

IMPROVING THE ENVIRONMENTAL PROPERTIES OF ARSENIC AND SULPHIDE RICH KOPSA AU–CU ORE TAILINGS THROUGH OPTIMISED MINERAL PROCESSING

by

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Mineral processing methods were applied to improve the environmental properties of Kopsa Au–Cu ore tailings containing arsenic-bearing and sulphide minerals. The effects of modification and optimisation of mineral processing flow sheet in the laboratory scale on tailings properties were studied using mineralogical and geochemical characterisation together with filled-in lysimeters which measured long-term behaviour together with drainage quality in field conditions. Most of the arsenic and sulphide minerals could be removed effectively from the tailings using a combination of fine grinding, froth flotation, high-gradient magnetic separation (HGMS), and sizing. The chemical composition and mineralogy of the tailings together with leaching of contaminants from the tailings changed significantly as a result of process development. E.g. leaching of As decreased from the level of hazardous waste to that of non-hazardous waste. The efforts made to improve the tailings quality also affected positively the process water quality. The filled-in lysimeter test results indicated that leaching of most elements in the drainage water decreased as a function of time during the monitoring period of one and a half years. Moreover, leaching of hazardous elements was generally less pronounced from the more processed tailings. Only the concentration of As in the seepage varied unexpectedly during the monitoring period. Further studies and more sampling is needed to confirm this observation and to predict the long-term behaviour.

Keywords: Mineral processing, tailings, arsenic, sulphide minerals, removal, environmental properties, mineralogy, geochemical characterisation, lysimeter test, seepage water

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1 INTRODUCTION

In gold production, huge amounts of rock need to be mined to yield just an ounce of gold. This is due to very low average gold grades in the ore deposits, usually a few grams per tonne at most. Therefore, large amounts of mining wastes are generated. A global estimate for the ratio of produced gold to the waste is particularly high, 1:950 000 (BRGM 2001). Only a small part of wastes can be used e.g. in mine site construction, most of them requiring long-term disposal.

Gold mining wastes typically contain sulphide minerals and metals hazardous to the environment, which prevents their further utilisation. Sulphide minerals are prone to generate low quality drainage from mine wastes. Acid mine drainage is considered to be one of the most significant environmental concerns associated with extractive industry (e.g. MEND 1991, Price 2003). Another major concern is arsenic (As), which is toxic and causes cancer in humans. Arsenic can be released to air, water, or land through various mining operations of which waste rock and tailings represent by far the largest arsenic fluxes for the gold industry to manage (Asselin & Shaw 2016). For example, in 2013, ca. 65% of total managed arsenic in the United State and 40% in Canada came from gold mining operations, and ca. 11% of total As directly emitted to the environment in Canada and Australia originated from these operations (Asselin & Shaw 2016).

Waste management is clearly a major challenge for the gold industry, and it will become more important and difficult to address as the ore grades decrease. Therefore, efficient waste management methods are needed. By removing As, sulphides and other hazardous metals from the gold mining waste, its utilisation potential and environmental properties could be improved. In addition, the volumes of harmful wastes could be minimized, which would facilitate their management and reduce costs.

Various mineral processing methods have been applied to increase raw material value of tailings and to improve their environmental properties. Liu et al. (2008) studied bioleaching and Lv et al. (2014) froth flotation after chemical pre-treatment to recover valuable metals from tailings. Desulphurisation of tailings by flotation was carried out e.g. by Benzaazoua and Kongolo (2003) and As removal by flotation by Choi et al. (2013). Also gravity concentration and magnetic separation have been applied. For instance, Savas (2016) studied recovery of colemanite from mine tailings using a Knelson concentrator, while Watson and Beharrell (2006) discussed concentration of valuables from mine dumps and tailings by high-gradient magnetic separation (HGMS).

In this work, mineral processing techniques were applied to decrease harmful minerals, especially As-bearing and sulphide minerals, from the tailings of the Kopsa gold–copper ore samples. These techniques included froth flotation, magnetic separation, gravity concentration, and classification. The main objective was to evaluate, whether it would be possible to reduce the amount of hazardous waste and to generate tailings that could be used as a cover material for mining waste facilities. Efforts were also made to increase the recovery of valuables to the concentrates. The influence of modified composition of tailings on their environmental performance was studied using mineralogical and geochemical characterisation together with filled-in lysimeters, which measured long-term behaviour together with drainage quality in field conditions.

This paper summarises the results of the study. More detailed descriptions of the investigations are provided in the GTK Open File Work Reports by Taskinen et al. (2018) and Tornivaara et al. (2018).

2 MATERIALS AND METHODS

2.1 Sampling and analyses

The ore samples for the study originated from the Kopsa Au–Cu deposit, located in Western Finland (Fig. 1). There were two ore samples, so-called sorted and unsorted sample. The sorted sample

had been pre-concentrated by sorting using X-ray transmission technique, while the unsorted sample had not been pre-concentrated by any way.

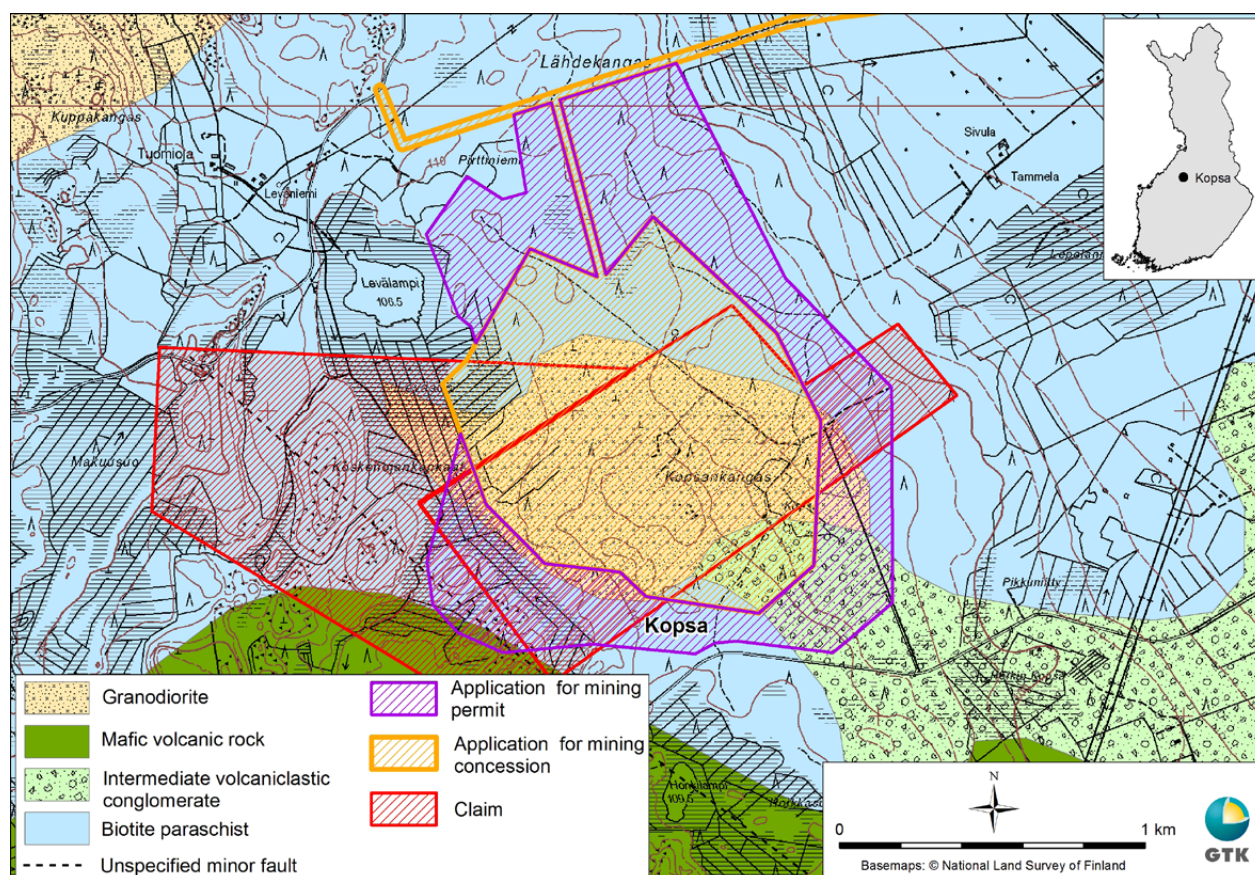


Fig. 1. Location and geology of the Kopsa Au–Cu deposit (Bedrock of Finland – DigiKP; Basemaps © National Land Survey of Finland and HALTIK 2013).

The Kopsa ore deposit is a porphyric Au–Cu mineralisation, which is hosted by tonalite and mica schist. The major ore minerals in the deposit are arsenopyrite, chalcopyrite and pyrrhotite with accessory löllingite, marcasite, pyrite, sphalerite, gold, cubanite, bornite, stannite, bismuth and Bi-bearing sulphosalts (Gaál & Isohanni 1979). The estimated ore reserves are 13.6 Mt with 0.81 g/t Au, 0.15% Cu and 2.15 g/t Ag (SRK 2013). Elevated

As grade is very typical for the mineralisation, the As contents varying between 0.1–1.2% in the deposit (Gaál & Isohanni 1979, Nurmi et al. 1991). Exploration has been carried out around the Kopsa deposit since the 1940s. The latest holder of the exploration claims, Belvedere Mining Oy, planned to open a mine, but went bankrupt in 2015. Therefore, no tailings existed at the site yet, providing good possibilities for tailings optimisation.

2.2 Sample preparation and analyses for the beneficiation tests

The ore samples for the beneficiation tests were crushed to <1 mm particle size using a small scale crushing circuit consisting of two jaw crushers in series and a roll crusher in closed circuit with a Sweco screen. The crushed samples were homogenised and divided into subsamples of 5.0 kg and 1.5 kg using Jones riffles and a sample divider (Retsch PT 100). The crushed subsamples were stored in a freezer to minimize oxidation of sulphide minerals.

Ground ore samples and slurry samples from the beneficiation tests were filtered by vacuum filtration and dried thermally at 90 °C. Representative

samples for chemical analyses and mineralogical characterisations were extracted by the sample divider (Retsch PT 100).

Size analyses of the samples were carried out by sieving. First, wet sieving was performed by hand to separate the finest –20 µm fraction. The oversized material was dry-sieved by a Ro-Tap sieve shaker using sieves with various apertures. Some particle size distributions were also determined by laser diffraction technique using Beckman Coulter LS 13320 MW Particle Size Analyser.

The chemical analyses of the ore samples and beneficiation test products were carried out by Labtium Oy. Total element concentrations were determined by XRF, Au and Ag grades by fire assay (FA) completed with flame atomic absorption spectroscopy (FAAS), and sulphur assays using an Eltra carbon/sulphur analyser. Some arsenic assays were also analysed by graphite furnace atomic absorption spectroscopy (GFAAS).

Modal mineralogy, grain size distribution, liberation and association of the ore and tailings samples

were studied using a mineral liberation analyser (MLA). The MLA equipment consisted of a standard modern scanning electron microscope (SEM; FEI Quanta 600) with two energy dispersive detectors (EDAX Genesis) and a special software package. Vertical polished sections were investigated. Electron probe microanalyser (EPMA; Cameca SX100) was applied for more detailed identification of some specific mineral phases and their quantitative composition.

2.3 Sampling and environmental characterisation of tailings

The environmental characterisation of the tailings and process waters from the beneficiation tests included mineralogical and chemical analyses of the tailings and determination of the process water quality. The purpose of the characterisation was to evaluate impacts of the modifications made in the ore processing on the environmental performance of waste materials and to determine the properties of tailings used in the filled-in lysimeter tests. In this paper, the focus is on the characterisation of the tailings and process water from the sorted ore sample. The results for the unsorted ore sample are provided in the report by Taskinen et al. (2018).

Tailings and process water samples were collected from the final slurry of the original and modified beneficiation tests using vacuum filtration (Table 1). Characterisation of tailings was carried out on freeze dried samples, sieved <2 mm for most of the analysis. The sieving was made mainly to break down clods generated during the drying. For total concentration measurements the samples were further ground to <100 µm (90%). The studied environmental properties included mineralogy, chemical composition, potential to produce acid mine drainage, and leaching and fractionation of

harmful elements. Mineralogy of the tailings was studied using MLA and EPMA as described above.

Total concentrations of elements in the tailings were determined by XRF and a mixture of concentrated acids (hydrofluoric acid, perchloric acid, hydrochloric acid and nitric acid) i.e. so-called four acid leach in combination with the ICP-OES/MS technique (method modified after Briggs (2002) and Briggs & Meier (2002)). Concentrations of total sulphur, total carbon, sulphide sulphur and carbonate carbon were measured pyrolytically with IR detection (ISO 15178, ISO 10694, CEN/TR 16376, SFS-EN 13137:en; Räisänen et al. 2010). Potential of the tailings to produce acid mine drainage was evaluated based on the ABA (SFS-EN 15875) and NAG tests (Amira 2002).

Leachability and fractionation of harmful elements from the tailings was studied using series of selective extractions in parallel. The applied extractions included: 1) 0.01 M NH_4 -chloride to extract easily dissolving fraction (Heikkinen & Räisänen 2008), 2) 1 M NH_4 -acetate at pH 4.5 to dissolve exchangeable and/or carbonate bound phases (e.g. Dold 2003, Heikkinen & Räisänen 2008), 3) 0.2 M NH_4 -oxalate at pH 3.0 in darkness to extract phases

Table 1. Tailings and process water samples used in the environmental characterisation.

Beneficiation test	Tailings sample	Process water sample
Original process (cf. Fig. 4)	TAIL 0A "As-rich"; used in filled-in lysimeter test	PWAT 0A
Modified process 1; finer grinding, higher reagent dosage, longer sulphide flotation than in the original (cf. Fig. 5)	TAIL 1A, "As-poor"; used in filled-in lysimeter test	PWAT 1A
Modified process 2; enhanced Cu and sulphide flotation, regrinding and (scavenger) flotation (cf. Fig. 8)	TAIL 2	PWAT 2
Modified process 3; high-gradient magnetic separation on scavenger tailings (cf. Fig. 8)	TAIL 3	PWAT 3

bound to Fe oxyhydroxides or oxides (Räisänen et al. 1992, Dold 2003, Heikkinen & Räisänen 2008), as well as 4) KClO_3 –12 M HCl + 4 M HNO_3 (Hall et al. 1996) and 5) aqua regia (1:3 HNO_3 :HCl) to digest sulphide bound fraction (modified from SFS–ISO 11466:2007, cf. also Doležal et al. 1968, Heikkinen & Räisänen 2009). The aqua regia concentrations are considered to indicate the elements that are most likely of concern in the drainage from waste (Price et al. 1997, Fosso Kankeu et al. 2015). In addition, they are used when evaluating whether mining waste is inert (Government Decree 2013a) by comparing the values with the threshold values of contaminated soils (Government Decree 2007). Element concentrations were measured from all the leachates with the ICP–OES/MS technique and pH of the tailings was determined potentiometrically from the 0.01 M NH_4Cl leach. Leaching of harmful elements from the tailings was further studied using standardized leaching tests (SFS–EN 14405 and/or SFS–EN 12457–3) and by analysing leachate from the NAG test (cf. Räisänen et al. 2010).

Process water samples were analysed for total and dissolved concentrations of elements with ICP–OES/MS techniques (SFS–EN ISO 11885, SFS–EN

ISO 17294–2), in which wet digestion technique was used for the total concentrations (SFS–EN ISO 15587–2). Anions (Br^- , Cl^- , F^- , NO_3^- , SO_4^{2-}) were measured using ion chromatography (SFS–EN ISO 10304–1) and phosphate content with flow injection analysis (FIA; SFS–EN ISO 15681–1). Ferrous iron was measured spectrophotometrically and total and dissolved concentrations of organic carbon (TOC, DOC) pyrolytically using IR detection (SFS–EN 1484). Alkalinity of the process waters was determined with titration (SFS 3005), suspended solids gravimetrically (SFS 872), and pH and EC potentiometrically (SFS 3021, SFS–EN 27888:en). Dissolved elements, ferrous iron and dissolved organic carbon were measured from filtered (0.45 μm) samples, while the rest of the analysis were made from unfiltered samples. Concentrated nitric acid, phosphorous acid and hydrochloric acid were used for the preservation of ICP–OES/MS, organic carbon and Fe^{2+} samples, respectively.

All the chemical analyses were carried out at an accredited laboratory of Labtium Oy and the mineralogical investigations were made at the mineralogical laboratories of GTK in Outokumpu and Espoo.

3 BENEFICIATION TESTS

Laboratory ball mills were used for grinding of the crushed ore samples and regrinding of tailings. Grind size was 80% <35–56 μm in most tests. Grinding was performed wet at room temperature, the pulp density generally being 50–63% solids by weight. Tap water was used. Grinding media was normally mild steel but stainless steel was also tested. Grinding of the crushed ore samples was undertaken immediately prior to flotation to minimize oxidation of sulphide mineral surfaces. In most cases, air was used as the grinding atmosphere but in one flotation test nitrogen was applied.

Flotation tests were performed using an Outotec GTK LabCell batch flotation machine and its older models. The operation principle was the same in all models. The flotation machines were equipped with automatic froth scrapers and a 45 mm rotor. The flotation cell size varied from 1.5 L to 14 L depending on the sample. In general, pulp density in the beginning of flotation was set to about 35%, and air was used as the flotation gas. Flotation chemi-

cals were added to the pulp as aqueous solutions or undiluted liquids and were measured out using pipettes. During flotation tests, pH of the pulp was measured with a calibrated glass electrode connected to a titrator (Metrohm 877 Titrino Plus). Pulp potential was monitored by the Consort C6020 multimeter using a platinum electrode as the sensing electrode and a saturated calomel electrode (SCE) as the reference electrode. Dissolved oxygen was measured using portable meter (Hach Sension+ DO6 or Hach HQ30D). The main variables studied in the flotation tests were flotation reagents and their dosages, flotation time, pulp pH, grind size, pre-oxidation of the pulp, grinding media, grinding atmosphere, and flotation gas.

Knelson gravity concentration tests were carried out using a 3" Knelson batch concentrator (model KC–MD3, Knelson Concentrators, Langley). The size of the feed batch varied between 0.5–1.5 kg. The flow rate of the feed slurry (ca. 10% w/w) introduced to the concentrator was about 1 litre/min. Rotational speed of the concentrate cone was set to 1500 rpm

and the fluidisation water pressure to 0.20 bar. Also 0.10 and 0.15 bar water pressures were applied.

For wet low-intensity magnetic separation (WLIMS), a drum separator ($\varnothing 200 \times 115$ mm) with a magnetic field strength of 0.07 T was used (Sala WS 201). A corresponding drum separator with higher intensity (0.30 T) was also tested. Concurrent configuration was applied, and pulp density was set to ca. 20% (w/w). For wet high-intensity magnetic separation, a high-gradient magnetic separator (Sala HGMS 10-15-20 SCR) was used and operated in batch mode. The matrix canister type was 3.5 XMGO, and the pulp density was set to 3–5% (w/w). Magnetic field strength in the HGMS tests varied from 0.1 to 2.0 T.

The size classification tests were carried out using elutriation which is a process based on different sedimentation velocities of particles of different size, shape, and density. First, the pulp was placed in a 4 L flotation cell. After that water was introduced into the cell at a controlled velocity. The small/light particles whose terminal sedimentation velocities were lower than the velocity of rising water rose to the top and were carried over in the water stream (overflow). The larger particles settled against the upward current. The terminal velocity could be calculated using Stoke's law.

4 FILLED-IN LYSIMETER TESTS

Filled-in lysimeter tests were conducted in the backyard of GTK Kuopio office in Eastern Finland (Fig. 2) to evaluate differences in long-term behaviour of As-rich (TAIL 0A) and As-poor (TAIL 1A) tailings. The experiment consisted of three plastic filled-in lysimeters of which one lysimeter was empty and filled naturally by rainwater. It was for the background monitoring of the local precipitation and for the potential contamination from the lysimeter materials. The other two lysimeters were each filled with 200 kg of fresh As-rich and As-poor

tailings from the beneficiation tests. Lysimeters were exposed to rainwater and other weather conditions by leaving their top open. Rainwater was allowed to percolate through the tailings and was collected to the plastic canisters from the base of the lysimeters.

Lysimeter tests were started at the beginning of July 2016, and the last water samples were taken at the beginning of November 2017. Sampling was conducted periodically 6 times, when the drainage water was unfrozen. After each sampling



Fig. 2. Plastic lysimeter filled with As-rich tailings and drainage water canister in Kuopio in summer 2016. Photo by A. Tornivaara, GTK

session, the seepage water canisters were emptied. During winter, the plastic canisters were removed and the tailings were allowed to freeze and be covered by snow. During each sampling, pH, T, EC, O₂ (mg/l), O₂ (%), and redox potential were measured by a portable multi-parameter instrument (YSI Professional Plus). The alkalinity (mmol/l) was additionally measured by titration method using a HACH digital titrator with 0.16N or 1.6N H₂SO₄ to an

end point of pH 4.5. Water samples were delivered to Labtium Oy for further analyses which included determination of dissolved solids, pH, alkalinity, dissolved and total element concentrations by ICP-OES/MS methods, anions by ion chromatography, dissolved (DOC) and total organic carbon (TOC) by pyrolytical method (SFS-EN 1484) and content of ferrous iron with spectrophotometer.

5 SUITABILITY OF MINERAL PROCESSING TECHNIQUES TO REMOVE ARSENIC AND SULPHIDE MINERALS

5.1 Mineralogy and chemical composition of the ore samples

The main valuable and harmful elements in the sorted ore sample were Au (1.0 g/t), Ag (2.4 g/t), Cu (0.10%), As (0.74%), and S (0.59%). The sample was composed mainly of various silicates such as quartz (23.5%), plagioclase (23.2%), potassium feldspar (22.0%), biotite (10.7%), actinolite (3.9%), epidote (2.8%), and muscovite (1.8%). The main sulphide minerals were arsenopyrite (1.7%), pyrrhotite (0.48%), chalcopyrite (0.32%), and pyrite (0.20%). Some goethite (0.15%) and iron oxides (0.03%) were found, too. Besides arsenopyrite, löllingite (0.01%) and various arsenate minerals such as pharmacosiderite, arseniosiderite, and scorodite (totally 0.04%) were determined as the hosts for arsenic. Goethite contained some arsenic, too. Gold was found to exist as native gold and electrum.

The unsorted ore sample contained less valuable and harmful elements than the sorted ore sample the ore grades being 0.8 g/t Au, 0.9 g/t Ag, 0.06% Cu, 0.48% As, and 0.38% S. Same minerals were

found as in the sorted ore sample but in different proportions. In general, the unsorted ore contained less sulphides and As-bearing minerals than the sorted ore sample. Interestingly, the unsorted sample contained more plagioclase (35.5%) and biotite (16.0%) than the sorted sample but less K-feldspar (7.2%).

The As-bearing minerals occurred mainly as liberated grains in the sorted ore sample comminuted for the beneficiation test (80% –44 µm). In other words, the degree of liberation was high: 97% of arsenopyrite and 80% of arsenates existed as totally free grains. The locked As mineral grains were mainly associated with silicate minerals. The degree of liberation of chalcopyrite (90%) and pyrrhotite (78%) was high, too, and the locked grains were associated with silicates for the most part. In the unsorted ore sample (80% –52 µm), liberation and association of arsenopyrite, arsenates, chalcopyrite, and pyrrhotite were similar.

5.2 Original process and As-rich tailings

Beneficiation tests were started by following the original process flow sheet planned by Belvedere Mining Oy (Ahma ympäristö Oy 2013). It consisted of crushing, grinding, copper flotation, sulphide flotation, and cyanide leaching (Fig. 3). Cyanide leaching was not investigated in this work. Some cleaner flotation tests were carried out but the main focus was on optimising the process which affected the properties of final tailings (e.g. grinding and rougher flotation in Fig. 3).

The baseline test is illustrated schematically in Figure 4. In short, it was comprised of ball mill grinding to 80% –52 µm, 6 min copper flotation

and 14 min sulphide flotation preceded by reagent addition and conditioning stages. In copper flotation, Ca(OH)₂ was used for pH adjustment, Aero 5100 as a selective copper sulphide collector, and methyl isobutyl carbinol (MIBC) as a frother. In sulphide flotation, H₂SO₄ was used as a pH regulator, CuSO₄ as an activator for sulphides and gold, potassium amyl xanthate (PAX) as a sulphide collector, Aero 7249 as a promoter for gold, and MIBC as a frother.

The Cu rougher concentrate assayed 13.0 g/t Au, 2.7% Cu, 7.7% As, and 8.1% S with recoveries of 28.0% for gold, 63.5% for copper, 27.2% for arsenic and 27.3% for sulphur. Thus, the recovery of

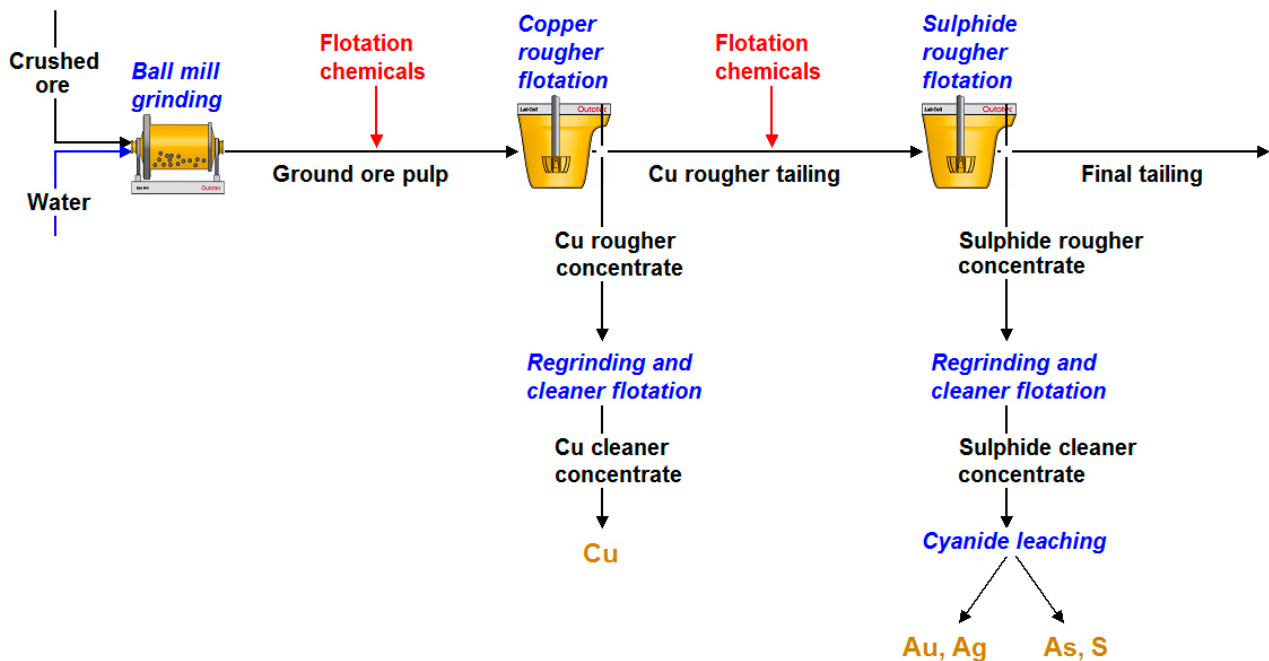


Fig. 3. Process flow sheet for beneficiation of the Kopsa ore by Belvedere Mining Oy.

copper was only moderate, and flotation was not very selective, either. The sulphide flotation gave a concentrate containing 7.1 g/t Au, 0.27% Cu, 5.6% As, and 5.5% S with recoveries of 53.5% for Au, 22.0% for Cu, 69.2% for As, and 64.0% for S. More details on the metallurgical performance and pulp chemistry can be found in the GTK Open File Work Report by Taskinen et al. (2018).

The baseline test yielded tailings called arsenic-rich in this study. The As-rich tailings assayed 0.21

g/t Au, 0.015% Cu, 0.025% As, and 0.064% S (Table 2), and contained 0.015% arsenopyrite, 0.024% arsenates, and 0.094% other sulphides. Thus, the recovery of arsenopyrite to the flotation concentrates was high, but the recovery of arsenates was much lower. The $-20\ \mu\text{m}$ size fraction of the tailings contained most of the As-bearing mineral grains, and their degree of liberation was over 97%. Coarser particles contained more locked grains. Liberation of chalcopyrite was poor in the tailings, only 5%.

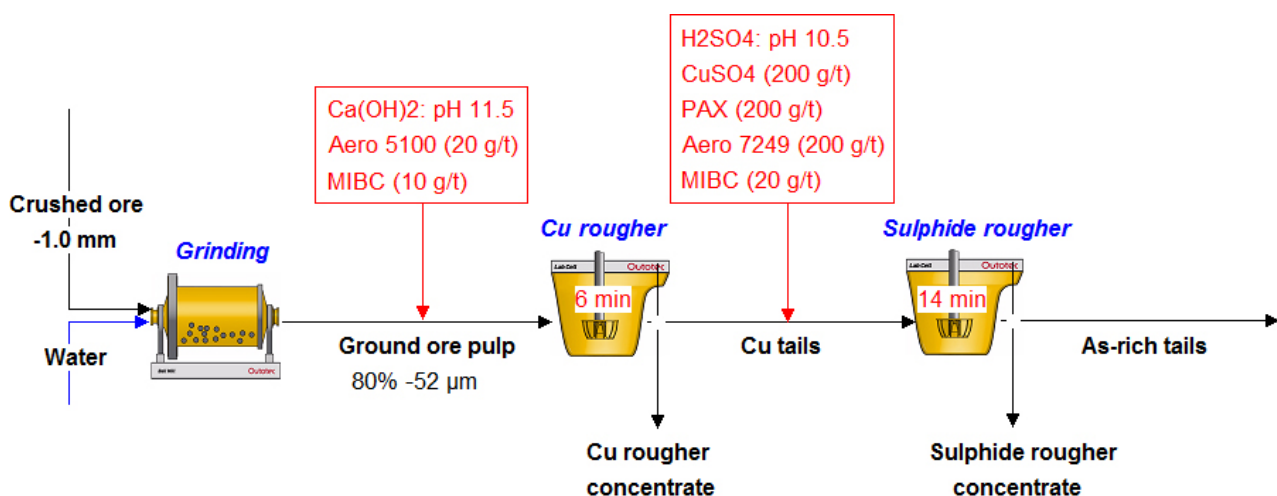


Fig. 4. Original, unmodified flow sheet including selective copper and sulphide rougher flotation stages. Grind size, total flotation times, pH regulators, and other flotation reagents with dosages are shown.

Table 2. Elemental and mineral assays in ore samples and various tailings. (n.d. = not detected)

Ore sample	Process sample	Weight (%)	Elemental assay (%)					Mineral assay (%)			
			Au (g/t)	Ag (g/t)	Cu	As	S	Arsenopyrite	Arsenate	Löllingite	Other sulphides
Sorted	Feed	100.0	0.99	2.4	0.104	0.74	0.59	1.71	0.039	0.012	1.01
	As-rich tails (Fig. 4)	90.1	0.21	—	0.015	0.025	0.064	0.015	0.024	n.d.	0.094
	As-poor tails (Fig. 5)	77.8	0.12	—	0.009	0.017	0.053	0.011	0.021	n.d.	0.042
	Scavenger tails (Fig. 8)	74.1	0.20	1.2	0.011	0.013	0.032	0.014	0.006	0.001	0.029
	HGMS tails (Fig. 8)	45.5	0.18	1.0	0.005	0.008	0.017	0.001	0.001	n.d.	0.005
Unsorted	Feed	100.0	0.82	0.9	0.056	0.48	0.38	1.10	0.010	0.016	0.63
	As-rich tails (Fig. 4)	92.7	0.15	—	0.005	0.017	0.057	0.004	0.003	0.003	0.039
	As-poor tails (Fig. 5)	76.1	0.07	—	0.003	0.010	0.036	0.002	0.006	0.000	0.015

5.3 Process modification and As-poor tailings

To improve recovery and selectivity of copper in Cu flotation and to reduce valuable and harmful element contents in the tailings, various modifications to the original flow sheet (Fig. 4) were studied. Pre-oxidation of the pulp after grinding increased selectivity of copper flotation (i.e. depressed arsenic and gold). However, it also increased As and S contents in the final tailings even though reagent dosages were increased and flotation time was extended by several dozens of minutes. More promising results with respect to tailings properties were obtained when the extended sulphide flotation was followed by regrinding of the rougher tailings to 80% –28 µm and its flotation. This procedure gave final tailings containing 0.010% Cu, 0.010% As, and 0.023% S.

As it would have been very time-consuming to carry out dozens of batch tests including regrinding in order to produce material for lysimeter tests (cf. later), another processing option was sought to improve the environmental properties of tailings. A flow sheet shown in Figure 5 was developed. Compared to the original flow sheet, it consisted of finer grinding (80% –35 µm) to improve liberation of locked copper, arsenic, and sulphide min-

erals, as well as higher reagent dosages and much longer sulphide flotation time to enhance reporting of those minerals to the sulphide concentrate. As a result, so-called arsenic-poor tailings were produced with 0.12 g/t Au, 0.009% Cu, 0.017% As, and 0.053% S (Table 2). Flotation kinetics of various elements in copper and sulphide flotation is illustrated in Figure 6. In Figure 7, tailings assays are presented as a function of flotation time. The assays decreased quickly during the first 20 minutes after which the reduction was significantly slower.

While arsenopyrite and arsenate grades decreased only slightly, the sulphide mineral content was roughly half of that in the As-rich tailings (Table 2). Liberation of chalcopyrite in As-poor tailings was better than in As-rich tailings but still poor, 20%, implying that even finer grinding would be needed to improve its recovery to the concentrates. On the contrary, liberation of As-bearing minerals was excellent in As-poor tailings, about 93%. The locked grains were mainly associated with silicates.

Tailings with reduced arsenic and sulphur could also be generated from the unsorted Kopsa ore sample by applying the modified process (Table 2).

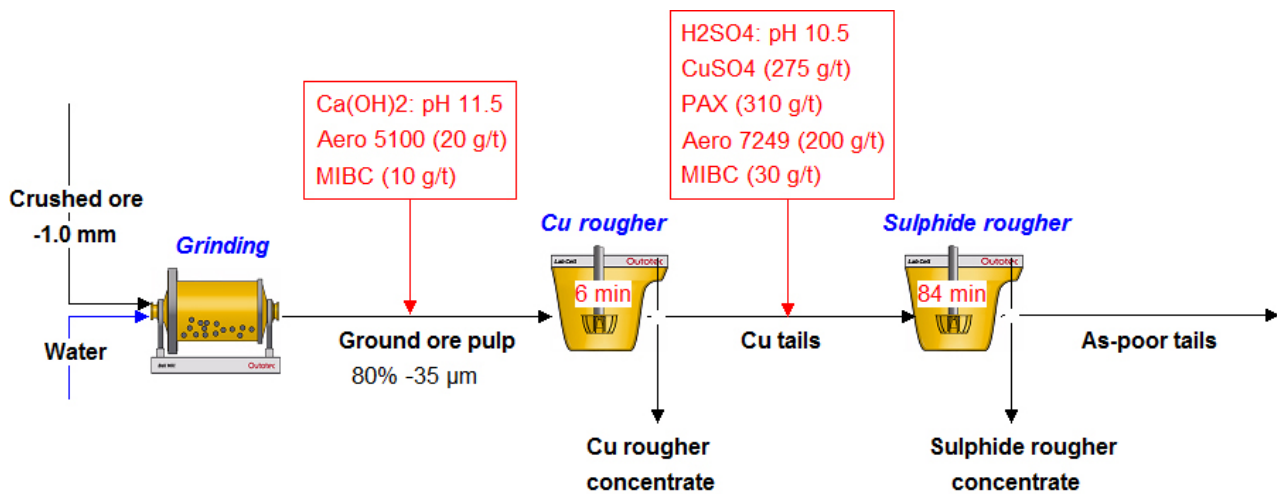


Fig. 5. Modified flow sheet including selective copper and sulphide rougher flotation stages. Grind size, total flotation times, pH regulators, and other flotation reagents with dosages are shown.

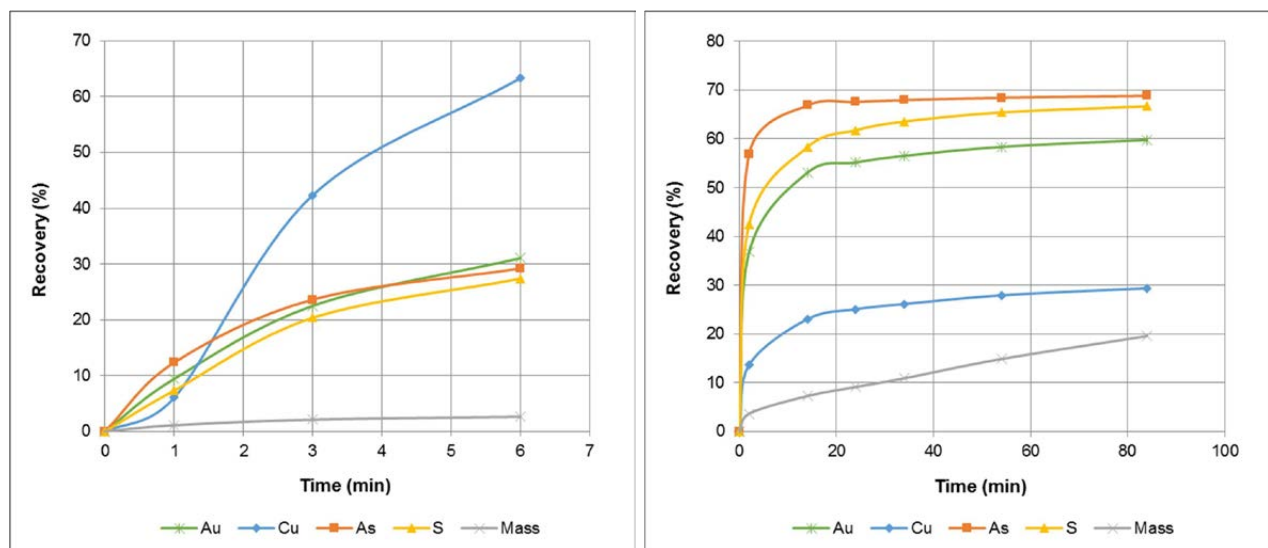


Fig. 6. Flotation kinetics of valuable and harmful elements in copper rougher flotation (left) and sulphide rougher flotation (right) of the modified flow sheet (Fig. 5).

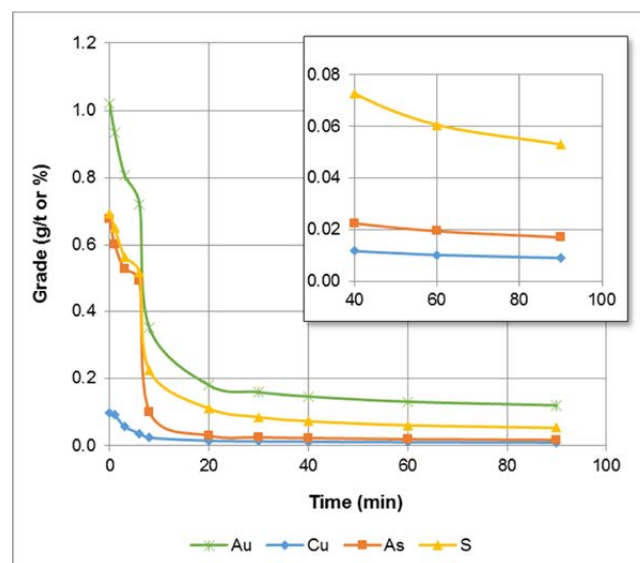


Fig. 7. Development of assays in tailings of the modified process (Fig. 5) as a function of flotation time. The inset plot is a magnification of the assays between 40 and 90 min.

5.4 Further process development and its results

To further reduce valuable and harmful elements in the tailings, several flotation, gravity concentration, magnetic separation, and classification tests were performed. Flotation alone seemed to be unable to reduce arsenic and sulphur concentrations to <0.01% and <0.02%, respectively. It was also found that both gravity concentration using a Knelson centrifugal separator and wet low-intensity magnetic separation were of little help in this endeavour. However, high-gradient magnetic separation using high magnetic fields (at least 1.0 T) appeared to be a feasible way to remove both As and S from flotation tailings. Consequently, the flow sheet optimised in this work consisted of selective copper and sulphide rougher flotation, regrinding of the rougher tailings, (scavenger) flotation, and HGMS on the scavenger tailings (Fig. 8).

Elemental and mineralogical composition of the scavenger tailings and the HGMS tailings (i.e. non-magnetic product in this case) showed that As-bearing minerals and sulphide minerals could be removed quite efficiently (Table 2). The HGMS tailings assayed 0.18 g/t Au, 1.0 g/t Ag, 0.005% Cu, 0.008% As, and 0.015% S. Therefore, the Cu, As, and S concentrations could approximately be halved by HGMS. The HGMS tailings contained only 0.002% of As-bearing minerals (excluding goethite) and only 0.005% of other sulphides. Arsenopyrite and arsenate grains were very small; ca. 80% of arsenopyrite existed as $\sim 4\ \mu\text{m}$ grains and 80% of arsenates as $\sim 9\ \mu\text{m}$ grains. Their degree of liberation was quite good, 70–80%.

As the process mineralogical results implied that As-bearing minerals were concentrated in the finest

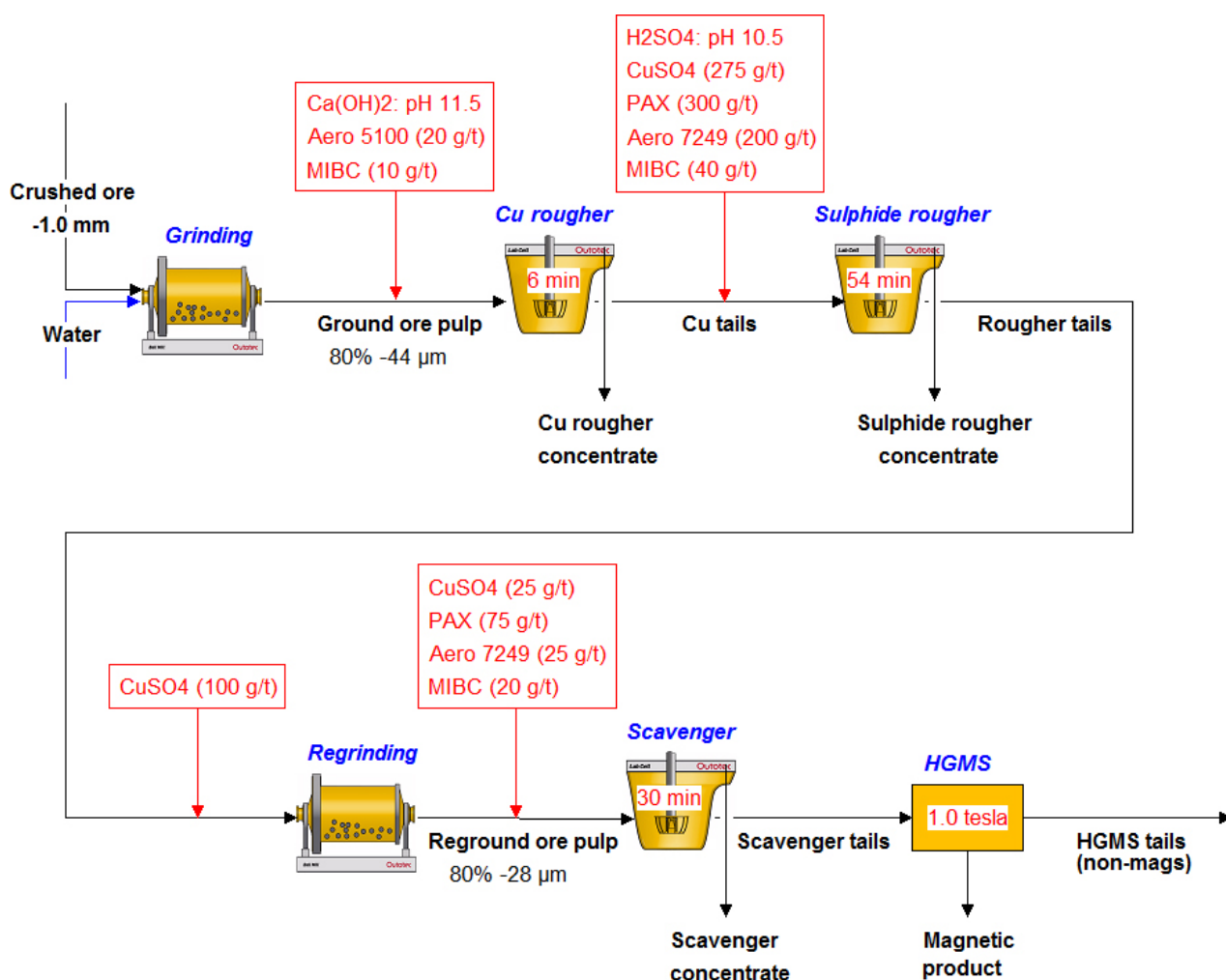


Fig. 8. Optimised flow sheet including selective copper and sulphide rougher flotation, regrinding and scavenger flotation of rougher flotation tailings, and high-gradient magnetic separation (HGMS). Grind size, total flotation times, pH regulators, and other flotation reagents with dosages are shown.

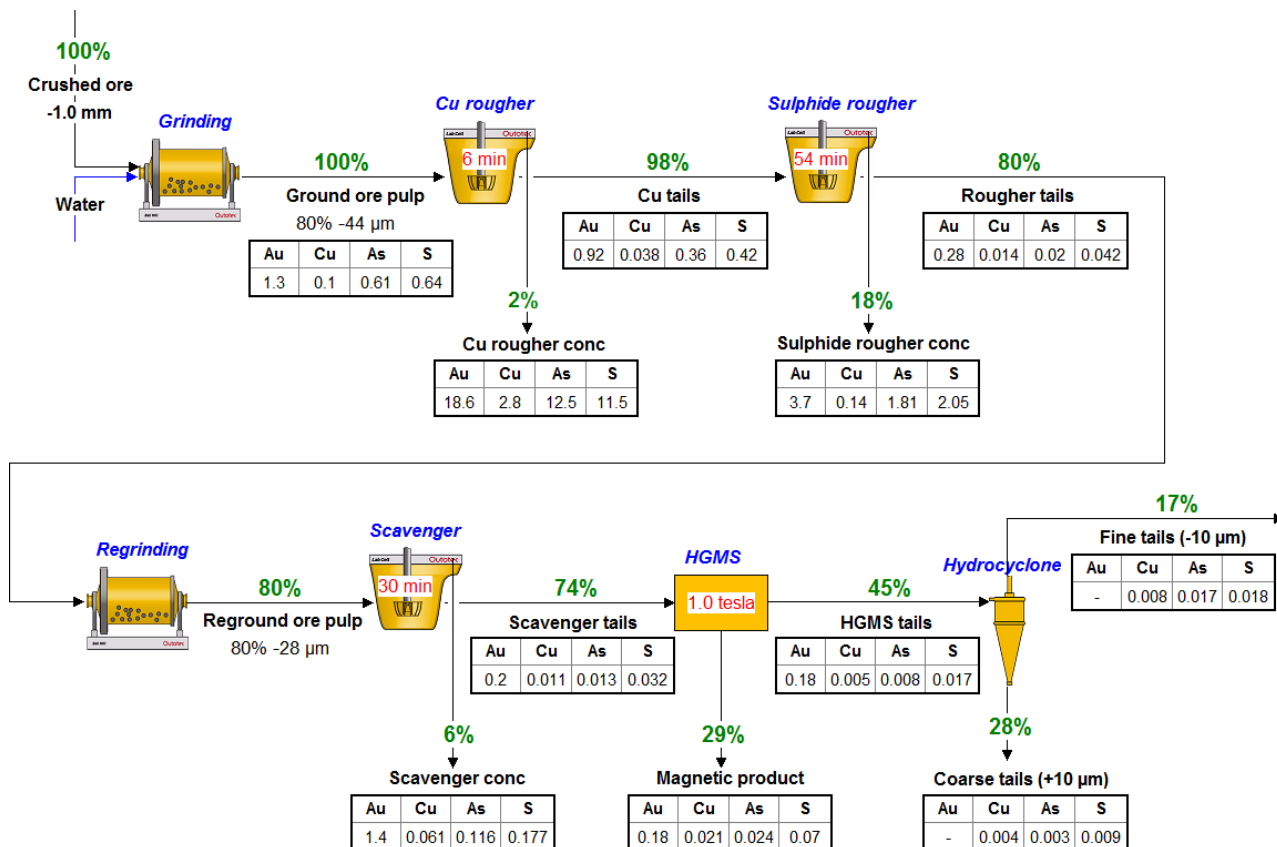


Fig. 9. Final flow sheet including classification of HGMS tailings into coarse and fine fractions by a hydrocyclone. The numbers in green denote mass of solids in each stream compared to the feed stream. Elemental assays in the streams are illustrated in the tables (Au in g/t, others in %).

particles of the HGMS tailings, it was inferred that classification could be utilised to produce a tailings fraction with even lower levels of arsenic. An elutriation process was applied to size the tailings. Arsenic concentration in the $-10\ \mu\text{m}$ fraction (36.7 Wt%) was analysed to be 0.014% by XRF (166 ppm by GFAAS), whereas As grade in the $+10\ \mu\text{m}$ fraction (63.3 Wt%) was as low as 0.001% by XRF (33 ppm by GFAAS). Thus, the coarse particles contained much less arsenic than the finest particles.

In the final process, it might be reasonable to separate the finest particles of the HGMS tailings by classification to generate waste with even lower levels of arsenic. The final flow sheet could look like the one in Figure 9 where a hydrocyclone is used to classify material into coarse and fine fractions. The mass of the coarse HGMS tailings is about 28% of the feed mass. It might be reasonable to combine the magnetic HGMS product and the fine HGMS tailings into another tailings fraction with mass of 46%, especially since their As concentrations are very similar. In continuous operation, one would probably return the scavenger concentrate to sul-

phide rougher flotation to increase the recovery of valuables into the sulphide rougher concentrate. As a result, three different tailings fractions would be formed during processing: the cyanide leach residue with high As content, combined magnetic HGMS product and fine HGMS tailings with low As content, and the coarse HGMS tailings with the lowest amounts of valuable and harmful elements.

Compared to the original flow sheet in Figure 4, the optimised flow sheet in Figure 9 is more complex and would cause higher costs for a concentrator due to longer sulphide flotation time (more/larger flotation cells), higher reagent consumption, regrinding, scavenger flotation, and a high-gradient magnetic separator. It should also be remembered that the mass percentages and elemental assays of the streams in Figure 9 were derived from open circuit, laboratory scale batch tests. In a continuous, industrial scale process including closed circuits these numbers could be different. A more accurate estimate of the tailings properties could be obtained by conducting a locked cycle test at the laboratory scale or, better, a test work at the pilot plant. The

continuous pilot-scale test run would also give information about energy consumption of various

process options, making it possible to compare the economics of various flow sheets.

6 IMPACTS OF PROCESS MODIFICATIONS ON THE ENVIRONMENTAL CHARACTERISTICS OF THE TAILINGS AND PROCESS WATER

Environmental characterisation of the Kopsa tailings and process waters was carried out to evaluate the influence of process modifications on their environmental properties and performance. The studies focused on the occurrence and long-term behaviour of arsenic, copper and sulphur in the

original versus modified tailings. In the following chapters, the main results of the environmental characterisation are discussed. Additional details of the results are provided in the report by Taskinen et al. (2018).

6.1 Influence on the properties of the Kopsa tailings

6.1.1 Chemical and mineralogical composition of the tailings and the occurrence of As-bearing minerals and sulphides

Based on the XRF results, the primary contaminants in the Kopsa tailings included As (0.01–0.03%), Cu (0.005–0.15%), and S (<0.01–0.09%). Concentrations of other potentially hazardous trace metals were low (<100 mg/kg), except for W. All the tailings were classified as non-inert mining waste, since the aqua regia leachable concentrations of As (106–292 mg/kg) exceeded the threshold value (5 mg/kg) of contaminated soils in the tailings (Government Decree 2007, 2013a). In addition, the Cu content (101–154 mg/kg) was above the threshold value (100 mg/kg) except for the HGMS tailings

(61 mg/kg). The total S content was, nevertheless, below the limit value (0.1%) for inert mining waste (Government Decree 2013a). Even though the trace metal concentrations were overall low, some of the trace metals occurred in elevated concentrations (e.g. Bi 5.7–10.6 mg/kg, Mo 0.2–2.7 mg/kg, W 116–162 mg/kg) compared e.g. with the fine fraction of Finnish tills (Koljonen 1992) or the subsoils in Europe (Salminen et al. 2005).

The highest aqua regia concentrations of As, Cu, and S occurred in the original Kopsa tailings (TAIL 0A), processed following the process by Belvedere Mining Oy, while the lowest were in the HGMS tailings (TAIL 3) (Fig. 10). Overall, the As content in the HGMS tailings was only one third of that in the original tailings, S content ca. 11%, and that

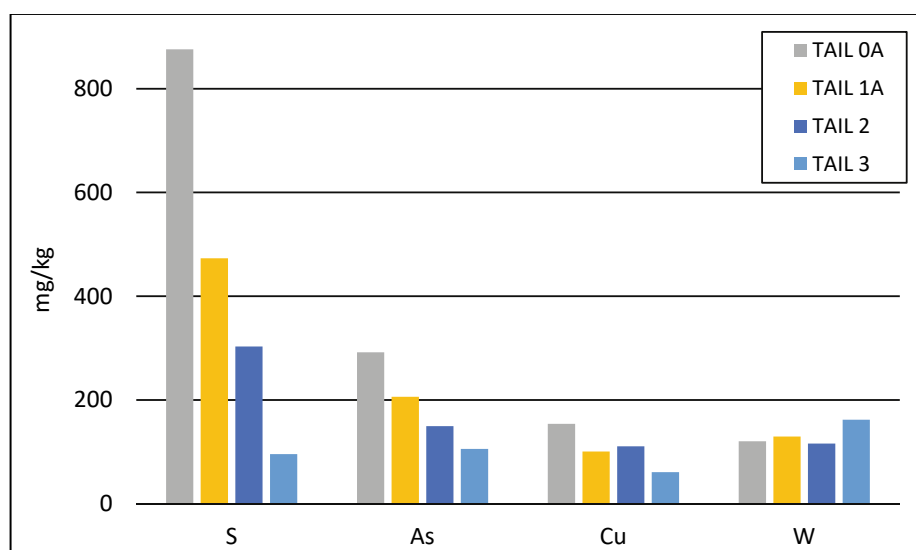


Fig. 10. Aqua regia leachable concentrations of S, As, Cu, and W in the Kopsa tailings. TAIL 0A = As-rich tailings from the original process, TAIL 1A = As-poor tailings from modified flotation, TAIL 2 = tailings from scavenger flotation, TAIL 3 = tailings from HGMS.

of Cu approximately 40%. This indicated that the modification of the process had been successful in reducing As, Cu, and S in the tailings. Interestingly, tungsten content (162 mg/kg) was, nevertheless, highest in the HGMS tailings. Despite the notable reduction of the As content during mineral processing, the HGMS tailings were still classified as non-inert mining waste, since the aqua regia leachable concentration of As was above the threshold limit of the contaminated soils.

The primary sources for As in the tailings included arsenopyrite (FeAsS), löllingite (FeAs_2) and arsenates, such as scorodite/parascorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and pharmacosiderite ($\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 6\text{H}_2\text{O}$) or arseniosiderite type ($\text{Ca}_2\text{Fe}_3^{3+}\text{O}_2(\text{As}_2\text{O}_4)_3$) mineral. In addition, based on the microprobe analysis, goethite contained As (As_2O_5 0.04–5.9%). The

main hosts for S, aside from the As-sulphides, were pyrrhotite, (FeS_{1-x}), chalcopyrite (CuFeS_2), pyrite (FeS_2), sphalerite (ZnS), covellite (CuS) and goethite. Cu originated mainly from chalcopyrite and covellite, and small amounts of Cu occurred also in goethite. The main source for W was scheelite (CaWO_4).

The mineralogical results showed that the reduced contents of As, Cu, and S in the HGMS tailings were a result of efficient removal of As-bearing mineral phases and sulphides with the modified process. Overall, the reduction of these minerals was notable: the amounts of As-bearing mineral phases decreased from 0.04% in the original tailings (TAIL 0A) to 0.002% in the HGMS tailings (TAIL 3), and those of sulphides from 0.09% to 0.005%, respectively (Fig. 11). Specifically, arseno-

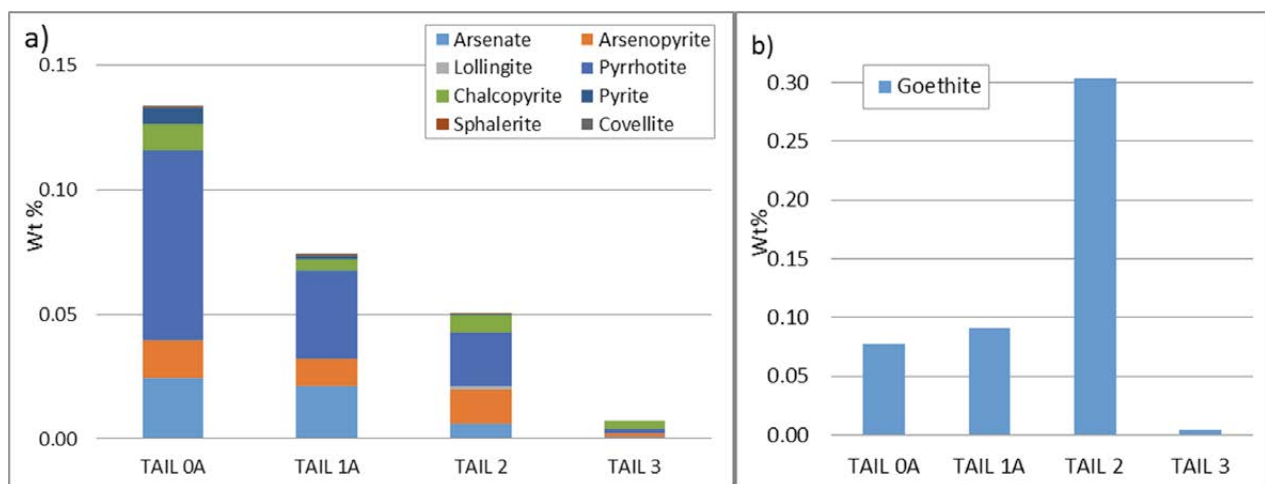


Fig. 11. Amounts of a) As and sulphide minerals and b) goethite in the Kopsa tailings. TAIL 0A = As-rich tailings from the original process, TAIL 1A = As-poor tailings from modified flotation, TAIL 2 = tailings from scavenger flotation, TAIL 3 = tailings from HGMS.

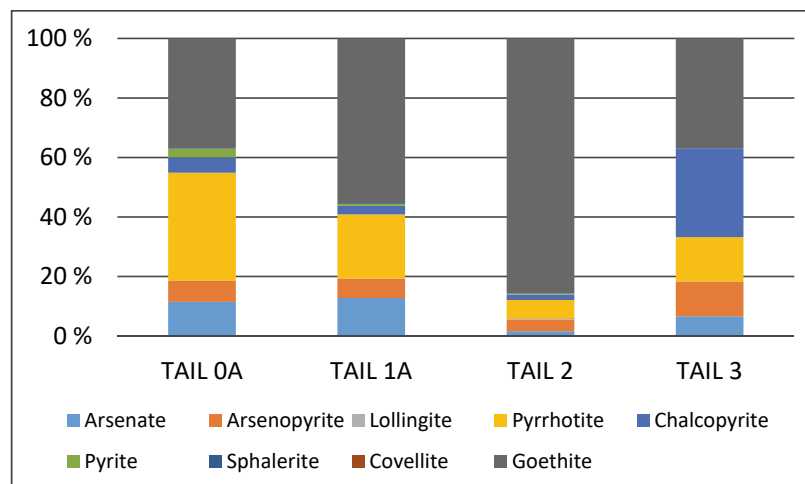


Fig. 12. Proportions of As-bearing minerals and sulphides in the Kopsa tailings. TAIL 0A = As-rich tailings from the original process, TAIL 1A = As-poor tailings from modified flotation, TAIL 2 = tailings from scavenger flotation, TAIL 3 = tailings from HGMS.

pyrite decreased from 0.015% to 0.001%, arsenates from 0.024% to 0.0007%, pyrrhotite from 0.08% to <0.002%, and chalcopyrite from 0.011% to 0.004%. In the HGMS tailings, goethite was the most abundant As-bearing mineral phase and also the most abundant source of Cu and S (Fig. 12).

Despite the successful removal of As and sulphide minerals, the scheelite content was somewhat higher in the HGMS tailings (0.05%) than in the original tailings (0.03%). In addition to As, W is a toxic metal and its aqua regia concentration was clearly elevated in the HGMS tailings (162 mg/kg) e.g. with respect to the concentration in Finnish tills (0.2 mg/kg, Koljonen 1992). The enrichment of W is most likely due to the fact that scheelite is heavy mineral (Koljonen 1992 and references therein), and as such ends up in the waste fraction. Similar concentrations of W have been observed in the tailings of the closed Ylöjärvi Cu–W–As mine (Parviainen et al. 2012).

Degree of liberation, grain size and mineral associations of the As-bearing mineral phases and sulphides were further studied to evaluate impacts of process modifications on their reactivity. Based on the results, these minerals occurred in the tailings mainly as well liberated grains in the finest fraction, but partly also associated with silicate minerals. In the HGMS tailings (TAIL 3), the portion of both As minerals and sulphides associated with silicates was slightly higher than in the original tailings (TAIL 0A), decreasing their liberation and also reactivity.

6.1.2 Leachability of As, Cu, and S from the tailings

Effects of process modifications on the distribution of As, Cu, and S in different mineral phases and their mobility were evaluated based on selective extractions, leaching tests (SFS EN 12457-3, SFS EN 14405) and leachates from NAG test.

The results of the selective extractions showed that both As and Cu were distributed in the tailings quite evenly mainly in three fractions: sulphide, oxalate, and acetate fractions, while S was mainly present in the sulphide fraction (Fig. 13). Small portion of S occurred also in the oxalate and soluble fractions. The sulphide bound As originated from arsenopyrite and löllingite, Cu from chalcopyrite and covellite, and S from sulphides in general. The oxalate and acetate fractions most likely represented As and Cu in goethite and (secondary) arsenates (cf. e.g. Parviainen et al. 2012). The host for S in the oxalate fraction was also goethite, while the soluble fraction of S was presumably largely from H_2SO_4 and $CuSO_4$ used in mineral processing (cf. Heikkinen 2009), but also from the sulphide mineral edges broken during processing (cf. Räisänen et al. 2002).

The distributions of As, Cu, and S clearly changed as a result of process modifications. In the original tailings (TAIL 0A), the sulphide fraction was the primary fraction for all these elements (As 49%, Cu 69%, and S 84%), but in the HGMS tailings (TAIL 3) the proportion of the sulphide fraction was noticeably smaller, particularly for As (As 33%, Cu 58%, S 71%). Instead, higher percentage of As, Cu, and S occurred in the HGMS tailings in the oxalate and acetate fractions (As 66%, Cu 41%, S 16%), i.e. in goethite and arsenates, than in the original tailings (As 49%, Cu 31%, S 8%). This change is in line with the mineralogical results according to which goethite was the most abundant host for these elements in the HGMS tailings (cf. Fig. 12). Unlike sulphide minerals whose dissolution is strongly dependent on oxygen availability, the solubility of goethite and arsenates is pH dependent and also relies on the crystallinity of these mineral phases (Paktunc & Bruggeman 2010). For example, synthetic scorodite has higher solubility at low (<2) and high pH (>6)

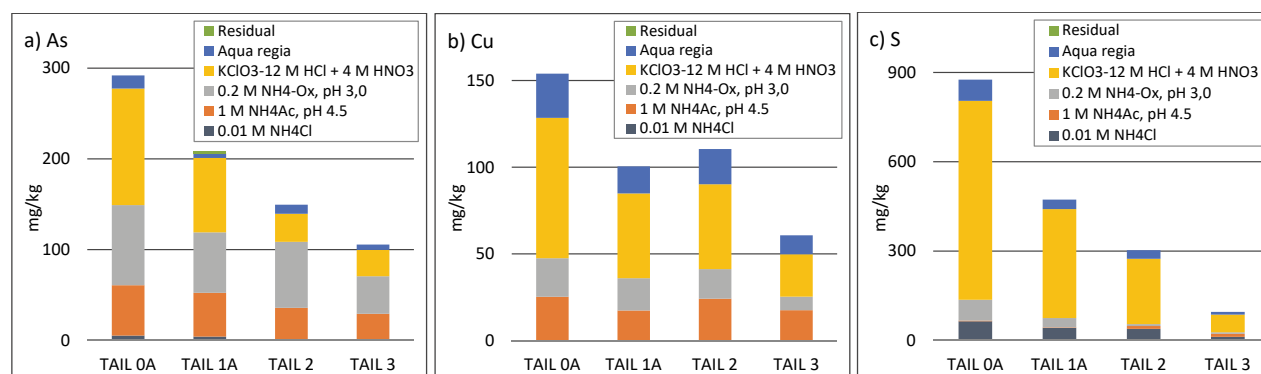


Fig. 13. Distribution of a) As, b) Cu, and c) S in different fractions based on selective extractions.

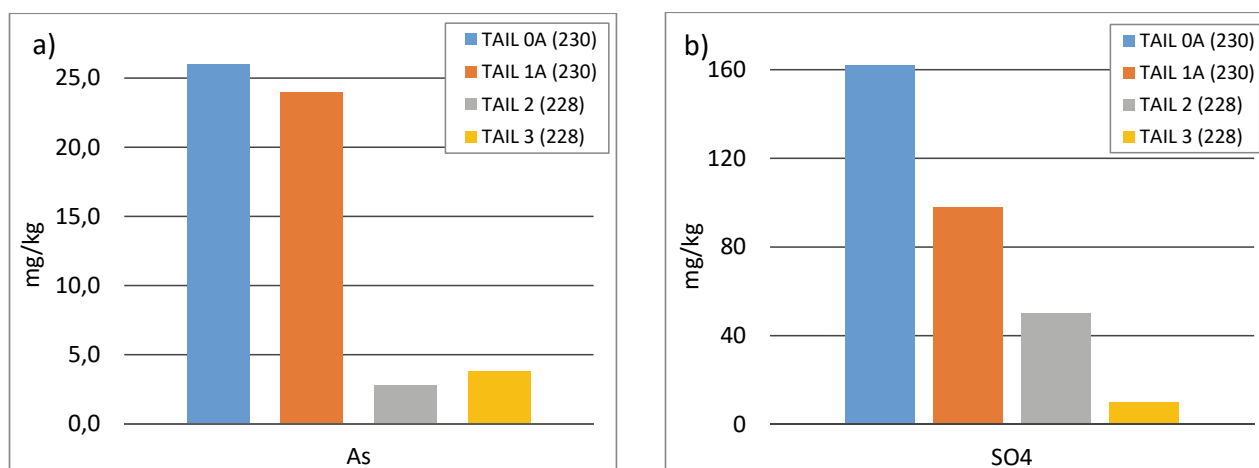


Fig. 14. a) As and b) SO₄ concentrations of the Kopsa tailings based on the leaching tests. TAIL 0A = As-rich tailings from the original process, TAIL 1A = As-poor tailings from modified flotation, TAIL 2 = tailings from scavenger flotation, TAIL 3 = tailings from HGMS. (230 = SFS-EN 14405, 228 = SFS-EN 12457-3).

than at around pH 3–4. The dissolution rate of e.g. Fe arsenates has been found to be slower than that of sulphides (Paktunc & Bruggeman 2010). Therefore, it seems that in the HGMS tailings As, Cu, and S are less mobile with respect to mineral oxidation than in the original tailings, but their leaching is more susceptible to changes in pH than initially.

The leaching tests and analysis of NAG leachate were further applied to evaluate mobility of As, Cu, and S/SO₄ as well as other trace elements from the tailings. Based on the tests, the leaching solutions and the NAGpH of all the tailings were alkaline (leaching tests: pH 9.0–9.3 (only TAIL 2 and TAIL 3); NAG leachate: 7.9–8.7). The tests showed leaching of mainly As and S together with dissolved organic carbon from all the tailings. In the NAG tests also some W was leached. Concentrations of other trace metals were mainly under detection limits, which is in accordance with the alkaline pH. The alkaline pH decreases mobility of most of the trace metals that occur in solution as cations (e.g. Cu, Ni, Zn), but increases that of metals/semimetals that

occur in anionic form, such as As, Mo, and W (e.g. Stumm & Morgan 1996, Bednar et al. 2009). The organic carbon most likely originated from residues of organic process chemicals used in mineral processing and is not discussed here any further. Results of these chemical residues are discussed in more detail in the report by Taskinen et al. (2018).

The process modifications clearly decreased the leaching of As and S from the Kopsa tailings (Fig. 14). Based on the leaching tests, leaching of As had decreased by ca. 85% and that of sulphate by ca. 94% from the original tailings to the HGMS tailings. Despite this, As concentration (3.8 mg/kg) in the leaching test solution (at L/S ratio 10) of the HGMS tailings exceeded e.g. the limit value (2 mg/kg) set by the European Council (2003) for the non-hazardous waste disposed at landfill sites (cf. also Government Decree 2013b). However, this was still a notable improvement, since in the original tailings the limit value for the hazardous waste (25 mg/kg) was exceeded (26 mg/kg).

6.2 Influence on the process water quality

In addition to the tailings solid, the impact of process modifications on the quality of process water was evaluated. Overall, the process waters were alkaline (pH 8.2–10.1) and contained elevated concentrations of As (33–775 µg/l) and SO₄ (37–310) with minor Mo, I, and B. The process modifications had similar effects on the process waters as were observed in the tailings quality and their leaching properties. Namely, the reduction of As and

SO₄ content in the process water from the original process to the HGMS process was notable (Fig. 15), being 96% for As and 89% for SO₄. This indicates that the efforts made to improve the tailings quality also affected positively the process water quality. However, part of the reduction in the concentrations is also due to dilution, since more water was used in the HGMS process than in the original process.

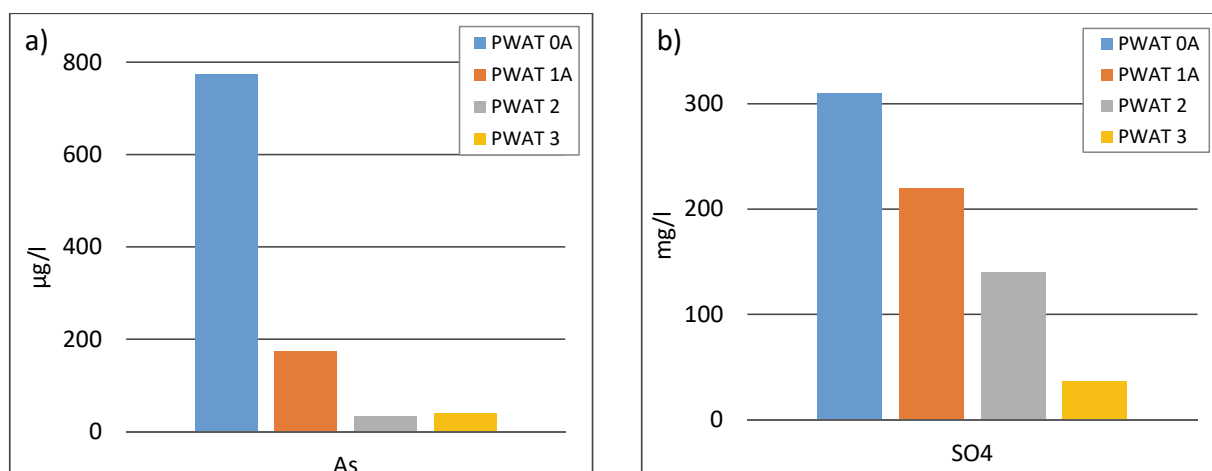


Fig. 15. As and SO₄ concentrations in the process waters from the Kopsa tailings. PWAT 0A = process water of the As-rich tailings from the original process, PWAT 1A = process water of the As-poor tailings from the modified flotation, PWAT 2 = process water of the tailings from scavenger flotation, PWAT 3 = process water of the tailings from HGMS scavenger flotation.

7 FILLED-IN LYSIMETER TESTS TO EVALUATE LONG-TERM BEHAVIOUR OF THE MODIFIED TAILINGS

Filled-in lysimeter test were carried out to study the effects of process modifications on the long-term behaviour of the tailings. In addition, suitability of the modified tailings for a cover material on top of other tailings was assessed.

The tailings used in the filled-in lysimeters included the As-rich tailings (TAIL 0A) from the original process of the sorted ore (Fig. 4) and

As-poor tailings (TAIL 1A) from the modified process (Fig. 5). Both tailings were non-inert, not acid generating mining waste (see above). The As-poor tailings were used in the lysimeter tests instead of the HGMS tailings (Fig. 8) or the coarse fraction of the HGMS tailings (Fig. 9), because they had the lowest As content at the time when the lysimeter test was set up.

7.1 Characteristics of the tailings of the lysimeter tests

Prior to the lysimeter tests, mineralogical and chemical characterisation of the tailings materials was carried out to describe material properties as a background for the interpretation of the test results. In the following, the main results of the characterisation are presented with an emphasis on the marked differences between the two lysimeter materials.

7.1.1 Tailings mineralogy

The differences in the occurrence of the As bearing minerals in the two tailings were rather small. The As-poor sample contained slightly smaller amount of arsenic minerals (arsenopyrite 0.01% and Fe arsenate 0.02%) than the As-rich tailings (both As minerals were 0.02%), but the As-poor tailings contained somewhat more goethite (0.09%) than

the As-rich tailings (0.08%). The sulphide mineral content of the As-rich tailings was higher (0.09%) than that of the As-poor tailings (0.04%). The carbonate content of both tailings was very similar.

The As minerals were in both tailings mainly well liberated and occurred as free grains (liberation degree approximately 90%; except for arsenopyrite 82% in the As-rich tailings). The rest of the As minerals were locked in silicates. The major difference between the two tailings was that in the As-poor tailings arsenate occurred clearly in higher portion as free mineral surfaces (97.5% as free surfaces and only 2% associated with silicates) than in the As-rich tailings (91.4% and 8.3% associated with silicates). In addition, in the As-poor tailings part of the arsenate occurred in association with unliberated mixed particles with Fe-hydroxides, but not in the As-rich tailings.

Furthermore, the As-poor tailings were somewhat finer grained (75% <32 µm) than the As-rich tailings (60% <32 µm), but the grain size of arsenate and arsenopyrite was the opposite way around.

The particle size distribution may affect the leaching of elements from the tailings, since fine grained material can retain more water, thus conducting it slower, which further affects weathering conditions.

7.1.2 Tailings chemistry

Based on the total concentrations and aqua regia leachable concentrations of the lysimeter tailings, the concentrations of As and S and several trace metals were clearly smaller in the As-poor tailings than in the As-rich tailings (Table 3). Particularly, As content had decreased from 300 mg/kg to 200 mg/kg, and S from 900 mg/kg to 500 mg/kg. Also Co, Cr, Cu, Ni, and Mo contents were lower in the As-poor tailings (Table 3).

Based on the selective extractions, most notable difference between the two tailings was in the distributions of As, Co, Cr, Ni, and Mo in different fractions (Fig. 16). For example, higher portion of As occurred in the acetate and oxalate fraction in the As poor tailings than in the As rich tailings, in which most of the As was in sulphides. This is in

line with the observations from the mineralogy. The As-poor tailings contained less arsenopyrite, but had same amount of arsenate and higher goethite content than the As-rich tailings. The latter minerals dissolve in oxalate extraction (cf. Dold 2003, Parviainen et al. 2012).

Both tailings showed elevated leaching of As and S in the leaching test (SFS-EN 14405) and the NAG test. However, in the NAG test the content of leachable As and S were clearly smaller in the As-poor tailings (As 37 mg/kg and S 433 mg/kg) than in the As-rich tailings (51 mg/kg and 799 mg/kg, respectively). In the leaching test, the As content in the As-rich tailings (26 mg/kg) exceeded the limit value set by the European Council (2003; also Government decree 2013b) for the hazardous waste (25 mg/kg) to be disposed in landfills, but in the As-poor tailings the content was only slightly lower (24 mg/kg), exceeding the limit value for the non-hazardous waste (2 mg/kg).

Process water quality was further analysed from both tailings samples. Both waters were alkaline in pH (8.7 and 10.1) and showed elevated concentrations of As, SO₄ and Mo (Table 4). Overall, pH, electrical conductivity and concentrations of As, SO₄ and Mo were higher in the As-rich tailings water than in the process water from the As-poor tailings (Table 4).

Table 3. Aqua regia leachable and total concentrations of selected elements in the As-poor and As-rich tailings (mg/kg). * P from the XRF-method has been calculated from P₂O₅ results. Values exceeding the threshold value of contaminated soils (Government Decree 2007) are marked with green shading, those over the lower limit value with yellow, and those exceeding the upper limit value with red shading. (Tail = tailings).

(mg/kg)	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	P	Pb	S	Sb	V	W	Zn
XRF-method (Total)															
As-poor tail	205	n.a.	n.a.	30	102	286	<10	<20	369*	<20	505	<100	71	n.a.	42
As-rich tail	310	n.a.	n.a.	40	149	278	<10	<20	331*	<20	919	<100	72	n.a.	43
Aqua regia 90 °C (AR)															
As-poor tail	206	0.1	1.6	24.6	101	228	1.3	8.3	308	3.6	473	1.3	52	130	26
As-rich tail	292	0.1	2.2	29.8	154	230	2.7	15.8	310	4.2	876	1.6	52	121	28

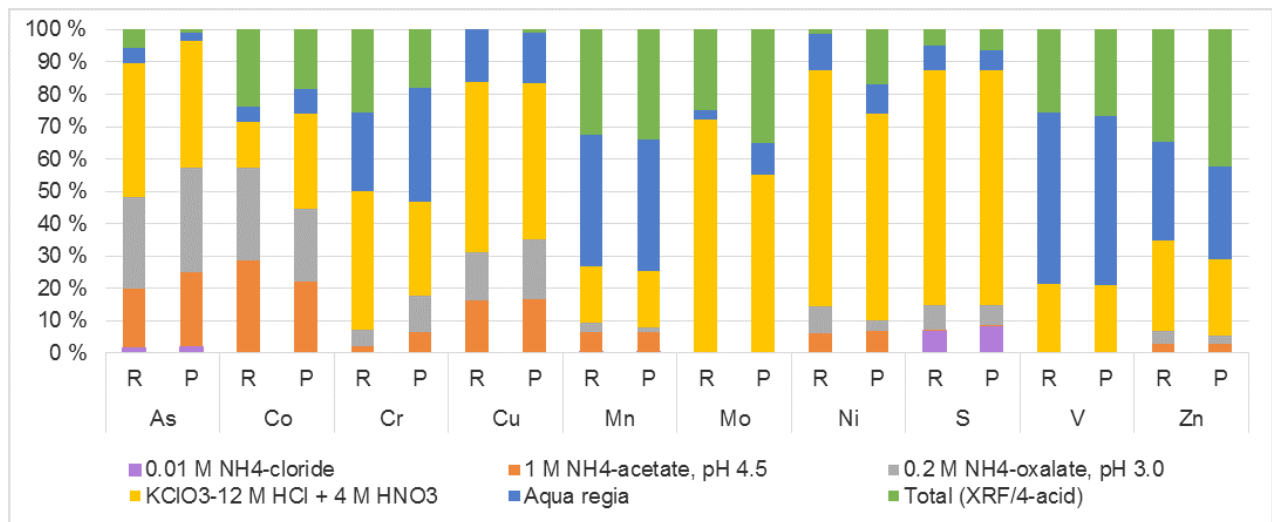


Fig. 16. Relative distribution of selected elements in different fractions based on selective extractions. P = As-poor tailings and R = As-rich tailings.

7.2 Results of the one and a half years of seepage monitoring

The quality of the drainage water from the lysimeters was monitored six times during the observation period of one and a half years. The drainage from both lysimeters was alkaline (7.1–8.0) and their electrical conductivity (EC) indicated elevated content of dissolved ions (Fig. 17). The alkaline pH was expected as the beneficiation process was carried out at alkaline pH, and the tailings materials were unoxidised and contained only minor sulphides. The pH values did not depend much on the lysimeter or the sampling time. The electrical conductivity (EC) suggested higher leaching of ions in the beginning of the monitoring period in the As-rich drainage than in the As-poor drainage, but towards the end

of the monitoring period the EC reached the same level in both drainages (ca. 40 mS/m). Redox potentials of both drainages decreased towards the end of the observation period being negative in the last measurement, thus suggesting a more reducing environment (Fig. 17). The alkalinity and oxygen ratios remained at the same level in both lysimeter drainage waters throughout the monitoring period.

Overall, the drainage waters contained elevated concentrations of As, SO₄, Mn, Mo, and P, while contents of Sb, Cu, and Ni were low (Figs. 18 and 19). This is in line with the tailings chemistry and the fact that alkaline pH of the lysimeter drainages increases the mobility of oxyanions like arsenate,

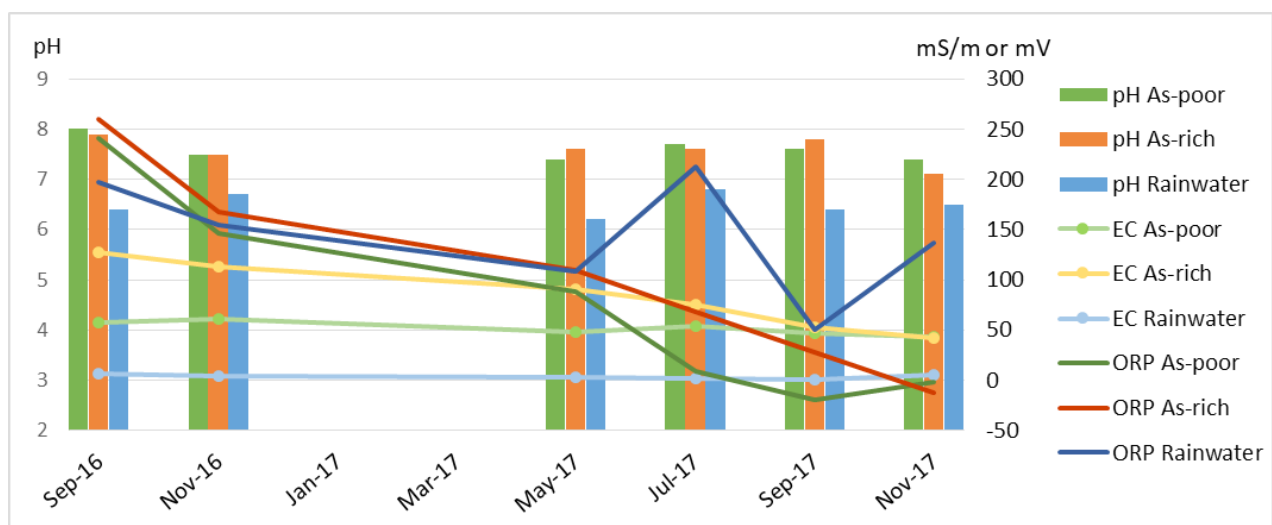


Fig. 17. pH, redox potential (ORP, mV), and electrical conductivity (EC, mS/m) in the As-poor and As-rich seepage waters and in the control lysimeter (rainwater).

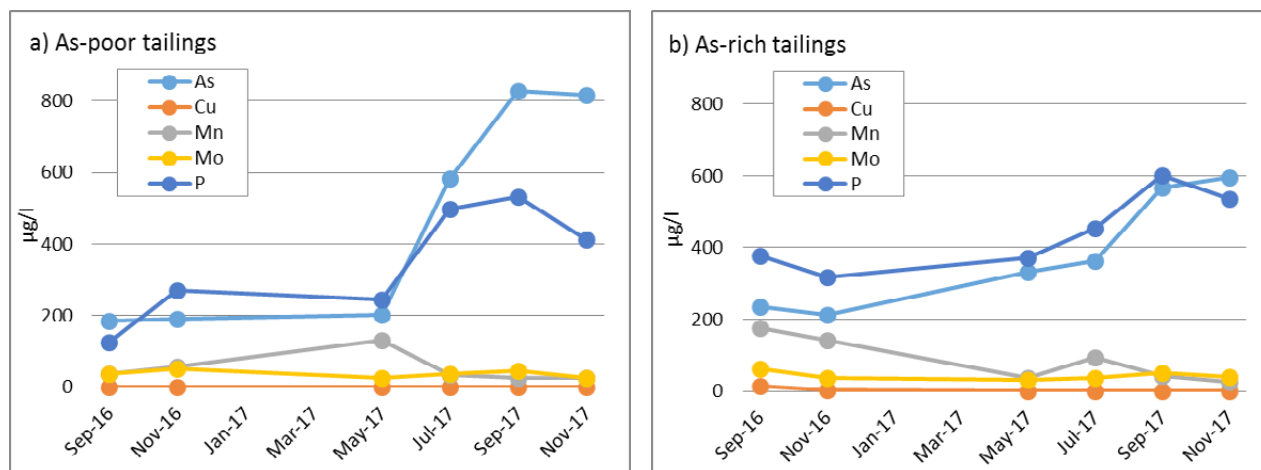


Fig. 18. Concentrations of As, Cu, Mn, Mo, and P in the drainage of the lysimeters of a) As-poor and b) As-rich tailings.

phosphate and molybdenate (cf. Stumm & Morgan 1996). The concentrations of these elevated compounds were clearly higher in the drainage from the As-rich lysimeter than from the As-poor lysimeter at the beginning of the test, which was expected based on the characteristics of the tailings in the lysimeters. Towards the end of the monitoring period, concentrations of SO_4 , Mn and Mo mainly decreased in the drainage from As-rich lysimeter reaching similar levels as the drainage from the As-poor lysimeter at the end. The concentrations of As and P nevertheless steadily increased. However, their concentrations also increased abruptly in the drainage from the As-poor lysimeter, and at the end of the monitoring period the As content (817 µg/l) eventually exceeded that of the drainage from the As-rich lysimeter (596 µg/l) (Fig. 18). During the

whole monitoring period, As concentrations in the drainages were much higher than for example the As threshold 10 µg/l for household consumption water (Decree of Ministry of social affairs and health 2015).

Table 4 emphasises the differences in the drainage quality from the lysimeters between the first three (from 9/2016 to 5/2017) and last three (from 7/2017 to 11/2017) analysis results (average concentrations of soluble concentrations of three measurements) to evaluate a possible first flush effect and longer term behaviour. In addition, the table shows the chemical assays of process waters from both tailings slurries to assess whether the remaining process water had influenced the lysimeter drainage quality. Overall, concentrations of most of the elements were higher in the first measurement period than in the last period suggesting the influence of

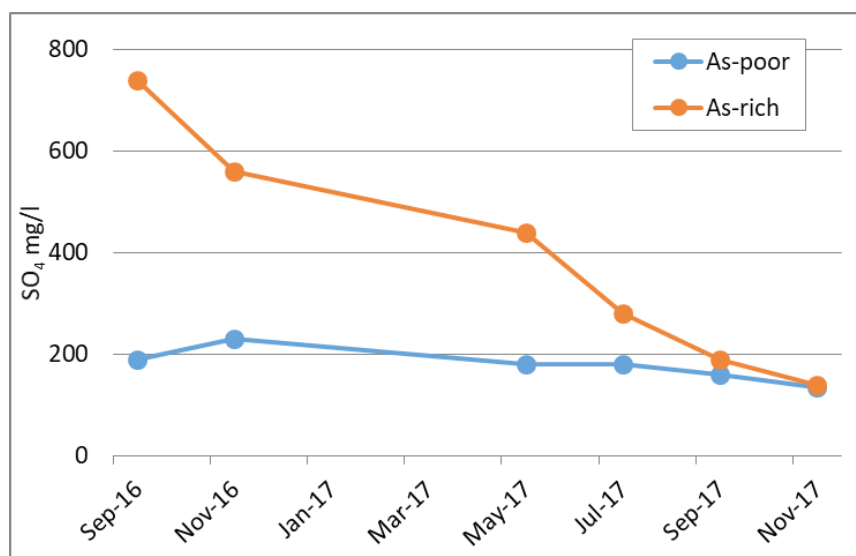


Fig. 19. SO_4 concentrations in the drainage of the lysimeters of As-poor and As-rich tailings.

Table 4. Average concentrations of seepage waters from the lysimeters of As-poor and As-rich tailings of two monitoring periods. Red shadings emphasise the monitoring period (I or II) with higher concentrations, the numbers in bold the lysimeter drainage (As-poor or As-rich) with higher concentrations and the green shadings notably elevated concentrations in the tailings water. (TW = Tailings water, I period = average of 3 seepage samples from 09/2016–05/2017 and II period = average of 3 seepage samples from 07/2017–11/2017.)

µg/l		As	Co	Cr	Cu	Mn	Mo	Ni	P	Sb	U	V	Zn	Al	S
As-rich	TW	775	0.03	1.8	<0.5	1.4	55	<0.5	4	<2	0.02	4	<1	337	344 000
	I	260	0.2	<0.2	5.8	118	43	1.6	355	11	7.6	0.2	1	18	181 000
	II	508	0	<0.2	0	54	42	0.2	530	6	0.4	0.2	1.8	23	70 000
As-poor	TW	174	0.02	<0.1	<0.5	4	21	0.6	2	<2	0.3	1	<1	77	269 000
	I	193	0.1	<0.2	0.6	74	38	0.4	214	10	2	0.2	4.9	17	71 000
	II	743	0	<0.2	0	28	36	0.1	482	8	0.4	0.1	0.5	23	57 000

first flush. The most notable exception was nevertheless As with the highest content in the last period (Table 4). Influence of the process water seemed to be quite minor, even in the first measurement period (Table 4).

Based on the seepage monitoring results, both tailings are prone to produce neutral drainage with high As concentration. Unexpectedly, the As-poor tailings produced eventually drainage with higher As content during the observation period than the As-rich tailings. Both soluble and total concentrations of all the other elements were low in the seepage.

The higher solubility of As from the As-poor tailings is most likely caused by the differences in the association, liberation and grain size of the As-bearing minerals, or better fracturing due to finer grind size. The grain size distributions of arsenopyrite and arsenates were finer in the As-rich lysimeter, which should have an opposite effect to arsenic weathering and mobility. However, in the As-poor tailings arsenates had more free surface area (ca. 7% more) and were less extensively associated with silicates (2.0%) than in the As-rich tailings (8.3%).

The elevated As concentration in seepage after one year of observation suggests that mineral

weathering reactions had eventually started in the tailings, even though part of the As also originated from the broken edges of As minerals. However, the increased SO_4 concentrations at the beginning of the monitoring period most likely originated mainly from the residues of processing chemicals, such as H_2SO_4 and CuSO_4 , and from the mineral edges broken in the processing, instead of sulphide oxidation. This is particularly since the sulphide content of the tailings was quite small and mineral grains were unoxidised at the beginning of the tests. During the tests, alkaline pH favours dissolution of arsenates (cf. Paktunc & Bruggeman 2010). In addition to the reasons mentioned above, the higher solubility of arsenic in the As-poor lysimeter can result from differences in water content, adsorption properties, hydraulic conductivity, pore size and quantity of tailings in the lysimeters. Seasonal variation in seepage concentrations, for instance as a result of an accelerated oxidation and increased element mobility, were not observed in this study. Overall, it is obvious that the As-poor tailings are not suitable for a cover material. Further studies and more sampling is nevertheless needed to confirm these observations and to predict long-term behaviour of the tailings.

8 CONCLUSIONS

Laboratory scale beneficiation tests were carried out to assess the suitability of various mineral processing techniques to improve environmental properties of tailings from the Kopsa Au–Cu ore samples. The influence of process modifications on the tailings was studied using mineralogical and geochemical

characterisation together with filled-in lysimeters which measured long-term behaviour together with drainage quality in field conditions.

The most promising process to reduce arsenic and sulphide minerals from the original, As-rich tailings consisted of froth flotation followed by

high-gradient magnetic separation (HGMS). The results showed that for example very fine grinding, long flotation time, and high magnetic fields were required to liberate and recover most of the harmful and valuable minerals. Sizing the HGMS tailings by classification could be a further option to produce a tailings fraction with even lower levels of arsenic.

Process development had a significant effect on the mineralogy, chemical composition and leaching of contaminants from the tailings. Successful removal of As minerals and sulphides from the tailings had resulted in more than 60% reduction in the content of As and almost 90% of S, and some 40% of Cu. In addition, leaching of As and SO_4 had decreased by ca. 85% and 94%, respectively. This was a major improvement, since even though the HGMS tailings were still classified as non-inert mining waste, the leaching of As had decreased from the level of hazardous waste to that of non-hazardous waste. The efforts made to improve the tailings quality also affected positively the process water quality, even though part of the reduction was due to a higher water amount in the HGMS process.

Filled-in lysimeter tests were performed to evaluate long-term behaviour of the original, As-rich tailings and the so-called As-poor tailings from a modified process. The results indicated that leaching of most elements in the drainage water

decreased as a function of time during the monitoring period of one and a half years. Furthermore, leaching of hazardous elements was generally less pronounced from the As-poor tailings. An interesting exception to this was arsenic. After one year of seepage monitoring, its concentration in the seepage from the As-poor lysimeter increased substantially and stayed higher than the As content of the seepage from the As-rich lysimeter for the rest of the monitoring period. This was most likely due to the changes in As mineral species and their liberations and associations in the tailings. Further studies and more sampling is needed to confirm this observation and to predict the long-term behaviour. Overall, the As-poor tailings proved unsuitable for a cover material. Instead, the environmental properties of HGMS tailings suggested that they could be suitable for a cover.

While the batch tests can provide information on possible ways to reduce harmful minerals from tailings, mini-pilot or pilot scale testing would be needed to provide the optimum conditions for removing the target minerals in a continuous, commercial plant. Economic pros (e.g. benefits in waste management) and cons (e.g. increased costs for energy, process chemicals, and equipment) should also be assessed during the pilot tests.

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