

# Laboratory flotation study of the DPM Krumovgrad gold ore (Bulgaria) – Effects from improved collector suite and ore desliming

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## ABSTRACT

A laboratory-scale investigation was conducted to study the effects of flotation reagents and clay minerals on the recovery of electrum from the ore treated at the Dundee Precious Metals Krumovgrad operation. The first part of the study focused on assaying the impact of clays on gold flotation by conducting desliming tests prior to flotation. It was observed that when a large portion of the fines (<10 μm) was removed through desliming, the gold grade in the concentrate increased by a factor of 9. However, this improvement was accompanied by a slight decrease in recovery. Furthermore, a new collector suite was tested in order to increase gold recovery and reduce the dosage of potassium amyl xanthate (PAX) by replacing the current promoter (AERO®238) with a new one called AERO MAXGOLD™900. The best combination was found to be 95 g/t of potassium amyl xanthate supplemented with 4.5 g/t of AERO MAXGOLD™900. The addition of this reagent was seen as a practical method to increase the gold grade in the concentrate, although it did not significantly improve the recovery rate. The potential relevance of the results to deposits and operations with similar characteristics are discussed.

## 1. Introduction

Gold flotation is a commonly practiced as a pre-concentration step before pressure oxidation or cyanidation of ores containing precious metals (Faraz et al., 2014). When gold is present in the gangue phase or hosted in minerals like quartz, mica, or iron oxides, its direct economic recovery by flotation is rare, unless the grades are sufficiently high (Allan & Woodcock, 2001). In such cases, flotation could become a cost-effective method for concentrating gold (Bulatovic & Wyslouzil, 2000). This is particularly true for the Krumovgrad mine in Bulgaria, where precious metals concentrate is recovered by floating electrum from the epithermal Ada Tepe deposit, which has average grades of 5 g/t Au and 3 g/t Ag.

### 1.1. Gold and electrum flotation

Despite gold's well-known hydrophobic nature, use of collector is quite often required to achieve satisfactory metallurgical results inside processing plants (Gardner & Woods, 1977b; Smith, 1980). For more than a century, a large panel of collectors have been studied to maximize the recoveries and rate of gold in flotation. The most commonly used

collectors for gold flotation are the xanthates, especially ethyl/butyl and amyl xanthate (NaC<sub>2</sub>H<sub>5</sub>OCSS). Potassium amyl xanthate (PAX) is not the collector offering the higher hydrophobicity of gold particles (because of its short alkyl chain), but it is a good compromise with its good surface coverage due to the few steric hinderances on the particles surface (Moncayo-Riascos & Hoyos, 2017). Several mechanisms can explain the interaction gold particles - xanthate, however, the chemisorption mechanism is considered as the preferred interaction route. It has the advantage to occur at wide ranges of pH and Eh (Allan & Woodcock, 2001). Xanthate oxidation is expected at the surface of gold particles producing dixanthogen, which participates in the formation of an hydrophobic layer around the gold grains (Wandelt & Thurgate, 2003; Woods et al., 1995). It is generally admitted that dixanthogen plays a key role in the flotation of free gold (Gardner & Woods, 1977; Miller et al., 1986; Woods et al., 1994). The fact that long chain xanthate, (such as PAX) oxidizes to dixanthogen at lower potential is another reason to use them preferentially in gold flotation (Dunne, 2016). The role of silver present inside electrum structure on its floatability using classical precious metals collectors described above is not well understood. Some authors suggest that higher silver content in electrum facilitates the adsorption rate of xanthate (Agorhom, Skinner, et al., 2015; Stefanova

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et al., 2018). On the other hand, some authors claim that silver-rich electrum may form a hydrophilic coating, significantly reducing its recovery by flotation (Bulatovic & Wyslouzil, 2000; Zhou & Cabri, 2004). New collectors based on phosphorous and nitrogen groups have been recently tested, as witnessed by published works (Chanturia et al., 2012; Ivanova et al., 2013). But rather than using them on a single basis, it is common to rely on their mixtures. For example, the inclusion of dithiophosphate as a promoter in the reagent blend for gold flotation is very common and aims to create a synergistic effect with xanthate as the collector, ultimately enhancing flotation performance (Agorhom et al., 2015; Allan & Woodcock, 2001; Bagci et al., 2007). Therefore, finding the most suitable collector for electrum flotation is a complex task and further research is required to identify optimal reagent mixtures for industrial implementation at operations like Krumovgrad.

The ore from the Ada Tepe deposit is processed at the Krumovgrad precious metals flotation plant, using a mixture of potassium amyloxanthate and dithiophosphate. Precious metals in the ore are primarily found as electrum, with some pure gold also observed (Demeusy et al., 2023).

### 1.2. Impact of fines on gold flotation

The comminution circuit at the Krumovgrad plant brings a flotation feed with a  $P_{80}$  of 30  $\mu\text{m}$ , the ore being characterized by a high amount of kaolinite, with a general formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . This latter feature is posing a significant processing challenge, as clay minerals like kaolinite are well-known to cause flotation issues, including particle coating, pulp rheology modification, increased reagent consumption, decreased concentrate grade, and formation of sticky and highly stable froth (Collins & Jameson, 1977; Taggart, 1927; Trahar & Warren, 1976; Wei et al., 2013). Kaolinite is also known to promote mineral dissolution, accelerate oxidation, and facilitate non-specific collector adsorption (Matis et al., 1993).

On the one hand, coatings formation promoted by electrostatic and Van der Waals interactions between negatively charged slimes and particles in suspension are not expected to be a major problem in the case of gold ores (Xing et al., 2019). Indeed, gold particles being “inert” seem to be immune towards such effects and hence are unlikely to be coated by clayey slimes (Liu et al., 2018). This is especially true in alkaline solutions where gold and kaolinite particles have negatively charged surfaces. For that reason, lime addition has been successfully used to cope with clay problems at Emperor gold mine Co, Fiji and at mines dealing with pyrophyllite containing South African Witwatersrand’s deposits, where flotation was carried out at pH 11 (Allan & Woodcock, 2001). The improvement in gold coated particles flotation can be done by adding more collector, chelating agents, organic acids, wash water or implementing acid treatment (Dunne, 2016).

On the other hand, in the case of Ada Tepe ore, modification of pulp characteristics is expected to occur due to clay content. Because of their colloidal size, charge, and anisotropic structure, clays may form a network like structure increasing the fluid viscosity inside the cell (Gupta, 2011). The intensity of this phenomena is known to be clay type dependant (Farrokhpay, 2012). The high viscosity harms the hydrodynamic regime in the system thus affecting sub-processes essential for an efficient flotation: gas dispersion, particle suspension, bubble-particle collision, attachment and detachment. Although concentration ranges when clays become problematic are not strictly defined, if kaolinite is present between 5 and 15 w%, it does not exercise marked effect on pulp rheology (Farrokhpay et al., 2016; Zhang & Peng, 2015). Moreover, the slight increase in pulp viscosity could bear a positive impact on the free gold recovery because when the viscosity is higher, the cell turbulence decreases, allowing for the complex bubble-high density gold particle to be stabilized. However, when the kaolinite content is as high as 36 %, both gold grade and recovery decrease tremendously (Liu et al., 2018). Likewise, rate constant and recovery of copper are virtually not affected by presence of around 15 % kaolinite, when copper ore is floated, but the

grade tends to decrease due to entrainment of gangue particles (Farrokhpay et al., 2016). Crystallinity of kaolinite also has an influence on its capacity to modify slurry characteristics: the lower the crystallinity, the higher the viscosity (Ndllovu et al., 2015).

### 1.3. Objectives of the work

The challenges associated with gold flotation, the presence of kaolinite in the ore, and the need for fine grinding have motivated the current investigation. The study has two main objectives: (i) to examine the role of slimes on gold recovery, and (ii) to test a new promoter with higher affinity for gold and silver as compared with dithiophosphate as a way to improve gold recovery. It addresses two key research gaps in the literature: (i) the lack of consensus on the effect of a thionocarbamate-type reagents on flotation of gold/electrum grains, and (ii) the way kaolinite clays influence flotation of gold from an epithermal deposit.

Additionally, the research aims to find ways to minimize gold losses into tailings, which could have broader implications for other operations involving precious metals ores (Yannopoulos, 1991). While increasing the grade of the concentrate is not the primary objective of the study, an increase in grade at similar recovery rates would be considered advantageous.

## 2. Material and methods

### 2.1. Materials

The Ada-Tepe deposit, which belongs to Dundee Precious Metals Inc., is unquestionably classified as a low-sulphidation epithermal type with a low abundance of base metals (Marchev et al., 2003, 2004; Márton et al., 2010; Tsintsov & Ivanov, 2012). Gold and silver are primarily found in the form of electrum within highly silicified sediments located above a detachment fault (Goranov & Atanasov, 1992; Marinova, 2006, 2007, 2008). The ore mineralogy is relatively simple, with precious metals being the sole economic commodity, and gangue minerals comprising silica polymorphs (microcrystalline, fine-grained, sugary quartz, and opaline silica), various carbonates (calcite, dolomite, ankerite, and siderite), and adularia. Electrum is consistently associated with quartz (Marchev et al., 2004).

Gold is found in majority in the form of electrum and to a lesser extent as pure gold. Being a low sulfidation deposit type, pyrite occurrence is about tenths of a percent and is known to be free of any gold (Demeusy et al., 2023). Gold head grades were back-calculated based on the fractions recovered after each flotation test, resulting in a mean head grade of 4 g/t. Assuming that gold is exclusively carried by electrum and disregarding the negligible quantities of pure gold and tellurides, the estimated electrum composition is  $73 \pm 4 \%$  Au and  $27 \pm 4 \%$  Ag.

### 2.2. Comminution

The sample used in this study is a crushed run-of-mine ore supplied by the Krumovgrad mine with a particle size giving  $P_{80}$  of 125  $\mu\text{m}$ . The ore has been further crushed to 100 % passing 2 mm using a Laarmann® LMFC250 lab jaw crusher and sampled with a riffle splitter into 1.8 kg lots. The material was ground immediately prior each flotation test using a fully instrumented laboratory mill Magotteaux® for 50 min at 70 % of the critical speed and 50 wt% solids to reach a  $P_{80}$  of 38  $\mu\text{m}$ . Stainless steel balls of 34 mm diameter, accounting for 20.5 kg in total have been used as media. The ground pulp was poured directly inside the flotation cell. To match the conditions applied at mine site, 100 % of the total  $\text{CuSO}_4$  and 80 % of the total  $\text{Na}_2\text{SiO}_3$  have been added inside the mill.

### 2.3. Desliming

Desliming has been performed using a laboratory micro-cyclone with

the ground pulp diluted to 10 wt% solids and introduced at a pressure of 1 bar. The cyclone has been equipped with different apex apertures enabling to change its cut-size and the respective partition curves have been plotted (Fig. 1). One could note that the 2.5 mm apex allows to considerably decrease the proportion of particles below 10  $\mu\text{m}$  in the underflow in comparison to the 5 mm apex. Therefore, three flotation feeds with differing granulometries have been produced: a non-deslimed feed with 42 vol% of particles below 10  $\mu\text{m}$ , a flotation feed deslimed using a 5 mm apex having 22 vol% of particles below 10  $\mu\text{m}$  and a feed with 13 vol% below 10  $\mu\text{m}$ , deslimed using an apex of 2.5 mm (Fig. 1). When hydrocycloning was tested for slimes removal, the underflow was used as flotation feed.

## 2.4. Flotation

### 2.4.1. Equipment and parameters

The flotation machine used is bottom-driven laboratory Magotteaux float Cell® equipped with a 5 L cell.

Air injection is realized from the bottom thanks to the valves located below the rotor. Agitation was kept constant at 900 rpm for all tests. Air flow rate was fixed at 15 L/min during the rougher stage (two first concentrates) and at 20 L/min during the scavenger stage (two last concentrates). The mass of the ground ore in each test (1.8 kg) has been chosen in order to maintain about 30 wt% solids in the cell,

corresponding to a pulp density of 1.23 g/cm<sup>3</sup>. This was likewise the case when the ore was deslimed. Values for pH and Eh were not controlled but were respectively monitored to be between 8 and 8.5 and 50–200 mV vs hydrogen standard electrode which corresponds to the range where gold and silver can be floated (Hintikka & Leppinen, 1995; Leppinen et al., 1991).

### 2.4.2. Reagent scheme

**2.4.2.1. Reference test.** The reference test procedure and reagents scheme has aimed to replicate the rougher and scavenger flotation stages practiced in the plant. The flotation test was divided in four steps with their respective reagents additions. The two first concentrates collected correspond to the rougher stage and the two last correspond to the scavenger stage. The flotation reagents suite for the reference test (plant conditions) is summarized on the left side of Fig. 2. Potassium amyl-xanthate (PAX, C<sub>6</sub>H<sub>11</sub>KOS<sub>2</sub>) and AERO®238 (A238, C<sub>8</sub>H<sub>6</sub>NaO<sub>2</sub>PS<sub>2</sub>) have been used as collector and promoter, in the rougher and scavenger stage, and in scavenger stage only respectively, as it is currently the case at mine site. Oreprep® F-549 (Cytac industry Inc., 2002) has been added as frother.

**2.4.2.2. AERO MAXGOLD™ 900 (MX900) trials.** The AERO

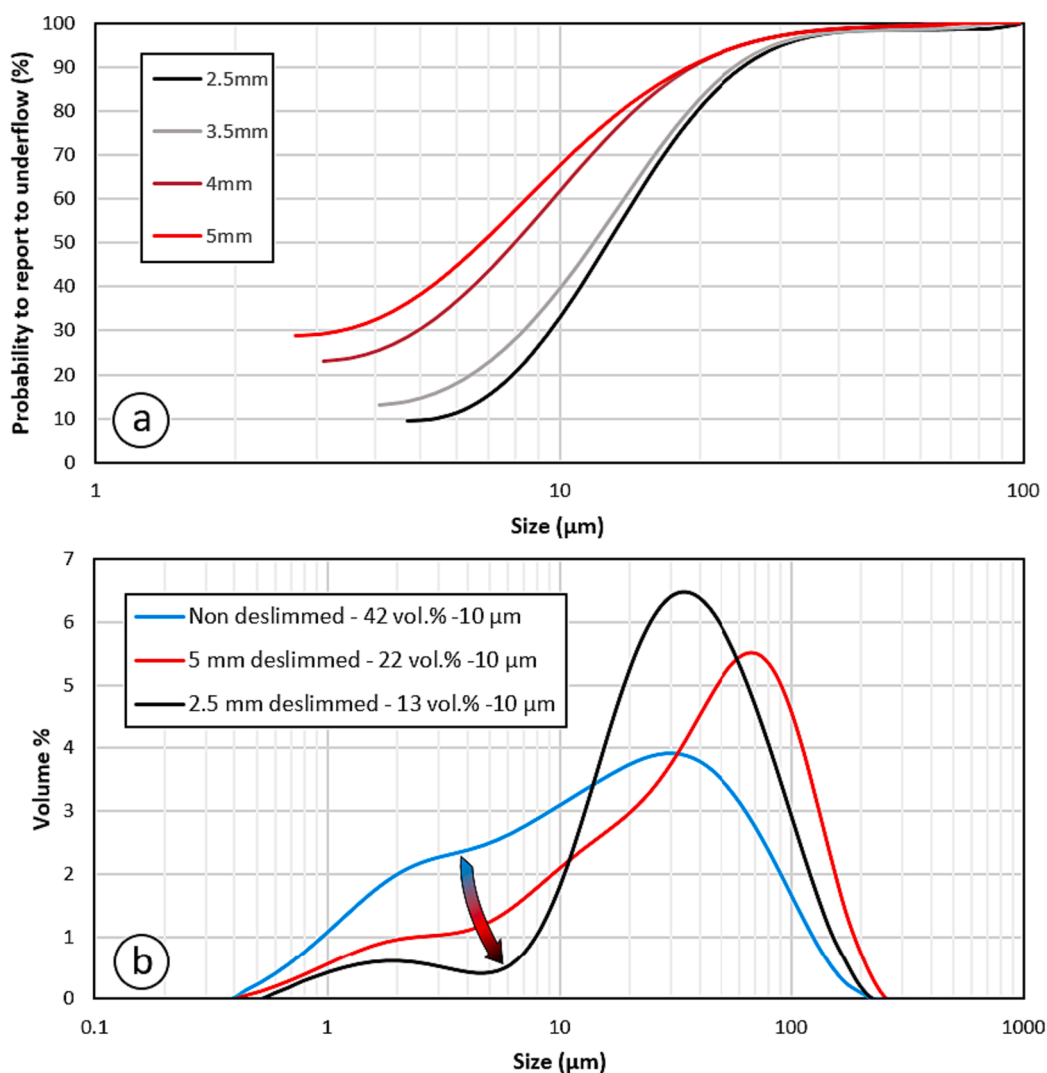


Fig. 1. (a) Partition curves of the micro-cyclone for its different apex openings; (b) Comparison of particle size distributions of hydrocyclone underflows for flotation feed.

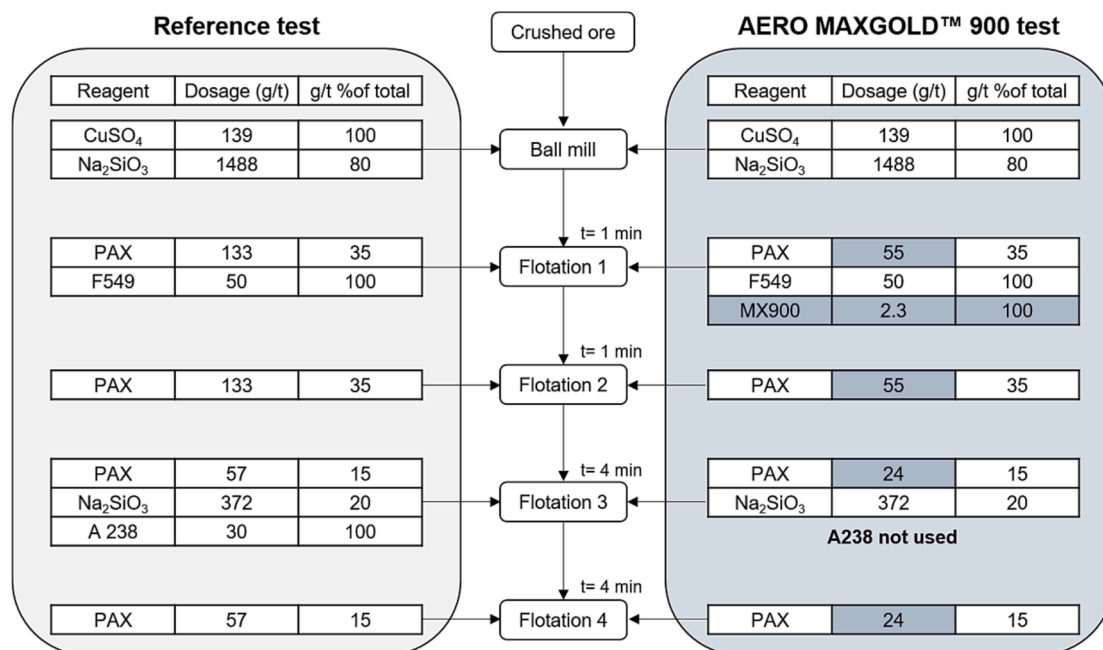


Fig. 2. Reagent scheme for reference tests (left) and AERO MAXGOLD™ 900 tests (right). AERO MAXGOLD™ 900 test presented on this figure corresponds to test 1 on Fig. 3.

MAXGOLD™ 900 is a modified thionocarbamate of general formula n-butoxycarbonyl-O-n-butyl thionocarbamate. In order to assess correctly its role in gold recovery, this reagent has been added just after the PAX at the rougher stage (right part of Fig. 2), since during our preliminary trials only a limited amount of froth has been recovered at the scavenger stages. Given that this new promoter is added together with xanthate at the rougher stage to replace A238, xanthate dosage has been decreased, while A238 was excluded. The PAX dosage has been varied stepwise between the xanthate dosage practice at the mine which is 380 g/t, and 95 g/t representing 25 % of it. For the MX900, three dosages were investigated: 2.3, 4.5 and 6.7 g/t. An experimental design has been built to represent the variability of the two parameters: PAX and MX900 dosages (Fig. 3). The selection of experimental points in the 2D design has been carried out with the aim of constructing the most robust and feasible model. The objective was to enable estimation of both

metallurgical parameters (gold recovery and grade), at any position of the design surface and to accordingly identify the optimal collector mixture.

The order of the tests has been randomized. A dosage of 25 g/t, laying out of the range represented in Fig. 3, has also been tested to evaluate the effect from promoter overdosing on recovery.

**2.4.2.3. Reagents preparation.** A fresh 1 % solution of xanthate was prepared on a daily basis. When used, A238 and AERO MAXGOLD™900 have been added neat with a micro-pipette. Although the activating effect of copper sulphate on gold is still debatable (Allan & Woodcock, 2001; Chandra & Gerson, 2009; Teague et al., 1999), 1 % solution of it was added as an activator directly in the mill. Sodium silicate was likewise added in the mill as gangue depressor and particles dispersant.

2.5. Material analysis

Gold grade has been delivered from fire assay realised by the SGS branch located at the Dundee Precious Metals Chelopech site in Bulgaria. Redox potential has been followed with a PtAgCl (silver chloride) probe and converted to a standard hydrogen electrode (SHE) while pH has been measured with an Ag/AgCl 3.0 mol/L KCl electrode. Particle size analysis has been performed on a laser diffraction analyser (Malvern Mastersizer 2000). Mineralogical analysis and quantification has been done using X-ray diffraction on a Bruker D8-ECO diffractometer, with CuK<sub>α</sub> radiations (λ = 1,9373 Å). The respective sample was pulverized before being scanned between 5 and 75° 2θ at a speed of 0.02°2θ per second. The identification of all minerals from the XRD patterns was done with a Panalytical Xpert suite and WebPDF4 + ICDD relational database.

3. Results and discussion

3.1. Ore characteristics

The ore has been ground down to 80 % passing 38 μm in order to approach the liberation target practiced at the processing plant. The particle size distribution of non-deslimed flotation feed (blue curve on

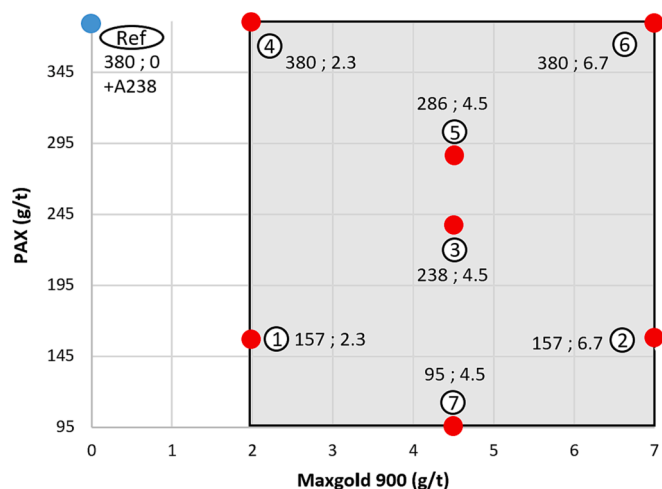


Fig. 3. Design of experiments to assess the role of AERO MAXGOLD™ 900 promoter and potassium amyl-xanthate (PAX) blend (red points). Blue point corresponds to reference test. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 1-b) shows a clear bimodal shape suggesting two distinguished particle populations: one centred around 2–3  $\mu\text{m}$  and another one at 30  $\mu\text{m}$ . The top size of the product is 100  $\mu\text{m}$ .

The flotation feed has been divided into four size fractions: +38  $\mu\text{m}$ , +20–38  $\mu\text{m}$ , +7–20  $\mu\text{m}$  and –7  $\mu\text{m}$ . The fraction –7  $\mu\text{m}$  has been obtained through a laboratory micro-cyclone, while the rest of the fractions via wet sieving. The XRD analysis done on each size fraction indicated that muscovite and adularia content are almost constant whatever the size fraction (Fig. 4). This is not the case for quartz and kaolinite. Quartz quantity decreases from 71 % to 42 % as the material gets finer, whereas kaolinite increases from 3 to 27 %. The sum of their proportions represents about 70 % of the material in all size fractions, meaning that quartz is literally replaced by kaolinite inside the finer fractions. This finding could be expected owing to the known difference in quartz and kaolinite hardness being respectively around 7 and 2–2.5 on Mohs scale.

The weight percent of the mineral phases and the gold distribution in the four size fractions have been respectively calculated based on the quantitative XRD and fire assays data (Table 1). For the fractions +38  $\mu\text{m}$  and +20–38  $\mu\text{m}$ , mineralogy and gold content are almost identical. The concentration of muscovite and kaolinite in the four size fractions does increase as particle size decreases. 62 % of kaolinite and 38 % of muscovite detected are in the fraction below 7  $\mu\text{m}$ . For gold, its content decreases drastically from the fraction +7–20  $\mu\text{m}$  down to the –7  $\mu\text{m}$  with respectively 48 % and 7 %. Since the behaviour of a particle inside a hydrocyclone is governed not only by its size but also by its density, it is likely that the proportion of Au reporting to the –7  $\mu\text{m}$  fraction has been underestimated. Indeed, even if electrum particles are finer than 7  $\mu\text{m}$ , their high density increases their probability to report to the fraction +7/–20  $\mu\text{m}$  (McGrath et al., 2015). Therefore, it is possible that the 48 % of total gold found in the +7–20  $\mu\text{m}$  fraction is overestimated on the expense of the –7  $\mu\text{m}$  fraction underestimation. In any case, more than half of the precious metals are contained in the –20  $\mu\text{m}$  fraction. Flotation of such a fine ore is expected to be difficult due to the very low particle-bubble collision probability (Chipfunhu et al., 2011). Nevertheless, Klimpel and co-workers state that finer gold particles can float faster and reach higher recoveries than coarser ones, while O'Connor

**Table 1**

Weight percent distribution of mineral phases inside the feed (following XRD and gold fire assay).

Fraction, $\mu\text{m}$	Quartz, %	Adularia, %	Kaolinite, %	Muscovite, %	Gold, %
+38	30	23	7	15	23
+20/–38	29	24	7	21	25
+7/–20	24	28	24	27	48
–7	18	26	62	38	5

and Dunne claim that it is possible to reach recovery as high as 80 % with gold particles sized under 12  $\mu\text{m}$  (Klmpel, 1999; O'Connor & Dunne, 1994).

### 3.2. Effect from ore desliming on flotation

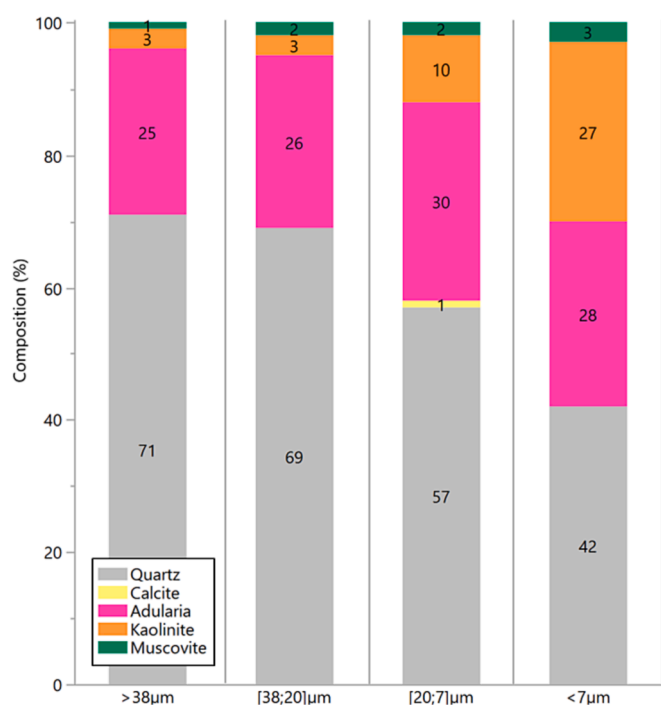
This section presents the results from the flotation tests performed with hydrocyclone underflows that contain different amount of fines (particles finer than 10  $\mu\text{m}$ ). The underflows have the following fines content: 42, 22 and 13 vol% (see section 2.3). XRD results indicate that one-third of the –7  $\mu\text{m}$  fraction is composed of kaolinite. When the ore was deslimed with the 5 mm apex opening, the content of kaolinite in underflow and overflow was 4 % and 19 % respectively. Therefore, the removal of fines mainly consist in removing the kaolinite from the flotation feed.

#### 3.2.1. Influence of desliming on mass recovery

Fig. 5 presents the concentrate mass pull as function of the amount of particles below 10  $\mu\text{m}$  in the ground ore subjected to flotation, referred to as “fines” in this section. It could be noted, that when the amount of fines in the feed is reduced, the concentrate mass pull has decreased from 7.6 % in the case of 42 vol% of fines, to around 1 % when 13 vol% of fines are present. Thus, the increased presence of fines drives a larger amount of mass to report to the concentrate. This could be explained by the fact that fines are easily entrained within the froth phase by water and their presence in the froth renders it more stable and able to carry out solids. The enrichment of the flotation concentrate with fines has been also directly observed in the flotation tests without desliming step. The four-fold increase in the frother dosage for the case of flotation feed containing 13 vol% of fines has allowed to partially compensate the absence of fines on mass recovery. When no sodium silicate is used during flotation, the mass recovery increases tremendously - up to 30 % when no desliming was practiced. These observations show, that in the case of the Ada Tepe ore, where the amount of valuable minerals that could stabilize the froth phase is limited, the presence of fine particles plays a key role in froth stabilization. However, this property has to be controlled by sodium silicate addition to find out an equilibrium point where the amount of fines going to the froth phase is sufficient to stabilize it, without leading to excessive mass recovery and therefore concentrate dilution.

#### 3.2.2. Influence of desliming on gold flotation

The general trend of gold recovery during flotation of the underflow after hydrocycloning undoubtedly suggests that the less fines in the flotation feed, the lower the overall gold recovery (Table 2). The latter one considers likewise the Au ‘losses’ in the overflow fraction. The gold recovery in the concentrate was respectively 88 %, 83 %, and 85 % when 42 vol%, 22 vol% and, 13 vol% of particles below 10  $\mu\text{m}$  have been respectively present in the feed. Therefore, the drop in gold recovery could be mainly attributed to gold which reported to the overflow during desliming prior to flotation, rather than to the different flotation conditions provoked by the decreased amount of fine particles. Indeed, when the micro-cyclone has been used with an apex of 2.5 mm, the mass recovery in the overflow was about 36 %, a fraction in which about 13 % of the total gold was lost. With an apex of 5 mm, these figures were



**Fig. 4.** Mineral composition of flotation feed per size fraction obtained by XRD analysis.

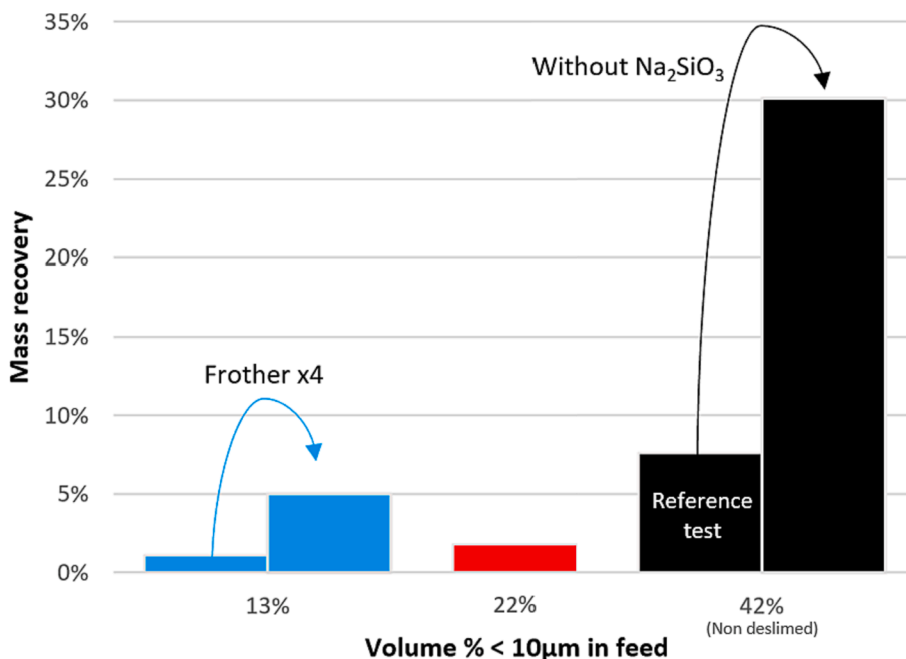


Fig. 5. Concentrate mass recovery as function of percentage of particles below 10 µm in feed.

**Table 2**  
Effect of micro-cyclone apex on gold partitioning in micro-cyclone streams and flotation products (OF = overflow, UF = underflow).

Cyclone apex (mm)	Vol.% < 10 µm in flotation feed	Cycloning		Flotation of UF		Global recovery
		OF	UF	tailing	Concentrate	
-	42	0 %	100 %	15 %	85 %	85 %
5	22	5 %	95 %	17 %	83 %	79 %
2.5	13	13 %	87 %	12 %	88 %	77 %

respectively 16 % and 5 % due to the finer cut size of the micro-cyclone (Table 2).

The presented results are showing that the variation of fines content in flotation feed did not cause a noticeable variation in gold recovery,

which somehow disagrees with findings reported by Teague and co-workers claiming that the higher froth stability, the better free gold recovery (Teague et al., 1999). However, the reduced fines proportion in the feed from 42 vol% to 13 vol% has provoked a nearly 8 fold increase in Au grade (Fig. 6), a phenomenon caused basically by the drop in mass recovery. The reduction of fines quantity at the flotation stage could therefore be a tangible way to substantially increase gold grade in the concentrate without degrading recovery. But as shown in Table 2, when the losses to hydrocyclone overflow are considered, the overall gold recovery of the process decreases. In the case of the Ada Tepe ore where the valuable minerals grains are finely disseminated, there is no choice, but to intentionally let the concentrate be diluted by fines to increase the overall plant recovery, unless a solution is found to remove fines without losing too much gold at this stage. Such approach could allow to keep the same recoveries and to increase significantly concentrate grades resulting in non-negligible energy saving on regrinding and offer avenues for increase in plant throughput.

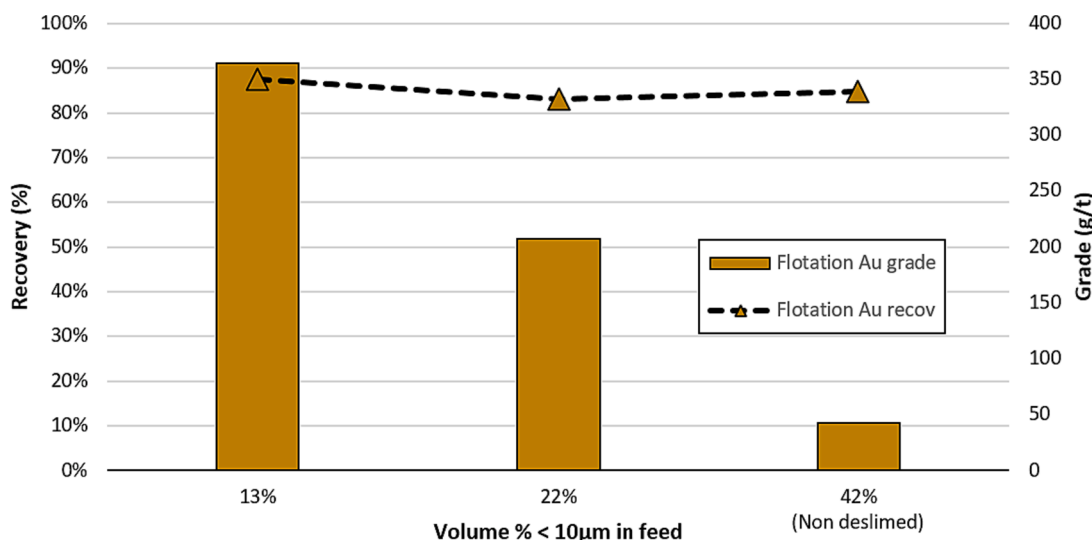


Fig. 6. Au grade and recovery as function of the percentage of particles below 10 µm.

The fact that the recovery of gold remained stable in parallel to mass yield decrease, suggests that electrum ability to report to the concentrate is unaffected. This means that entrainment could not be the principal mechanism responsible for carrying out gold into the concentrate, although such conditions are likely created when desliming is omitted, as demonstrated by Fig. 5. This situation could be explained by the following two assumptions. At first, electrum grains being sufficiently liberated have a lower probability to be carried out as entrained particles together with gangue minerals and hence report to the froth. The second reason could be, that the grains are too heavy to report in the concentrate without being lifted up by a bubble. It is known, that the larger the gold particles, the more difficult they are to be floated because of their high density and enhanced detachment probability (Allan & Woodcock, 2001; Klimpel, 1999). In the present case, we may have an intermediate situation because the majority of gold grains are fine. They may be too heavy to be entrained, but not heavy enough to overcome the attachment forces when fixed to bubbles, thus keeping their detachment probability unchanged.

Likewise, gold recoveries are not affected when the amount of fines in the flotation feed is reduced, which indirectly suggests that fines do not create deleterious effects to precious metals flotability, e.g. particles coating. For direct detection of particle coatings, methods like electrophoretic mobility, induction time measurement or atomic force microscopy need to be deployed, which is out of scope of the current work (Yu et al., 2017).

### 3.3. Effect from AERO MAXGOLD™ 900 addition

#### 3.3.1. Gold recovery

Fig. 7 depicts the influence of PAX and MX900 dosage levels on gold recovery and grade. It could be noted, that whatever the MX900 dosage, when the xanthate is raised from 95 to 380 g/t, the recovery of gold decreases by about 25 % (test 7 versus test 4 and 6).

At 380 g/t PAX, when the dosage of MX900 increases from 2 g/t (test 4) to 7 g/t (test 6), the Au recoveries decrease, but the grade slightly increase. When only 41 % of PAX regular dosage is used (158 g/t instead of 380 g/t), the addition of either 2 or 7 g/t of MX900 gave better gold recoveries (see for comparison tests 1 versus 4, and 2 versus 6 in Fig. 7). This observation supports the assumption that it is necessary to decrease PAX dosage when MX900 is used, even at lower dosage to avoid collector over-dosage. It is known, that collector over-dosage may provoke a

lateral orientation of collector molecules leading to chain-chain configuration and interactions causing a second, inversed adsorption layer rendering ultimately the mineral surface hydrophilic. In such a way, the number of particles covered by a collector monolayer decreases, which reduces mass recovery and consequently increases grade. This is especially relevant in the present case where gold is very finely disseminated and hence it could require less collector dosage than a coarser one to form a stable particle/bubble complex (Lins & Adamian, 1993).

#### 3.3.2. Gold grade

The results shown in Fig. 7 suggest that the dosage rate of both PAX and MX 900 seem to influence Au grade. The highest grades are found in the region where both PAX and MX900 dosage tend to be low, respectively between 95 and 250 g/t and 2.3–4.5 g/t. One could note, that the observed maximum difference between the lowest achievable gold grades (between 46 and 63 g/t, tests 2, 4, 5 and 6) at high PAX or at high MX900 dosages, and the highest ones (between 81 and 85 g/t, tests 1, 3 and 7) achieved at low PAX or at low MX900 dosage is about 30 %.

On one hand, when 2 g/t MX900 is used and PAX dosage decreased from 380 to 158 g/t (tests 4 and 1 respectively), Au grade increases to reach 85 g/t. But on the other hand, when 7 g/t MX900 is used, and PAX dosage drops from 380 g/t to 158 g/t (tests 6 and 2 respectively), Au grade decreases. This observation may indicate that in this case there is not enough PAX to interact with the available MX900, thus part of the virtuous synergism effect between the two molecules is lost. When MX900 was added at 25 g/t (result not presented in this paper), its critical concentration has seemed to be reached. Indeed, in comparison with reference test, concentrate mass yield was multiplied by 3, bringing increased recoveries, but on the expense of lower grades.

#### 3.3.3. Electrum floatability observations

The results pictured in Fig. 7 showed that the recovery and grade of gold vary to a relatively large extent as function of collector mixture variation. Accordingly, one could assume that collector adsorption and true flotation phenomena are predominantly the governing mechanisms for gold flotation. This observation could be discussed on the background of the lack of consensus on the role of silver in the floatability of electrum. On one hand, some authors suggest that the adsorption rate of xanthate onto electrum grains is facilitated when the ratio Au:Ag decreases (Agorhom, Skinner, et al., 2015, Stefanova et al., 2018). Work

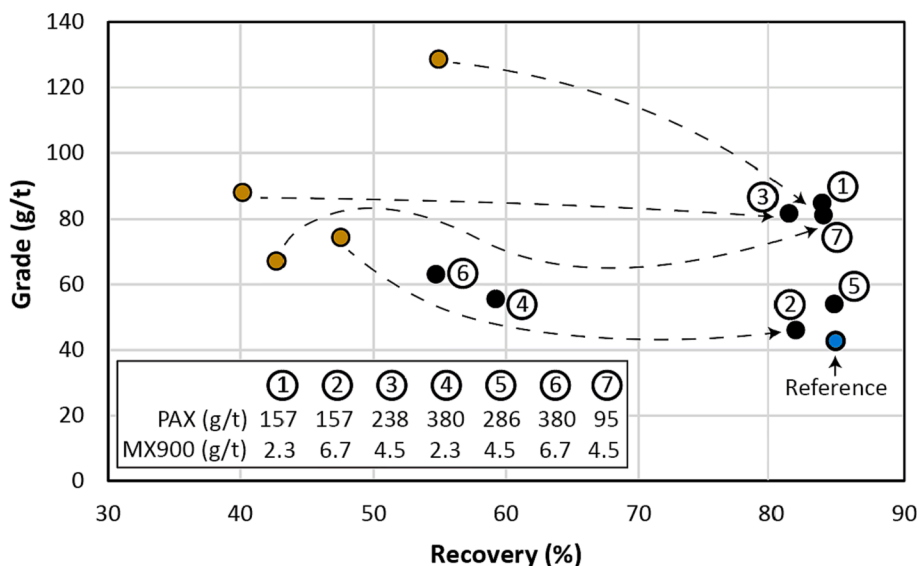


Fig. 7. Grade VS recovery plot of gold for PAX/MX900 mixtures. Yellow and dark points are rougher and scavenger steps respectively. Tests 6, 4 and 5 appear as a single step because rougher and scavenger concentrates were merged. Numbering corresponds to the experimental design in Fig. 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

carried by Leppinen et al., 1991 and Woods et al., 1994 compiled with other works by Wandelt & Thurgate, 2003 show that the monolayer of metal xanthate is proportional to the silver content of the alloy. On the other hand, studies done by Zhou & Cabri, 2004 and Bulatovic & Wyslouzil, 2000, claim that silver-rich electrum may form a hydrophilic silver-rich coating, which reduces considerably its recovery by flotation. According to our observations and taking into account the metallurgical data for silver (plant data not shown) we could assume that in the case of the Krumovgrad ore with electrum predominating, the AERO MAX-GOLD™ 900 collector tends to be preferentially adsorbed on Au rather than on Ag.

### 3.3.4. AERO MAXGOLD™ 900 trials – Overall observations

The test conditions described at positions 5, 3, 1 and 7 as pictured in Fig. 3 have secured the highest recoveries and grades for gold. When compared with the baseline test (plant conditions), it appears that using MX900 does not contribute to a marked increase in gold recovery (Table 3). However, gold grade has increased by several magnitudes. Therefore, the separation efficiencies (Equation (1) below) for Au are higher for tests 3, 1, and 7, than for the reference one. This could be explained by the observed decrease in mass recovery within those three tests, due to potential higher selectivity of MX900 than PAX towards electrum, and also due to the lower concentration of both reagents thus avoiding overdosage.

$$SE = \frac{C \times m \times (c - f)}{F \times f \times (m - f)} \quad (1)$$

where  $C$  is the concentrate mass,  $F$  is the feed mass,  $m$  is the metal content in the mineral,  $c$  is the concentrate grade and  $f$  is the tailing grade.

The use of MX900 under the tested conditions has proven to maintain similar gold recovery levels, but higher grades compared to the PAX/A238 mixture currently used at the mine. The optimal MX900/PAX ratio is found as 4.5 g/t of MX900 and 95 g/t PAX, corresponding to a nearly 75 % decrease in PAX consumption and entire exclusion of A238 addition.

### 3.4. Relevance of the study to other deposit types

The above findings provide useful insights when processing deposits having gold carried by electrum or pure gold particles, and when these need to be separated from a siliceous matrix mainly composed of quartz. This is gladly the case for the intermediate and low sulfidation epithermal and orogenic deposits (Kesler & Simon, 2015). The results bear also relevance for placer deposits where flotation is preferred over gravity separation. If gold is however hosted inside other mineral phases, such as pyrite/arsenopyrite, in Carlin-type hydrothermal or volcanogenic massive sulphides deposits, or in Cu-bearing minerals like in porphyry Cu deposits, then the proposed reagent mixture may not be the tangible way to increase concentrate quality. It could be nevertheless proposed for porphyry Au-Cu and Cu deposits containing economic portion of pure gold, such as deposits when Au is mobilized by early hydrothermal fluids before being trapped inside the sulphides (Jébrak & Marcoux, 2008). These gold deposit types could witness proven resources often overpassing 100 tons of Au (Singer & Kouda, 1999).

## 4. Conclusions

The role of clays in controlling froth phase features has been confirmed. They tend to stabilize froth by increasing bubble loading, which in the studied case is relatively weak due to the low amount of precious metals grains. The increase in clay content therefore increases mass recovery in the concentrate and if no depressant is used, mass recovery is increased by four.

Desliming tests with a cyclone having a very fine apex aperture

**Table 3**

Metallurgical comparison of the best DOE test against PAX/A238 mixture currently used at the mine corresponding to plant conditions - Ref. R = recovery, G = Grade, SE = separation efficiency.

	Position (Fig. 3)	Mass R %	Au R %	Au G g/t	Au SE %
DoE	5	6.0	84.7	54.0	72.1
best	3	3.9	81.3	81.7	77.4
tests	1	4.0	83.8	84.9	79.9
	7	4.2	83.9	81.2	87.2
	7bis	5.1	82.9	59.4	77.8
Ref		7.6	84.8	42.8	77.2

illustrate that part of electrum minerals still report to the overflow. The overall recovery (cycloning and flotation) is therefore slightly below the one obtained without desliming. All in all, keeping fine clays in flotation feed is beneficial for the overall recovery of gold because it prevents losses of fine grained electrum into tailings and stabilize the weakly charged froth.

The presented results from a laboratory scale study suggest that given its enhanced selectivity, the AERO MAXGOLD™900 promoter could be used to partially replace PAX in the rougher flotation stage at the Krumovgrad concentration plant. The inclusion of this reagent under the tested conditions has proved to maintain gold recovery at levels similar to the baseline case (actual plant practice), however achieving higher grades. The optimal MX900/PAX suite has been established as 4.5 g/t of MX900 and 95 g/t PAX, corresponding to a PAX consumption decrease of 75 % and entire exclusion of AERO 238. This combination could bring only slight improvement of the global gold recovery, but it offers an ultimate advantage of reducing the material flow entering the regrinding circuit. Therefore, it could lead to a non-negligible economic benefits in terms of increased plant throughput and decreased energy expenditure.

The study opens further opportunities for seeking improved metallurgy of the gold from the Ada Tepe ore, such as trying alternative collectors having stronger affinity for silver in electrum (e.g. AEROPHINE 3418A), testing selective dispersing agents, and delineating the copper sulphate activating role in gold flotation.

### CRedit authorship contribution statement

**Bastien Demeusy:** Experiments execution, Data compilation and interpretation, Original draft-preparation. **Deyan Madanski:** Industrial support, Research formulation, Material supply. **Stoyan Gaydardzhiev:** Conceptualization, Interpretation, Writing-reviewing, Paper polishing.

### 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.

### Data availability

Data will be made available on request.

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## References

- Agorhom, E.A., Skinner, W., Zanin, M., 2015. Post-regrind selective depression of pyrite in pyritic copper–gold flotation using aeration and diethylenetriamine. *Miner. Eng.* 72, 36–46. <https://doi.org/10.1016/j.mineng.2014.11.019>.
- Allan, G.C., Woodcock, J.T., 2001. A review of the flotation of native gold and electrum. *Miner. Eng.* 14 (9), 931–962. [https://doi.org/10.1016/S0892-6875\(01\)00103-0](https://doi.org/10.1016/S0892-6875(01)00103-0).
- Bulatovic, S., Wyslouzil, D.M., 2000. GOLD RECOVERY: FLOTATION. In *Encyclopedia of Separation Science*. Elsevier, pp. 2965–2975.
- Chandra, A.P., Gerson, A.R., 2009. A review of the fundamental studies of the copper activation mechanisms for selective flotation of the sulfide minerals, sphalerite and pyrite. *Adv. Colloid Interface Sci.* 145 (1–2), 97–110. <https://doi.org/10.1016/j.cis.2008.09.001>.
- Chanturia, V.A., Nedosekina, T.V., Gapchich, A.O., 2012. Improving gold flotation selectivity by using new collecting agents. *J. Min. Sci.* 48 (6), 1031–1038. <https://doi.org/10.1134/S1062739148060111>.
- Chipfunhu, D., Zanin, M., Grano, S., 2011. The dependency of the critical contact angle for flotation on particle size – Modelling the limits of fine particle flotation. *Miner. Eng.* 24 (1), 50–57. <https://doi.org/10.1016/j.mineng.2010.09.020>.
- Cytec industry Inc. (2002). *Mining Chemicals Handbook* (K. A. Day, Ed.). <https://www.911metallurgist.com/wp-content/uploads/2017/03/2002-cytec-mining-handbook924751.pdf>.
- Demeusy, B., Madanski, D., Bouzazhah, H., Gaydardzhiev, S., 2023. Mineralogical study of electrum grain size, shape and mineral chemistry in process streams from the Krumovgrad mine, Bulgaria. *Minerals Eng.* 198, 108080 <https://doi.org/10.1016/j.mineng.2023.108080>.
- Dunne, R., 2016. Flotation of Gold and Gold-Bearing Ores. In: *Gold Ore Processing: Project Development and Operations, Second edition*. Elsevier, pp. 315–338.
- Farrokhpay, S., 2012. The importance of rheology in mineral flotation: A review. *Miner. Eng.* 36–38, 272–278. <https://doi.org/10.1016/j.mineng.2012.05.009>.
- Farrokhpay, S., Ndlovu, B., Bradshaw, D., 2016. Behaviour of swelling clays versus non-swelling clays in flotation. *Miner. Eng.* 96–97, 59–66. <https://doi.org/10.1016/j.mineng.2016.04.011>.
- Gardner, J. R., & Woods, R. (1977). *The hydrophilic nature of gold and platinum*. 6.
- Gupta, V., 2011. Particle interactions in kaolinite suspensions and corresponding aggregate structures. *J. Colloid Interface Sci.* 9.
- Hintikka, V.V., Leppinen, J.O., 1995. Potential control in the flotation of sulphide minerals and precious metals. *Miner. Eng.* 8 (10), 1151–1158. [https://doi.org/10.1016/0892-6875\(95\)00080-A](https://doi.org/10.1016/0892-6875(95)00080-A).
- Ivanova, T.A., Chanturia, V.A., Zimbovsky, I.G., 2013. New experimental evaluation techniques for selectivity of collecting agents for gold and platinum flotation from fine-impregnated noble metal ores. *J. Min. Sci.* 49 (5), 785–794. <https://doi.org/10.1134/S1062739149050134>.
- Jébrak, M., Marcoux, É., 2008. *Géologie des ressources minérales*. Ministère Des Ressources Naturelles Et Faune.
- Kesler, S.E., Simon, A.F., 2015. *Mineral resources, economics and the environment* (Second edition). Cambridge University Press.
- Klimpel, R.R., 1999. Industrial experiences in the evaluation of various flotation reagent schemes for the recovery of gold. *Mining, Metallurgy & Exploration* 16 (1), 1–11. <https://doi.org/10.1007/BF03402850>.
- Leppinen, J.O., Yoon, R.-H., Mielczarski, J.A., 1991. FT-IR studies of ethyl-xanthate adsorption on gold, silver and gold-silver alloys. *Colloids Surf.* 61 [https://doi.org/10.1016/0166-6622\(91\)80309-C](https://doi.org/10.1016/0166-6622(91)80309-C).
- Lins, F.F., Adamian, R., 1993. The influence of some physical variables on gold flotation. *Miner. Eng.* 6 (3), 267–277. [https://doi.org/10.1016/0892-6875\(93\)90035-L](https://doi.org/10.1016/0892-6875(93)90035-L).
- Liu, S., Chen, X., Lauten, R.A., Peng, Y., Liu, Q., 2018. Mitigating the negative effects of clay minerals on gold flotation by a lignosulfonate-based biopolymer. *Miner. Eng.* 126, 9–15. <https://doi.org/10.1016/j.mineng.2018.06.021>.
- McGrath, T.D.H., O'Connor, L., Eksteen, J.J., 2015. A comparison of 2D and 3D shape characterisations of free gold particles in gravity and flash flotation concentrates. *Miner. Eng.* 82, 45–53. <https://doi.org/10.1016/j.mineng.2015.04.022>.
- Miller, J.D., Misra, M., Gopalakrishnan, S., 1986. Gold flotation from Colorado River sand with the air-sparged hydrocyclone. *Mining, Metallurgy & Exploration* 3 (3), 145–148. <https://doi.org/10.1007/BF03402651>.
- Moncayo-Riascos, I., Hoyos, B.A., 2017. Effect of collector molecular structure on the wettability of gold for froth flotation. *Appl. Surf. Sci.* 420, 691–699. <https://doi.org/10.1016/j.apsusc.2017.05.197>.
- Ndlovu, B., Farrokhpay, S., Forbes, E., Bradshaw, D., 2015. Characterisation of kaolinite colloidal and flow behaviour via crystallinity measurements. *Powder Technol.* 269, 505–512. <https://doi.org/10.1016/j.powtec.2014.09.029>.
- O'Connor, C.T., Dunne, R.C., 1994. The flotation of gold bearing ores—A review. *Miner. Eng.* 7 (7), 839–849. [https://doi.org/10.1016/0892-6875\(94\)90128-7](https://doi.org/10.1016/0892-6875(94)90128-7).
- Singer, D.A., Kouada, R., 1999. Examining risk in mineral exploration. *Nat. Resour. Res.* 8 (2), 111–122. <https://doi.org/10.1023/A:1021838618750>.
- Stefanova, V., Serafimovski, T., Tasev, G., 2018. Native gold composition and morphology through the mineral processing stages at the Bucim copper mine, Republic of Macedonia. *Geol. Macedonica* 34 (1), 59–74.
- Teague, A.J., Van Deventer, J.S.J., Swaminathan, C., 1999. A conceptual model for gold flotation. *Miner. Eng.* 12 (9), 1001–1019. [https://doi.org/10.1016/S0892-6875\(99\)00087-4](https://doi.org/10.1016/S0892-6875(99)00087-4).
- Wandelt, K., Thurgate, S., 2003. *Solid-liquid interfaces: Macroscopic phenomena, microscopic understanding*. Springer.
- Woods, R., Basilio, C.I., Kim, D.S., Yoon, R.-H., 1994. Chemisorption of ethyl xanthate on silver—Gold alloys. *Colloids Surf. A Physicochem. Eng. Asp.* 83 (1), 1–7. [https://doi.org/10.1016/0927-7757\(93\)02649-Y](https://doi.org/10.1016/0927-7757(93)02649-Y).
- Woods, R., Kim, D.S., Basilio, C.I., Yoon, R.-H., 1995. A spectroelectrochemical study of chemisorption of ethyl xanthate on gold. *Colloids Surf. A Physicochem. Eng. Asp.* 94 (1), 67–74. [https://doi.org/10.1016/0927-7757\(94\)02964-T](https://doi.org/10.1016/0927-7757(94)02964-T).
- Xing, Y., Xu, M., Gui, X., Cao, Y., Rudolph, M., Butt, H.-J., Kappl, M., 2019. The role of surface forces in mineral flotation. *Curr. Opin. Colloid Interface Sci.* 44, 143–152. <https://doi.org/10.1016/j.cocis.2019.11.005>.
- Yu, Y., Ma, L., Cao, M., Liu, Q., 2017. Slime coatings in froth flotation: A review. *Miner. Eng.* 114, 26–36. <https://doi.org/10.1016/j.mineng.2017.09.002>.
- Zhang, M., Peng, Y., 2015. Effect of clay minerals on pulp rheology and the flotation of copper and gold minerals. *Miner. Eng.* 70, 8–13. <https://doi.org/10.1016/j.mineng.2014.08.014>.
- Zhou, J.Y., Cabri, L.J., 2004. Gold process mineralogy: Objectives, techniques, and applications. *JOM* 56 (7), 49–52. <https://doi.org/10.1007/s11837-004-0093-7>.