

Article

Environmental Impact Variability of Copper Tailing Dumps in Fushe Arrez (Northern Albania): The Role of Pyrite Separation during Flotation

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Abstract: Acid mine drainage and potentially toxic elements release are a major source of pollution in sulfide-rich mining sites. Pyrite is the most impacting mineral due to its high acidification potential when it reacts with water under oxidizing conditions. At the Fushe Arrez dressing plant in Northern Albania, a volcanic massive sulfide copper mining district, pyrite was in past separated, with a double flotation process, to produce a pyrite concentrate and relatively-pyrite-poor tailings. In the last twenty years single flotation has replaced the double flotation process and pyrite has been deposited in pyrite-rich tailings stacked separately from the old ones. The study of the solid tailing materials and natural waters flowing through the dumping area, together with leaching tests show that waters interacting with single flotation tailings are slightly more acidic and much higher in total metal contents than those interacting with double flotation tailings. Also, the metal distribution is different, with the former being higher in sulfide-hosted metals and the latter higher in gangue-hosted metals. It is thus suggested that separation of pyrite can play an important role in the sustainable mining of pyrite-rich ores, either for dumping high hazardous pyrite concentrate separately or for marketing it as a by-product. An implementation of studies for the industrial uses of pyrite is pivotal in this last case.

Keywords: pyrite; Albania; circular economy



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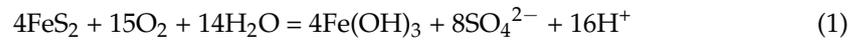
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1. Introduction

Copper mining is a major source of environmental pollution, mainly related to water acidification and dispersal of potentially toxic elements (PTE) in what is known as the acid mine drainage (AMD) process (e.g., [1–3]). As a result, active and abandoned copper mines and beneficiation plants are sites of high environmental hazards. The high sulfide content and the rich polymetallic association are the main background of such high hazards. Volcanic massive sulfide (VMS) copper deposits, like those of the Northern Albania mining district, add to this frame the high concentration of sulfides in the massive ore and the high pyrite content (e.g., [4–6]). Pyrite is, by far, the main responsible of AMD in these ores due to its abundance and its high sulfur to metal ratio that leads to the highest sulfuric acid production per mass unit (e.g., [6–12] and references therein). Moreover, pyrite is nowadays always dumped with the tailings during beneficiation as it is no longer used to produce sulfuric acid as in the past. Pyrite is still used in small amounts for increasing malleability of steel, for the production of amber colored glass, brake pads and grinding wheels. New uses have also been developed, such as pyrite as an electrode material for rechargeable lithium batteries [13] and for sodium batteries [14], as reaction material for sulfate waste

decomposition [15] or as thin film for solar absorber in photovoltaic materials [16], but these innovative uses are not fully developed yet, leading to a low demand for this commodity.

The strong acidification of waters in VMS copper deposits can be attributed to pyrite oxidation according to the generic reaction (1) [17]:



At pH values below 4 the biogenic acidification becomes dominant, biologically mediated by iron-oxidizing bacteria [17].

The high environmental impact of copper mining and copper separation plants in the Northern Albania mining region has already been reported [18,19]. The river pollution in the district has specifically been addressed by Kumanova et al. [20]. The authors showed a correlation between river sediment metal pollution and mining activity, even though they do not infer the relative proportion of pollution to be attributed to the mines and to the plants. The recent work of Fantone et al. [21] on the Reps tailing dumps, where an abandoned separation plant was operative in the last decades, was addressed to define AMD from the tailings. Their results show the presence of two different materials in the dumps: high and a low sulfide tailings, whose distribution within the dump follows irregular patterns. Most of the net potential acid production from the two studied dumps is attributed to the high sulfide materials, although they represent no more than 20% of the tailings volume. The authors infer, on the basis of the little information available on the operating conditions, that low and high sulfide tailings were produced by single and double flotation, respectively: the former separating only a chalcopyrite concentrate and the latter a chalcopyrite and a pyrite concentrate. The present work was planned as a continuation of that of Fantone et al. [21] in order to confirm the reason for the highly variable acid potential and to clarify the different contributions of single and double flotation tailings, exploiting the opportunity to sample an active plant where the two different tailings have been stocked separately.

The present study aims to ascertain the metal pollution in waters that drain tailings dumps and the change in tailings environmental impact due to the transition from double to single flotation. In the first case pyrite is separated as a by-product, while, in the second case, pyrite is not separated and is mixed with the tailings. The northern Albania copper mining district was chosen as a case study because, due to its industrial policy, this country was one of the last to abandon sulfuric acid production from pyrite, so the transition can be studied in recent and present-day tailings. Moreover, strongly different tailings due to changes in the flotation process have already been described at the abandoned Reps beneficiation plant in the same copper mining district [21].

The study was carried out on samples collected from the working Fushe Arrez copper enrichment plant, which was operating during the sampling. At the Fushe Arrez plant the separation of pyrite was abandoned in the late 1990s. Here the old pyrite-poor and the still active pyrite-rich tailings were stacked in the same valley impoundments but in two well separated areas. Differently from Reps, where tailings resulting from single or double flotation had to be inferred, at Fushe Arrez, the location of single and double flotation tailings is perfectly known by company working there. The different tailings were stacked in close but completely separate dumps. This makes conditions at Fushe Arrez favorable to the study of the effect of different flotation scenarios.

The overall pollution of waters flowing out of the tailings system was determined through in situ pH and conductivity analyses followed by determination of selected metals content. To assess the environmental impact of tailings produced with different flowsheet configurations (i.e., with or without pyrite separation) leaching tests were conducted on both pyrite-rich and pyrite-poor tailings. Leachates were also compared with sampled waters. The possible effect of other parameters affecting AMD and metals release were also considered.

2. Materials and Methods

The Northern Albania copper mining district has 25 contemporaneously active mines and three enrichment plants, located at Reps, Rubik and Fushe Arrez. Waste dumps are scattered all over the area and millions of tons of tailings lie in dumps close to the three flotation plants.

Since 2004, the Fushe Arrez flotation plant has produced a copper concentrate at 21–22 wt.% Cu from the only two mines still active in the district: Lak Roshi and Munella. These provide ore to the plant, that, after comminution, is sent to a set of flotation cells producing the copper concentrate and pyrite-rich tailings that are deposited in the nearby tailings impoundment. This covers an area of about 50,000 m² in the valley of a small stream tributary of the Fan I Madh river. The dump is contained downward by an earth dam.

Till 2000, a second flotation line separated a pyrite concentrate from the discarded chalcopyrite flotation line. Pyrite concentrate was then sent to a sulfuric acid production plant at Rubik, while the resulting, pyrite-poor, tailing was stacked in another impoundment located downstream in the same valley (Figure 1).

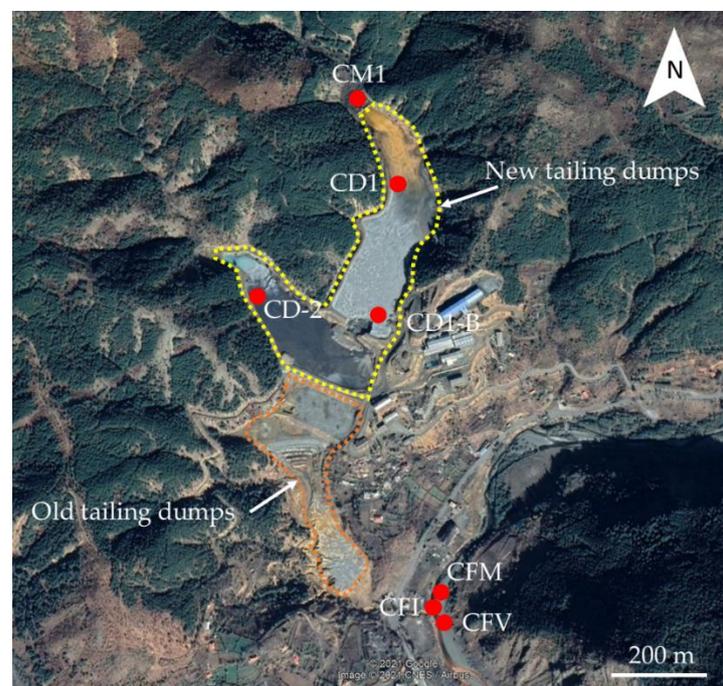


Figure 1. Satellite view of the Fushe Arrez plant area with location of water samples.

The study of solid materials was based on two samples provided by the mining company. They were produced by mixing materials from different parts of the dumps: FA3 from the new dumps and FA4 from the old dumps. They were assembled to be the most representative possible of each dump material. This sampling method prevents the possibility to perform a statistical study of the internal variability of solid materials of each dump, but, on the other hand, it can be considered as representative of the average composition of each dump.

Feed (FA1) and concentrate (FA6) at the moment of sampling were also collected and characterized. The former, due to technical reasons, was collected after crushing but before grinding.

Seven water samples were collected, and their type and location are reported in Table 1 and Figure 1. One sample (CM1) was collected from the stream waters upstream of the dumps, three samples CD1, CD1-B, CD-2 were collected from the pounding waters above new dumps and 3 samples (CFM, CFI, CFV) were collected at the confluence of the stream into the Fan I Madh river (Figure 2).

Table 1. Localization and type of water samples collected in the Fushe Arrez dumping area.

Sample	Latitude	Longitude	Type
CM1	42° 5' 02.37"	20° 2' 10.96"	Stream waters upriver of the dumps
CD1	42° 4' 54.80"	20° 2' 12.89"	Pounding waters over the new dumps: North
CD1-B	42° 4' 44.96"	20° 2' 08.01"	Pounding waters over the new dumps: South
CD-2	42° 4' 48.72"	20° 1' 57.10"	Pounding waters over the new dumps: West
CFM	42° 4' 24.99"	20° 2' 07.88"	Fan I Madh waters just upstream of the confluence of the stream flowing from dump waters
CFI	42° 4' 24.03"	20° 2' 07.02"	Stream flowing from dumps waters
CFV	42° 4' 23.10"	20° 2' 07.50"	Fan I Madh waters just downstream of the confluence of the stream flowing from the dumps



Figure 2. Confluence of the discharge stream flowing out of the dumps and the Fan I Madh River, showing deposition of red muds along the stream bed and transport of the same material into the Fan I Madh waters.

Field surveys, in situ analyses and sampling of waters were conducted in early summer, under conditions of moderate water flow from upstream of the dumps. A total of seven water samples were collected. The pH and conductivity of waters were measured at the moment of sampling with a WTW Multiline P3 multifunction potentiometer (Labexchange, Burladingen, Germany).

Double flotation (old) and single flotation (new) dumps were located in the field according to reports from the plant personnel. In each dump a 5 kg tailing material sample was assembled by collecting several subsamples from different points in the active dump pound at different distances from the discharge pipe. As for the old dump a 5 kg sample was assembled by collecting several subsamples from different layers in a vertical cut of the dump. All analyses, unless otherwise, were performed at the Department of Earth Sciences of the University of Milan.

Grain size analyses were performed on 1 kg subsamples employing cone and quarter method, by use of a pile of sieves with the following openings: 1, 0.5, 0.25, 0.125, 0.063 and 0.038 mm.

Polished sections of dump materials were prepared embedding glued sand in resin. Sections were then observed under reflected light by use of a reflected light microscope.

XRD analyses were performed on samples by use of a high-resolution X-ray powder diffractometer (X'pert Pro, Panalytical, Malvern, UK). This powder diffractometer is equipped with an incident beam monochromator, which separates the $K\alpha_1$ and the $K\alpha_2$ and can work with the Bragg Brentano geometry (divergent beam) as well as with a parallel beam geometry.

The values of pH of water leachates were measured with a WTW Multiline P3 multifunction potentiometer on water left in contact with the solid material for 24 h after filtering.

Solid samples were analyzed for trace elements through TD-ICP-OES and for sulfur content through IR spectroscopy performed at Activation Laboratories Ltd. (Ancaster, ON, Canada).

Leaching tests followed the Synthetic Precipitation Leaching Procedure (SPLP, U:S: EPA Method 1312). Leachates were analyzed for pH using the WTW Multiline P3. Leachates and water samples collected in situ were analyzed for selected metals using a 4100 MP-AES system (Agilent, Santa Clara, CA, USA). Co, Ni and Pb were determined applying the FLIC correction, on the basis of the overlap of blank and standard spectra in order to avoid Fe interferences [22]. Sulfate contents were determined with the turbidimetry technique by use of an Orbeco-Hellige photometer (Farmingdale, NY, USA).

3. The Northern Albania Cu Mining District and the Fushe Arrez Beneficiation Plant

The geology of northern Albania is dominated by the units of the Mirdita Zone (Figure 3), a ~40 km wide, SW-NE trending segment within the Dinaride-Hellenide sector of the Alpine-Himalayan orogenic system. The Mirdita Zone includes part of the Albanian ophiolite belt. These ophiolites represent an ocean floor evolution that took place in Early-Middle Triassic with the thinning of a continental margin [23,24].

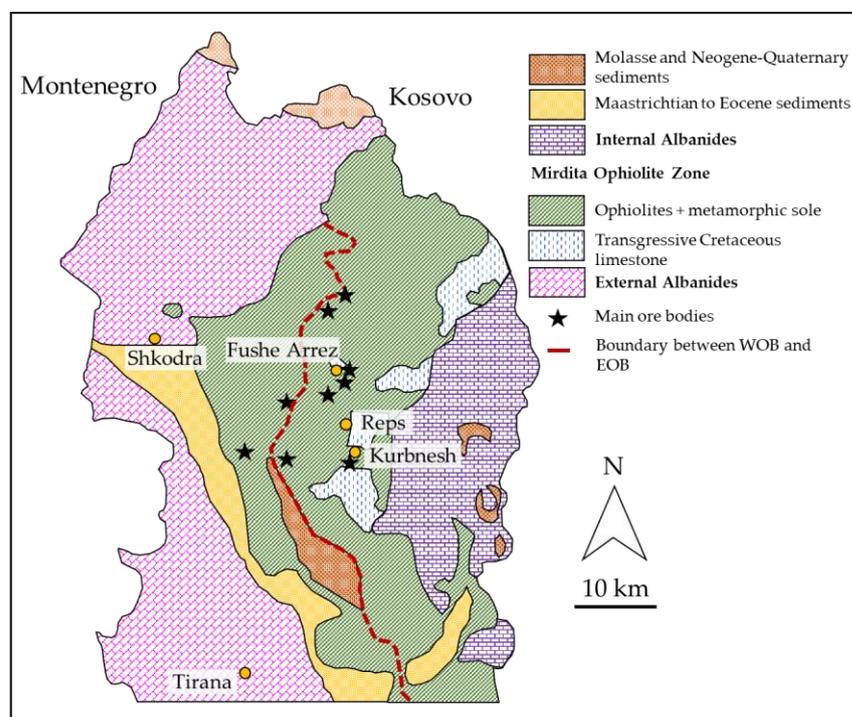


Figure 3. Simplified tectonic map of Northern Albania with location of the main volcanic massive sulfide (VMS) copper ore bodies (modified after [24]).

These upper mantle and crustal units show features varying from the west to the east in thickness, internal stratigraphy and chemical compositions. In particular, the Western Ophiolite Belt (WOB) is a harzburgitic-harzburgitic-dunitic upper mantle unit, overlain by a plutonic sequence and extrusive rocks characterized by MORB affinity. On the other hand, in the thicker Eastern Ophiolite Belt (EOB) the basement is mainly made up of harzburgites and dunites, overlain by a plutonic sequence. The sheeted dyke complex is well developed and the effusive units consist of basalts and andesites with affinities of the supra subduction zone type [25–27].

Sulfide orebodies occur both in the WOB and in the EOB (Figure 1). In the western belt massive sulfides and stockwork veins are mainly hosted into the volcano-sedimentary series (volcanites, mélanges, with variable content of shales, slates, cherts). Within the EOB, a NNE trending, 25 km long belt between Chafe Mal and Reps hosts the majority of and the biggest deposits, classified as volcanic massive sulfide [28–30]. Both mines providing

ore to Fushe Arrez plant are located in this belt. Major ore bodies are distributed along a discontinuous line, and minor occurrences lie along sub parallel orientations. Host rocks are massive lava flows, pillow basalts, pyroclastics and, in few cases, also intrusions and mélanges [28–30]. Massive pyrite deposits are also documented within the rhyolitic dyke complex [27]. Pyrite is the dominant sulfide mineral throughout. The copper ores are comprised of chalcopyrite, bornite, tennantite. Sphalerite and, to a lesser extent, covellite, chalcocite, arsenopyrite and galena, are also found, as minor constituents, in the mineral associations. The main sulfide related metals are Cu, Zn, Au, associated to variable contents of Pb, Ag, As, Cd, Ge, Sb, In [30–33].

4. Results

4.1. Water Samples

Waters of the stream flowing through the valley used for dumping tailings showed very different visual characters during the field survey. Upstream of the dumps they are clear and do not show any evidence of sulfate or oxy-hydroxide precipitates. Waters collected at the new dump were turbid, but no precipitates were visible, probably due to the high and continuous inflow of tailing muds in the dump. No water was visible on the old dump. Water flows within the dump material and gets back to the surface only close to the stream confluence into the Fan I Madh river, when a widespread deposition of red muds is evident as well as the transport of the same muds from the stream to the Fan I Madh river (Figure 2). In this area the old dump is partially eroded, especially in the central part of the impoundment and shows an orange surface due to precipitates, but just few centimeters below surface the color changes into grey.

In situ pH and conductivity values are reported in Table 2. The waters that were not affected by dumps, those from the watercourse upstream of the dumps (sample CM1) and from the Fan I Madh river upstream of the water's confluence (sample CFM) show very similar pH (6.61 and 6.62) and conductivity (154 and 156 $\mu\text{S}/\text{cm}$) values. Waters ponding on the new dumps (CD1, CD1-B, CD2) are highly acidic ranging from pH 3.14 and pH 3.48 and show variable but generally high conductivity ranging between 415 and 876 $\mu\text{S}/\text{cm}$.

Table 2. Values of pH, conductivity and sulfate content of water samples.

Sample	pH	σ ($\mu\text{S}/\text{cm}$)	Sulfate ($\mu\text{g}/\text{L}$)
CM1	6.61	154 at 26.1 °C	46.4
CD1	3.36	442 at 27.0 °C	423.0
CD1-B	3.48	415 at 26.0 °C	472.0
CD-2	3.14	876 at 28.9 °C	545.0
CFM	6.62	156 at 21.0 °C	23.5
CFI	4.59	1814 at 21.4 °C	2450
CFV	5.81	650 at 21.0 °C	373.5

Waters flowing out of dumps (CFI) are weakly acid (4.59) and show a very high conductivity (1814 $\mu\text{S}/\text{cm}$). Finally, waters just downstream of confluence (CFV) show to be affected by polluted waters from the dumps. In comparison with waters of Fan I Madh river not affected by dumps, they show a pH decrease of 0.81 and a conductivity increase of 494 $\mu\text{S}/\text{cm}$.

Sulfate contents of waters are correlated with the conductivity data, showing that they are the most abundant anions. Very low sulfate contents in unpolluted waters change into high contents (472–545 $\mu\text{g}/\text{L}$) in dump waters and very high contents in waters downstream of dumps (2450 $\mu\text{g}/\text{L}$). Finally, Fan I Madh river waters show a strong increase in sulfate content due to the confluence with waters from the dumps, the waters downstream having 16 times higher sulfate contents than those upstream.

The metal contents of waters are shown in Table 3. All metals whose content is systematically above the detection limits show a similar pattern of concentration distribution in the samples, the only exception being Ca. This latter cation is present in high amounts

in waters downstream of dumps, is still present in the Fan I Madh waters after confluence but is below detection limits in all other samples. Other metals show the lowest contents in unpolluted waters upstream of dumps and confluence, peak values downstream of dumps and intermediate values in the Fan I Madh river waters downstream of confluence.

Table 3. Concentration of selected metals in water samples.

Sample	Zn (mg/L)	Fe (mg/L)	Cu (mg/L)	Co (mg/L)	Al (mg/L)	Mn (mg/L)	Ca (mg/L)	Ni (mg/L)	Mo (mg/L)	Pb (mg/L)	Cr (mg/L)	Cd (mg/L)	As (µg/L)
CM1	0.01	1.00	0.03	0.01	0.06	0.17	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	4.96
CD1	1.15	2.52	0.77	0.02	2.11	0.36	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	7.85
CD1-B	1.08	1.30	0.84	0.02	1.94	0.33	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	8.11
CD-2	5.38	3.90	3.54	0.01	6.27	0.64	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	6.91
CFM	0.05	0.02	0.02	0.00	0.05	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	2.27
CFI	6.17	62.19	1.01	0.14	19.70	7.20	214.84	<0.01	<0.01	<0.01	<0.01	<0.01	10.23
CFV	1.63	24.68	0.29	0.03	3.73	2.00	63.25	<0.01	<0.01	<0.01	<0.01	<0.01	3.78

4.2. Characterization of the Dump Material

Based on the way dump material samples were assembled, the following results have to be considered as average values referred to the whole dumps, respectively the old and new one. A statistical analysis of internal variability of each dump is beyond the possibility and the aim of the present work.

Grain size distribution of the four solid samples is shown in Figure 4. The feed sample is obviously coarser as it was collected before grinding. Current concentrate and new dump samples have a very similar grain size distribution, showing that since reopening the comminution procedure has not changed. Old dump sample is coarser. This result can be partially due to an artifact, as some portions of the old dump show an incipient cementation, anyway the sample used for grain size analysis was carefully shaken in order to break weak cement bonds, so it is suggested that before closure in 2000 the feed was ground to a coarser grain size. Semi-quantitative determination of mineralogy from XRD data is reported in Table 4.

The feed sample contains mainly pyrite with minor chalcopyrite and quartz, that is the same mineralogy observed under transmitted light microscopy in the ore stocked at the plant: during sampling a massive sulfide ore was being processed resulting in a very low 4% silicates in the feed. The high chlorite content of dump materials is related to the ore host rock, an andesitic to dacitic volcanite, where all feldspar had been altered into chlorite.

Observations in reflected light show that sulfide phases are dominated by pyrite in sub-millimetric to millimetric grains, with minor mounts of chalcopyrite, often associated to pyrite in aggregates. Degree of alteration is low in both old and new dumps materials. Pyrite grains are mostly euhedral to subhedral with only rare evidence of corroded rims (Figure 5).

Table 4. Semi-quantitative determination of mineralogical composition of feed, new dump, old dump and concentrate (data in wt.%).

Sample		Pyrite	Chalcopyrite	Quartz	Gypsum	Chlorite
FA1	Feed	89	7	4		
FA3	New dump	68		23	3	6
FA4	Old dump	18		34		48
FA6	Concentrate	49	51			

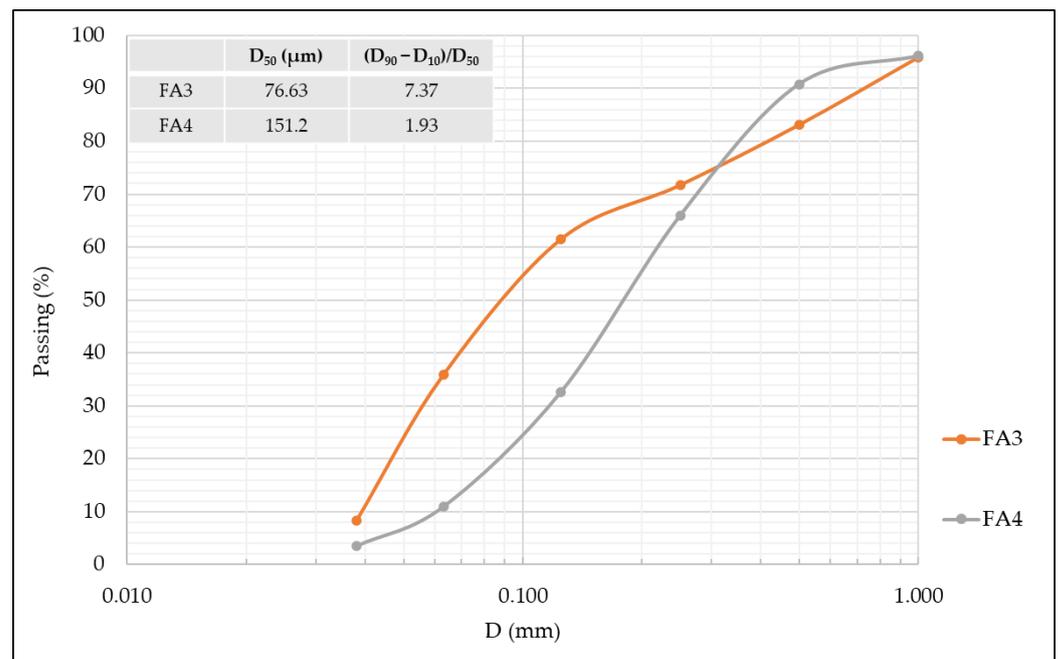


Figure 4. Grain size curves of new and old dumps solid materials. Statistical parameters reporting median grain size (D_{50}) and standard deviation $(D_{90} - D_{10})/D_{50}$.

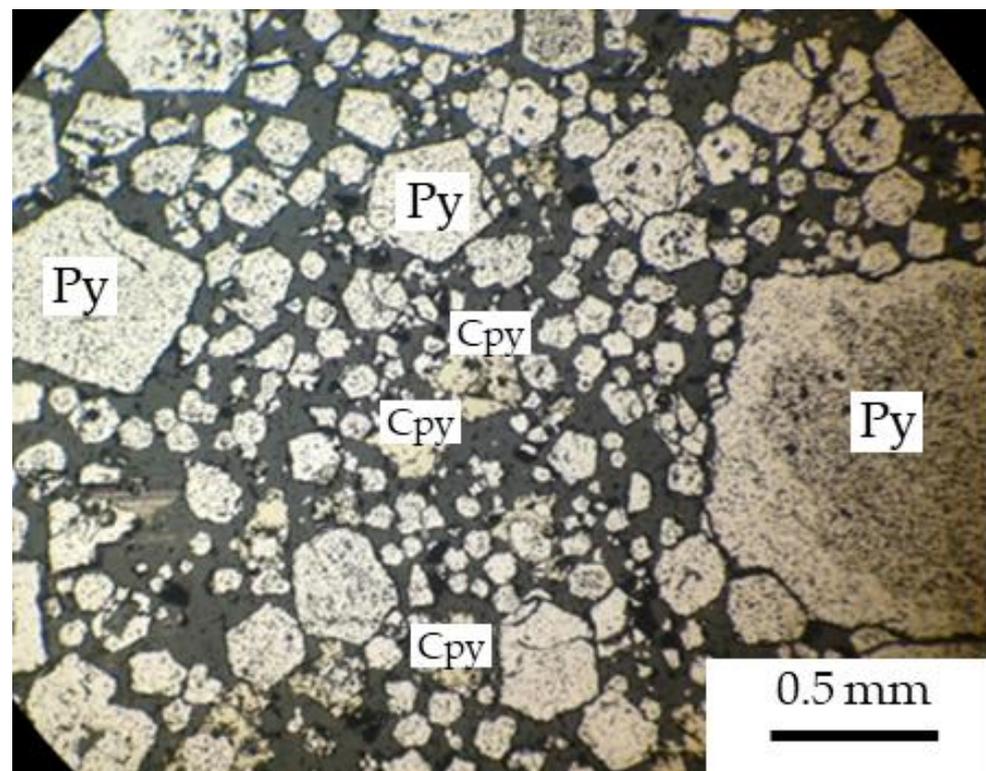


Figure 5. Reflected light microscopy image showing the mineralogy of the feed sample. Py: pyrite, Cpy: chalcopyrite.

Old and new dump samples show the same mineralogy but with a different proportion among phases. The old dump sample is strongly depleted in pyrite (18 wt.%) when compared with the new dump sample (68 wt.% pyrite) reflecting the double flotation process that separated most of the pyrite, left in a second concentrate. The presence of gypsum in the new dump can be attributed to the initial alteration of sulfides caused by

meteoric waters. Sulfates in old dumps were not found and reported, probably due to their low amount in this S-depleted material or to their leaching during the longer time span of residence of material in the dump.

The values of pH and conductivity of leachate waters, derived from soaking of the, are reported in Table 5. All samples are strongly acidic, with pH values below 3 in the dump samples and show low conductivity with a maximum for new dump samples, probably due to the faster dissolution of sulfates.

Table 5. Values of pH and conductivity of leachates from feed, new dumps, old dumps and concentrate.

Sample		pH	σ ($\mu\text{S}/\text{cm}$)
FA1	Feed	3.88	2.45
FA3	New dump	2.59	8.58
FA4	Old dump	2.87	4.81
FA6	Concentrate	3.08	6.78

The concentrations of selected metals and sulfur in the samples are reported in Table 6. The distribution of metals in the feed (FA1), tailing of the new dump (FA3), tailing of the old dump (FA4) and concentrate (FA6) is very different. In particular, Ni, Al, Ca, Cr, Mg, Mn, Na and Ti are more concentrated in the tailings, with the highest concentration in the old ones, while Au, Ag, Cu, Cd, Mo, Pb, Zn and Sb are strongly enriched in the concentrate. Co shows the highest concentration in the new dump, and As is strongly enriched in the feed and in the new dump.

4.3. Leaching Tests

In order to increase the reliability of the results, leaching tests were performed six times on previously homogenized portions of old and new dump samples through mixing and quartering. Results of pH and conductivity of leachate solutions are reported in Table 7.

Results show a strong acidification of waters, with slightly but statistically meaningful lower pH values for the new dumps. The difference is larger for conductivity values, that are almost 3 times higher for new dump material.

Two leachate waters (L1 and L2) for each sample were analyzed for a selection of 11 metals and are reported in Table 8. Two elements, Ni and Pb, show very low concentrations, below their detection limits, in both samples, and their differential distribution cannot be assessed. All other analyzed metals have very different distributions between old and new dumps, with the only exception of Co. Fe and Ca are strongly enriched in the new dump, Zn, Mg, Mn and As are slightly enriched in the new dump and only Cu and Al are enriched in the old dump.

Table 6. Concentration of selected metals and sulfur in solid materials from feed, new dumps, old dumps and concentrate.

Sample	Al	S	Fe	K	Mg	Na	Ti	Cu	Ca	As	Ag	Au	Cd	Mo	Pb	Co	Ni	Zn	Cr	Mn	Sb
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	w%	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
FA1	0.39	48.4	39.9	0.06	0.08	0.03	0.02	>1	0.24	980.0	6.2	1350	3.0	16	127	6	18	914	10	72	15.5
FA3	1.46	36.8	33.4	0.20	0.62	0.09	0.09	0.156	0.71	890.0	2.4	1280	1.0	14	61	217	12	206	34	333	10.0
FA4	4.67	15.9	19.8	0.19	2.58	0.42	0.20	0.207	1.03	276.0	0.7	290	0.7	4	15	177	40	121	86	750	2.1
FA6	0.07	n.a.	34.8	<0.01	0.04	0.01	<0.01	>1	0.25	625.0	19.6	2480	29.3	22	140	15	16	13,400	14	45	37.7

Table 7. Values of pH and conductivity of leachates from new (FA3) and old (FA4) dump solid materials.

Sample	FA3		FA4	
	pH	σ ($\mu\text{S/cm}$)	pH	σ ($\mu\text{S/cm}$)
L1	2.94	2.99	3.19	1.02
L2	2.91	2.89	3.12	1.06
L3	2.94	2.92	3.15	1.04
L4	2.89	3.02	3.14	1.00
L5	2.88	2.91	3.14	1.03
L6	2.91	2.93	3.16	1.00
average	2.91	2.94	3.15	1.02

Table 8. Concentration of selected metals in leachates from new (FA3) and old (FA4) dump solid materials.

Sample	Zn	Fe	Cu	Co	Ni	Pb	Ca	Mg	Al	Mn	As
	mg/L	mg/L	mg/L	mg/L	$\mu\text{g/L}$	$\mu\text{g/L}$	mg/L	mg/L	mg/L	mg/L	$\mu\text{g/L}$
FA3-L1	2.11	360.38	4.61	0.03	<50	<50	369.00	36.98	39.63	3.24	12.90
FA3-L2	1.87	351.28	4.43	0.03	<50	<50	409.79	36.30	38.21	3.12	11.62
FA4-L1	1.39	31.90	11.31	0.04	<50	<50	38.38	27.21	80.58	1.06	7.39
FA4-L2	1.26	31.94	10.36	0.04	<50	<50	35.47	26.03	76.40	1.02	5.46

5. Discussion

The distribution of metals in feed, concentrate and the two tailings strongly reflects their behavior during flotation, that, in turn, depends on the mineralogic phase hosting the metals. A first group of elements (Ni, Al, Ca, Cr, K, Mg, Mn, Na, Ti) is mainly hosted in gangue phases (feldspar, quartz, chlorite). These metals show the highest concentrations in old dump samples, that are strongly depleted in sulfides and hence indirectly enriched in gangue minerals. A second group of elements (Au, Ag, Cu, Cd, Mo, Pb, Zn, Sb) is strongly enriched in the concentrate, showing that these elements are mainly hosted in chalcopyrite and sphalerite, in microscopic inclusions within them or in accessory phases that also report to the concentrate. Hence, they are preferentially accumulated in the concentrate. A third group composed of As and Co shows the highest concentrations in the new dump, being related to pyrite but not chalcopyrite. Finally, Fe, by far the most abundant metal in the system, is only depleted below 20% in the old dump due to its abundance in gangue minerals.

Sulfur contents mainly reflect the distribution of pyrite and hence the single or double flotation process employed. Due to separation of a pyrite concentrate old dump material is strongly depleted in pyrite and sulfur when compared to the new dump material.

The results of the leachate tests also reflect the different nature of the two tailing materials. The two elements strongly enriched in the new dump leachates can be ascribed to the much higher abundance in this dump of pyrite (Fe) and gypsum (Ca). Higher values of Zn and As in leachates from the new dump also reflect a higher content of these metals in the dump material, while Mg and Mn, whose content is higher in the old dump material must reflect a different solubility of the phases that host them. Finally, higher contents of Cu and Al in the leachates from the old dump can be ascribed to a lower chalcopyrite separation efficiency of the old flotation plant and to the high chlorite content of old dump material.

At Fushe Arrez, the predominant role of pyrite in AMD processes is confirmed by the very high pyrite content of feed (89% pyrite). The only other sulfide present in significant amounts is chalcopyrite but, as it is mostly reported to the concentrate, its role in the tailing acidification is much lower than that of pyrite. All other sulfides do not play a significant role in water acidification. These minerals are, anyway, important sources, together with pyrite and chalcopyrite, of potentially toxic elements, that are easily released in acidic waters.

Tailings at Fushe Arrez are fine grained and relatively recent as they were stacked in the dumps in the last 20 years for new dumps and no more than 30 years ago for the old dumps. The relatively young age of the dumps, together with the fine grain size of the material, that reduces the filtration of water, can be the main cause of the low content of secondary phases, such as iron oxides, sulfates, and oxi-hydroxides, that were detected only as orange crusts at the surface of the old dump, or along the outflow stream bed. In comparison copper tailings from VMS mine at Libiola are very rich in secondary iron phases with a low amount of sulfides, below 5% in average [2]. At Libiola the grain size of tailings is coarser and they were produced probably in the fifties of last century and underwent a much longer and more intense AMD process. The low degree of alteration of Fushe Arrez sulfides can result in a low rate of acid production and PTE release, but, on the other hand, it means that the AMD related pollution is just at the beginning and its persistence in time will be very long, decades or even centuries.

The role of factors other than the flotation settings in affecting the pyrite content of tailing must be taken into account. A first possibility is that the old dump underwent long and deeper alteration and the secondary sulphates were leached by the percolating waters. While this process is confirmed by the high sulphate contents of waters it can hardly explain the huge difference in sulfur and pyrite amount between old and new dumps. Firstly, the time span between old and new dumps is quite short. A second important clue is the low degree of alteration showed by pyrite under reflected light study. A third clue is the sharp contact and large difference in sulfur and pyrite contents of single and double flotation tailings interbedded in the same dump at Repts, where materials and conditions were very similar to those at Fushe Arrez. We infer that even if the different ages of dumps and the different degree of alteration can play a role in the pyrite content of tailings, this is subordinate if not negligible when compared to the role played by differing flotation settings.

Also differences in primary ore mineralogical composition worked at different times at the Fushe Arrez plant can have affected the pyrite content of dumps. This however cannot explain the detected differences in pyrite content VMS ore deposits are known to show quite homogeneous mineralogy and this is the case also of the Northern Albania mining district [27,29,30]. Moreover, a single mine, the Munella Mine, has been the main provider of ore during the whole life span of Fushe Arrez plant.

AMD processes at Fushe Arrez are verified by the pH value of dump waters that react with pyrite and lower their pH from close to neutrality (Sample CM1; pH = 6.61) to around 3.5 (samples CD-). The higher pH of waters downstream of dumps is puzzling as there are no outcrops of buffering rocks, such as limestones, in the area, while the high Ca content, detected only in these waters, suggests buffering through reaction with carbonates. We can just assume that some neutralizing material, now buried by tailings, was deliberately placed, probably at the bottom of the new dumps, to treat the tailings.

The metal contents show, when reported in a Ficklin diagram, a negative correlation with pH (Figure 6A). As a whole the Fushe Arrez waters fall in the core of the VMS waters field defined by Plumlee et al. [34], but with a strong differentiation among different waters. Stream waters upstream of the dumps and Fan I Madh river waters before confluence of dump waters discharge are very similar and can be classified as “near-neutral low-metals”. This suggests that there is low natural pollution or contribution from mining works upstream in the area and that the background values of metal concentrations are very low. Waters that reacted with tailings are all “acid high-metal”, but waters from the dumps discharge have higher pH. Finally, Fan I Madh waters just after discharge confluence are clearly affected, falling in the “near neutral-high metal” field. The effect is higher on metals than on acidity due to the low acidity of discharge waters.

In Figure 6B results were plotted in a Ficklin diagram together with those of waters from Repts tailings, deriving from the nearby dressing plant that enriched ore from several copper mines located within the EOB, and those from the Iberian pyrite belt. This last one is a large VMS copper district in southern Spain and Portugal that was widely studied for

its AMD processes [35–40]. Background waters conditions are similar in all three areas, with a slightly higher metal content at Reps, probably due to the presence of other mines upstream of the Reps dumps. Impacted river waters show the same trend of increasing metal content and acidity, with differences among the three areas not easy to evaluate as they strongly depend on several factors. Among the factors affecting impacted waters, the ratio between discharge and river waters flow and the distance from the source of pollution are the most important. Tailings and open pit waters are invariably the most polluted, both in terms of metal content and acidity. The lower metal content at Reps can be interpreted as the effect of a poorer base sulfide mineral assemblage, widely dominated by pyrite.

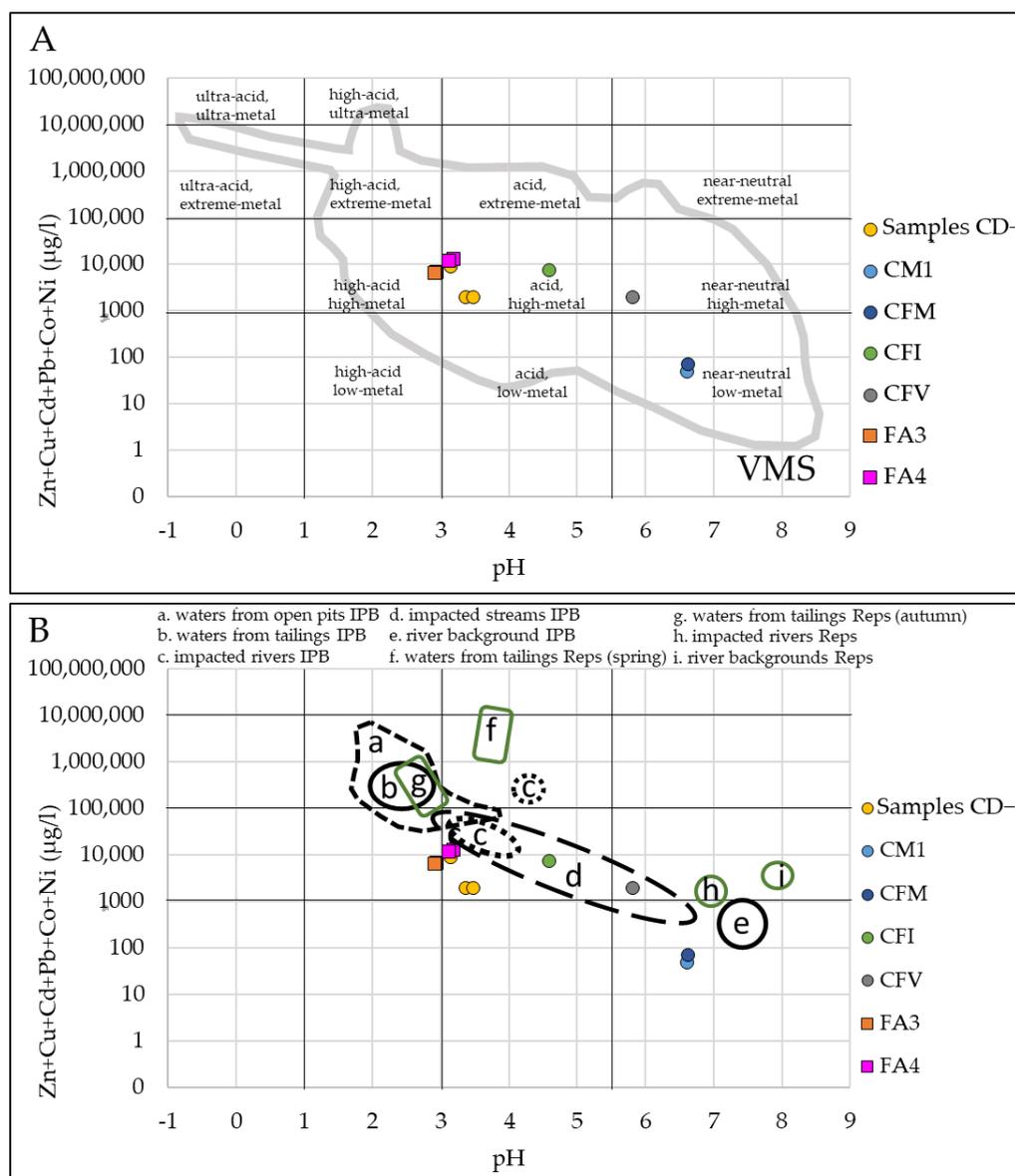


Figure 6. Ficklin diagram [41] of pH vs. dissolved metal content in Fushe Arrez water samples and leachates compared to (A) VMS waters field [34] and (B) waters from tailings, open pits, impacted rivers and river backgrounds of the Iberian Pyrite Belt (IPB) [35–39] and Reps [42].

In pyrite-dominated systems, like those of the Fushe Arrez dumps, the dissolution of Fe has a major role in water pollution. When compared to the VMS field of Plumlee et al. [34] in the pH vs. Fe chart (Figure 7), dump ponds waters at Fushe Arrez plot in its upper portion, while discharge waters are outside the field due to the extremely

high Fe content. In a similar environment like that of the IPB as well as at Reps, the high Fe enrichment is also present [35–40]. Leachates from old and new dumps are high in Fe, overlapping the field of tailing waters from Reps and IPB. New dump leachates are particularly high in Fe, due to the very high pyrite content of the dumps. Discharge waters are also high in Fe showing intermediate contents among new and old dumps leachates that confirm their derivation from a mixture of waters draining old and new dumps.

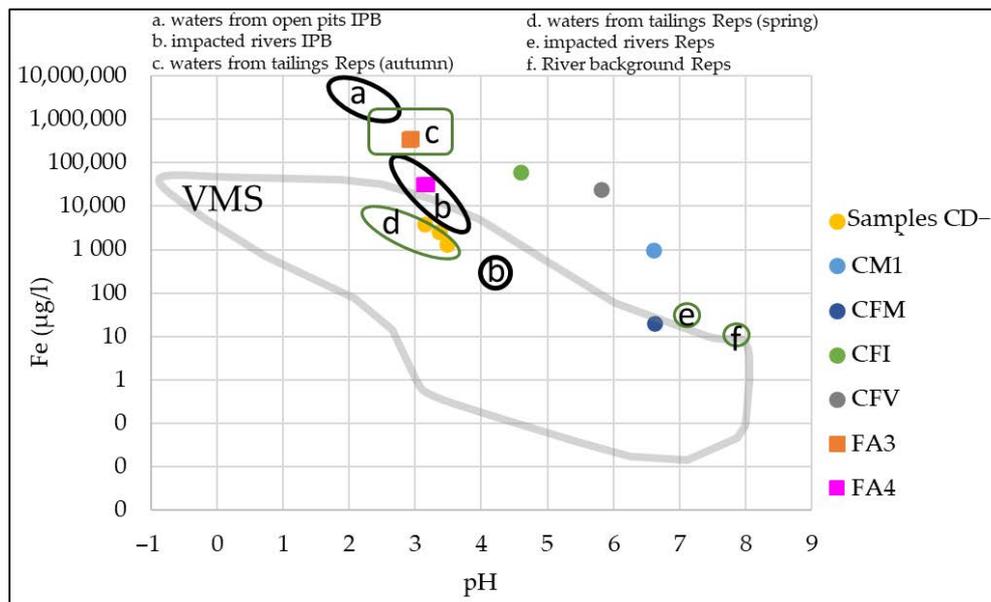


Figure 7. pH vs. dissolved Fe content in Fushe Arrez water samples and leachates compared to VMS field [34], waters from open pits, tailings, impacted rivers and river backgrounds of the IPB [35–39] and Reps [42].

As a whole the release of metals into the waters at Fushe Arrez like in the other VMS copper mines is strictly related to AMD processes and driven by dissolution of pyrite and other sulfides in contact with waters and atmospheric oxygen. Acidification is a self-sustaining process as solubility of pyrite is inversely correlated to pH of waters [43–45].

The relative contribution of old and new dumps to water pollution cannot be assessed through water analyses as no waters that interacted only with old dumps could be collected. Leaching tests provide a good proxy of polluted waters and, moreover, due to the standardization of procedures allow to rule out the contribution of other parameters that affect waters in situ, like the time of residence of waters in the dumps or their flow rates.

Leaching tests, repeated six times, show very consistent results. In agreement with their higher S contents new tailings leachates are more acidic than old ones. A leachates plot in the Ficklin diagram chart at the top end of the AMD trend for the Fushe Arrez waters, provides a confirmation of the use of these waters as a proxy of the leaching processes at Fushe Arrez. Both leachates are more acidic than any water analyzed in situ. Anyway, values are quite close to those of waters collected on top of the new dump, the difference being probably due to a more intense interaction between solid materials and waters in the leaching tests. They are also consistent with tailing and open pit waters from Reps and IPB.

Comparison among old and new dump leachates shows a quite different distribution of metals (Tables 7 and 8; Figures 6 and 7). Leachates from the new dumps show much higher total metal content and slightly lower pH values. The biggest difference is in Fe content as concentration of this element is more than ten times higher in the new dump leachates. This high ratio can be attributed to the combined effect of the higher pyrite content and lower grain size of new dump materials. A minor contribution of a partial coating effect on old dump pyrite can be also envisaged. Zn and As, that are both hosted in sulfides are also enriched in the new dump leachates but to a lower extent. Cu is hosted in chalcopyrite and its higher concentration in the old dump leachates reflects the lower

efficiency in chalcopyrite separation by the old flotation plant and the consequent higher Cu content of old dump solid sample. Mg, Al and Mn are mostly found in non-sulfide gangue phases and probably reflect a difference in composition and abundance of gangue minerals in the two dumps. Finally, the much higher Ca content of new dump leachates can be referred to the presence of low amounts of gypsum in the dump.

The metal contents of both dump leachates are compatible with the contents of the same metals in the dump solid materials. In detail, the latter confirms the higher Cu, Al, Mg and Mn contents of the old dumps. On the other hand, Fe concentration in leachates cannot be explained only by different Fe contents of the two dumps, which are not so high. Thus, the role of the grain size and the possible partial coating of pyrite in old dumps are confirmed to enhance the Fe concentration differences among leachates. The very low Ca content in the old dump leachates in spite of a higher Ca content in the old dump solid materials can be due to its presence in insoluble gangue phases such as clinopyroxenes and Ca-amphiboles unlike the Ca content in leachates from the new dumps containing gypsum.

Comparison of leachate metal contents with metal contents of waters collected in situ shows that all waters that did not deeply interact with dumps have quite low concentrations of metals. Water samples collected upstream of the dumps and from the Fan I Madh river belong to this group. Although the waters collected on the top of the new dumps are very acidic and have a low metal content due to their interaction in the beginning also belong to this group. The best comparison can be done with the stream waters downstream of both old and new dumps. The total metal content of outflow waters is intermediate between the two types of leachates. While Fe content can be explained by a simple mixing of water outflows from old and new dumps, other metals show some differences. While the order of magnitude of the metal concentrations is the same, confirming the validity of the leaching tests, outflow waters are anyway higher in Zn, Mn and lower in Al and Cu than both leachates. This is indicative of some difference between the natural system and the laboratory leaching tests. It is possible that Cu and Al-bearing phases are solubilized more quickly in laboratory condition whereas Mn and Zn phases are less soluble.

Environmental treatment of AMD is pivotal on the way towards sustainable mining and several techniques have been proposed and discussed (e.g., [46] and references therein). The present work suggests a new way to approach the problem that can lead to two typologies of actions depending on the conditions of the mines. This new approach has been validated for VMS Cu mines where pyrite separation not always occurred together with chalcopyrite separation. It can be implemented also for any other mining operations where separation followed articulated patterns. The approach can be summarized as follows:

- Abandoned mines: study of the beneficiation process during all mine lifetime in order to assess if and when single or double flotation were in exercise; on the basis of historical data and dumps sampling study the distribution of low and high sulfide tailings according to the procedures of Fantone et al. [21] and plan environmental treatment actions accordingly.
- Active mines: shift from single to double flotation to produce a low and a high sulfur tailing that will be treated and stocked separately.

6. Conclusions

The analysis of tailing materials, waters from leaching tests and natural waters flowing in the system show that changes in separation processes can have a major role in the environmental impact of tailing dumps. Pyrite separation during flotation has a key role as a single flotation setting that deposits pyrite to the tailings produces lower pH acid waters with a much higher total metal content than double flotation where pyrite concentrate is produced. This occurs at Fushe Arrez even though double flotation with much lower separation efficiency was utilized a long time ago, as verified by the relatively high Cu content in the tailings. Due to such low separation efficiency during double flotation, a significant amount of pyrite is reported to the tailings. Today, a highly efficient double flotation would result in even S-poorer tailings than those observed at Fushe Arrez.

Double or single flotation separation processes affect not only the global environmental impact, but also the distribution of metals in the dumps and consequently in the impacted waters. Double flotation tailings show lower Fe and other sulfide-related metal and higher gangue minerals metal contents. The only exception to this scenario is Cu whose content in tailings is more closely related to the changes in separation efficiency with time than to the double or single flotation setting of the plant.

The present results show that pyrite separation is an effective way to reduce the environmental hazards of copper mine separation plants and, as can be inferred, of all pyrite-rich ores. By separating pyrite during flotation, it is possible to achieve very important environmental goals like strongly reducing the acidity and total metal contents of waters interacting with tailing dumps. It is finally suggested that a great effort should be done to implement pyrite industrial uses as the production of a pyrite concentrate at many types of sulfide ore mines can strongly decrease environmental pollution and help achieve a more sustainable management of mining dumps.

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References

1. Balistrieri, L.S.; Seal, R.R.; Piatak, N.M.; Paul, B. Assessing the concentration, speciation, and toxicity of dissolved metals during mixing of acid-mine drainage and ambient river water downstream of the Elizabeth Copper Mine, Vermont, USA. *Appl. Geochem.* **2007**, *22*, 930–952. [\[CrossRef\]](#)
2. Marescotti, P.; Carbone, C.; De Capitani, L.; Grieco, G.; Lucchetti, G.; Servida, D. Mineralogical and geochemical characterisation of open-air tailing and waste-rock dumps from the Libiola Fe-Cu sulphide mine (Eastern Liguria, Italy). *Environ. Geol.* **2008**, *53*, 1613–1626. [\[CrossRef\]](#)
3. Servida, D.; Grieco, G.; De Capitani, L. Geochemical hazard evaluation of sulphide-rich iron mines: The Rio Marina district (Elba Island, Italy). *J. Geochem. Explor.* **2009**, *100*, 75–89. [\[CrossRef\]](#)
4. Barrie, C.T.; Hannington, M.D. Classification of volcanic-associated massive sulfide deposits based on host-rock composition. *Rev. Econ. Geol.* **1999**, *8*, 1–11.
5. Ferreira da Silva, E.; Bobos, I.; Xavier Matos, J.; Patinha, C.; Reis, A.P.; Cardoso Fonseca, E. Mineralogy and geochemistry of trace metals and REE in volcanic massive sulfide host rocks, stream sediments, stream waters and acid mine drainage from the Lousal mine area (Iberian Pyrite Belt, Portugal). *Appl. Geochem.* **2009**, *24*, 383–401. [\[CrossRef\]](#)
6. Marescotti, P.; Azzali, E.; Servida, D.; Carbone, C.; Grieco, G.; De Capitani, L.; Lucchetti, G. Mineralogical and geochemical spatial analyses of a waste-rock dump at the Libiola Fe–Cu sulphide mine (Eastern Liguria, Italy). *Environ. Earth Sci.* **2010**, *61*, 187–199. [\[CrossRef\]](#)
7. Akcil, A.; Koldas, S. Acid Mine Drainage (AMD): Causes, treatment and case studies. *J. Clean. Prod.* **2006**, *14*, 1139–1145. [\[CrossRef\]](#)
8. Dong, Y.; Di, J.; Wang, X.; Xue, L.; Yang, Z.; Guo, X.; Li, M. Dynamic Experimental Study on Treatment of Acid Mine Drainage by Bacteria Supported in Natural Minerals. *Energies* **2020**, *13*, 439. [\[CrossRef\]](#)
9. Jamieson, H.E. Geochemistry and Mineralogy of Solid Mine Waste: Essential Knowledge for Predicting Environmental Impact. *Elements* **2011**, *7*, 381–386. [\[CrossRef\]](#)

10. Kefeni, K.K.; Msagati, T.A.M.; Mamba, B.B. Acid mine drainage: Prevention, treatment options, and resource recovery: A review. *J. Clean. Prod.* **2017**, *151*, 475–493. [[CrossRef](#)]
11. Liu, Y.; Hu, X.; Xu, Y. PropS-SH/SiO₂ nanocomposite coatings for pyrite oxidation inhibition to control acid mine drainage at the source. *J. Hazard. Mater.* **2017**, *338*, 313–322. [[CrossRef](#)] [[PubMed](#)]
12. Servida, D.; Comero, S.; Dal Santo, M.; de Capitani, L.; Grieco, G.; Marescotti, P.; Porro, S.; Forray, F.L.; Gál, Á.; Szakács, A. Waste rock dump investigation at Roşia Montană gold mine (Romania): A geostatistical approach. *Environ. Earth Sci.* **2013**, *70*, 13–31. [[CrossRef](#)]
13. Strauss, E.; Golodnitsky, D.; Peled, E. Study of phase changes during 500 full cycles of Li/composite polymer electrolyte/FeS₂ battery. *Electrochim. Acta* **2000**, *45*, 1519–1525. [[CrossRef](#)]
14. Hu, Z.; Zhu, Z.; Cheng, F.; Zhang, K.; Wang, J.; Chen, C.; Chen, J. Pyrite FeS₂ for high-rate and long-life rechargeable sodium batteries. *Energy Environ. Sci.* **2015**, *8*, 1309–1316. [[CrossRef](#)]
15. Huang, P.; Deng, S.; Zhang, Z.; Wang, X.; Chen, X.; Yang, X.; Yang, L. A sustainable process to utilize ferrous sulfate waste from titanium oxide industry by reductive decomposition reaction with pyrite. *Thermochim. Acta* **2015**, *620*, 18–27. [[CrossRef](#)]
16. Zhang, X.; Manno, M.; Baruth, A.; Johnson, M.; Aydil, E.S.; Leighton, C. Crossover From Nanoscopic Intergranular Hopping to Conventional Charge Transport in Pyrite Thin Films. *ACS Nano* **2013**, *7*, 2781–2789. [[CrossRef](#)]
17. Johnson, D.B.; Hallberg, K.B. Acid mine drainage remediation options: A review. *Sci. Total Environ.* **2005**, *338*, 3–14. [[CrossRef](#)]
18. Daci, A.; Kaza, G.; Deda, T.; Hoti, S. The environmental impact of the Copper industry in the Fani River Valley (Repsi “Hot spot”) Mirdita, Albania. *Bull. Geol. Soc. Greece* **2018**, *40*, 1387. [[CrossRef](#)]
19. Demi, G. *Waste Assessment of Copper Mines and Plants in Albania and Their Impact in Surrounding Areas*; Report for Mining and Processing; Technology Institute: Tirana, Albania, 2003.
20. Kumanova, X.; Leka, G.; Nilsson, B.; Jacks, G. Assessing the mobility of metals in an aquatic environment: River Fani and River Mati, Albania. *Environ. Earth Sci.* **2015**, *74*, 6293–6301. [[CrossRef](#)]
21. Fantone, I.; Grieco, G.; Sinojmeri, A.; Cavallo, A. A quantitative approach to the influence of pyrite separation on Cu-processing tailings: A case study at Repts, Mirdita district, Albania. *Environ. Earth Sci.* **2017**, *76*, 774. [[CrossRef](#)]
22. Hettipathirana, T. *Determination of Metals in Soils Using the 4100 MP-AES*; Application Notes; Agilent Technologies: Melbourne, Australia, 2011.
23. Bortolotti, V.; Chiari, M.; Marcucci, M.; Marroni, M.; Pandolfi, L.; Principi, G.; Saccani, E. Comparison among the Albanian and Greek ophiolites: In search of constraints for the evolution of the Mesozoic Tethys Ocean. *Ophioliti* **2004**, *29*, 13–35.
24. Gawlick, H.-J.; Frisch, W.; Hoxha, L.; Dumitrica, P.; Krystyn, L.; Lein, R.; Missoni, S.; Schlagintweit, F. Mirdita Zone ophiolites and associated sediments in Albania reveal Neotethys Ocean origin. *Int. J. Earth Sci.* **2008**, *97*, 865–881. [[CrossRef](#)]
25. Shallo, M.; Dilek, Y. Development of the ideas on the origin of Albanian ophiolites. *Spec. Papers-Geol. Soc. Am.* **2003**, *373*, 351–364.
26. Dilek, Y.; Furnes, H.; Shallo, M. Suprasubduction zone ophiolite formation along the periphery of Mesozoic Gondwana. *Gondwana Res.* **2007**, *11*, 453–475. [[CrossRef](#)]
27. Phillips-Lander, C.M.; Dilek, Y. Structural architecture of the sheeted dike complex and extensional tectonics of the Jurassic Mirdita ophiolite, Albania. *Lithos* **2009**, *108*, 192–206. [[CrossRef](#)]
28. Economou-Eliopoulos, M.; Eliopoulos, D.G.; Chryssoulis, S. A comparison of high-Au massive sulfide ores hosted in ophiolite complexes of the Balkan Peninsula with modern analogues: Genetic significance. *Ore Geol. Rev.* **2008**, *33*, 81–100. [[CrossRef](#)]
29. Hoxha, L. The Jurassic-Cretaceous orogenic event and its effects in the exploration of sulphide ores, Albanian ophiolites, Albania. *Eclogae Geol. Helv.* **2001**, *94*, 339–350.
30. Hoxha, L.; Scott, P.W.; Eyre, J.M. The geological setting of volcanogenic sulphide orebodies in Albanian ophiolites. *Appl. Earth Sci.* **2005**, *114*, 33–52. [[CrossRef](#)]
31. Sinojmeri, A. Sea-floor sulfide mineralizations of Munella deposits, central Mirdita, Albania. In Proceedings of the 7th Congress on Bulletin of Geological Society of Greece, Thessaloniki, Greece, 1994; p. 3.
32. Tsoupas, G.; Economou-Eliopoulos, M. High PGE contents and extremely abundant PGE-minerals hosted in chromitites from the Veria ophiolite complex, northern Greece. *Ore Geol. Rev.* **2008**, *33*, 3–19. [[CrossRef](#)]
33. Daci, A. *Geochemical and Mineralogical Characteristics of the Copper Industry Pollution in the Fan River Valley (Reps-Rubik Region), Environmental Impact and Measures for the Rehabilitation of Damaged Soils*. Ph.D. Thesis, University of Tirana, Tirana, Albania, 2013. Unpublished work.
34. Plumlee, G.S.; Smith, K.S.; Montour, M.R.; Ficklin, W.H.; Mosier, E.L. Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. *Environ. Geochem. Miner. Depos. Rev. Econ. Geol.* **1999**, *6*, 373–432.
35. Da Silva, E.F.; Patinha, C.; Reis, P.; Fonseca, E.C.; Matos, J.X.; Barrosinho, J.; Oliveira, J.M.S. Interaction of acid mine drainage with waters and sediments at the Corona stream, Lousal mine (Iberian Pyrite Belt, Southern Portugal). *Environ. Geol.* **2006**, *50*, 1001–1013. [[CrossRef](#)]
36. Durães, N.; Bobos, I.; da Silva, E.F. Speciation and precipitation of heavy metals in high-metal and high-acid mine waters from the Iberian Pyrite Belt (Portugal). *Environ. Sci. Pollut. Res.* **2017**, *24*, 4562–4576. [[CrossRef](#)]
37. Cánovas, C.R.; Ollás, M.; Macías, F.; Torres, E.; San Miguel, E.G.; Galván, L.; Ayora, C.; Nieto, J.M. Water acidification trends in a reservoir of the Iberian Pyrite Belt (SW Spain). *Sci. Total Environ.* **2016**, *541*, 400–411. [[CrossRef](#)]

38. Nieto, J.M.; Sarmiento, A.M.; Olías, M.; Canovas, C.R.; Riba, I.; Kalman, J.; Delvalls, T.A. Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. *Environ. Int.* **2007**, *33*, 445–455. [[CrossRef](#)]
39. Da Silva, E.F.; Fonseca, E.C.; Matos, J.X.; Patinha, C.; Reis, P.; Santos Oliveira, J.M. The effect of unconfined mine tailings on the geochemistry of soils, sediments and surface waters of the lousal area (Iberian Pyrite Belt, Southern Portugal). *Land Degrad. Dev.* **2005**, *16*, 213–228. [[CrossRef](#)]
40. Sánchez España, J.; López Pamo, E.; Santofimia, E.; Aduvire, O.; Reyes, J.; Baretino, D. Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Appl. Geochem.* **2005**, *20*, 1320–1356. [[CrossRef](#)]
41. Ficklin, W.H.; Plumlee, G.S.; Smith, K.S.; McHugh, J.B. Geochemical classification of mine drainages and natural drainages in mineralized areas. In Proceedings of the International symposium on water-rock interaction, Park City, UT, USA, 13–18 July 1992; pp. 381–384.
42. Fantone, I. A Flow-Sheet Approach to the Issue of Sulfide-Rich Tailings. Ph.D. Thesis, University of Milan, Milan, Italy, 2016.
43. Descostes, M.; Vitorge, P.; Beaucaire, C. Pyrite dissolution in acidic media. *Geochim. Cosmochim. Acta* **2004**, *68*, 4559–4569. [[CrossRef](#)]
44. Rimstidt, J.D.; Vaughan, D.J. Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. *Geochim. Cosmochim. Acta* **2003**, *67*, 873–880. [[CrossRef](#)]
45. Todd, E.; Sherman, D.; Purton, J. Surface oxidation of pyrite under ambient atmospheric and aqueous (pH = 2 to 10) conditions: Electronic structure and mineralogy from X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **2003**, *67*, 881–893. [[CrossRef](#)]
46. Rezaie, B.; Anderson, A. Sustainable resolutions for environmental threat of the acid mine drainage. *Sci. Total Environ.* **2020**, *717*, 137211. [[CrossRef](#)]