailings from Kutahya (Turkey) (Güven et al., 2012)	*4.77*	–	*< 212 μm* *< 106 μm* *< 74 μm* *< 38 μm* –	*Xa* *Xa*	–	*$Na_2S_2O_5$ (dispersant) [1000]* *$Na_2S_2O_5$ (dispersant) [1000]*	–	*16.24* *22.98* *17.36* *11.6* *52.26*	*20.3* *25.0* *31.7* *18.3* *7.6*
Kütahya-Uşak region, Turkey (Gülcan et al., 2019)	~ 0.65–3.02	As (0.059–0.151); Cu (0.01–0.058); Ni (0.009–0.024)	Hydrosizer OF/ slimes (<1 mm) 80% < 75 μm	Xa or Xa/O Xa or Xa/O	Clay	Na_2SiO_3 [1000]	–	2.39–2.69 2.09–9.06	6.27–7.58 6.27–16.24
Not reported (US Patent) (Brinker, 1935)	–	–	–	Xa	Stibnite Pyrite	NaOH [680.4–907.2] NaCN + Pb compound	> 7 –	– –	– –
Bolivia (Lepetic, 1978)	2.18	–	39.5% <74 μm 70.5% <74 μm	Xa	Fe sulphides (e.g. pyrite)	Zn-CN salt (ZnO, NaCN) (C) [500]	< 6	63.4 60.1	76.4 87.7
Bolivia (tailings) (Lepetic, 1978)	*~1.6*	–	*69.4% < 74 μm*			*CaO + NaCN (G, C)* *Zn-CN (C) [500]*	*<7 (R); >7 (C)* –	*26.5* *53.6*	*43.2* *43.8*
Nullagine, WA, Australia (Lager and Forssberg, 1989b)	–	As, Au	–	DTP	–	Na_2SiO_3 (dispersant)	~ 8.5	60	~ 60
Hillgrove, NSW, Australia (Lager and Forssberg, 1989b)	4.5	Au (9 g/t); As	60% < 74 μm	Xa	–	–	–	60	≥ 90
Kaapvaal Craton, South Africa (Lager and Forssberg, 1989b; Davis et al., 1986)	6–12 1.8	As (0.1–0.2) As (0.1–0.3); Au (2 g/t)	– 99% < 300 μm; 65–75% < 75 μm; ~ 45% < 25 μm	Xa Xa/DTP	– – Talc Arsenopyrite, gersdorffite	– Na_2SiO_3 (dispersant) Dextrin [500] NaCN (R, C) [50–80]	– 6–7	>56 >56	80–85 80–88
Republic of Macedonia (	1.30–1.65	As (0.4)	95% < 147 μm	Xa	As sulphides (e.g. realgar, arsenopyrite)	Dextrin (G) [150]; NaCN (G) [40]	6.5	20.5–38 29.5–49.4	43.2–61.3 45.5–82.8

(*continued on next page*)

Table 6 (*continued*)

Region/Country of the mineral deposit and source	Ore feed characteristics			Collector Type [1]	Depressed mineral(s)	Depressant [g/t] [2]	pH	Grade (g) and recovery (r) in final Sb conc.	
	Elements (%)		Particle size specification						
	Sb	Other						g (%)	r (%)
Krstev et al., 2003)						$KMnO_4$ (G, C1–C3) [150–200; 0–200; 0–25; 0–25]; NaCN (G) [40]			
Hunan, China (Hu, 1988)	–	W; Au	–	Xa	–	–	7–8	41.7	–
Papua New Guinea (Ealedona and Fujita, 2006)	15.93	Au (27 g/t); Ag (36 g/t); As (0.59)	80% < 108 μm	Xa	Au-bearing arsenopyrite	Starch [25]	6	35.8	78
Southwest of Ordu, Turkey (Celep et al., 2010)	1.64	Au (20 g/t); Ag (220 g/t); As (262 g/t)	80% < 25–11 μm	Xa	Silicates	Na_2SiO_3 [1000]	~7 (6.7–7.3)	–	75–80
Russia (Kanarskii et al., 2012)	0.3	Au (3.6 g/t); As (0.4)	80% < 74 μm (R)	Xa	–	–	7.5	6.3	≥ 87.5
			95% < 74 μm (C)	Xa	Arsenopyrite	H_2O_2 (oxidising agent) [100–150]	–	38.2	86
Balochistan, Pakistan (Bhatti et al., 2014)	20.04	Pb (0.36)	80% <75 μm (R); 98% <75 μm (C)	Xa	Quartz, clay, silicates Pyrite	Na_2SiO_3 (R, C) [800; 200] NaCN (C) [100]	9	65.12	> 85
Not reported (Senchenko et al., 2016)	0.42	FeAsS (2.4); Au (2.2 g/t); Ag (7.76 g/t)	80% <71 μm	DTP	–	–	–	30.1	70.91
Not reported (Chinese patent) (Wei et al., 2017)	1.35–3.12	As (1.54–3.63)	–	DTC/Xa	Realgar, other minerals	Cassava starch (R,S, C) [200–250; 50–100; 100–150]; $C_6H_5FeO_7$ (R,S,C) [300–500; 200–300; 200–300]	–	48.39–51.24	91.25–93.67
Shaanxi province, China (Wu et al., 2019)	2.18–2.25	As (0.27); Cu/Pb/Zn (<0.01)	60% < 74 μm	O	Kaolinite, illite Pyrite, arsenopyrite	TZ-10 (R) [500] $KMnO_4$ (C) [30]	–	65.12	91.56
Alaska, USA (Erspamer and Wells, 1956)	2.7	Hg (1.6); As (0.73)	100% < 208 μm	Xa or Xa/O	Pyrite	NaCN (G) [453.6]	6	30.7	76.1
			–		Stibnite (R)	$Na_2Cr_2O_7$ (G,R, C) [1361–2722]	8.5 (R); 4.9 (S)	49.4	33.3
Alaska, USA (Wells et al., 1958)	2.87	Hg (1.55); As (0.67)	90% < 147 μm	Xa	–	–	–	34.6	82.6
Alaska, USA (Town and Stickney, 1964)	0.73–1.08	Hg (1.56–1.74)	~ < 147 μm	Xa	Stibnite (R2)	$Na_2Cr_2O_7$ (R2) [503.5]	6 (R2)	37	88.8
Hunan, China (Hu, 1988)	–	Hg	–	Xa	Stibnite	ACMC + Na_2SiO_3	9	–	–
Anzob, Tajikistan (Abdusalyamova et al., 2013)	3.57–3.61	Hg (0.27–0.29); Au (~2.3 g/t); Tl; Se; Te	–	Xa/O	–	–	–	42.6–45.46	90.28–94.82

[1] Xa = Xanthate type; DTP = Dithiophosphate type; DTC = Dithiocarbamate type; O = Other (unknown type or not classified as Xa, DTP or DTC).
[2] Reagent dosage expressed in g/t (square brackets) when available. Capital letters in round brackets indicate the stage of reagent addition when reported: (G) = Grinding; (R) = Roughing or Conditioning; (S) = Scavenging; (C) = Cleaning.

This is likely to be related to the use of dithiophosphate as a selective stibnite collector towards arsenopyrite, as observed in many of these studies and pointed out by some authors (Hu, 1988; Lager and Forssberg, 1989b). In other cases, however, even a relatively low content of arsenic may demand the use of arsenic sulphide depressant, especially with low-grade stibnite ores (~1.3–2.3% Sb) (Table 6).

Lead is another impurity found in some stibnite-bearing ores in amounts usually below 2% (Table 6). The presence of lead in the stibnite-bearing ore does not seem to have caused any difficulty in the flotation process or, at least, no special treatment for the removal of this metal from the final concentrate has been reported in the literature (Table 6). Some smelters, however, may have special requirements; for instance, the lead content in stibnite concentrates should be less than 0.15% to be suitable for Chinese smelters (Cao et al., 2018a). Lead contained in stibnite-bearing deposits may originate from small amounts of lead sulphides such as galena (Cao et al., 2015; Davis et al., 1986; Morizot and Ollivier, 1993) or polymetallic antimony-bearing minerals such as jamesonite (Anderson, 2012; Davis et al., 1986; Gülcan et al., 2019; Lager and Forssberg, 1989a), boulangerite and bournonite (Anderson, 2012; Lager and Forssberg, 1989a), zinckenite and andorite (Anderson, 2012; Celep et al., 2010), and others (Anderson, 2012). Gold, on the contrary, is a valuable co-product that is frequently found in some stibnite-bearing deposits as coarse or very finely disseminated gold (Davis et al., 1986), and mostly associated with pyrite or arsenopyrite (Davis et al., 1986; Hu, 1988; Kanarskii et al., 2012; Lager and Forssberg, 1989b), although it can also be associated with stibnite (Haque, 1987) and occur in gold-antimony minerals such as aurostibite (Anderson, 2012; Lager and Forssberg, 1989b).

Typical antimony content in the feed to flotation varies widely among stibnite froth flotation testwork carried out in the reviewed studies, which covers industrial operations as well as bench-scale studies on ore samples from stibnite-bearing deposits worldwide. A few studies have reported antimony content between 10% and 20%, while the majority of the studies report an antimony content in the flotation feed within the range 2–10%. In a few other studies, the antimony grade in the flotation feed is particularly low (<2% Sb), and some of these include attempts of tailings reprocessing (Table 6 and Figure 5). For the latter, the overall recovery of antimony in the final concentrate has not been as satisfactory (<45%) as in the case of primary ores (usually > 80%). This may be due to several reasons, including the presence

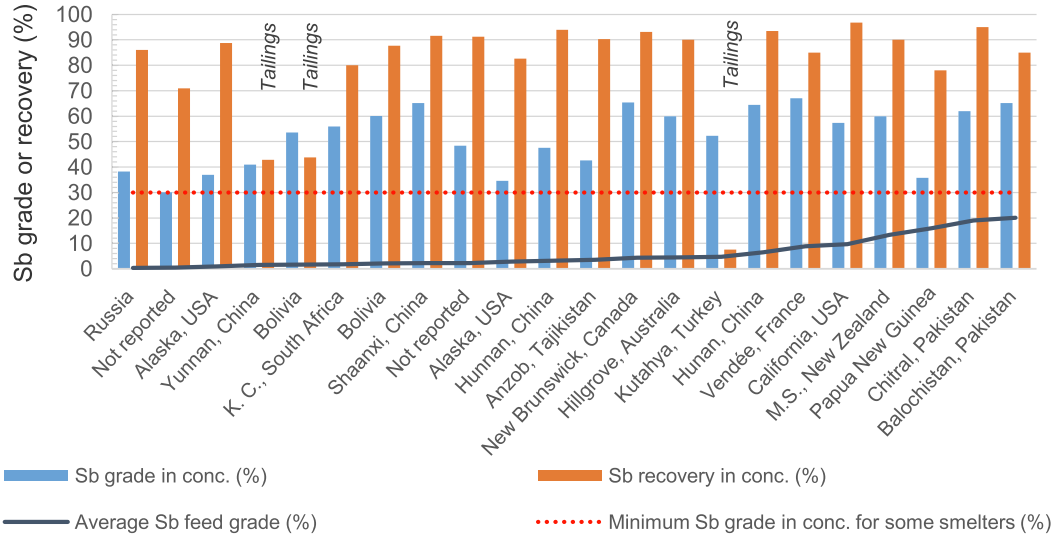


Fig. 5. Relationship between antimony content (%) in flotation feed and antimony recovery (%) and grade (%) in the final flotation concentrate for selected industrial and bench-scale studies on froth flotation of stibnite-bearing ores around the world. Data from Table 6 (minimum values for Sb grade and Sb recovery in concentrate have been reported in some cases).

of mineral particles partially liberated and/or containing antimony in an oxidised state (especially in old tailings), the presence of high amounts of slimes and/or other gangue compounds that interfere with the recovery of stibnite, and a lack of assertiveness with respect to optimal operating conditions (pH, reagent types, depressant dosage, etc.). Nevertheless, recovering antimony from tailings by froth flotation, although challenging, may be feasible, especially if most of the antimony content in tailings (comparable to that of some primary ores, as observed in Figure 5) is found as stibnite. If that is the case, tailings reprocessing may not only offer a revenue stream but a better opportunity for improving the environmental management of waste throughout the mine life cycle. Additionally, it would allow a partial reduction in some of the highest operating costs involved in conventional mining and processing, such as those related to blasting and comminution (Segura-Salazar and Tavares, 2018).

Antimony losses in tailings may be caused by the poor response to floatability of native antimony and antimony oxides (e.g. cervantite, valentinite, senarmontite) occurring in stibnite-bearing ores, and by the relatively slow floatability of certain antimony-bearing sulphides (berthierite, gudmundite) present in the ore to be floated (Davis et al., 1986). Another characteristic that affects the recovery of stibnite by froth flotation is its high friability (Ealedona and Fujita, 2006; Engel, 1949; Gülcan et al., 2019; Lager and Forssberg, 1989b), which may easily lead to overgrinding the ore and concentrate the antimony in the fine fractions. The presence of friable clay minerals such as kaolinite and illite can also contribute to the generation of undesirable slimes that increase the viscosity of the pulp and make it difficult to float stibnite (Wu et al., 2019). In this regard, an adequate geometallurgical plan that involves detailed mineralogical characterisation combined with sampling protocols as well as replicate comminution-flotation testwork and modelling tools should be adopted in evaluating any mineral resource (greenfield or brownfield projects) (Lotter et al., 2014; Thompson, 2016), either primary or secondary (e.g. tailings, waste rock) in nature. Such a plan should also consider the inherent variability across the orebody and, therefore, be based on representative samples of the different ore typologies (geometallurgical units) that can be potentially exploited and beneficiated at the mine site (Lotter et al., 2014; Thompson, 2016). In that sense, Erspamer and Wells (1956), for instance, illustrated how an unrepresentative, higher-grade sample of the Run-of-Mine ore may affect the flotation results and mistakenly result in an overestimation of the stibnite recovery and grade in the flotation concentrate.

The decrease in recovery and grade of stibnite in the concentrate at very fine or coarse particle sizes ("elephant curve"), a widely recognized phenomenon in froth flotation, was also reported at the microscale by Richards (1977). Indeed, some losses may occur at coarse sizes as stibnite may occur in finely disseminated grains within the host gangue matrix (Davis et al., 1986).

In a stibnite-cinnabar deposit from Alaska it was found that, although stibnite and cinnabar may be mostly liberated from gangue minerals at a particle size of about 150 μm (Erspamer and Wells, 1956; Town and Stickney, 1964; Wells et al., 1958), some finely disseminated grains of the target minerals may remain locked even in the −75 μm size fraction (Erspamer and Wells, 1956; Wells et al., 1958). In other stibnite deposits with relatively simpler mineralogy, it has been indicated that an optimal liberation of the stibnite even with finely disseminated grains can be achieved by grinding to approximately −105 μm (Engel, 1949). Richards (1977), on the other hand, reported that the optimal particle size for flotation of a relatively simple stibnite-bearing ore from New Zealand was found between 63 and 150 μm, on the basis of microflotation and bench-scale studies (the former are usually carried out on medium- to high-purity samples within this particle size range, as observed in Table 1).

Other authors have also reported stibnite liberation sizes relatively close to the aforementioned values. Bhatti et al. (2008), for instance, estimated that most of the stibnite analysed in an ore sample from Pakistan was liberated for a particle size around 150 μm. Gülcan et al. (2019) established that 86% or more of the stibnite from an ore sample from the Kütahya-Uşak region of Turkey appeared as liberated in the size fraction −106 μm. Among the studies analysed herein, the particle size specification for flotation has been defined in terms of the mass proportion of material passing a selected sieve, usually 150, 106 or 74 μm (Table 6). Some studies have evaluated the effect of characteristic particle size on the floatability of stibnite; it has been made clear that finer grinding increases the recovery of antimony in the final concentrate, although in some cases there might be a slight decrease in the antimony grade of the product due to entrainment (Table 6). In complex stibnite-bearing ores, a subsequent regrinding stage after a rougher bulk flotation might be required (Bhatti et al., 2014; Kanarskii et al., 2012).

Summarising, it is clear that aspects related to mineral liberation of

stibnite have been considered to a certain extent in a few studies. However, from the authors' perspective, there is still a need for a greater understanding of the effect of particle size and the degree of liberation of stibnite (and other valuable minerals, where applicable) per size fraction (as well as other key process variables) in the context of antimony recovery and grade in the flotation concentrate. In this sense, valuable insights could be obtained from quantitative mineralogical characterisation techniques such as Scanning Electron Microscopy (SEM) combined with Energy-Dispersive X-ray Spectroscopy (EDS or EDX) or X-ray micro tomography (μCT or XMT).

With regard to grinding, it is noteworthy to mention that a few publications have reported the addition of chemicals used as flotation reagents to the pulp at the grinding stage (Table 3, Table 4, and Table 6). However, the benefits of adding flotation reagents at this stage for stibnite-bearing ores have not been systematically studied. Additionally, there is a lack of knowledge regarding the physicochemical interactions that might occur in grinding and their impact on stibnite flotation.

4. Flowsheet design for stibnite recovery by froth flotation

Different flowsheets have been designed for the production of antimony concentrate from the exploitation and processing of stibnite-bearing ores. In cases where high-grade ores are combined with affordable and available labour, it is usual to find traditional hand-sorting as a pre-concentration stage (Schwarz-Schampera, 2014), as in the case of some mines in China, Bolivia and South Africa (Anderson, 2019, 2012; Grund et al., 2011), and as it was at New Zealand stibnite mines over a century ago (Richards, 1977). Further ore processing involves conventional stages of crushing and screening, followed by grinding alternating with classification and gravity concentration, and subsequent froth flotation (Anderson, 2019, 2012; European Commission, 2017a; Schwarz-Schampera, 2014), as observed in Figures 6, 7 and 8.

Typically, stibnite froth flotation at both industrial-scale and bench-scale for simple stibnite-bearing ores is performed using at least one rougher stage, and at least one cleaning stage to significantly enhance the antimony grade in the final concentrate. Various studies also report the incorporation of one or more scavenger stages (Figure 6). The complexity of the circuit configuration depends largely on the ore characteristics, more specifically of the proportion and association of certain gangue minerals, the presence of highly toxic components that must be removed from the product (e.g. As, Hg) and the presence of other commercially valuable minerals or metals (e.g. Au-bearing sulphides, cinnabar, etc.). While certain smelters can handle concentrates containing 30% of antimony (Senchenko et al., 2016; Thom, 1962), it has been widely reported that a saleable stibnite concentrate should contain 55–65% antimony (Ozkan, 2007; Richards, 1977; Thom, 1962). Also, as discussed in Section 3, some penalty elements such as arsenic could affect the quality of the concentrate. Thereby, some stibnite-bearing concentrates might need further processing before being marketable, examples being those obtained from bulk stibnite-cinnabar flotation (Table 6 and Figure 8a) or from the beneficiation of stibnite-bearing ores containing recoverable amounts of gold and scheelite (Hu, 1988) (Figure 8b). The latter is becoming one of the main sources of tungsten (another metal persistently listed as critical by the European Commission (2020, 2017b, 2014, 2010)) and is frequently recovered by froth flotation (Kupka and Rudolph, 2018).

For stibnite-bearing ores containing very finely disseminated and/or occluded gold (i.e. refractory gold ores (Haque, 1987)), antimony recovery in the final concentrate may be affected by the addition of cyanide in upstream gold leaching stages, as stibnite is soluble at high pH and binds cyanide (Lager and Forssberg, 1989b). Furthermore, stibnite decomposes to form thioantimonite (SbS_3^{2-}) and sulphide (S^{2-}) ions which inhibit gold to react with cyanide as these ions are adsorbed on the gold surface (Yannopoulos, 1991). Improved extraction techniques for these refractory gold-bearing concentrates (Figure 7) consist of oxidative pre-treatments including low-alkalinity high-pressure cyanidation (Davis et al., 1986; Haque, 1987; Morizot and Ollivier, 1993), bioleaching with *At. Ferrooxidans* (de Carvalho et al., 2019; Haque, 1987; Morizot and Ollivier, 1993; Torma, 1989; Ubaldini et al., 2000) and other microorganisms (Haque, 1987; Solozhenkin and Alekseev, 2010a; van Aswegen et al., 2007), nitric acid digestion and roasting, as

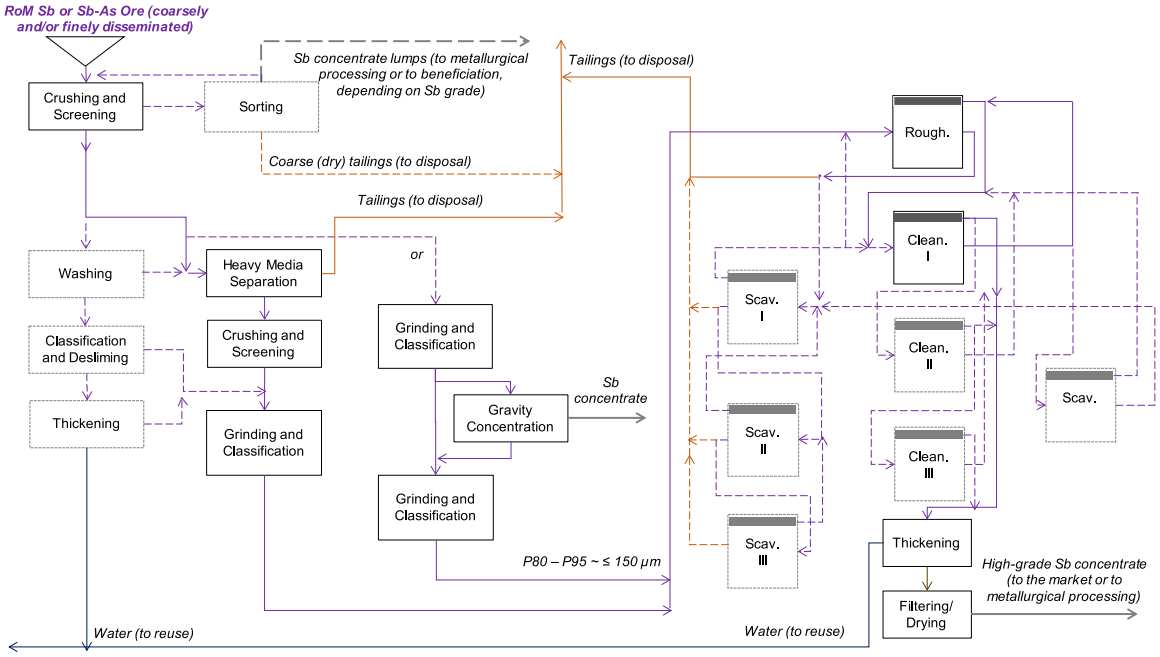


Fig. 6. Flowsheet of stibnite beneficiation for simple stibnite-bearing ores, based on the Xikuangshan plant (China) and other selected operations, as well as conceptual designs (laboratory testwork). Adapted from: Anderson (2019); Bhatti et al. (2008); Hu (1988); Lager and Forssberg (1989b); Morizot and Ollivier (1993); Richards (1977); Schwarz-Schampera (2014); Wu et al. (2019). Solid arrows represent the simplest processing route. Dashed lines represent alternative pre-concentration or beneficiation stages, depending on the mineralogy: ore grade and occurrence (coarse- or fine-grained), abundance of certain gangue minerals (e.g. talc, silicates), etc.

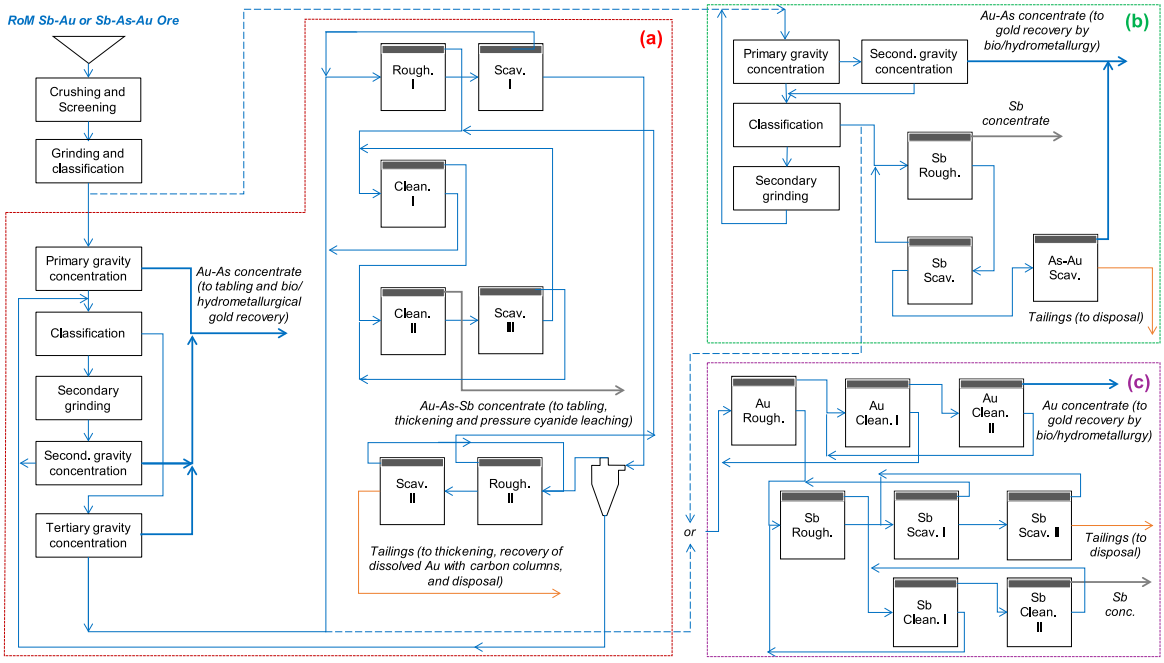


Fig. 7. Flowsheet of stibnite beneficiation for complex stibnite-bearing ores containing recoverable amounts of gold. Flowsheet based on the Consolidated Murchison operation in South Africa (a) and other processing circuits (b, c).
Adapted from: Ai et al. (2019); Davis et al. (1986); Lager and Forssberg (1989b); Morizot and Ollivier (1993)

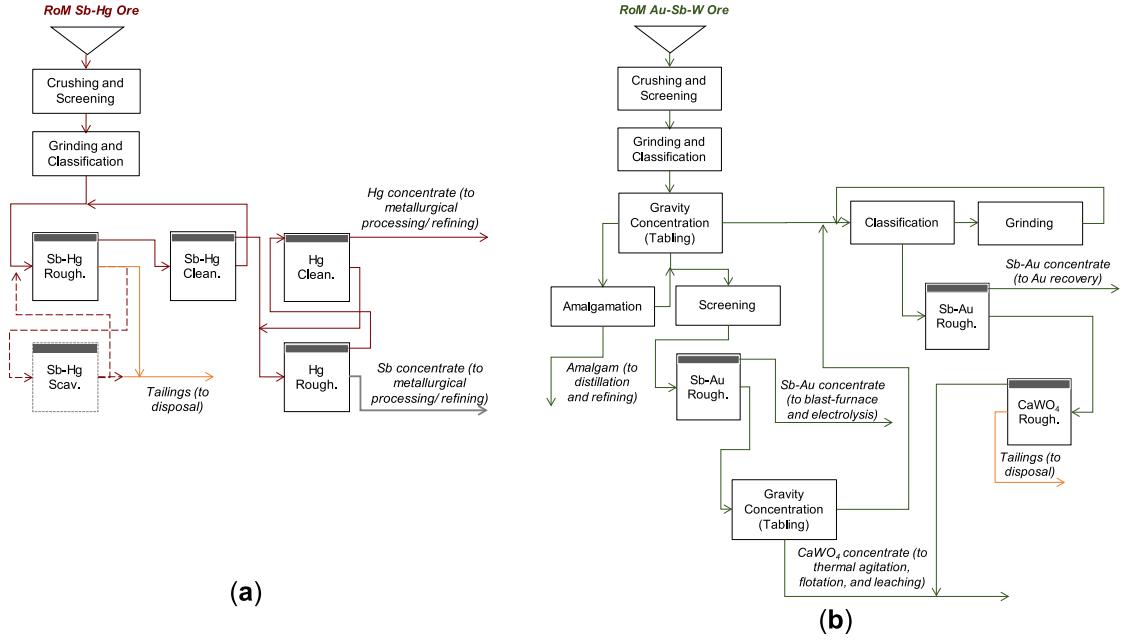


Fig. 8. Flowsheet of stibnite beneficiation for complex stibnite-bearing ores containing other valuable minerals. (a) Conceptual design of selective flotation of cinnabar and stibnite from Red Devil Ore, USA (Adapted from: Town and Stickney (1964); Wells et al. (1958)); (b) Flowsheet for the recovery of stibnite, gold and scheelite at the Xiangxi mine, China (Adapted from: Hu, 1988).

well as dissolution of gold with thiourea (Haque, 1987; Morizot and Ollivier, 1993), and microwave heating (Haque, 1999).

5. Environmental aspects and broader utilisation of antimony resources via froth flotation

5.1. Antimony in stibnite flotation tailings and wastewater

Antimony release to the environment is a major cause of concern, as it is a potentially toxic and carcinogenic element. Mining of antimony ores, often also associated with other toxic elements such as As, Hg and other heavy metals, risks pollution via the release of those elements to the air, water and soil, with significant environmental consequences. In line with the focus of this review, this section reports on the literature on environmental aspects directly related to stibnite flotation tailings and wastewater. For a broader discussion on environmental aspects linked to Sb mining, the reader is referred to Multani et al. (2016) and references therein.

Direct environmental impacts of stibnite flotation can be linked to the toxicity of reagents used and contaminants associated with the ore (as discussed in Section 2 and Section 3), the water consumed, and the flotation wastewater and tailings. Zhou et al. (2020) report that for every ton of stibnite ore processed in the flotation circuit at the Xikuangshan Antimony Mine in Hunan, China, 3.5 m^3 of water are consumed, while producing 920 kg of tailings and 0.2 kg of dust. Their comprehensive environmental study quantified the contribution of the tailings from the concentrator to the release of potentially toxic elements associated with mine waste, which is linked to inefficiencies in the processing stage.

Guo et al. (2018) studied the levels and speciation of antimony and other contaminants in waters and sediments from the Xikuangshan mine area. They found high concentrations of Na^+ as well as a direct link between Sb and Na^+ concentrations, which was attributed to the use of SBX in the flotation of stibnite. Sb speciation results confirmed the stability of Sb(V) in the water samples tested. One of the suggested mechanisms was that Sb(III) is generated during stibnite flotation that oxidises to Sb(V) when Fe/Mg (hydro)oxides (from reactions of pyrite in the slurry) act as catalysts. Importantly, particulate Sb was also suggested to be significantly present in the waters from the mine. According to Gradberg and Ou (1994) *apud* Zhu et al. (2011), Sb speciation in flotation wastewater heavily depends on pH, with variations found for $pH < 4$ or $pH > 9$.

Antimony speciation in aqueous systems occurs in the form of Sb(III) and Sb(V) (Multani et al., 2016). Thermodynamic data for Sb(III) and Sb (V) is, however, limited in the literature compared to other species, which might explain some discrepancies between experimental measurements and calculated Pourbaix diagrams for Sb (Multani et al., 2016). This can also occur if the oxidation of antimony has not achieved an equilibrium condition (Majzlan et al., 2011). Nevertheless, on the basis of the Pourbaix diagram, Sb has been reported to be mainly present as Sb(V) in the waters and tailings from the Beaver Brook antimony deposit in Canada (Borčinová Radková et al., 2020), and from the Dúbrava abandoned mine site in Slovakia (Ondrejková et al., 2013). Arsenic, whose main source is the weathering of arsenopyrite, has been predominantly reported in mine tailings and waters as As(V) (Borčinová Radková et al., 2020; Flakova et al. 2012; Ondrejková et al., 2013). Borčinová Radková et al. (2020) also reported dissolved arsenic as As (III) in tailings pore water samples, which suggested, according to the authors, that As oxidation kinetics was slower compared to that of Sb.

The treatment of Sb flotation wastewater from the Xikuangshan mine has also received some attention in the literature. Zhu et al. (2011) studied electrocoagulation as a technique to treat Sb flotation wastewater (also containing SBX as a pollutant), particularly investigating the effect of operating conditions on the removal efficiency, including the current density, redox potential, pH and the collector concentration. The authors reported that the treated flotation wastewater had concentrations below 1 mg/L (which is still high for a wide range of regulatory frameworks (Hansen et al., 2010)), while low removal rates of SBX were reported.

A review of other potentially useful techniques for Sb removal from aqueous solutions is also discussed briefly in Zhu et al. (2011) and Li et al. (2018). These include adsorption, coagulation, membrane separation, ion exchange, coagulation-flocculation, and solvent extraction. However, none of the publications cited, with the exception of a study on coagulation (Du (1995) *apud* Zhu et al. (2011)), correspond to applications specifically for Sb flotation wastewater. X. Wang et al. (2020) used Life Cycle Assessment (LCA) to quantify the potential environmental impacts of two different technologies for the remediation of Sb-rich water as a result of mine drainage. They concluded that bioreactors are environmentally advantageous compared to adsorption systems in several impact categories, although there is room for improvement in terms of the use of greener construction materials for the former. In general, there is a lack of LCA studies for antimony production and treatment, and more robust and detailed inventories for different ore types and geographical contexts are needed.

Majzlan et al. (2011) studied both Sb- and As-bearing tertiary minerals for the flotation tailing impoundments from the historic exploitation of the Sb-Au Pezinok deposit in Slovakia. While a significant fraction of stibnite from flotation reported into the tailings, the study found stibnite to be currently absent in the tailings, which was attributed to its rapid weathering. Tripuhyite ($FeSbO_4$) was identified as the main tertiary Sb mineral. Notably, Sb was found to be significantly retained in the impoundment, as opposed to As which was found to be mobile. According to Flakova et al. (2012), who also studied the behaviour of Sb and As at the Pezinok mining site, there seems to be a competition for the adsorption sites between those species and, thereby, the adsorption of Sb (V) affects the adsorption of As(V).

An example of phytoremediation of flotation tailings is discussed by Ranđelović et al. (2019), in which the technique is assessed as a potential remediation strategy for material from the flotation tailings dam from Stolice, Serbia, which collapsed following heavy rains in 2014. Phytostabilisation via *E. ramosissimum* showed potential as a complementary strategy for Sb and other heavy metals present in the tailings and soil around the site.

5.2. Recovery of antimony oxides from stibnite-bearing deposits by froth flotation

The use of sulphidising agents (Na_2S, NaHS) as potential activators of oxidised antimony minerals has been attempted in stibnite froth flotation. This application has been recommended for oxidised minerals of metals such as Pb, Zn and Cu (Wills and Finch, 2016). However, the addition of these reagents might result in an increase in the pH of the pulp and the formation of hazardous gases (H_2S). Moreover, an excess in their dosage could compromise the flotation efficiency by causing a depressing effect in the sulphide minerals (e.g. stibnite) and also by reducing the availability of dissolved oxygen, which is required for the adsorption of sulfhydryl collectors on the mineral surface (Wills and Finch, 2016). The possible occurrence of such phenomena might explain the fact that a marginal or no benefit in the overall Sb recovery was observed when adding sulphidising agents to the pulp, according to the results reported by Ealedona and Fujita (2006), Gülcan et al. (2019), and Güven et al. (2012).

Indeed, antimony oxides are difficult to recover by froth flotation, especially due to their poor response to xanthate collectors (Lager and Forssberg, 1989a) and also because of the challenge that involves separating such minerals from gangue minerals that frequently occur in stibnite-bearing deposits, such as quartz and calcite (Qin et al., 2017). Some of the reasons argued by Qin et al. (2017) that contribute to the poor floatability of antimony oxide are: the relatively low hardness of these minerals, and the consequent trend to overgrind them and create slimes that affect flotation efficiency; the possible similarity in the

flotation behaviour between quartz and antimony oxides such as cervantite; and the tendency of antimony oxides to form hydrophilic compounds such as $HSbO_2$ or $HSbO_3$.

Improving antimony oxide froth flotation at laboratory scale has drawn research attention in recent decades. Recovery enhancement of antimony oxides by froth flotation has been sought through the combination of metal salts (copper, manganese or lead salts) as activators with a range of alternative collectors (oleic acid, sodium dodecyl sulphate, dodecylamine, hydroxamic acid, and others) (Qin et al., 2017; Y. Wang et al., 2017). Microflotation tests carried out by Changhuai (1997) at pH 7.5 indicated that manganese ions (Mn^{2+}) activated the antimony oxide surface and enhanced its floatability and selective separation from silicified limestone when a composite collector containing hydroxamic acid was also used. X-ray diffraction analysis revealed the presence of Sb_2O_3, Sb_2O_5 and $MnSb_2O_4$ in the antimony oxide concentrate. Moreover, the addition of modified water glass improved the depression of the gangue mineral without affecting the floatability of the antimony oxides. More recent microflotation studies supported by zeta potential and other measurements showed that cervantite (Sb_2O_4) could be selectively separated from quartz either by: 1) using sodium oleate collector and a copper salt ($CuCl_2$) as an activator through direct flotation at slightly acidic to neutral pH (around 6.5–7.0) (Wang et al., 2018); or by 2) using dodecylamine as a collector by reverse flotation at pH 10.5 (J. Wang et al., 2017).

Gravity concentration (e.g. shaking tables) has been traditionally used to recover antimony oxides (Changhuai, 1997). It can also be combined with enhanced antimony oxide flotation to facilitate the sourcing of antimony from oxides (Qin et al., 2017), which occur in primary deposits but are also contained in other resources, including mining waste and tailings. Furthermore, recent studies have suggested that ore pretreatment by sulphidisation roasting followed by froth flotation with stibnite flotation reagents (e.g. lead nitrate activator, xanthate/dithiophosphate collector, pine oil frother) allows the recovery of antimony from cervantite, an important antimony oxide (Qin et al., 2017; Wang et al., 2014). The formation of a sulphide layer of Sb_2S_3 has been considered to be the key factor that turns cervantite hydrophobic. Furthermore, the floatability of sulphidised cervantite improves with the increase in the sulphide layer thickness, the latter depending on the operating conditions (Y. Wang et al., 2017).

6. Final remarks and opportunities for future work

An abrupt drop in publications regarding the flotation of stibnite at micro-, bench-, and industrial-scale has been observed between the 90s and early 2000s, which might have been related to the decline in antimony prices in the global market during that period. This trend was reversed over the last two decades (USGS, 2020b) and now antimony raises concerns in terms of its future supply and environmental management, which has also been reflected in the increased research on stibnite froth flotation. Interestingly, what used to be a low-grade stibnite-bearing ore over a century ago (around 20% Sb (Hulst, 1919)) is now considered as a high-grade flotation feed (Figure 5). This has been largely possible thanks to the technological improvements in mineral processing, and particularly in froth flotation, which have made it profitable to exploit increasingly complex ores.

While microscale flotation studies have allowed us to get insightful views on the phenomena that occur at the stibnite mineral surface with and without the influence of certain reagents, these studies have fallen short when it comes to bringing the results into practical application at a larger scale. Contact angle measurements based on improved capillary penetration methods (Chau, 2009), and the systematic study of those measurements as a function of physical and chemical parameters (particle size, particle shape, heterogeneity, roughness, surface active agents) have been suggested as a way to gain insights for further correlation with batch flotation tests and thus move towards a more practical implementation (Chau, 2009). Another approach to compare the performance of collectors could be in terms of the dynamic bubble surface coverage at the bubble-particle scale, as suggested by P. Wang et al. (2020). This approach relies on a combination of kinetic particle attachment tests with image processing (P. Wang et al., 2020) and has proved to provide more information than conventional contact angle measurements on polished plates, allowing differentiation of the collecting ability between reagents by considering the kinetics of attachment. Such type of studies can also be benefited from detailed investigations on zeta potential measurements to assess the effect of flotation reagents on mineral surface potential changes.

On the other hand, fundamental research on froth flotation has increasingly benefited from the use of molecular simulation tools based on Density Functional Theory (DFT) and other methods over the last decade or so (Foucaud et al., 2019). This has not been the exception for stibnite, as observed in Table 1 and in other studies where molecular simulation has been used to explore the interaction of stibnite with different types of collectors (Kanarskii and Solozhenkin, 2014; Solozhenkin, 2016). Nevertheless, there is still room in terms of having a deeper knowledge concerning the differences in adsorption behaviour of long-chain vs. short-chain xanthates and their interactions with metal salts, depressant mechanisms, among others. Therefore, molecular simulation seems a promising approach for the evaluation and formulation of alternative reagents and/or mixtures for the flotation of complex stibnite-bearing ores, especially when it is complemented with experimental research.

Regarding bench-scale and industrial-scale studies, these have been useful to test reagent combinations and their effect on the recovery and grade of the concentrate obtained from stibnite-bearing ores of varying complexity. There have been, however, some challenges in terms of the lack of adequate reporting in some of these studies, particularly concerning reagent types and dosages, which in some cases could be understood due to confidentiality reasons.

Exploring the relationship between ore characteristics, upstream processing and froth flotation is also another topic that might be examined in future work on stibnite-bearing ores. This could be achieved, for instance, by evaluating the benefits of using advanced technology (e.g. preconcentration, comminution, and grinding assisting technologies) and/or different grinding conditions (grinding media, dry vs wet grinding, grinding electrochemistry, etc.) on the selective recovery of stibnite and co-products, and on the overall process performance. Quantitative mineralogical characterisation techniques (SEM/EDS, XMT) could provide valuable support for this type of studies. Furthermore, it is worth highlighting the importance of adopting a geometallurgical plan for stibnite-bearing deposits that allows the new (flotation) operations to deal with technical difficulties that might arise from the lack of knowledge about the inherent variability of the Run-of-Mine ore and its effect on process performance (Lotter et al., 2014; Thompson, 2016).

The use of systemic, rather than an approach based on “silos” is progressively becoming more necessary in the context of more sustainable mineral processing operations, such as in the case of water reuse (Liu et al., 2013). As water demand is unavoidable in froth flotation, it is also of paramount importance that future research efforts are focused on the understanding and quantification of the effects of water quality on stibnite froth flotation performance; this could allow envisaging improvements in the water reuse system if required by a particular mine site.

Regarding the use of reagents, while long chain xanthate collectors and lead nitrate as activator have become the standard formula in stibnite froth flotation for many decades, it has also been clear that it is feasible to use alternative reagents without compromising stibnite flotation performance. Those include copper sulphate activator (less toxic than lead salts), dithiophosphate (optimal performance at acidic pH, good selectivity towards arsenopyrite) or mixed collectors, and various (bio)depressants. The synergy between the first two, however, has been overlooked (as observed in Table 3, with an exception made for

the study of Ealedona and Fujita (2006)), and should be confirmed in practice, particularly at acidic pH. In relation to (bio)depressants, these have been mostly evaluated at laboratory-scale, which certainly demands more efforts directed towards the application of these reagents at a commercial scale. Moreover, a holistic evaluation of new combinations of flotation reagents across scales (i.e. from micro-flotation tests to bench-scale, pilot-scale and industrial-scale application) should consider key aspects including technical performance (e.g. kinetic behaviour, selectivity), possible differences in the properties of the reagents obtained from different suppliers, cost-benefit analysis and potential hazards to health and to the environment (Fuerstenau et al., 2007; Pradip, 1988) throughout the life cycle of these products, among others.

Reprocessing of antimony legacy deposits is also seen as a potential contribution to more sustainable sourcing of antimony. Nevertheless, there are some challenges that should not be overlooked from the perspective of froth flotation, particularly in fine tailings management, such as dealing with high amounts of ultrafine clays and/or oxidised antimony minerals, the latter being hardly recoverable by froth flotation with conventional reagents and flotation technology. From a conceptual point of view, a combination of processing methods involving gravity concentration, grinding in closed circuit with classification, desliming, sulphidisation roasting and/or enhanced flotation would be a potential approach that needs to be confirmed in industrial practice.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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