Journal of Geochemical Exploration xxx (xxxx) xxx-xxx

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: http://ees.elsevier.com

Revalorization of Haveri Au-Cu mine tailings (SW Finland) for potential reprocessing

Annika Parviainen[a,b,*], Fabián Soto[c,d,e], Manuel A. Caraballo[c]

[a] Instituto Andaluz de Ciencias de la Tierra (IACT, UGR-CSIC), Universidad de Granada, Avda. de las Palmeras 4, Armilla, Granada E-18100, Spain
[b] Departamento de Edafología y Química Agrícola, Universidad de Granada, Granada, Spain
[c] Department of Mining Engineering, Universidad de Chile, Avenida Tupper 2069, 8370451 Santiago, Chile
[d] Advanced Laboratory for Geostatistical Supercomputing (ALGES), Universidad de Chile, Avenida Tupper 2069, Santiago, Chile
[e] Advanced Mining Technology Center, Universidad de Chile, Avenida Tupper 2007, Santiago, Chile

ARTICLE INFO

Keywords
Mine wastes
Circular economy
Extractive industry
Cobalt
Copper
Gold

ABSTRACT

The aim of this work was to make an estimate of the remaining metal resources of the Haveri tailings (SW Finland) that were deposited for 60 years ago. We used existing databases (Cu, Zn, Ni, Co, As, Pb, Ag, Au, Fe, S) of previous valorization performed in the 1980's with high sample density; a total of 1201 tailings samples from 165 drill cores. Cobalt, Cu, and Au were chosen for further statistical evaluation, 3D block modeling, and feasibility analysis. We performed also a volume estimate of the tailings based on the depth of drill cores, which was used for the calculation of the total resources. The grade and total tonnage of remaining Au resources present economic potential in comparison to current Au production, whereas the remaining resources for Co and Cu are less promising for reprocessing. However, further feasibility studies are required. This work may serve as an example to make use of existing databases by means of geostatistical modeling techniques in combination with more profound understanding of the mineralogical associations of the metals.

1. Introduction

Modern functioning societies, developing technological applications, and growing demand for green energies increase the future demand for raw materials. The European Commission launched the European Raw Materials Initiative in 2008, which is a strategy to ensure raw materials' supply for the European Union (European Commission, 2018). A list of Critical Raw Materials (CRMs) was created including materials with economic importance and supply risk. The 27 CRMs include for instance Co (European Commission, 2018), and in addition, there is a high demand for other metals such as Ag, Au, Cu, and Ni. The European Commission acknowledges mine wastes as potential sources of secondary raw materials, and reprocessing of extractive wastes is encouraged in the framework of circular economy (Directive 2006/21/EC on the management of waste from extractive industries). The European Union member states are periodically required to make an inventory of closed and abandoned waste facilities, which cause or have the potential to produce negative environmental impacts to human health or the environment (Directive 2006/21/EC). The sustainable use of metallic raw materials requires reuse, recycling, and rehabilitation of mine wastes (De Villiers, 2017; Lottermoser, 2011; Tayebi-Khorami et al., 2019). The environmental and social aspects are increasingly part of the sustainable development of mineral resources. In accordance with the European Union Mineral Policy, Finland's Mineral Strategy is committed to reducing the environment impact of the minerals sector and increasing its productivity, including the recycling and re-use of stockpiled waste materials and tailings (http://projects.gtk.fi/export/sites/projects/minerals_strategy/documents/FinlandsMineralsStrategy_2.pdf). There are 418 historic metal mines in Finland that operated from 1520 to 2001 (Puustinen, 2003) leaving mine wastes on site and near processing plants. During the 21st century the metal mining industry has experienced a significant increase and currently Finland is one of the biggest producers of battery minerals in Europe (https://www.gtk.fi/en/services/mineral-economics/mining-maps/, https://www.gtk.fi/en/research-area/battery-minerals/). The pressure to reuse wastes from the past activities of extractive industry is growing, yet to our knowledge none of the mine waste deposits in Finland have been reprocessed so far. Few of the old mine waste facilities have been revalorized for potential reprocessing (Kokkola, 1981, 1982a, 1982b), and recently, Aijala tailings in SW Finland were surveyed for remaining metal resources using geophysical and geochemical methods (Markovaara-Koivisto et al., 2018). However, closed and abandoned mine sites have been the target of extensive surveys of the post-mining land-use, current environmental

* Corresponding author at: Instituto Andaluz de Ciencias de la Tierra (IACT, UGR-CSIC), Universidad de Granada, Avda. de las Palmeras 4, Armilla, Granada E-18100, Spain.
E-mail addresses: aparviainen@iact.ugr-csic.es (A. Parviainen); fsoto@alges.cl (F. Soto); mcaraballo@ing.uchile.cl (M.A. Caraballo)

https://doi.org/10.1016/j.gexplo.2020.106614
Received 11 June 2020; Received in revised form 17 July 2020; Accepted 18 July 2020
Available online xxx

state, and environmental impact assessments (Kivinen, 2017; Räisänen et al., 2013, 2015; Tornivaara et al., 2018). The Haveri Au—Cu mine operated from 1942 to 1960 leaving 1559 Mt. of tailings (Puustinen, 2003). These mine wastes were revalorized in the early 1980's by the Outokumpu Oy mining company, though at that time the tailings were not considered profitable for reprocessing (Kokkola, 1986a). For instance, the recovery of Au after magnetic separation and flotation tests (50%) and by gravitational separation (Knelson separator; 35%) were found too low, whereas cyanide leaching (75–80%) was discarded due to environmental implications (Kokkola, 1986b).

Modeling of historical tailings may be challenging because of the lack of important information. Typical examples of this type of information are the bottom surface (former topography) that is necessary to generate accurate tailings volume estimates, or the concentration of some elements that were not considered as economic or environmentally relevant at that time. Commonly, the former topography (prior to the tailings deposition) is not available. However, the geometry of the tailings is crucial information to calculate the final volume for the resource estimation, which has a direct impact on tonnage and, therefore, on the amount of resources.

In the view of the growing demand for raw materials and improved extraction technologies, here we present a 3D block model for revalorization of Co, Cu, and Au and an evaluation of the volume of the tailings by rescuing old databases. This work will present a way to overcome the lack of knowledge of tailings bottom topography by using the georeferenced information of the drill cores touching the underlying subsurface. This punctual information of the bottom is statistically interpolated to generate a bottom surface analogous to the former topography of the basin were the tailing was deposited. Additionally, based on the block model, we present a feasibility analysis for the elements of economic interest. This work may serve as an example to make use of existing databases –with high spatial density, but low number of measured elements– by means of geostatistical modeling techniques supported with more profound understanding of the mineralogical associations of the metals of interest obtained during more recent drilling campaigns (characterized by a much lower spatial density sampling, but a much more detailed mineralogical and geochemical characterization).

2. Field site background information

The Haveri formation, located in Ylöjärvi (SW Finland), is composed by metavolcanic mafic rocks, and the sulfide deposit is considered as a Cyprus-type volcanic-exhalative deposit (Mäkelä, 1980). The Haveri Au—Cu mine was operated during nearly two decades producing a total of 4440 kg Au (2.8 g/t, ore grade) and 6085 t Cu (0.37%) in a three-step process including initial sulfide froth flotation for a pre-concentrate, cyanide treatment, and final froth flotation for chalcopyrite concentrate. As a result of the metal recovery process, a total of 1559 Mt. of mill tailings were produced and deposited in a bay of the adjacent Lake Kirkkojärvi (Fig. 1). Most of the tailings were drained in an impoundment restricted by a dam structure (18.4 ha), and additionally, through the end of the mining activity, tailings were also discarded directly in the lake Kirkkojärvi north of the dam. The tailings thickness ranges from approx. 2 to 9 m (average 6.5 m; Parviainen, 2009).

The subarctic climate in the study area is characterized by humid weather and cold winters with mean annual temperature of 4 °C and mean annual rainfall of 600 mm (Finnish Meteorological Institute; https://en.ilmatieteenlaitos.fi/climate). The snow typically covers the ground from mid-December to mid-April.

The main gangue minerals include hornblende [$Ca_2(Mg,Fe_{2+},Fe_{3+},Al)_5(Si,Al)_8O_{22}(OH)_2$], albite [$NaAlSi_3O_8$], quartz [$SiO_2$], microcline [$KAlSi_3O_8$], clinochlore [$Mg_5Al(AlSi_3O_{10})(OH)_8$], and biotite [$K(Mg,Fe)_3[AlSi_3O_{10}(OH,F)_2]$], as well as, small amounts of calcite and dolomite (Parviainen, 2009). Pyrrhotite [$Fe_{(1-x)}S$] and pyrite [FeS_2] are the most abundant sulfide minerals in the tailings, followed by scarce chalcopyrite [$CuFeS_2$] (Parviainen, 2009). Cobaltite [CoAsS], glaucodote [(Fe,Co)AsS], arsernopyrite [FeAsS], gersdorfite [NiAsS], sphalerite [ZnS], molybdenite [MoS_2], hessite [As_2Te] and tellurobismuthite [Bi_2Te_3] are minor ore minerals (Mäkelä, 1980; Paarma, 1947). Magnetite [Fe_3O_4] and ilmenite [$FeTiO_3$] are the only

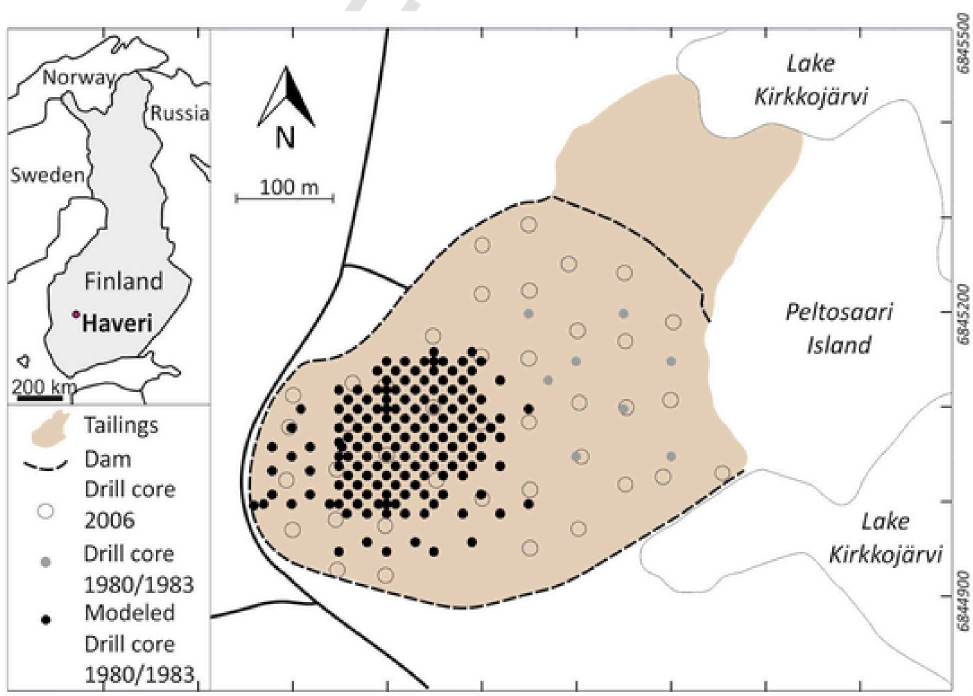

Fig. 1. Schematic map of the Haveri tailings impoundment. The open circles represent drill cores collected in 2006 (Parviainen, 2009), whereas dots represent drill cores taken in 1980/1983 (Kokkola, 1986a). The drill cores marked with black dots were used for the 3D block modeling.

oxide minerals present in the tailings, and minor barite [$BaSO_4$] and scheelite [$CaWO_4$] can also be found (Parviainen, 2009).

The Haveri tailings have been exposed to chemical weathering for 60 years since mine closure, and the surface layer has experienced alteration processes. Due to contact with meteoric water and oxygen in the air, sulfide minerals have oxidized producing acid mine drainage and, subsequently, secondary mineral precipitates. The thickness of the alteration layer varies from 40 to 140 cm according to the depth of the vadose zone (*i.e.* above phreatic level) and moisture content of the tailings (Parviainen, 2009). According to Parviainen (2009), the top most 15 cm is depleted from sulfide minerals. Biotite, calcite and dolomite have partially also been depleted in the intensively altered tailings. Below this depletion zone, partial sulfide alteration may be observed in the transition zone and unaltered sulfide grains are encountered below the phreatic zone. In the alteration layer, secondary minerals, such as, gypsum [$CaSO_4 \cdot 2H_2O$], Fe oxyhydroxides, jarosite [$KFe_3(SO_4)_2(OH)_6$], schwertmannite [$Fe^{3+}{}_{16}O_{16}(OH)_{12}(SO_4)_2$] and elemental sulfur are observed (Parviainen, 2009). According to Parviainen (2009), native gold is not detected in the tailings, but in the ore deposit it occurs as free grains together with sulfarsenides and as fine-grained nebulous disseminations in cobaltite (Mäkelä, 1980; Paarma, 1947).

The grain size of the tailings ranges from 1 to 850 µm, though silt and fine to medium sand fractions are most abundant. The silt fraction is generally more abundant in the surface layer where alteration processes have impacted the mineral composition with abundant fine-grained secondary minerals, whereas the deeper unaltered tailings consisted principally of fine to medium sized sand (Parviainen, 2009; Supplementary Fig. S1). However, the grain size varies even in the deep tailings, and grain size separation and stratigraphic layering occurs (Fig. 2A). The sulfides and sulfarsenides occur mainly as free grains, especially in the more finely ground tailings (*ca.* <100 µm), but in the coarser tailings (*ca.* >100 µm) they are trapped in silicate mineral aggregates (Fig. 2B).

Due of the continuous acid mine drainage from the tailings impoundment (Parviainen, 2009; Parviainen et al., 2012) to the Lake Kirkkojärvi, remediation actions were implemented from 2015 to 2017. The remediation consisted of covering the northern part of the tailings with natural soils to avoid wind and rain erosion, repairing the broken dam structure, and erosion protection of the ditches.

3. Materials and methods

3.1. Data collection

The data used in the present work was compiled using both previously published and unpublished research work (Parviainen, 2009; Kokkola, 1986a). In the early 1980's the mining company Outokumpu Oy explored the remaining ore resources in the Haveri tailings. Two sampling campaigns were performed in 1980 and 1983 with 165 drill cores and a total of 1201 samples that were collected at one meter intervals from the surface to the bottom of the tailings (Fig. 1). The main characteristics (*i.e.*, year, number of drill cores/samples, analyzed elements, chemical analysis methods) of the compiled drill core samples are summarized in Table 1. The samples were analyzed at the laboratory facilities of Outokumpu Oy (Kokkola, 1986a) and the comparison for Au measurements by Fire Assay and Atomic Adsorption Spectrometry are shown in Supplementary Table S1.

In 2006, additional 40 drill cores were collected, and 239 tailings samples were also obtained in one meter intervals from the surface to the interface of underlying silt-clay subsoil (Fig. 1; Parviainen, 2009). More details of the sampling and analytical methods can be found in the previously cited publications.

3.2. Statistical analysis and modeling

The statistical evaluation of the chemical data was performed using IBM SPSS Statistics 24 software. The normality of the data was evaluated by the Kolmogorov-Smirnov and Shapiro-Wilk–tests. Due to the non-normal distribution of the dataset, Spearman's correlation was performed. Principal Component Analysis (PCA) was also run using Minitab 19.2020.1 using a correlation matrix.

Resource assessment using geostatistics was based in the theory of regionalized variables (Matheron, 1970). Traditional methods like kriging or geostatistical simulation use second order stationarity condition, thus, modeling was performed using a variogram (Journel, 1986). Cobalt, Cu, and Au modeling was performed for the Haveri tailings using the dataset obtained from Kokkola (1986a); Co was modelled through kriging, whereas Cu and Au were joint modelled using co-kriging (Chilès and Delfiner, 1999). Multivariate modeling was performed using the ANDES software (Soto et al., 2017). From the available dataset 1980–1983, 158 drill cores (1015 samples) were selected (black dots in Fig. 1). This dataset reduction was performed to obtain a high spatial drill core density and to ensure a robust geostatistical model. The samples were composited at one meter intervals. The three experimental distribution models showed exponential and/or lognormal shapes, similar to the typical behavior observed in ore deposits (Supplementary Fig. S2).

Due to the lack of information of the previous topography underlying the tailings, the tailings bottom surface was modelled by kriging the length of the drill cores at the studied domain. The tailings surface was assumed to be flat at the time of drill core sampling. The estimation of the bottom surface was done in two parts. First, the bottom surface was defined to estimate the total volume of the restricted modelled area (after data by Kokkola, 1986a). Second, we defined the bottom surface of the whole tailings impoundment, restricted by the dam structure, to

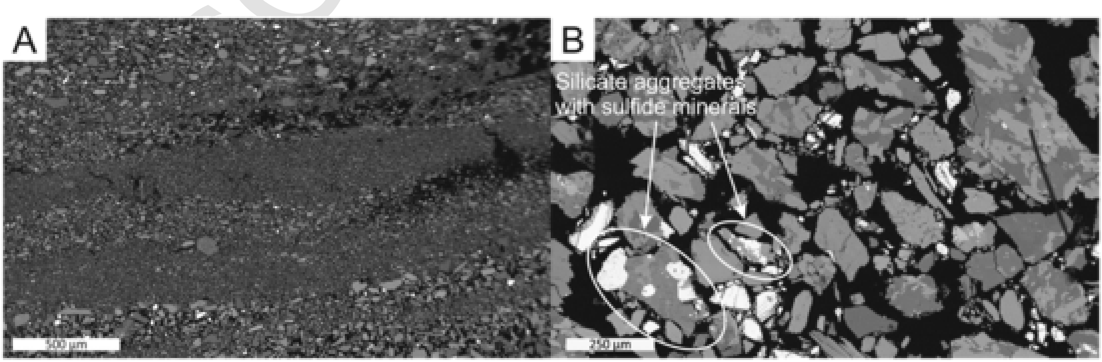

Fig. 2. Back-scattered SEM images of unaltered deep tailings showing A) stratigraphic layering and grain size separation of tailings, and B) silicate aggregates with trapped sulfide grains and free sulfide grains.

Table 1
Summary table for drill cores assessed in this work with year of sampling, number of drill cores and samples, elements analyzed, and the used techniques. *Information omitted because only drill core depths are used in the present work.

Year	Number of drill cores/samples	Analyzed elements	Chemical analysis method	Reference
1980	29/193	Cu, Zn, Ni, Co, As, Pb, Ag, Au, Fe, S	Au by Fire Assay; other elements by Atomic Adsorption Spectrometry (AAS)	Kokkola (1986a)
1983	136/1008	Cu, Co, As, Ag, Au, Fe	Au by Fire Assay; Atomic Adsorption Spectrometry (AAS)	Kokkola (1986a)
2006	40/239	–*	–*	Parviainen (2009)

estimate the volume of the whole impoundment (after data by Parviainen, 2009).

We estimated the total resources of Co, Cu, and Au using a 3D block model (Deutsch and Journel, 1997). This model was arranged according to a sampling grid with horizontal distances of five meters and depth intervals of one meter (block size of 5mx5mx1m) resulting in a total of 14,557 blocks. Cobalt, Cu, and Au were modelled in each block using a discretization cell of 3mx3mx2m (Deutsch and Journel, 1997). It is important to mention that geostatistical modeling of abandoned tailings differs from traditional modeling (Journel, 1986), because of the following two geometrical phenomena are of great influence:

1. The amount of mineral resources depends on the total volume under study. However, abandoned tailings volume is usually uncertain since accurate information about the previous topography where the tailings were deposited (and consequently information about the tailing bottom surface) is not available. Different approaches can be used to estimate the tailing bottom surface, like the use of geophysical techniques inferring the surface from its physical properties or the use of drill hole information (*i.e.*, the geological record verifying that the drill hole hit underlying rock bottom or natural subsoil layer). The latter was the approach used in the present study.
2. Anisotropy is represented by variogram, which is fully parameterized by angles and ranges in three ranges along principal axes (Martin et al., 2018). In tailings, the length of the horizontal direction is much longer than vertical direction. Thus, special care ought to be taken in modeling of vertical direction.

Therefore, the modeling workflow consisted of three steps. Firstly, a 2D estimation of the tailings' depth was performed using the records of drill cores. Secondly, Co, Cu, and Au grades were estimated using a 3D block model with the volume defined according to the results from the previous step. Anisotropy modeling was performed in omni-horizontal and vertical directions for the metals of interest. Finally, a feasibility analysis was performed to have a first approximation to the probable resources and to the economic potential of the tailings revalorization. This analysis was done using tonnage-grade curves and benchmarking with similar deposits.

4. Results and discussion

4.1. Correlation of chemical data

Table 2 summarizes the geochemical composition and basic statistics of the Haveri tailings (using the chemical analyses obtained in 1980 and 1983). Silver concentrations range from 1.0 to 8.0 mg/kg (mean 3.2 mg/kg), As from 22 to 1063 mg/kg (157 mg/kg), Au from 0.02 to 8.0 mg/kg (1.1 mg/kg), Co 3.0 to 1222 mg/kg (142 mg/kg), Cu from 64 to 3560 mg/kg (934 mg/kg), Ni from 25 to 331 mg/kg (131 mg/kg), Pb from 9.0 to 249 mg/kg (18 mg/kg), and Zn from 38 to 491 mg/kg (170 mg/kg). The mean S content of the tailings is 3.1 wt% which is in accordance with the most recent results presented by Parviainen (2009) and Placencia-Gómez et al. (2010). This translates into approx. 50,000 t of remaining S, as in approx. 8% of sulfide minerals. Sulfur occurs in sulfide and sulfarsenide minerals in the unaltered tailings, whereas sulfides are depleted in the upper-most layer of the tailings where secondary minerals (such as gypsum, $CaSO_4$ Fe-oxyhydrixide, and oxyhydroxysulfate (jarosite and schwertmannite) have precipitated (Parviainen, 2009) during the weathering processes at the surface tailings.

The Spearman's correlations and PCA were performed using the database from 1980 containing 193 samples. This database was used instead of the bigger database from 1983 to include S in the statistical analysis, because it is an essential component of most minerals hosting valuable elements. Sulfur exhibits a strong positive correlation with Fe (0.838) and good positive correlations with Co, Cu, and Ni (*ca.* 0.600; Table 3), which according to the mineralogical information available could be attributed to the presence of different sulfides such as pyrite, pyrrhotite, and chalcopyrite, as well as sulfarsenides (including cobaltite and glaucodote). However, As shows merely a weak positive correlation with Co (0.355) and no correlation with Ni (0.147), but Co and Ni are well-correlated with each other (0.671). Gold exhibits moderate positive correlations with Cu and Fe (*ca.* 0.500), whereas Ag pre-

Table 2
Basic statistics of the Haveri tailings with Min., Max., Mean, Median concentrations, standard deviation (SD), and percentiles (25, 50, 75, and 95) (values in mg/kg except in wt% for Fe * and S *) according to Kokkola (1986a) (N = number of samples).

	N	Min.	Max.	Mean	Median	SD	Percentiles			
							25	50	75	95
Ag	*1201*	1.0	8.0	3.2	3.1	0.8	2.7	3.1	3.7	4.7
As	*1201*	22	1063	157	100	140	100	100	136	471
Au	*1201*	0.02	8.0	1.1	1.0	0.7	0.7	1.0	1.4	2.3
Co	*1201*	3.0	1222	142	118	102	80	118	174	310
Cu	*1201*	64	3560	934	852	402	634	852	1129	1690
Ni	*193*	25	331	131	121	56	90	121	155	245
Pb	*193*	9.0	249	18	16	18	14	16	18	23
Zn	*193*	38	491	170	159	72	125	159	209	293
Fe *	*1201*	2.6	17	10	10	2.0	8.5	10	11	14
S *	*193*	1.0	6.0	3.1	3.0	1.1	2.4	3.0	3.7	5.3

Table 3
Spearman's correlations for Ag, As, Au, Co, Cu, Fe, Ni, Pb, S, and Zn in 193 samples after Kokkola (1986a). The *p*-value at level 0.01 ** and at level 0.05 *, respectively.

	Ag	As	Au	Co	Cu	Fe	Ni	Pb	S	Zn
Ag	1.000									
As	0.003	1.000								
Au	0.421 **	−0.002	1.000							
Co	−0.047	0.355 **	−0.171 **	1.000						
Cu	0.602 **	0.131 **	0.427 **	0.280 **	1.000					
Fe	0.411 **	0.067 *	0.540 **	0.338 **	0.509 **	1.000				
Ni	0.172 *	0.147 *	−0.222 **	0.671 **	0.210 **	0.268 **	1.000			
Pb	0.037	0.082	−0.052	0.372 **	0.286 **	0.239 **	0.341 **	1.000		
S	0.283 **	−0.043	0.286 **	0.641 **	0.614 **	0.838 **	0.591 **	0.382 **	1.000	
Zn	0.157 *	−0.160 *	−0.276 **	0.345 **	0.274 **	0.213 **	0.605 **	0.353 **	0.434 **	1.000

sents good positive correlation with Cu (0.600) and moderate correlation with Au (0.42).

The PCA shows that 67% of the variability can be explained using three principal components, whereas the first two components can explain a 53% of the data variability. The location of the studied elements in a diagram plotting the PC1 against PC2 loading factors reveals some interesting groups that can be explained by the mineral phases hosting these elements (Fig. 3). Copper and Fe, in close relationship with S can be attributed to the primary sulfide minerals in the Haveri tailings including pyrrhotite, pyrite, and chalcopyrite. The position of Co and Ni between S and As reflect the presence of sulfarsenides. Additionally, Ag and Au could form a group that shows a delicate relationship (more predominant for Ag) with chalcopyrite and, apparently, with no potential association with sulfarsenides.

4.2. Modeling of Co, Cu, and Au contents

An estimation of the spatial variation of the tailings' depth and, subsequently, the bottom topography of the impoundment is shown in the Fig. 4. The thickness of the impoundment varies from one to 8.5 m. The thickest parts of the tailings are located in the central and north-eastern parts of the impoundment, conforming the shape of the bay where tailings were deposited. Most of the blocks typically vary from 6 to 8 m presenting yellowish and light orange colors (Fig. 4). However, in the western and north-western border, the thickness tends to vary from 1 to 3 m. Large variations in the thickness of a small tailings impoundment –as the one in Haveri– might lead to erroneous volume estimations, unless the variation is well-documented. Therefore, the tailings depth estimate allowed us to better evaluate the total volume.

Modeling the tailings' current surficial topography is also important because it can slightly affect the calculations of the tailings volume, as well as, it can influence the physical stability of a future operations and control the formation of ditch network eroding the tailings surface. However, to fulfill the objectives of the present work, priority was given to the tailings bottom surface interpolation, and the tailings surficial topography was considered as if it was a flat surface at the time of drill core sampling.

For a general overview of ore grades worldwide, we present here some examples. Mudd et al. (2017) studied 851 different types of deposits and observed that the dominant mean grades for Ag, Au, Cu, Pb, and Zn were 16.4 g/t, 0.12 g/t, 0.28 wt%, 0.44 wt%, and 1.2 wt%, respectively. In addition, Mudd and Jowitt (2018) reported Cu grades from 0.18 to 1.5 wt% in ore deposits around the World ranging, as well as, Ni ore grades from 0.1 to 1.5 wt% and Au grades associated to Cu-ore deposits typically ranging from 0.002 to 0.3 g/t. Regarding Co grades of ore deposits around the World, Mudd et al. (2013) reported values ranging from 0.019 to 0.24 wt%. Mudd et al. (2017) also reported the following grades for 15 tailings in Canada, Peru, and Australia: 10 to 64 g/t of Ag, 0.54 to 0.87 g/t of Au, 0.09 to 0.20 wt% of Cu, 0.09 to 1.07 wt% of Pb, and 0.33 to 2.52 wt% of Zn. Also, it is important to notice that reprocessing mine tailings have some economic advantages if compared with mining of rock ore deposits (*e.g.*, less mineral processing and transport needed with concomitant savings in energy and infrastructure) that allows to exploit lower elemental ore grades. This situation is perfectly exemplified by the case study of Minera Valle Central (Rancagua, Chile) that is economically reprocessing a mixture of fresh mine tailings from El Teniente mine and old mine tailings from the Cauquenes tailings deposit, with Cu grades of 0.1 wt% and 0.25 wt%, respectively (Henderson, 2018).

Taking into account this information and considering the mean concentrations for these elements reported in the Haveri tailing deposit (Table 2), only Co, Cu, and Au present economic interest for a revalorization. Hence, based on the concentration ranges and statistical evaluation, we chose Co, Cu, and Au for further evaluation and 3D block modeling.

The experimental and spatial distributions of Co, Cu, and Au in the 3D block model are presented in Figs. 5 and 6, respectively. Based on the block model, the Co mean grade is 141 mg/kg, ranging from 21 to 614 mg/kg. The histogram of Co in Fig. 5 shows a bimodal behavior, with minor mode concentration around 85 mg/kg and another around 171 mg/kg. The block model distribution exhibits values below 70 mg/

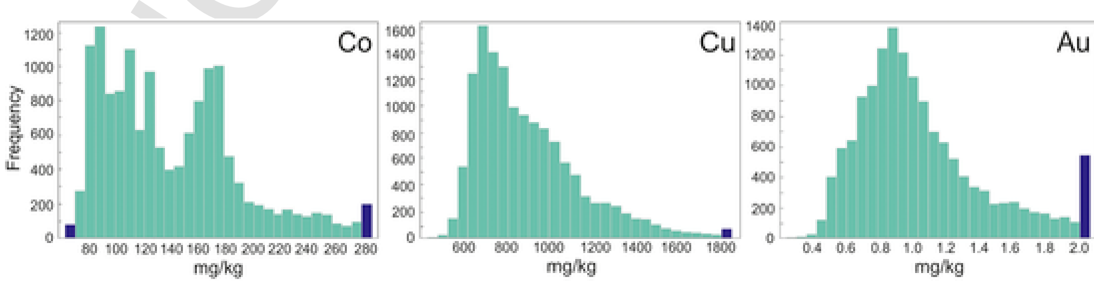

Fig. 3. PCA for Ag, As, Au, Co, Cu, Fe, Ni, Pb, S, and Zn based on dataset published by Kokkola (1986a).

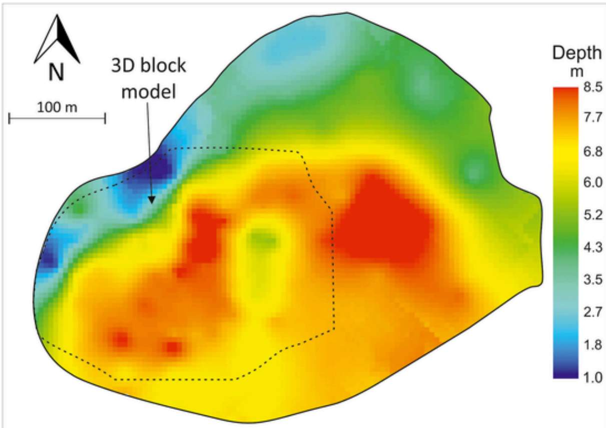

Fig. 4. Spatial variation of the depth of the Haveri tailings.

kg in the left tail and values above 280 mg/kg are accumulated in the right tail (the accumulated bins of the histogram correspond to the blue columns that were calculated by adding all values lower and higher than 70 mg/kg and 280 mg/kg, respectively). The spatial distribution of Co content exhibits higher concentrations (>200 mg/kg) in the northern and north-eastern end of the modelled area, in the central part of the impoundment (Fig. 6). The highest concentrations are found in the uppermost three meters of the tailings.

The modelled mean grade for Cu is 903 mg/kg, ranging from 438 to 2445 mg/kg, and the mode is around 680 mg/kg. The block model distribution exhibits values above 1600 mg/kg accumulated in the right tail (Fig. 5). The spatial distribution of Cu concentrations, exhibits enriched layers with >1400 mg/kg at depths ranging from one to two meters and from six to seven meters in the north-eastern end (Fig. 6). In between these layers (3 to 5 m), Cu concentration range roughly from 1200 to 1400 mg/kg.

According to the model, Au mean grade is 1.1 mg/kg, ranging from 0.24 to 4.6 mg/kg, and the mode is around 0.85 mg/kg (Fig. 5). The block model distribution for Au in the Haveri tailings exhibits similar distribution as for Cu with values above 2.0 mg/kg in the right tail (Fig. 6). The spatial distribution pattern of Au is similar to Cu, and it appears to be concentrated in the north-eastern part of the modelled area at the depths ranging from 4 to 7 m. Here the concentrations vary from 1.6 to 2.0 mg/kg. Higher Au concentrations in the deeper layers may be due to the gravitational deposition of heavier Au mineral particles in the tailings slurry that was deposited in the impoundment. The mean grades of Co, Cu, and Au based on the block model are in good agreement with the mean concentrations presented in the Table 2. Variograhpic study and validations of the model can be found in Supplementary Material (Supplementary Figs. S3 and S4).

It is important to take into account that the present resource estimate is based in chemical data obtained almost 40 years ago and that the tailings deposit has been subjected to weathering processes since then. On this respect, Parviainen (2009) estimated the amount of sulfide-bound metals and S that have been leached –as a consequence of sulfide oxidation– from the upper-most sulfide-depleted tailings (15 cm) since mine closure. The amount of leached sulfide-associated elements from the tailings increase in the following order: Cd (0.07 t), Pb (0.1 t), Mo (0.2 t), As (0.7 t), Ni (4.3 t), Co (4.5 t), Zn (6.0 t), Cu (14.7 t), Fe (1330 t), and S (2,070 t). The real amount of leached elements is probably higher as the sulfide alteration has progressed deeper in large parts of the tailings (Parviainen, 2009).

4.3. Metal resources and potential treatment methods

The 3D block models of the remaining Co, Cu, and Au resources are restricted to the western half of the Haveri tailings (Figs. 1 and 6), where the higher density of information was available. Hence, the density of information in the rest of the tailings deposit needs to be increased and more detailed studies are required to make a reliable estimation of the total resources. Nevertheless, the results of the present study can be considered an excellent exploratory study to settle the economic potential of this residue. On this respect, a feasibility analysis is performed using the proportion-grade curves (Fig. 7). These curves show the proportion of the blocks that have a higher grade than the cut-off grade and the mean grade of the remaining blocks. The optimum cut-off grade will depend on the metal price and operation costs. However, this curve can be considered as a first approximation to determine the amount of potential resources.

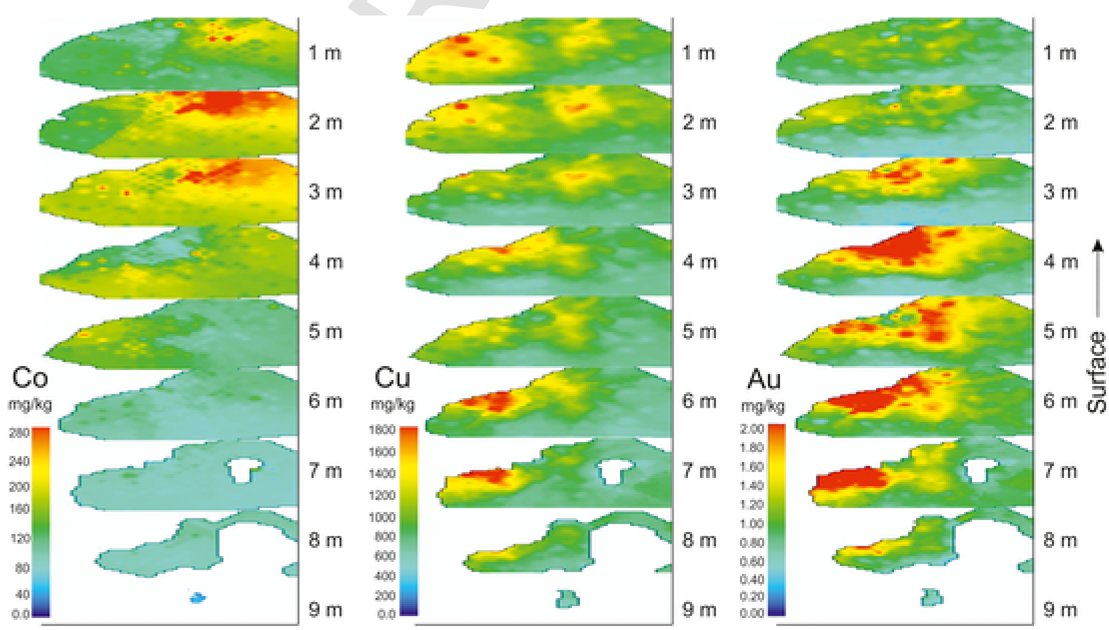

Fig. 5. Experimental distribution for Co, Cu, and Au according to the block model. Dark blue bars represent the accumulated bins. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

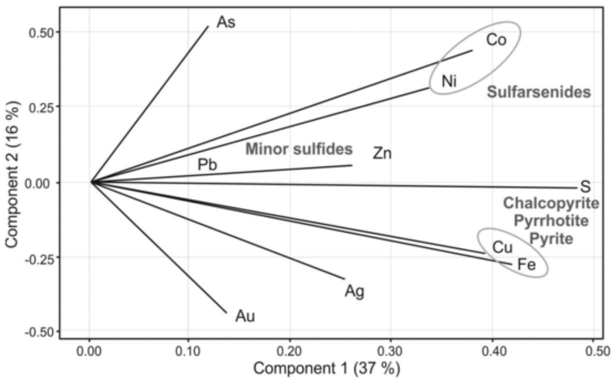

Fig. 6. Spatial distribution of Co, Cu, and Au grades in the Haveri tailings according to the block model (data from Kokkola, 1986a).

An estimated 15% of the blocks are profitable for Co, with a cut-off grade of 190 mg/kg, resulting in a mean grade of 240 mg/kg. A cut-off grade of 1000 mg/kg for Cu implies that 25% of blocks are economically profitable with a mean grade of 1240 mg/kg. For Au, 45% of blocks are profitable, with a cut-off grade of 1.0 mg/kg resulting in a mean grade of 1.4 mg/kg. These values were chosen according to current operations for Au (Yamana Gold, 2019), known ore deposit for cobalt (Mudd and Jowitt, 2018), and current operations extracting Cu from mine tailings (Henderson, 2018). Based on the mean grades of the elements of interest, we made a rough estimation of the total remaining resources for Co, Cu, and Au using the volume of the whole impoundment, considering a tonnage of 1559 Mt. According to this estimation, potential resources for minimum cut-off values can be observed in the Table 4.

However, due to the small size of the Haveri tailings, costs would probably increase leading to an increase in the cut-off grade. It is important to emphasize that this analysis was made using benchmarking, not with an exhaustive study –which is recommended–, and employing cut-off grade of other current mines with similar potential as the main concept (Rendu, 2014). Further analysis should consider the tailings as a polymetallic deposit. On this regard, the multivariate statistical analyses performed in this study shows a close correlation of Fe and S with Cu (in chalcopyrite), of Ni and As with Co (in sulfarsenides) and, of Ag with Au (as native elements). These correlations corroborate the geochemical and mineral associations already proposed by previous studies (Parviainen, 2009; Placencia-Gómez et al., 2010). Therefore, if the tailings are reprocessed to obtain Co, Cu, and Au as the main valuable elements governing the mining process, other elements like Ag, As, Fe, Ni, Pb, Zn, and S will also be extracted. This polymetallic situation will generate inherent difficulties (mostly during the metallurgical extraction of the valuable elements), but at the same time it could imply some relevant economic and environmental benefits.

For a feasible reprocessing, tests need to be run to select optimal methods. Tailings have the advantage that they already are fine-grained, which generally is a prerequisite for ore processing. At Haveri, the ore was milled prior to the three-step extraction procedure. However, there are still relatively large particles in the tailings ranging up to 850 μm in size. Silicate aggregates with Ø > 100 μm host sulfides, oxides, and potentially also Au (Fig. 2). Gentle milling of the tailings may improve the recovery of metals by disaggregating the minerals of interest. Yet, remilling of the tailings would increase the pretreatment expenses.

Gravity separation and froth flotation may be performed to recover a Cu and Au bearing pre-concentrate. For instance, flotation is suggested to be an optimal approach to recover Cu—Co tailings the Republic of Congo and Cu in China (Shengo and Maloba, 2013; Shengo et al., 2019; Yin et al., 2018). Particle size of copper tailings has been proven to have an effect on the froth stability and flotation performance (MacKay et al., 2020). These authors suggest carrying out froth stability tests to find the optimal particle size distribution to improve mineral recoveries prior to reprocessing tailings by froth flotation. These findings will both contribute to a more efficient recovery of resources and the reduction of environmental impacts of sulfide tailings. Han et al. (2018) also suggested copper recovery process for chalcopyrite from flotation tailings using high–pressure leaching followed by solvent extraction.

Flotation and gravity separation have been tested for waste rocks in Malartic mine in Quebec, Canada (Amar et al., 2020 in this issue). In this case, laboratory gravity separation (Knelson separator and Mozley table) –applied on the fraction < 2.4 mm– was found more efficient than flotation. Additionally, pyroanalysis of Au and Ag on the concentrate after desulphurization with gravity methods was found beneficial.

4.4. Environmental aspects

According to the Finnish Government Degree 214/2007 on assessment of contaminated soils and remediation needs, the Haveri tailings can be considered as polluted soils as the mean concentrations of As and Cu surpass the upper guideline values for contaminated soils (100 mg/kg and 200 mg/kg, respectively; industrial areas), whereas Co and Ni surpass the lower guideline values (100 mg/kg and 100 mg/kg, respectively; residential areas). Furthermore, occasionally Zn concentrations exceed the lower guideline values (250 mg/kg) (Table 2).

Prior to any remediation actions, large parts of the tailings surface were barren, hence, they were prone to wind and rain erosion, flushing of dissolved metals, and the meteoric water also infiltrated into the tailings. Chemical weathering of the tailings generated acid mine drainage over 60 years with drainage waters flowing to the lake Kirkkojärvi. Metal mobilization from the tailings affected the quality of the surface waters and was registered in the lake sediment records. According to Parviainen et al. (2012), metal concentrations in the lake sediments gradually increased during active mining with respect to pre-mining

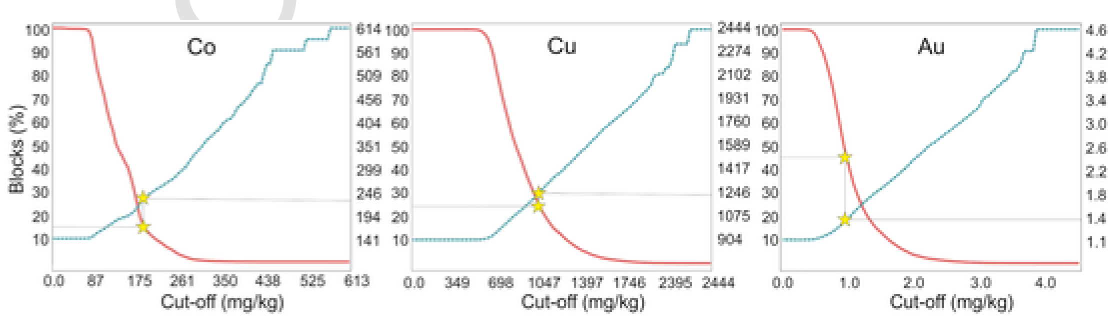

Fig. 7. Modelled blocks' proportion-grade curves for Co, Cu, and Au. Red lines represent the percentages of the blocks and blue dashed lines the mean ore grades of these blocks. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4
Rough estimation of potential resources of Haveri tailings.

	Cut-off (mg/kg)	Mean grade (mg/kg)	Percentage (%)	Reserves (Mt)
Co	190	240	15	0.056
Cu	1000	1240	25	0.483
Au	1.0	1.4	45	0.001

conditions, but major post-mining acid mine drainage impact was observed peaking approximately 5 to 15 years after mine closure. Higher concentrations (*e.g.* Ag, As, Cd, Co, Cu, Fe, Mo, Ni, U, S, and Zn) than the pre-mining values were still recorded in the sediment cores corresponding to the beginning of the 21st century. In addition to acid mine drainage in the surface water bodies, geophysical studies have suggested that the acid drainage percolated downwards potentially affecting the groundwater quality (Placencia-Gómez et al., 2010). Large part of the deeper tailings remains unaltered and contain approx. 3 wt% of S in the form of sulfides (mainly pyrrhotite, pyrite, chalcopyrite, and minor sulfarsenides) prone to future oxidation. Subsequently, reuse of the Haveri tailings, for instance, for backfilling and construction purposes is not recommended due to their acid generation character.

Many recent publications suggest froth flotation as a viable option for desulphurization to minimize the environmental footprint of the mineral processing industry (Shengo and Maloba, 2013; Nuorivaaraa et al., 2019). Removing sulfide minerals from tailings reduces the acid generation potential and –at the same time– eliminates the potentially toxic elements. Desulphurization by gravity separation has, as well, been proposed for improving the environmental quality of mine waste rocks in Malartic mine in Quebec, Canada (Amar et al., 2020 in this issue).

Subsequently, desulphurization of the Haveri tailings would reduce their acid generation potential and even could favor the potential reuse of the remaining silicate gangue minerals. Even though, reprocessing of old tailings could be an alternative tailings management tool aiming to improve environmental, social, and economic outcomes (Edraki et al., 2014), it may have negative environmental impacts when stacks are excavated and disturbed. Disturbing the geochemical balance gained over years through natural attenuation mechanism, *e.g.*, precipitation of secondary Fe(III) phases retaining potentially toxic elements, may lead to low-quality drainage to the groundwater and surface water bodies. Milling and metallurgical processes may also have negative environmental impacts during the reprocessing of tailings. Therefore, considering the remediation actions taken place at Haveri tailings (including covering part of the tailings, repairing the broken dam structure, and erosion protection of the ditches), the potential economic benefits and potential environmental damages derived from reprocessing need to be properly assessed and weighted. We recommend that the economic benefits with further feasibility studies and environmental risk assessment are necessary in order to evaluate the potential reprocessing of Haveri tailings.

5. Conclusions

As the World's need for metallic raw materials grows, reprocessing of old mine wastes gains importance in the scenery of the extractive industry. The European Commission encourages the use of mine wastes as potential sources of secondary raw materials. However, for instance in Finland, revalorization and reprocessing of tailings is still advancing slowly on the way to become a solid part of the extractive industry. In this work we present revalorization of the Haveri tailings in SW Finland by rescuing old drill core databases from a former revalorization in the 1980`s as a way to make an initial inventory of the remaining resources. We performed a volume estimate by modeling the tailings bottom topography based on drill core depths, followed by a 3D block model for elements of economic interest, including Co, Cu, and Au. Additionally, we performed statistical evaluations and a feasibility analysis using proportion-grade curves presenting the portion of blocks surpassing the cut-off grade of the selected metals. Au concentrations show economic potential, with values similar to active mines, whereas the potential for Co and Cu is less considerable. On the one hand, Cu remains below economic feasibility compared to for instance the Minera Valle Central tailings (Chile). On the other hand, Co presents a major possibility, even though only 15% of the blocks surpass the cut-off compared to other ore deposits. The potential reduction in operation costs can move up the amount of Co resources. Our recommendation is to continue studies to better characterize Au and Co content by collecting more drill core samples from the whole tailings impoundment for detailed geochemical analysis and recovery tests. Additionally, analysis and estimation of other CRMs is recommended. Scale considerations need be studied in order to estimate associated costs (capital and operational expenditures). In case re-milling is needed, it adds up to the expenses. Further analysis should be performed adding mine planning studies in order to analyze in more detail the feasibility, as well as, environmental risk assessment of reprocessing.

Uncited references

Directive 2006/21/EC, 2006
Finnish Government Decree on the Assessment of Soil Contamination and Remediation Needs 214, 2007

CRediT authorship contribution statement

Annika Parviainen: Conceptualization, Resources, Formal analysis, Investigation, Visualization, Writing - original draft. **Fabián Soto:** Formal analysis, Methodology, Software, Writing - review & editing. **Manuel A. Caraballo:** Conceptualization, Formal analysis, Writing - review & editing.

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.

Acknowledgements

The authors acknowledge the funding received from the European Union Life Environment program (LIFE04ENV/FI/000300). The drill core sampling in 2006 was performed as part of RAMAS project (http://projects.gtk.fi/ramas/). The authors would also like to acknowledge the National Research and Development Agency of Chile (ANID) that support this work through the project AFB180004, UNESCO International Geoscience Programme for the project IGCP682 Mine Tailing Revalorization, and CORFO and Codelco through the project 16PTECME-66524.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2020.106614.

References

Amar, H, Benzaazoua, M, Elghali, A, Bussière, B, Duclos, M, 2020. Upstream environmental desulphurisation and valorisation of waste rocks as a sustainable AMD management approach. J. Geochem. Explor. 215, 106555. doi:10.1016/j.gexplo.2020.106555.

Chilès, J P, Delfiner, P, 1999. Geostatistics: Modeling Spatial Uncertainty. Wiley, New York, p. 734 (ISBN: 978-0-470-18315-1).

De Villiers, J P R, 2017. How to sustain mineral resources: beneficiation and mineral engineering opportunities. Elements 13, 307–312. doi:10.2138/gselements.13.5.307.
Deutsch, C, Journel, A, 1997. GSLIB: Geostatistical Software Library and User's Guide. Oxford University Press, New York, p. 369 (ISBN-13: 978-0195100150).
Directive 2006/21/EC, 2006. of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC - Statement by the European Parliament, the Council and the Commission. OJ L 102, 15–34 11.4.
Edraki, M, Baumgartl, T, Manlapig, E, Bradshaw, D, Franks, D M, Moran, C J, 2014. Designing mine tailings for better environmental, social and economic outcomes: a review of alternative approaches. J. Clean. Prod. 84, 411–420. doi:10.1016/j.jclepro.2014.04.079.
European Commission, 2018. Report on Critical Raw Materials and the Circular Economy. p. 80.
Finnish Government Decree on the Assessment of Soil Contamination and Remediation Needs 214 https://www.finlex.fi/en/laki/kaannokset/2007/en20070214.pdf200731 May 2020
Han, B, Altansukh, B, Haga, K, Stevanović, Z, Jonović, R, Avramović, L, Urosević, D, Takasaki, Y, Masuda, N, Ishiyama, D, Shibayama, A, 2018. Development of copper recovery process from flotation tailings by a combined method of high–pressure leaching–solvent extraction. J. Hazard. Mater. 352, 192–203.
Henderson, R D, 2018. Minera Valle Central Operations Rancagua, Region VI, Chile. 43–101 Technical report. p. 118. http://www.amerigoresources.com/_resources/Technical_Report_March_2019.pdf (Accessed 7/6/2020).
Journel, A, 1986. Geostatistics : models and tools for the earth sciences. Math. Geol. 18, 119–140.
Kivinen, S, 2017. Sustainable post-mining land use: are closed metal mines abandoned or re-used space? Sustainability 9 (10), 1705. doi:10.3390/su9101705.
Kokkola, M, 1981. Jätealueen soijatutkimus, Kisko, Orijärvi. Outokumpu OY Report 061/2014 06D/MK/1981. p. 12. http://tupa.gtk.fi/raportti/arkisto/061_2014_06d_mk_1981.pdf (in Finnish).
Kokkola, M, 1982. Jätealueen soijatutkimus Kisko, Aijala. Outokumpu OY Report 067/2014 03/MK/1982. p. 20. http://tupa.gtk.fi/raportti/arkisto/061_2014_03_mk_1982.pdf (in Finnish).
Kokkola, M, 1982. Jätealueen soijatutkimus Ylöjärvi. Outokumpu OY Report 061/2124 04A/MK/1982. p. 20. http://tupa.gtk.fi/raportti/arkisto/061_2124_04a_mk_1982.pdf (in Finnish).
Kokkola, M, 1986. Jätealueen soijatutkimus. Outokumpu Oy Report 061/2124/02b/MK/1986. p. 83. http://tupa.gtk.fi/raportti/arkisto/061_2124_02b_mk_86.pdf (in Finnish).
Kokkola, M, 1986. Kaivoslain 19 §:n mukainen tutkimustyöselostus Viljakkala, "Haveri", kaivosrekisterinumero 3058/1. In: Outokumpu Oy Report 080/2124 02b/MK, PE/1986. p. 3. https://tupa.gtk.fi/raportti/arkisto/080_212402b_mk_pe_1986.pdf (in Finnish).
Lottermoser, B G, 2011. Recycling, reuse and rehabilitation of mine wastes. Elements 7, 405–410. doi:10.2113/gselements.7.6.405.
Mäkelä, K, 1980. Geochemistry and origin of Haveri and Kiipu, Proterozoic strata-bound volcanogenic gold-copper and zinc mineralizations from southwestern Finland. Bull. Geol. Surv. Finland 310, 17–39.
Markovaara-Koivisto, M, Valjus, T, Tarvainen, T, Huotari, T, Lerssi, J, Eklund, M, 2018. Preliminary volume and concentration estimation of the Aijala tailings pond – evaluation of geophysical methods. Res. Policy 59, 7–16.
Martin, R, Machuca-Mory, D, Leuangthong, O, Boisvert, J B, 2018. Non-stationary geostatistical modeling: a case study comparing LVA estimation frameworks. Nat. Resour. Res. 28, 291–307.
Matheron, G, 1970. La théorie des variables régionalisées et ses applications. In: Cahiers du Centre de Morphologie Mathématique de Fontainebleau: Ecole nationale supérieure des mines. p. 212 (in French).
Mudd, G M, Jowitt, S M, 2018. Global resource assessments of primary metals: an optimistic reality check. Nat. Resour. Res. 27, 229–240. doi:10.1007/s11053-017-9349-0.
Mudd, G M, Weng, Z, Jowitt, S M, Turnbull, I D, Graedel, T E, 2013. Quantifying the recoverable resources of by-product metals: the case of cobalt. Ore Geol. Rev. 55, 87–98.
Mudd, G M, Jowitt, S M, Werner, T T, 2017. The world's lead-zinc mineral resources: scarcity, data, issues and opportunities. Ore Geol. Rev. 80, 1160–1190.
Nuorivaaraa, T, Björkqvist, A, Bacher, J, Serna-Guerrero, R, 2019. Environmental remediation of sulfidic tailings with froth flotation: reducing the consumption of additional resources by optimization of conditioning parameters and water recycling. J. Environ. Manag. 236, 125–133.
Paarma, H, 1947. Haverin Kiisumalmin Mineraaliparageneesi (Mineral Paragenesis of the Haveri Sulfide Ore) MSc thesis. University of Helsinki (in Finnish).
Parviainen, A, 2009. Tailings mineralogy and geochemistry at the abandoned Haveri Au–Cu mine, SW Finland. Mine Water Environ. 28 (4), 291–304.
Parviainen, A, Kauppila, T, Loukola-Ruskeeniemi, K, 2012. Long-term lake sediment records and factors affecting the evolution of metal(loid) drainage from two mine sites (SW Finland). J. Geochem. Explor. 114, 46–56.
Placencia-Gómez, E, Parviainen, A, Hokkanen, T, Loukola-Ruskeeniemi, K, 2010. Integrated geophysical and geochemical study on AMD generation at the Haveri Au–Cu mine tailings, SW Finland. Environ. Earth Sci. 61 (7), 1435–1447.
Puustinen, K, 2003. Mining industry and production of raw materials in Finland during 1530–2001, a historic review in the light of production figures. In: Geological Survey of Finland, Report M 10.1/2003/3. p. 578 (in Finnish).
M.-L. Räisänen A. Tornivaara T. Haavisto K. Niskala M. Silvola Suljettujen ja hylättyjen kaivosten kaivannaisjätealueiden kartoitus. Ympäristöministeriön Raportteja, 24, 45https://helda.helsinki.fi/handle/10138/41486201326 May 2020 Finnish
Räisänen, M-L, Beucher, A, Tornivaara, A, Kauppila, P, 2015. Suljettujen ja hylättyjen metallikaivosalueiden nykytila ja arvio jätealueiden ympäristöriskipotentiaalista. In: Geological Survey of Finland, Archive Report 46/2015. p. 129.
Rendu, J M, 2014. An Introduction to Cut-off Grade Estimation. Society for Mining, Metallurgy, and Exploration (SME), Englewood, Co, p. 168 ISBN-13: 978-0873353939.
Shengo, M L, Maloba, B, 2013. Recovery of cobalt and copper through reprocessing of tailings from flotation of oxidised ores. J. Environ. Chem. Eng. 1, 1085–1090.
Shengo, M L, Kime, M-B, Mambwe, M P, Nyembo, T K, Nyembo, T K, 2019. A review of the beneficiation of copper-cobalt-bearing minerals in the Democratic Republic of Congo. J. Sustain. Min. 18, 226–246.
Soto, F, Garrido, M, Díaz, G, Silva, C, 2017. Rapid multivariate resource assessment. In: GEOMIN-MINEPLANING, 5th International Seminar on Geology for the Mining Industry. GECAMIN, Santiago de Chile.
Tayebi-Khorami, M, Edraki, M, Corder, G, Golev, A, 2019. Re-thinking mining waste through an integrative approach led by circular economy aspirations. Minerals 9 (5), 286. doi:10.3390/min9050286.
Tornivaara, A, Räisänen, M-L, Kovalainen, H, Kauppi, S, 2018. Suljettujen ja hylättyjen kaivosten kaivannaisjätealueiden jatkokartoitus (KAJAK II). Suomen Ympäristökeskuksen Raportteja 12. p. 162. https://helda.helsinki.fi/bitstream/handle/10138/235617/SYKEra_12_2018.pdf?sequence = 1&isAllowed = y in Finnish; accessed 11/7/2020.
Yamana Gold, 2019. Summary of Mineral Reserve and Mineral Resource Estimates. p. 6. http://q4live.s22.clientfiles.s3-website-us-east-1.amazonaws.com/899716706/files/Yamana-AR19_RR_V2-for-website_12-02-20.pdf. (Accessed 26 May 2020).
Yin, Z, Sun, W, Hu, Y, Zhang, C, Guan, Q, Wu, K, 2018. Evaluation of the possibility of copper recovery from tailings by flotation through bench-scale, commissioning, and industrial tests. J. Clean. Prod. 171, 1039–1048.