A Brief Review of Auriferous Sulphide Flotation Concentration; Pyrite and Arsenopyrite Mineral Separation

P. Forson, 1,2M. Zanin, 1W. Skinner and 1R. Asamoah
1University of South Australia, Future Industries Institute, SA, 5000, Australia
2MZ Minerals, Mineral Processing Consulting, SA, 5000, Australia


Abstract

Pyrite, the most abundant sulphide mineral in the earth crust is mostly found in close association with arsenopyrite in most auriferous complex ore bodies. Previous studies on occurrence of gold in these sulphides has shown the preferential preconcentration of gold in arsenopyrite compared with pyrite. Notwithstanding, in the separation of gold bearing sulphides during froth flotation, a concentrate made up of both pyrite and arsenopyrite is obtained due to their similar characteristics and flotation response. Separation of gold predominated arsenopyrite minerals from less economical pyrite phase maximises downstream unit feed and improves financial performance of the operation. This paper briefly reviews attempts made thus far in exploiting subtle differences between pyrite and arsenopyrite for separation. The underlying reported flotation mechanism for both minerals is illustrated.

Keywords: Differential flotation, Grade engineering, Selectivity, Pyrite, Arsenopyrite

1 Introduction

Froth flotation is an important step in concentrating mineral of interest from their gangue (Shean and Cilliers, 2011). The technique relies on differences in the surface wetting properties of minerals to separate them, that is, hydrophobic particles are floated as concentrate whereas the hydrophilic fraction are depressed and remain in the pulp as tailings (Farrokhpay, 2011).

Sulphide minerals are important sources of metals extracted in the world (Vaughan, 2013). For refractory gold ores characterised by nanoparticulate inclusion of gold in sulphide matrices, pyrite and arsenopyrite are the major economic host (Arehart et al., 1993; McCarthy et al., 2018; Zhang et al., 2016; Asamoah et al., 2014). These are jointly floated as concentrate for downstream processing. Notwithstanding, arsenopyrite and arsenic-rich pyrite have shown preferential association with gold compared to arsenic-free pyrite (Asamoah et al., 2019a; Asamoah et al., 2019b; Chryssoulis and McMullen, 2016; Reich et al., 2005; Asamoah et al., 2015). This preferential occurrence is of the order arsenopyrite > arsenian pyrite > arsenopyrite. Reich et al. (2005) demonstrated the relationship between arsenic content and gold concentration from a compilation of SIMS and EMPA data from several deposits (Figure 1) and proposed an equation (Equation 1) which evince and define limits where native and solid solution gold is observed. Thus, the addition of a process step that separate gold-rich pyrite and arsenopyrite fraction from pyrite is preferred and holds promise in favoring project economics. Additionally, recalcitrant secondary
mineral formation due to complex relationship between some barren sulphides and other gangue phases will be eliminated in a highly selective float and its impact on downstream pretreatment process nullified (Asamoah, 2020; Asamoah et al., 2018; Asamoah et al., 2014). It is noteworthy that, although the formation of arsenian pyrite and subsequent gold occurrence is not fully understood at present, the inclusion of nanosized gold-bearing arsenopyrite in pyrite has been proposed (Reich et al., 2005; Simon et al., 1999; Wells and Mullens, 1973).

\[ C_{Au} = 0.02C_{As} + 4 \times 10^{-5} \]  

(1)

This brief review paper presents a summary of the attempts made thus far to separate pyrite from arsenopyrite. Control of pulp chemistry parameter in xanthate system is elucidated shedding light on the mechanism involved in the separation process. The use of depressants and selective collectors is also briefly discussed.

2 Surface Oxidation and Collector Adsorption Mechanism

2.1 Oxidation of pyrite and Arsenopyrite

Froth flotation is a physicochemical process and warrants an in depth understanding of mineral surface alteration typically in aqueous solution for flotation (Dong et al., 2019, Wills and Finch 2016). The mineral oxidation dictates the surface species formation as well as flotation kinetics (Bonnissel-Gissinger et al., 1998; Corkhill and Vaughan, 2009). Presented herein is a brief classification of the surface oxidation species formed on pyrite and arsenopyrite in the acidic and alkaline regimes in aqueous solution.

Under acidic condition, the surface of arsenopyrite is depleted in Fe and As coupled with surface restructuring forming a pyrrhotite-like phase (Buckley and Walker, 1988; Mikhlin and Tomashevich, 2005; Richardson and Vaughan, 1989). Contrary to this observation, a surface dominated with As(III) and As(V) along with Fe(II)-arsenite, Fe(III)-arsenate and minor elemental sulphur was observed by Costa et al. (2002). In a systematic study using XANES, a surface composed of Fe and As-rich overlayer with S-enriched layer beneath was confirmed by Mikhlin and Tomashevich (2005). On the other hand, Fe(II) and Fe(III) (hydr)oxides constituting about 19% of the total Fe was found on the surface of pyrite (Bonnissel-Gissinger et al., 1998). At low pH conditions, surface-bound thiosulphate in addition to elemental surface has been reported elsewhere (Druschel and Borda, 2006; McGuire et al., 2001; Schippers et al., 1996). Clearly, contradictory reports on arsenopyrite and pyrite surface species exists in literature under acidic conditions.

Arsenite, Fe(II), Fe(III) and S are the main products of oxidation on arsenopyrite surface in alkaline solutions (Buckley and Walker, 1988; Richardson and Vaughan, 1989). In addition to an overlayer composed of Fe(III)-arsenite, Fe(III)-arsenate and Fe(III)-sulphate, Hacquard et al. (1999) demonstrated that arsenopyrite surface was heavily oxidised in a solution at pH 10. Using XPS, the authors observed an almost complete oxidation of
Fe(II) to Fe(III) and the oxidation of As(-1) to As(V). Polysulfide, sulfate and disulfide were also present on the mineral surface (Hacquard et al., 1999).

An increase in the growth of surface iron (hydr)oxides is observed on pyrite surface at alkaline pH with a stoichiometry close to that of ferric hydroxide (FeOOH) (Bonnissel-Gissinger et al., 1998). A predominance of OH groups generally populates the mineral surface in alkaline solutions (Bonnissel-Gissinger et al., 1998).

Generally, ferric (hydr)oxide and arsenate species confer hydrophilicity on the mineral surface (Abeidu and Almahdy, 1980; Sirkeci, 1993). More so, they inhibit the collector adsorption and subsequent flotation (López Valdivieso et al., 2005). Conversely, elemental sulfur and pristine surface promote collectorless flotation and interaction with collector respectively (López Valdivieso et al., 2005; Trahar et al., 1994). The flotability of the mineral at any given condition is dependent on the ratio of hydrophilic surface oxidation product and hydrophobic collector species (Bulut et al., 2002; Fuerstenau et al., 1969; Tao et al., 2018).

2.2 Collector Adsorption Mechanism

Thiol collectors, specifically xanthates are mostly used in the flotation of sulphides (Dunne, 2005) and require careful control of pulp chemistry parameters to achieve selectivity in flotation (Hu et al., 2010). To this effect, a wide range of investigations have been carried out to understand the collector adsorption mechanism (Hu et al., 2010). This endeavour has been extensive in systems where both gangue and mineral of interest share same mechanism of collector adsorption as is for pyrite and arsenopyrite. Amongst several mechanisms proposed for flotation of these minerals, the mixed potential model is widely accepted (Cheng and Iwasaki, 1992; Hu et al., 2010; López Valdivieso et al., 2005). This mechanism proposes an anodic oxidation of xanthate to dixanthogen on the mineral surface with a corresponding reduction of oxygen as the cathodic half equation. A more refined form of this mechanism suggests a simultaneous removal of ferric hydroxide from the mineral surface when dixanthogen is formed (López Valdivieso et al., 2005). The overall reaction is given in Equation 2 and demonstrated in Figure 2.

$$2\text{Fe(OH)}_3(s, \text{surf}) + 2X^- + 6H^+ = X_2(l, \text{surf}) + 2\text{Fe}^{2+} + 2\text{Fe}^{3+} + 6H_2O \quad (2)$$

![Figure 2 Schematic of the adsorption of xanthate ion on mineral surface (López Valdivieso et al., 2005)](image-url)
3 Separation of Pyrite and Arsenopyrite

3.1 Pulp Chemistry Control

Pulp pH is one of the most significant parameters in deciding the flotability and selectivity of sulphides (López Valdivieso et al., 2006). For both pyrite and arsenopyrite, high flotation recoveries are achieved under acidic pH conditions proposed to be as a result of elemental sulphur as well as a high ratio of dixanthogen to surface oxidation product (Choi et al., 2013; Guongming and Hongen, 1989; Park et al., 2015; Zhang and Zhang, 2014). Conversely, a window for selectivity exists between near neutral and middle alkaline condition. Chanturiya et al. (1998) investigated the floatabilities of pyrite and arsenopyrite with different mineralogical peculiarities and observed a decrease in adsorbed dixanthogen and subsequent depression of arsenopyrite whereas pyrite retained good collector absorptivity between pH 6.5-12 (Figure 3). Their observation agrees with the works of Li et al. (1992) and Abeidu and Almahdy (1980). Along this line, Kim (1993) floated pyrite while depressing arsenopyrite at pH 10.5. Depression of the arsenopyrite in alkaline conditions was associated with an increase in surface oxidation product which has a higher coverage on arsenopyrite than pyrite treated under the same conditions (Abeidu and Almahdy, 1980; Li et al., 1992; López Valdivieso et al., 2006; Zhang and Zhang, 2014). It is important to note that, the depression of the minerals at alkaline conditions is nullified with an increase in collector concentration and hence a critical collector concentration is often required for high selectivity (Mu et al., 2016).

From both electrochemical and thermodynamic standpoint, flotation of sulphides is strongly Eh-dependent (Plackowski et al., 2012). Interestingly, pulp pH interplays with pulp potential in the flotation process. Typically, a unit increase in solution pH leads to a decrease in the oxygen reduction process by 59 mV (Bonnissel-Gissinger et al., 1998). As a result, low pulp potentials are recorded in alkaline solutions.

![Figure 3 Floatability of pyrite and arsenopyrite as a function of pH (Asp-Arsenopyrite; Py-pyrite). Adapted from Chanturiya et al. (1998)](image_url)

Using cyclic voltametric study, Vreugde (1982) prescribed the addition of oxidants to increase Eh and facilitate the formation of ferric hydroxide on arsenopyrite surface whereas pyrite remained unaffected. Park et al. (2015) proposed that, the flotation separation of pyrite from arsenopyrite was possible at high Eh because ferric arsenate; a stable hydrophilic species on arsenopyrite was affected by high Eh than pyrite. On the contrary, Kydros et al. (1993b) used reducing modifiers sodium dithionite and sodium sulphite to depress arsenopyrite while floating pyrite. A similar observation was made by Matis et al. (1992) who used sodium metabisulphite and hydrazinium sulphate to control pulp potential. These showed promising results in the depression of pyrite from a bulk concentrate made up of pyrite and arsenopyrite although pyrite recovery was generally low (<60%).
3.2 Selective Oxidation

Pyrite and arsenopyrite exhibit different oxidation kinetics (Ma and Bruckard, 2009; Monte et al., 2002; Ran et al., 2019). Primarily, crystal structure differences and atom arrangement are the reason for this observation (Plaksin, 1959). Under acidic conditions, oxidation rate 3-4 orders of magnitude have been reported for arsenopyrite higher than pyrite (McKibben et al., 2008). Furthermore, using density functional theory, Fe is arsenopyrite has been shown to be more reactive than that found in pyrite (Li et al., 2015). Pursuance of this difference in their separation had led to the use of several oxidants in the flotation process.

Chlorinated lime was used to depress arsenopyrite during the flotation of pyrite (Guongming and Hongen, 1989; Qian et al., 1993). The formation of a hydrophilic films made up of arsenate and sulphate was proposed to be a major contributor to the depression of arsenopyrite. It can be concluded from these studies that, the surface oxidation product formed on pyrite was easily washed off whereas that on arsenopyrite was very stable. In the same way, potassium permanganate, hydrogen peroxide, sodium and calcium hypochlorite and potassium dichromate have been exploited (Chen et al., 2019; Herkenhoff, 1944; Lin et al., 2018; Monte et al., 2002; Subramanian et al., 2005; Tuteja et al., 1992; Vreugde, 1982). An increase in surface oxidation species on arsenopyrite compared with pyrite was the assigned reason. Removal of the surface oxidation products using EDTA extraction can restore floatability (Wang and Forssberg, 1990). Inference based on differences in flotation recoveries for selected studies in which two or more oxidants were compared reveal oxidant selectivity in the order; Hydrogen peroxide > potassium permanganate > (sodium/calcium) hypochlorite > potassium dichromate (Chen et al., 2019; Tuteja et al., 1992; Vreugde, 1982).

To achieve a high Au:S ratio, John (2017) used different acids (nitric acid and sulphuric acid) to ascertain their oxidation potential on pyrite and arsenopyrite and inform conditions for selectivity. Amongst the acids tested, nitric acid excelled in oxidising arsenopyrite more than pyrite, thus, its use in separation of pyrite and arsenopyrite was proposed. A novel approach which involves the use of low temperature oxygen plasma pretreatment was also used to successfully depress arsenopyrite while pyrite was floated. The dissolution rate of arsenopyrite under this treatment was high than pyrite and aided in their differential flotation (Ran et al., 2019).

Galvanic interaction between minerals and with grinding media has an impact on the oxidation of pyrite and arsenopyrite (Pozzo and Iwasaki, 1989). Pyrite is the noblest of sulphide minerals and acts as a cathode and enhances the oxidation of less noble minerals (Hu et al., 2010) as shown in Figure 4.

Monte et al. (2006) showed that pyrite rest potential was doubled while that of arsenopyrite drop by 50% when both minerals were placed in galvanic contact. This observation corroborates with the work Urbano et al. (2008) who noticed that oxidation of pyrite in arsenopyrite was delayed and displaced to more negative potential using a combination of cyclic voltammetry and SEM EDS study. Additionally, the use of electrochemically active grinding media
contributes to high production of oxidised species on the surface of arsenopyrite (Huang, 2005; Huang et al., 2006).

### 3.3 Depressants and Selective Collectors

Magnesium ammonium mixture (MAA) made from a combination of MgCl$_2$.6H$_2$O + NH$_4$Cl + NH$_4$OH dissolved in distilled water has been employed in the depression of arsenopyrite (Abeidu and Almahdy, 1980; Li et al., 2019; Tapley and Yan, 2003). An admixture of pyrite and arsenopyrite was separated in the presence of MAA by Tapley and Yan (2003) where the authors conjectured the formation of a hydrophilic AsO$_4$NH$_4$Mg$_2$H$_2$O layer exclusive to the surface of arsenopyrite. Recoveries of 62.1% and 25.5% for pyrite and arsenopyrite, respectively, were achieved under an optimal condition of 250 mg/l MAA, pH 8 and 2.14 x 10$^{-4}$ sodium ethyl xanthate concentration as shown in Figure 5. Similarly, flotation involving the use of several amines showed that 2-coco 2-methyl ammonium chloride was able to produce a concentrate rich in arsenic and gold, however, solids recovery was low (Mavros et al., 1993).

![Figure 5 Separation of pyrite and arsenopyrite in the absence and presence of MAA and pre-aeration (Tapley and Yan, 2003)](image)

Kydros et al. (1993a) employed cetyltrimethylammonium bromide as collector in the selective flotation of arsenopyrite from pyrite. The pH of solution was held between 3.5-4.5 and required careful control of collector addition. Arsenopyrite and pyrite recovery of 87% and 40% were achieved in the concentrate.

A combination of xanthate, 2-hydroxypropyl ester diethylidithiocarbarnino acid (HPEDEDCA) and oak bark extract (OBE) in a ratio of 1:0.5:(0.5-1.5) showed promise in separating pyrite from arsenopyrite (Chanturiya et al., 2011). The reagent recipe succeeded in depressing arsenopyrite but had little effect on the flotation of pyrite (Chanturiya et al., 2011). Potassium cyanide has shown good depression potential for arsenopyrite (David and Quast 1991). Qian et al. (1993) used a new reagent ‘L’ to effectively depress arsenopyrite and float pyrite even in the presence of cuprous ions. Physisorption of Portland cement on arsenopyrite and subsequent depression aided in its differential flotation from pyrite (Kim, 1993). Patented by Beattie and Duteroue (1992), sulphitic depressing agent (SO$_2$ gas) and xanthates were used to depress arsenopyrite at elevated temperature (40-70 °C). Chen et al. (2010) found the use of tertiary dodecyl mercaptan (TDM) as an effective collector in producing bulk arsenopyrite and pyrite concentrate. The high recovery (90.8%) and grade of concentrate (81.1 g/t from a feed assaying 2.9 g/t) suggests good selectivity with the collector.

Thiol collectors other than xanthates have been investigated with proven selectivity. A two-stage flotation process involving dithiophosphate float at pH 11 and copper sulphate plus dithiocarbamate float developed by O’Connor et al. (1990) produced a concentrate with 74.8% arsenopyrite and 8.4% pyrite. Parameters such as aging of the ore and particle size had an impact on the selectivity. Wilcox et al. (2012) reported a sequential flotation scheme where pyrite was depressed at pH 11 using lime followed by copper activation and thionocarbamate
flotation of arsenopyrite at the same pH. 90% arsenopyrite and 18% pyrite recovery was achieved but no light was shed on the mechanism involved in the separation of the mineral pair.

Sirkeci (1993) investigated the use of a chelating agent; hexylthioethylamine hydrochloride (HTA) in selective flotation of pyrite from arsenopyrite and quartz. Pyrite recovery into the concentrate was 69.1% with 4.9% arsenopyrite recovery (Figure 6). The author proposed out of several possible adsorption mechanisms that, above pH 9.3, -NH+3 group in HTA losses its proton so a lone pair of electrons is left in the -NH2 group. The electron is donated to Fe in a higher oxidation and per the crystal arrangement of these minerals, Fe fully exposed on the surface of pyrite compared to arsenopyrite facilitated the interaction of HTA and subsequent flotation of pyrite (Sirkeci, 1993; Sirkeci, 2000a; Sirkeci, 2000b).

![Figure 6 Flotation recovery of pyrite, arsenopyrite and quartz with 10^{-5} mol/l HTA concentration](image)

4 Conclusion

Dixanthogen is the collector species responsible for the flotation of both pyrite and arsenopyrite using xanthates. Although both minerals interact with collector the same way, differences in the surface oxidation rate and extent can be employed in a selectively floating pyrite and depressing arsenopyrite. Separation using differences in surface oxidation is more feasible in the alkaline environment than acidic pH where contradictory mechanisms are reported.

Use of chelating agents such as hexylthioethylamine hydrochloride have great potential in obtaining a high selectivity. An understanding of their interaction with the mineral surface would go a long way to help streamline the process for optimization.

Interaction of amines with arsenates on the surface of arsenopyrite can also be exploited in the development of new reagents that are mineral-specific in obtaining a finer separation.

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Authors

Philip Forson holds a BSc. (Hons) in Minerals Engineering from the University of Mines and Technology, Tarkwa, Ghana in 2017. He did a year of National Service with Golden Star Resources at its Bogoso Mine as a Graduate Metallurgist and later for the Group as a Business Improvement Officer-Lean Six Sigma. Currently, he is a PhD candidate at the Future Industries Institute of the University of South Australia in Adelaide. He is a member of the South African Institute of Mining and Metallurgy (SAIMM) and the Australasian Institute of Mining and Metallurgy (AusIMM).

Richmond K. Asamoah obtained his BSc. (Mineral Engineering) and PhD (Minerals and Resources) degrees from the University of Mines and Technology (UMaT), and the University of South Australia (UniSA), respectively. He has over nine years of experience in mining companies, consulting firms and education institutions. He is currently a Senior Research Officer at the Future Industries Institute of the University of South Australia.

Max Zanin is an Associate Research Professor in Mineral Processing and the CEO of MZ Minerals; a mineral processing consulting firm. He holds a BEng (Hons) in Mineral Processing Engineering (University of Trieste) and a PhD in Geo-engineering (University of Cagliari). He holds a solid network of contact within the industry and other research institutions worldwide.
William Skinner is a Research Professor and Strand Leader for Minerals and Resource Engineering at the Future Industries Institute at the University of South Australia. He is an Applied Physicist, specializing in surface and interface science and application of surface spectroscopies, including synchrotron-based techniques. He has 26 years of experience in minerals processing and geochemical sciences and the role of surface chemistry in flotation and hydrometallurgy.